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Surface and subsurface manifestations of gas movement through a N–S transect of the Gulf of Mexico

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Abstract

Large volumes of gas have vented through a north–south transect of the offshore northern Gulf of Mexico. An overview of surface and subsurface manifestations of this gas venting is presented. This gas movement has caused extensive alteration of reservoir oils to the north of the transect which are estimated to have equilibrated with, or been gas washed by, as much as 30 volumes of gas for every volume of oil. This gas washing entrains and carries upward the most volatile oil components depositing them in either shallower reservoirs or venting them to the overlying sediments and the water column. A significant amount of this gas bypasses the reservoirs and vents upward into the overlying sediments and waters. In spite of the significant amounts of the gas involved, the venting at the seafloor appears to occur primarily through highly localized faults and fractures. This gas discharge is spatially and temporally heterogeneous, making it difficult to estimate the actual hydrocarbon fluxes involved. This upward gas movement leaves characteristic signatures at the sediment water interface including carbonate pavements in older seep areas, and chemosynthetic biological communities, methane hydrates, and gas seeps in more recent long-term seep areas. In some cases where gas venting is very recent, massive disruption of surface and subsurface sediments is observed to be occasionally accompanied by mud volcanoes. Venting can be vigorous enough to produce methane gas bubbles, which appear to be injected rapidly into surface waters and which may constitute a significant source of methane, a greenhouse gas, to the atmosphere.

In the northern Gulf of Mexico, gas venting is sometimes accompanied by natural oil slicks at the sea surface, which can be tracked for many miles in non-productive areas. These gas-venting signatures are not unique to the Gulf of Mexico; similar seep features are observed in sediments worldwide. The widespread occurrence of these seep features, which may or may not be related to subsurface oil and gas deposits, may explain why use of surface seeps has often proved to be so controversial in oil exploration. Indeed, most seeps are probably not linked with economic subsurface petroleum reservoirs.

The relationships between surface seep features and productive subsurface reservoirs along a N–S transect of the northern Gulf of Mexico are presented as an example of how all surface and subsurface geochemical, geological, geophysical data might be used together to better constrain interpretations regarding the nature and dynamics of subsurface oil and gas deposits and their plumbing in frontier areas.

Keywords: Methane; Hydrate; Seep; Migration; Petroleum; Gas; Biodegradation

1. Introduction

The goals of this paper are to present an overview of the dynamic nature of gas movement along a north–south transect in the northern Gulf of Mexico (Fig. 1); demonstrate the apparent relationship between subsurface gas movement and surface sediment seep features, and; show how these processes might impact interpretations of surface seepage as related to the presence of underlying gas and oil reservoirs. The effects of Gulf of Mexico gas movement on subsurface oil reservoirs, surface sediments, the water column, and the overlying atmosphere are summarized. The manifestations of dynamic gas movement described here are not unique to the Gulf of Mexico. Examples of similar seep features in other geographic areas worldwide are presented to demonstrate that surface

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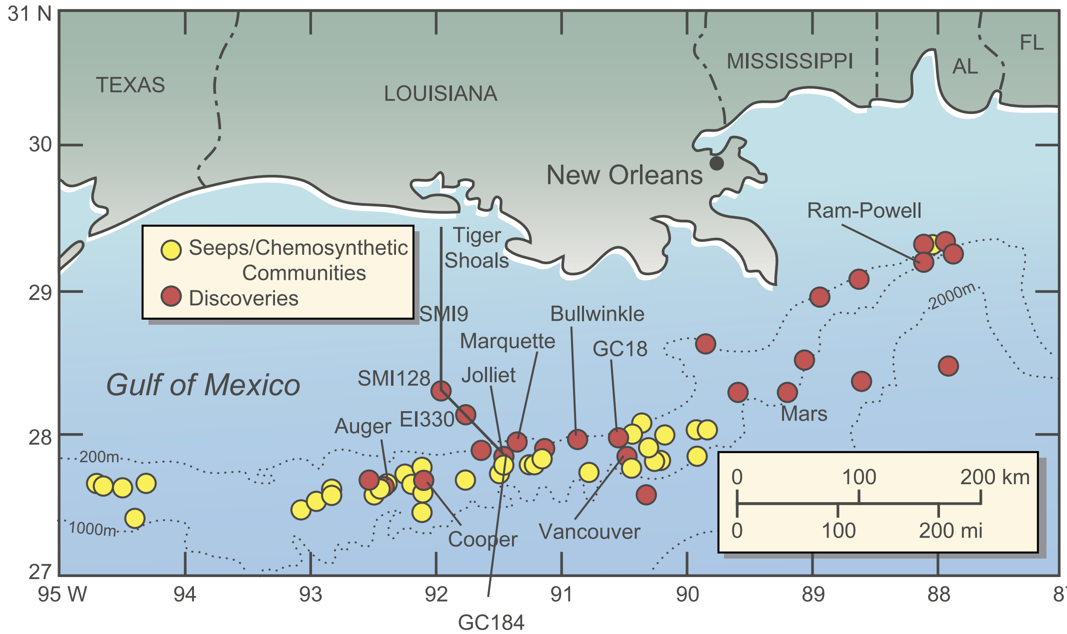

Fig. 1. Map of oil and gas seeps/chemosynthetic communities and recent petroleum discoveries (adapted from Sassen et al., 1993a,b). The location of N–S well transect on upper slope of northern Gulf of Mexico is indicated by the heavy black line.

seepage occurs very widely in some parts of the ocean floor, particularly along the edges of continents and in ocean margins, even when no viable producible petroleum reservoirs appear to be present. The widespread occurrence of these seep features, which may or may not be related to subsurface oil and gas deposits, may explain why use of surface seeps has often proved to be so controversial in oil exploration. The relationship between the surface seep features and subsurface gas migration through reservoirs along a N–S transect in the Gulf of Mexico is presented as one example of the relationship between surface seep geology, chemistry, and biology, and the dynamics of subsurface gas and oil movement into and through subsurface petroleum reservoirs.

2. Summary of effects of gas venting in the northern Gulf of Mexico

Extensive research has been carried out in the offshore Green Canyon (GC184) area of the upper continental slope of the northern Gulf of Mexico (Fig. 1) near the Conoco Jolliet oil field. Extensive work has been carried out in this area, including mapping seafloor gas and oil seep features (Fu and Aharon, 1998; Aharon et al., 1997; Brooks et al., 1984, 1986, 1987, 1990; Kennicutt et al., 1985, 1988a,b; Paull et al., 1989; Roberts et al., 1990a,b; 1999a,b; Roberts, 2001; Roberts and Carney, 1997; MacDonald, 1998; Milkov and Sassