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9. MICROBIAL GASES IN BLACK SHALE SEQUENCES ON THE DEMERARA RISE[1]

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ABSTRACT

The amounts and compositions of interstitial gases found at the five sites cored on the Demerara Rise during Leg 207 are related to sediment lithology. Concentrations are low in the sedimentary units overlying Cenomanian–Santonian black shales, where they increase to maximum values. A microbial origin for most of the gases is inferred from the low thermal maturity of organic matter and the predominance of methane in their compositions. Active in situ gas generation is postulated to compensate for migration of methane out of the black shale units. Trace amounts of C_4–C_6 gases found in the black shale units likely migrated from deeper in the section.

INTRODUCTION

Concentrations of the light hydrocarbon gases methane (C_1), ethane (C_2), and propane (C_3) were routinely measured during Leg 207 to monitor the possible presence of petroleum hydrocarbons and to investigate the existence of active microbial communities in the passive margin sediment sequences of the Demerara Rise. By analogy to Mediterranean sapropels (Coolen et al., 2002), it was anticipated that the organic carbon–rich Cretaceous black shales that were a major objective of Leg 207 coring might support active populations of prokaryotes.

Elevated amounts of gas have previously been reported in Cenozoic and Mesozoic sediments cored during Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) legs (e.g., Kvenvolden and Barnard, 1983; Meyers and Brassell, 1985; Kvenvolden and McDonald, 1986;

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Meyers and Snowdon, 1993; Meyers et al., 1998; Shipboard Scientific Party, 2002, 2003). Possible origins of these sedimentary gases are (1) residues of relict microbial degradation of sediment organic matter, (2) active generation by existing microbial communities, (3) in situ thermal decomposition of sediment organic matter, and (4) thermal degradation of deeply buried organic matter and migration into the sequences cored by DSDP and ODP legs. In very gassy sediments, gas can exist in the free state or as gas hydrate. However, the hydrostatic and lithologic pressures and temperatures that exist beneath the seabed typically keep gases dissolved in the interstitial fluids of sediment sequences.

If sufficiently abundant, gases exsolve from sediment pore waters during core recovery as pressure is released and sediments are warmed. None of the cores recovered during Leg 207 contained either the large gas bubbles or the gas expansion pockets that are two of the benchmarks of sediments especially rich in interstitial gases. Nonetheless, elevated gas concentrations were consistently measured in the black shale units present at the five sites drilled on the Demerara Rise. Both the amounts and compositions of these gases initially caused concern during drilling operations. This contribution describes the gas contents of these passive margin Cretaceous sedimentary sequences and considers their possible origins.

DEPOSITIONAL REGIMES AND SEDIMENTARY SEQUENCES ON THE DEMERARA RISE

The Demerara Rise is a prominent submarine plateau located at ~5°N off the coasts of Surinam and French Guyana (see Fig. **F1,** p. 58, in the "Leg 207 Summary" chapter). This feature is built on rifted continental crust that subsided as Africa and South America separated during Early Cretaceous time. Seismic stratigraphy reveals that its sediments thin from south to north. The five Leg 207 sites were drilled on the northern edge of the Demerara Rise to recover as much of the Cretaceous section as possible (see Fig. **F2,** p. 59, in the "Leg 207 Summary" chapter). The sites consequently share very similar passive-margin depositional environments that differ principally in their depths below sea level but also in some features of the five lithostratigraphic units that were found at all five sites (see Fig. **F8,** p. 65, in the "Leg 207 Summary" chapter).

GAS ANALYSIS METHODS

Gas samples were obtained by the headspace procedure (Kvenvolden and McDonald, 1986), which involves placing a nominal 5-cm^3 plug of sediment into a septum-sealed vial that is then heated at 60°C for 30 min to evolve sediment gases. Methane and ethane contents of gas samples were routinely analyzed using the shipboard GC3 gas analysis system, which consists of a Hewlett-Packard 5890 II Plus gas chromatograph equipped with a 2.4 m × 3.2 mm stainless steel column packed with HaySep S connected to a flame ionization detector (FID). When elevated gas contents were encountered, samples were also analyzed using the natural gas analyzer (NGA), which is a Hewlett-Packard 5890 II Plus gas chromatograph equipped with a multiport valve system that directs gases into two analytical pathways. The first measures hydrocarbons from methane to hexane using a 60 m × 0.32 mm DB-1 capillary column connected to an FID. The second measures nonhydrocarbon gases such as CO_2 and H_2S using a packed column connected to a thermal conductivity detector. Both gas chromatographs were calibrated using Scotty IV gas mixtures. Gas concentrations are reported as parts per million by volume (ppmv) relative to the standard volume (5 cm^3) of the headspace sample that is injected into the gas chromatograph.

The ODP gas analysis techniques are designed to provide rapid determinations of the relative amounts and compositions of the residual interstitial gases recovered during drilling. In particular, a goal of the analyses is to help avoid situations where dangerously elevated concentrations of thermogenic gas might occur. The procedures were not designed to deliver quantitatively correct in situ concentrations of the gaseous components of sediments but rather the concentrations of gas that remain after core recovery. Although samples for gas analysis are collected almost immediately after sediment cores reach the ship, a significant amount of the gas is lost because of the decrease in pressure and increase in temperature experienced by the cores. Moreover, the gas concentrations measured by the headspace procedure represent the gas concentrations of the headspace vial. Gas concentrations relative to the volume of interstitial water in the sediment plugs can be estimated, but are not normally determined. The results of the headspace gas analysis techniques nonetheless provide useful comparisons of the relative amounts and compositions of sedimentary gases at different depths at a single drill site and between different drill sites.

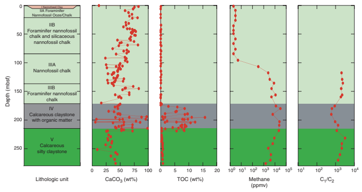
CALCIUM CARBONATE, ORGANIC CARBON, AND HYDROCARBON GAS CONCENTRATIONS

The amounts and compositions of headspace gases exhibit similar patterns that are related to the lithostratigraphic units and carbon concentrations at the five Leg 207 sites. The general pattern is that interstitial methane concentrations start to increase near the top of the nannofossil chalks and clays of Unit III, reach maximum values in the black shales of Unit IV, and decrease near the base of Unit V. In addition, a weak odor of hydrogen sulfide was noted in the black shale sequences at all the sites, although detectable concentrations (>1 ppmv with the NGA) of this gas were not found. A petroliferous odor present in parts of some of the black shale units may indicate the presence of organosulfur compounds. Concentration patterns of $CaCO_3$, total organic carbon (TOC), and headspace methane at each site are summarized in the following sections.

Site 1257

Concentrations of $CaCO_3$ in the five lithostratigraphic units generally diminish with depth (Fig. F1). However, Unit IV still contains relatively high $CaCO_3$ (average = 50 wt%) but the concentrations of individual sediment samples vary greatly, largely because of the calcite laminae in the black shales of this unit and because the claystones are interbedded with limestones. The sediments of Units I, II, and III contain <0.1 wt% TOC. In marked contrast, the black shales have TOC concentrations of 1–16 wt%. The calcareous siltstones that compose Unit V have TOC values of ~0.6 wt%, which is double the average DSDP value

F1. $CaCO_3$, TOC, and CH_4, Site 1257, p. 12.



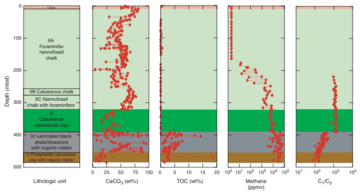
(TOC = 0.3 wt%) compiled by McIver (1975). The Unit V siltstones are hence relatively rich in organic matter.

Concentrations of headspace methane remain at background levels (<3 ppmv) until Unit III, where they start to increase in conjunction with the depletion of concentrations of interstitial sulfate (see **"Interstitial Gas Contents,"** p. 23, in "Organic Geochemistry" in the "Site 1257" chapter). Maximum headspace methane concentrations of ~25,000–30,000 ppmv are reached in black shale Unit IV. These values are not particularly large. The maximum concentrations are accompanied by sharp decreases in C_1/C_2 ratios from 2300–1900 ppmv in Unit III to 1300–600 ppmv in the black shales (Fig. **F1**). Propane also appears at minor but significant concentrations (14–48 ppmv). Methane concentrations decrease below the black shale unit, and C_1/C_2 ratios are larger than values in Unit IV.

Site 1258

Concentrations of $CaCO_3$ vary between 5 and 95 wt% in the sediments and rocks of Site 1258 (Fig. **F2**). Sediments of Units I, II, and III average 0.1 wt% TOC, whereas the black shales of Unit IV have an average of 7.9 wt% TOC. The calcareous mudstones that compose Unit V have an average TOC value of 4.2 wt%, which is much higher than in Unit V at the other four sites.

F2. $CaCO_3$, TOC, and CH_4, Site 1258, p. 13.



Concentrations of interstitial gases in lithostratigraphic Units I, II, and III at Site 1258 are low, but they increase in Units IV and V (Fig. **F2**). Methane concentrations first exceed 1000 ppmv at 220 meters below seafloor (mbsf) and thereafter increase slowly to the top of the black shale Unit IV at ~390 mbsf. Here, methane increases abruptly from ~10,000 to 43,300 ppmv and ethane concentrations exceed 100 ppmv for the first time at this site (see **"Interstitial Gas Contents,"** p. 25, in "Organic Geochemistry" in the "Site 1258" chapter). The methane concentrations reach a maximum of 65,000 ppmv at 430 mbsf and then slowly decrease to ~30,000 ppmv at the bottom of the hole. The concentrations of ethane and propane are relatively low compared to the yields in methane, yet they also seem to show a depth-related increase. The C_1/C_2 ratio decreases to values between 500 and 100 in the black shales and remains relatively low throughout Unit V.

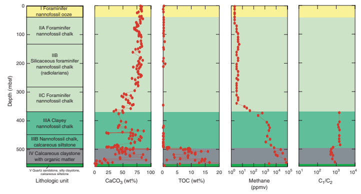
Because gas concentrations are higher at Site 1258 than those at Site 1257, the NGA was employed to monitor the higher molecular weight volatile hydrocarbons butane (C_4), pentane (C_5), and hexane (C_6) that occur in trace amounts below 425 mbsf (see **"Interstitial Gas Contents,"** p. 25, in "Organic Geochemistry" in the "Site 1258" chapter). These hydrocarbons are usually not considered to be microbially generated (Claypool and Kvenvolden, 1983). Because the organic matter in these sediments is thermally immature (see **"Organic Matter Source Characterization,"** p. 24, in "Organic Geochemistry" in the "Site 1258" chapter), the presence of the C_4–C_6 hydrocarbons suggests that some gases have migrated into Unit IV from an unidentified source deeper in the sedimentary section.

Site 1259

$CaCO_3$ concentrations of the five lithostratigraphic units generally decrease with greater depth. However, the black shales that compose most of Unit IV still contain ~50 wt% $CaCO_3$, largely because calcite laminae are interspersed among the black shale laminae. Sediments in Units I, II, and III contain <0.8 wt% TOC. The average TOC content for the black shale unit is 9.3 wt%. Unit V has TOC values that are <0.5 wt%.

Concentrations of headspace methane remain at background levels (<3000 ppmv) until near the base of Unit II, when they start to rise as concentrations of interstitial sulfate decrease (see **"Interstitial Gas Contents,"** p. 29, in "Organic Geochemistry" in the "Site 1259" chapter). Concentrations remain below 5000 ppmv until the black shale in Unit IV (Fig. **F3**). Maximum concentrations on the order of 62,000–76,000 ppmv are reached near the base of this unit. The maximum concentrations are accompanied by sharp decreases in C_1/C_2 ratios from 1600–1200 in Unit III to 800–500 in the black shales (Fig. **F3**). Propane also appears at minor concentrations near the base of Unit IV. The methane concentration decreases abruptly to 2300 ppmv in the sandstone unit underlying the black shale unit.

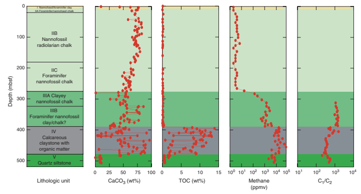
F3. $CaCO_3$, TOC, and CH_4, Site 1259, p. 14.



Site 1260

Concentrations of $CaCO_3$ generally decrease with depth in the sedimentary succession of Site 1260. The black shale Unit IV averages ~50 wt% $CaCO_3$ because calcite laminae are interspersed in this unit. The quartz sandstones of Unit V are low in calcite (Fig. **F4**). Most of the sediments of lithostratigraphic Units I, II, and III contain <0.1 wt% TOC. The black shales of Unit IV have TOC concentrations that average 7.2 wt% and reach as high as 13.9 wt%.

F4. $CaCO_3$, TOC, and CH_4, Site 1260, p. 15.

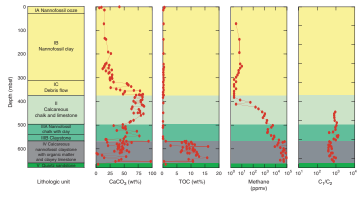


Concentrations of headspace methane first increase above background levels at the top of Unit III. Concentrations remain <4,000 ppmv until the top of black shale unit, where they abruptly increase to 17,000 ppmv (Fig. **F4**). A maximum concentration of 68,000 ppmv is attained near the middle of this unit. C_1/C_2 ratios sharply decrease from 1500 to 1000 ppmv in Unit III and from 900 to 300 ppmv in the black shales. Propane also appears at concentrations of 30–5 ppmv near the middle of Unit IV. Methane concentrations decrease moderately to 7000–2000 ppmv in the siltstone unit underlying the black shale unit, and C_1/C_2 ratios increase slightly (Fig. **F4**).

Site 1261

The sedimentary succession at Site 1261 differs from the other four Demerara Rise sites by its 350-m-thick clay-rich Unit I. Concentrations of $CaCO_3$ are between 15 and 30 wt% through most of this unit and reach ~80 wt% only in the debris flow layer that is its base (Fig. **F5**). Unit II is composed of calcareous chalk and averages 75 wt% $CaCO_3$, whereas the clayey calcareous chalks of Unit III average 47 wt%. The black shale unit is again quite variable in carbonate content, and the underlying sandstone is carbonate poor. Sediments of Units I, II, and III contain <0.5 wt% TOC, and the black shales of Unit IV have an average TOC concentration of 9.3 wt%,

F5. $CaCO_3$, TOC, and CH_4, Site 1261, p. 16.



Methane concentrations increase above background values within Unit I to reach 10 ppmv at 250 mbsf before decreasing to <3 ppmv. The appearance of methane coincides with the disappearance of interstitial sulfate at this depth (see **"Interstitial Gas Contents,"** p. 25, in "Organic Geochemistry" in the "Site 1261" chapter). Methane concentrations increase again above baseline levels starting at ~400 mbsf in Unit

II to reach 19,300 ppmv at the base of Unit III (Fig. F5). The amount of methane increases sharply to 62,000 ppmv at the top of the black shale Unit IV, and ethane appears at concentrations above 100 ppmv (see **"Interstitial Gas Contents,"** p. 25, in "Organic Geochemistry" in the "Site 1261" chapter). Methane concentrations remain high through the black shale unit, reaching a maximum of 111,000 at 586 mbsf. The C_1/C_2 ratio decreases from >1000 in Unit III to values ~500 in the black shales.

DISCUSSION

Origin of the Gases

Several possible origins exist for the relatively abundant gases found in the black shale units of the five Leg 207 sites:

1. Hydrocarbon gases from deeper, more thermally mature sediments may have migrated into the gas-rich zone.
2. The gases can originate from some combination of in situ thermogenic and biogenic degradation of the organic matter in the black shales.
3. The gases could be a mixture of in situ and migrated gases.

Evidence for migration of presumably thermogenic methane into porous sediments from deeper sources has been found at other ODP sites. For example, a thermogenic source exists in the Jurassic rocks that underlie Sites 762 and 763 on the Exmouth Plateau (Meyers and Snowdon, 1993). Potential Mesozoic sources of thermogenic gas are indeed known on the South American margin between Trinidad and Surinam.

The C_1/C_2 ratio is particularly useful for distinguishing between biogenic and thermogenic gaseous hydrocarbons; biogenic gases commonly have ratios >1000, whereas values <200 imply gas generation related to increasing depth and temperature (cf. Claypool and Kvenvolden, 1983; Stein et al., 1995; Whiticar, 1999). High C_1/C_2 ratios and the absence of major contributions of higher molecular weight hydrocarbon gases (see the "Organic Geochemistry" sections in the site chapters) suggest that little of the gas in the sites drilled during Leg 207 is derived from the thermal degradation of organic matter.

The most likely source of most of the methane, the dominant hydrocarbon gas in these sediments, is in situ formation by methanogenic microorganisms. Methanogenesis becomes important in sediments devoid of interstitial sulfate but containing metabolizable organic matter. This process has two stages, in which a consortium of microorganisms first converts various components of organic matter into short-chain alcohols and acids, CO_2, and H_2. In the second stage, some of these products are converted to CH_4 by a metabolically limited group of obligate anaerobic microbes (Mechalas, 1974; Whiticar, 1999). The general reactions that represent the production of methane in the second stages are

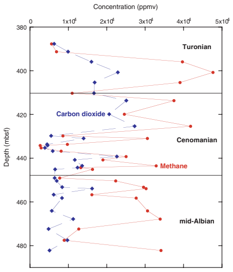
$$CH_3COOH \rightarrow CH_4 + CO_2 \text{ (acetic acid fermentation) and}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ (}CO_2\text{ reduction).}$$

The reduction of CO_2 to methane is the dominant process in marine sediments (Wiese and Kvenvolden, 1993; Whiticar, 1999).

Comparison of concentrations of methane and CO_2 in the black shale unit of Hole 1258A indicates that these two components of interstitial gases are indeed related. Although methane is usually more abundant than CO_2, higher concentrations of the two gases generally coincide in the Cenomanian–Turonian black shales (Fig. F6). However, this relation is not obvious in the underlying mid-Albian claystones of Unit V. One important difference between the two lithostratigraphic units is their TOC concentrations; the black shales average 7.9 wt%, whereas the claystones average 4.2 wt%. Another difference is that Rock-Eval pyrolysis identifies the organic matter as Type II in Unit IV and a mixture of Types II and III in Unit V (see **"Organic Matter Source Characterization"** p. 24, in "Organic Geochemistry" in the "Site 1258" chapter). The organic matter in Unit V is evidently less suitable for gas generation.

F6. NGA methane vs. carbon dioxide, p. 17.



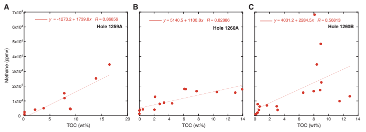
At all five Leg 207 drill sites, the disappearance of interstitial sulfate coincides with the top of the black shales and the increase in methane concentrations (see the "Organic Geochemistry" sections in the site chapters). A microbial origin of the methane is implied by this observation, inasmuch as Claypool and Kvenvolden (1983) observe that the presence of interstitial sulfate inhibits microbial methanogenesis in marine sediments. Similar in situ microbial production of methane has been inferred from high microbial gas concentrations at numerous DSDP and ODP sites. Examples include Pliocene–Pleistocene sediments from under the Benguela Current (Meyers and Brassell, 1985; Meyers et al., 1998), at Sites 618 and 619 on the northern margin of the Gulf of Mexico (Burke et al., 1986; Pflaum et al., 1986), at Leg 112 sites on the Peru margin (Kvenvolden and Kastner, 1990; Kvenvolden et al., 1990), at Sites 897 and 898 on the Iberian Abyssal Plain (Meyers and Shaw, 1996), and in middle Miocene sediments at Site 767 in the Celebes Sea (Shipboard Scientific Party, 1990). The tops of the Leg 207 black shale units are between 176 and 565 mbsf (see the "Lithostratigraphy" sections in the site chapters), which places them within the range of microbial viability (surface to ~500 mbsf) reported by Cragg et al. (1992) in sediments from the Japan Sea.

The origin of the methane probably involves mainly reduction of interstitial CO_2 in the sediments and minor in situ microbial fermentation of marine organic matter. Because these two processes are carried out by distinct microbial populations, the production of methane ultimately depends on satisfying the metabolic requirements of the separate pathways. Comparison of the carbon isotopic contents of CO_2 and CH_4 in sediments at DSDP Site 533 on the Blake Plateau indicates that most of the CH_4 originates from reduction of CO_2 (Galimov and Kvenvolden, 1983). Inasmuch as the obligate anaerobes involved with CO_2 reduction are particularly metabolically limited (Mechalas, 1981; Whiticar, 1999), this pathway can become blocked despite an abundance of interstitial CO_2 and thereby limit CH_4 production.

Comparison of Methane Abundance and Organic Carbon Concentration

The possible relation between interstitial methane concentrations and sediment organic matter contents was investigated by measuring the TOC concentrations of the headspace sediment samples from Holes 1259A, 1260A, and 1260B. A rough correspondence exists between larger gas concentrations and higher TOC values (Fig. F7). Marked excursions from a simple linear relation suggest that organic matter quality, and not simply quantity, affects gas generation from the black shales. Moreover, dramatic changes in methane concentrations at lithostratigraphic boundaries (e.g., Figs. F3, F4) suggest either that gas does not freely migrate from its origin in the black shales or that it migrates and is being quickly replenished from the organic matter in this unit so that elevated concentrations are maintained.

F7. TOC vs. methane, p. 18.



Inferential evidence for migration of methane out of the black shale units exists. Concentrations of interstitial sulfate start to increase and those of ammonium to decrease at the top of the black shale sequences at all five sites (see **"Organic Geochemistry"** p. 45, in "Discussion and Conclusions" in the "Leg 207 Summary" chapter). These results indicate the existence of an important sulfate sink and ammonium source in the Cretaceous black shales, which in turn implies diffusion of methane from the black shales to support metabolic activity above the black shale unit, most likely as anaerobic methane oxidation. Because maximum concentrations of methane are found in the black shale units at each site, methanogenesis must be active to replace the methane that migrates out of these units.

The weak correspondence between concentrations of carbonate carbon and organic carbon and concentrations of CH_4 in sediments from the five sites implies that only a small percentage of organic matter is converted to gases. For example, even at saturation, methane represents only ~0.1% of the organic matter that is present in unconsolidated sediments (Whiticar, 1999). The limiting factor to microbial gas production is generally not the availability of organic matter but the availability of terminal electron receptors.

SUMMARY

Concentrations of interstitial methane in the sediment sequences at all five Leg 207 sites increase abruptly in the black shales, where they reach their maximum values. A weak correspondence exists between higher TOC and greater methane concentrations, but marked excursions from a simple linear relation suggest that the type of organic matter, and not simply the amount, affects gas generation in the black shales. Because of the low thermal maturity of organic matter at all five sites and the predominance of methane in the interstitial gases, the origin of most of the gases is likely from in situ microbial activity. Dramatic decreases in methane concentration at the tops of the black shale boundaries suggest that methane oxidation, which consumes interstitial sulfate, proceeds in overlying units. Evidence of migration of some hydrocarbon gases into the drilled sequences from deeper, more thermally mature sediments is reflected in the presence of small amounts of heavier hydrocarbon gases. Active generation of methane in the black shale units likely replaces gas that may migrate out of these lithostratigraphic units to maintain the elevated methane concentrations that exist within the black shales.

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Figure F1. Concentrations of $CaCO_3$, total organic carbon (TOC), and headspace CH_4 in sediments at Site 1257. Elevated methane/ethane (C_1/C_2) ratios indicate microbial origins for these hydrocarbon gases.

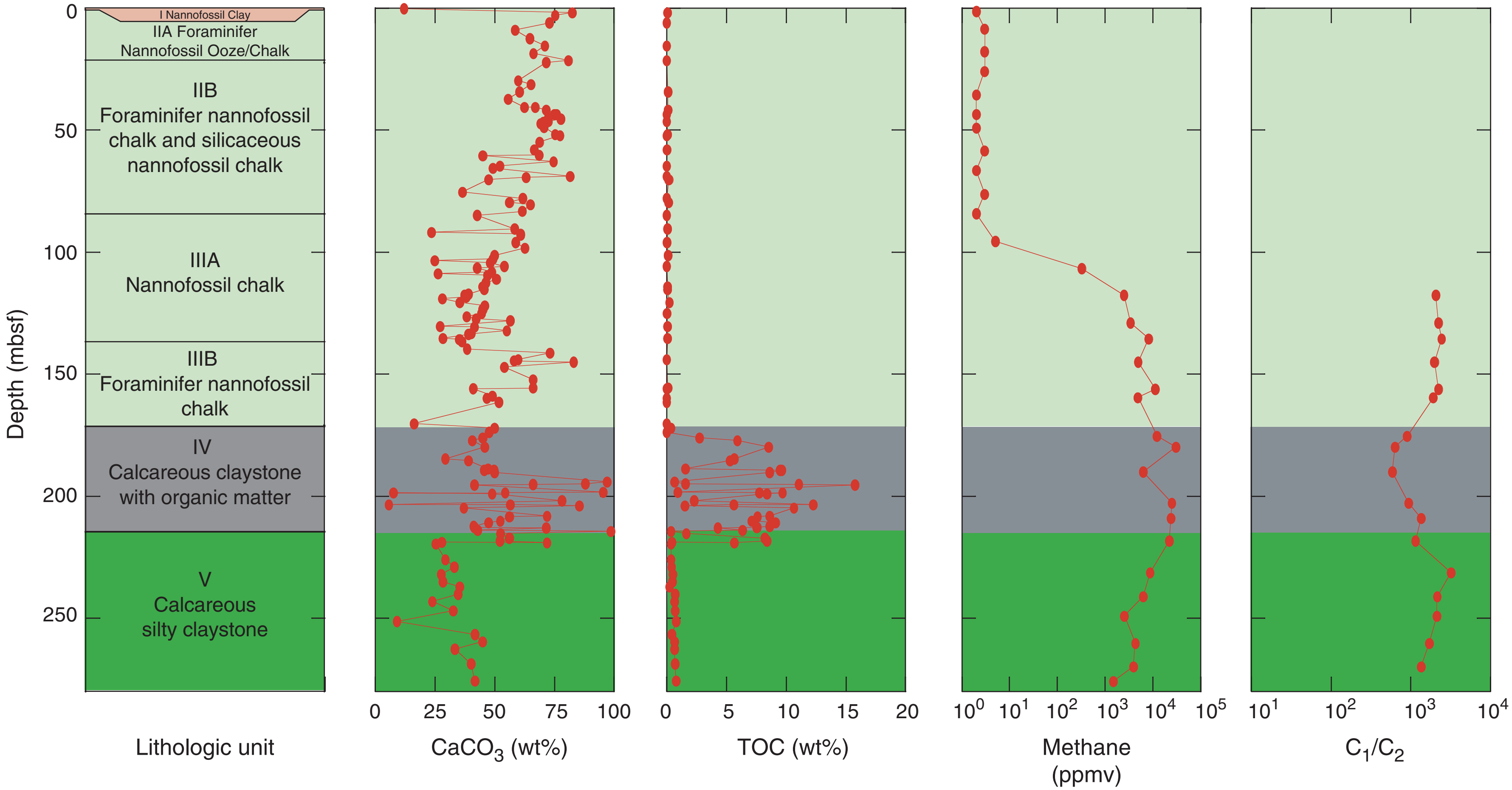

Figure F2. Concentrations of $CaCO_3$, total organic carbon (TOC), and headspace CH_4 in sediments at Site 1258. Elevated methane/ethane (C_1/C_2) ratios indicate microbial origins for these hydrocarbon gases.

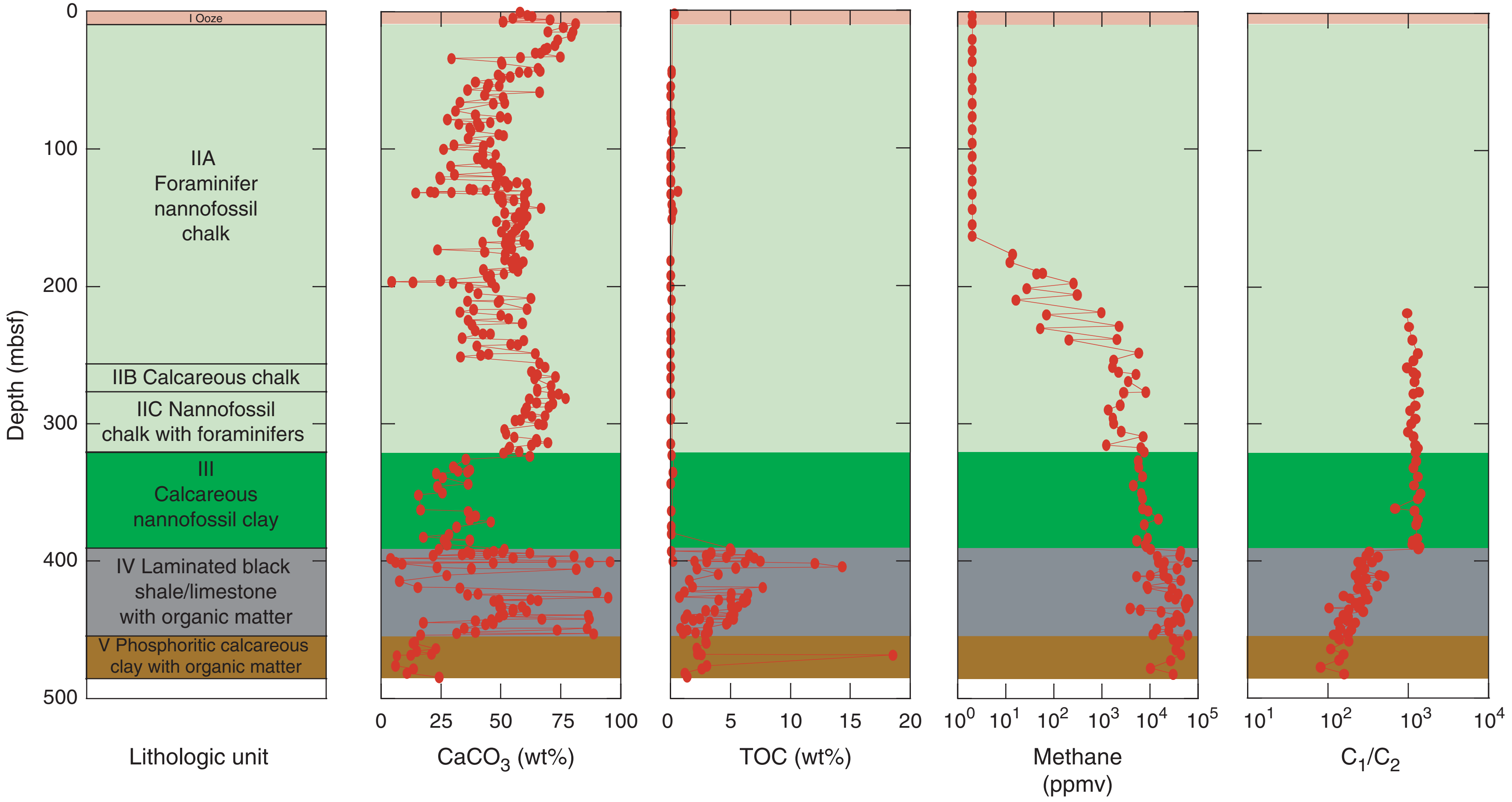

Figure F3. Concentrations of $CaCO_3$, total organic carbon (TOC), and headspace CH_4 in sediments at Site 1259. Elevated methane/ethane (C_1/C_2) ratios indicate microbial origins for these hydrocarbon gases.

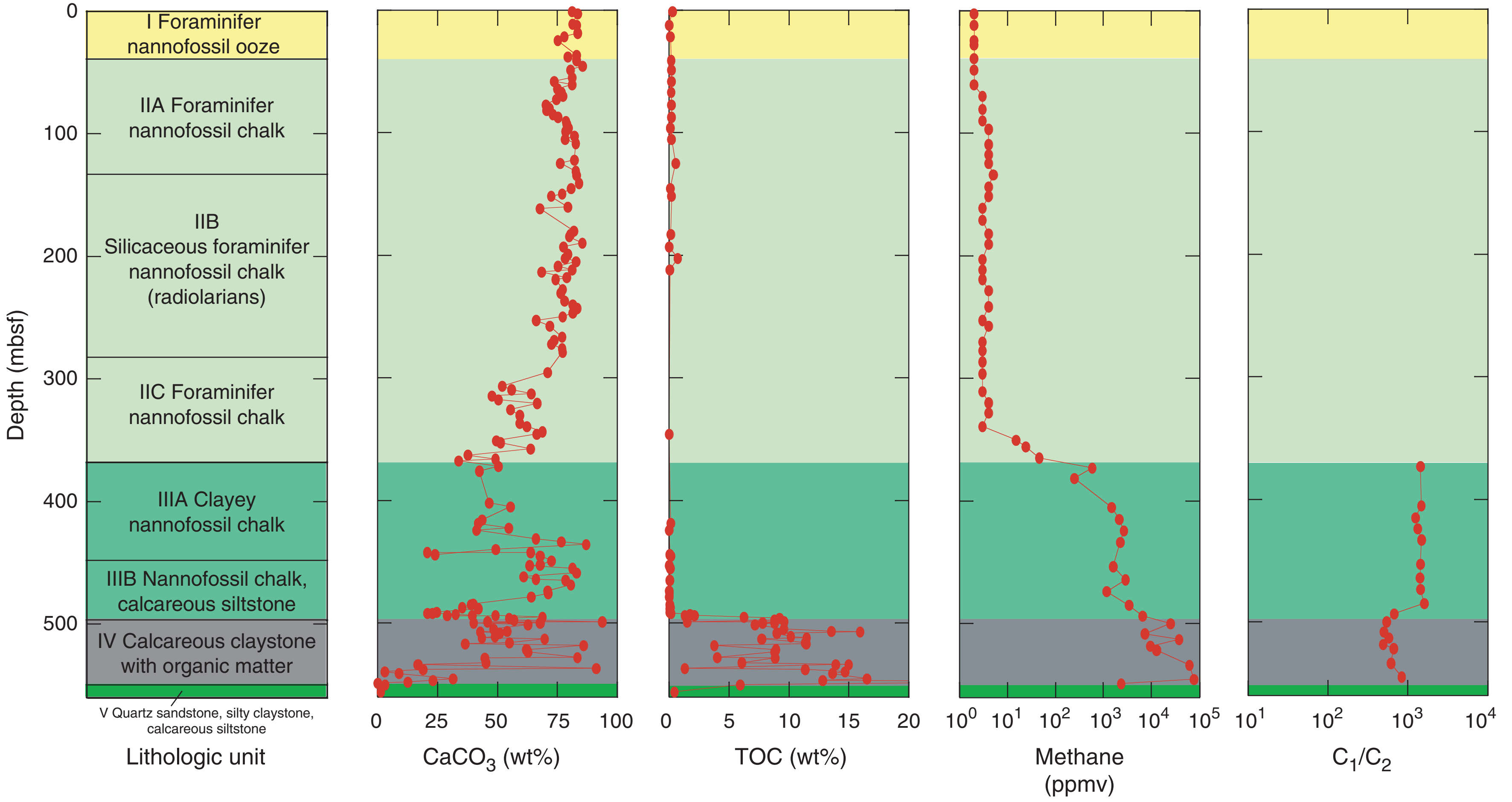

Figure F4. Concentrations of $CaCO_3$, total organic carbon (TOC), and headspace CH_4 in sediments at Site 1260. Elevated methane/ethane (C_1/C_2) ratios indicate microbial origins for these hydrocarbon gases.

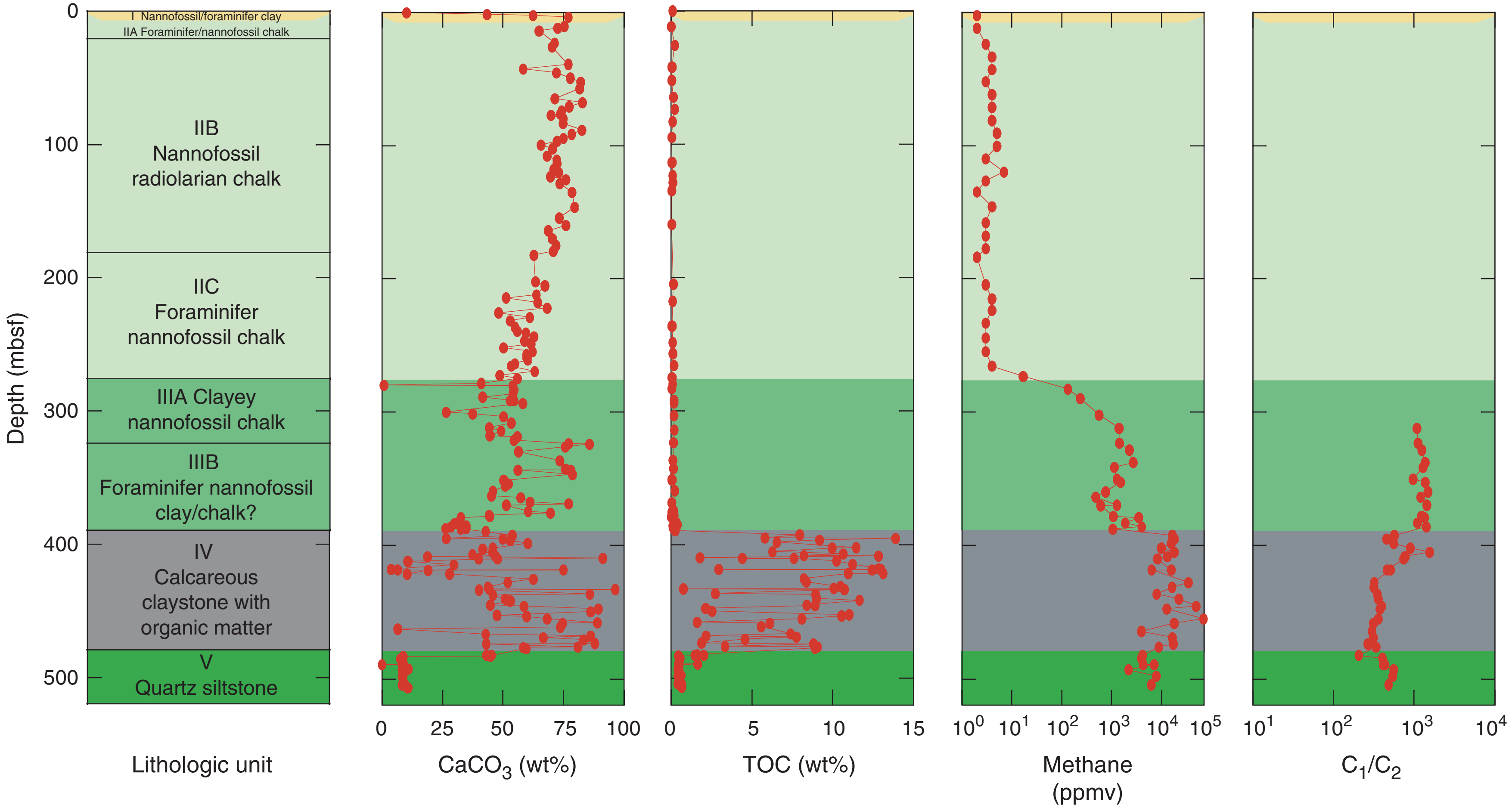

Figure F5. Concentrations of $CaCO_3$, total organic carbon (TOC), and headspace CH_4 in sediments at Site 1261. Elevated methane/ethane (C_1/C_2) ratios indicate microbial origins for these hydrocarbon gases.

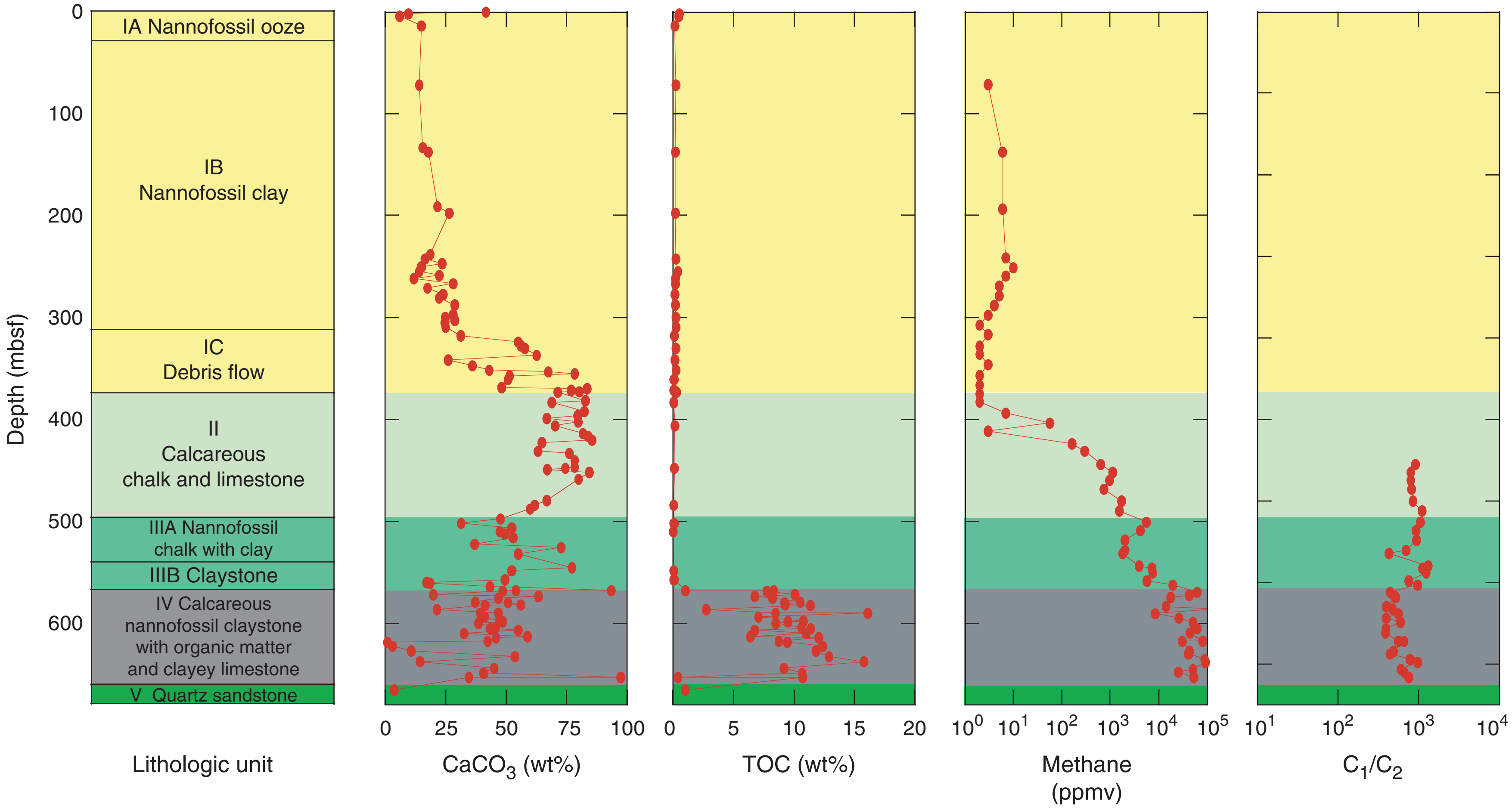

Figure F6. Comparison of concentrations of interstitial methane and carbon dioxide measured with the Natural Gas Analyzer (NGA) (see the "Site 1258" chapter) in sediments from Hole 1258A.

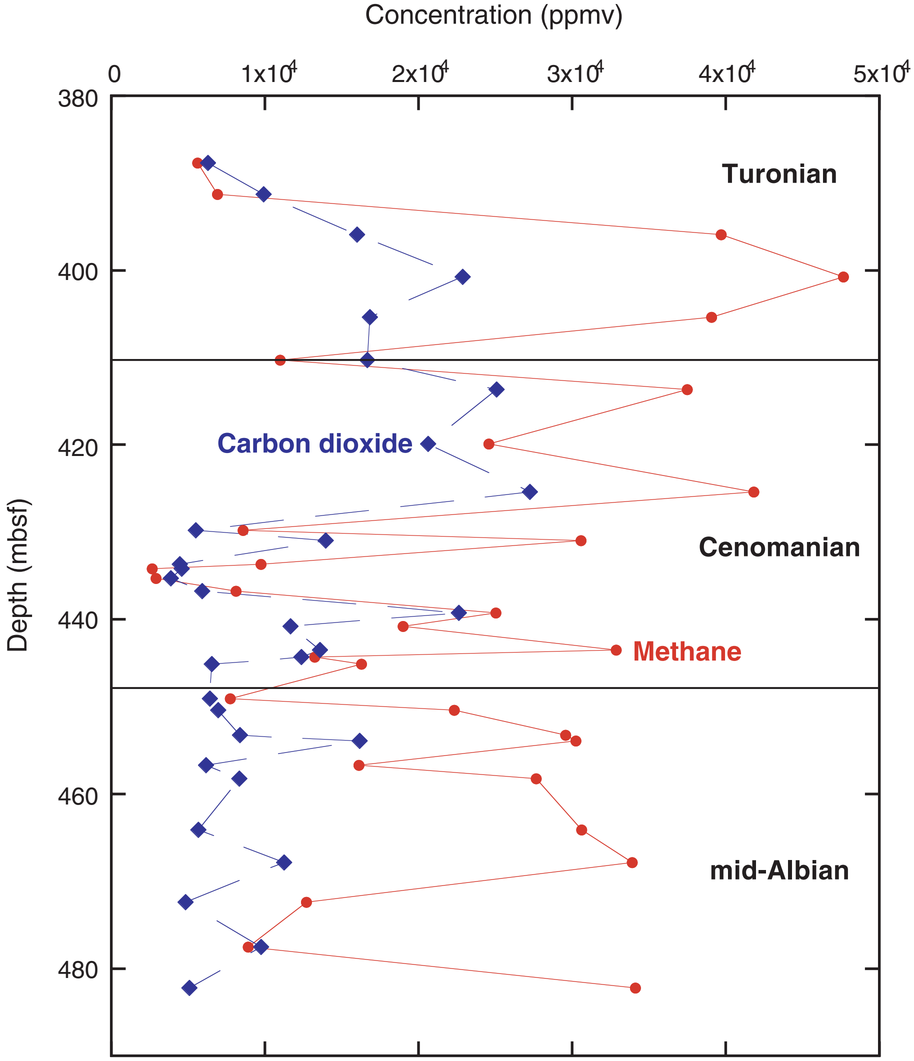

Figure F7. Comparison of total organic carbon (TOC) and methane concentrations in headspace samples from Holes (**A**) 1259A, (**B**) 1260A, and (**C**) 1260B.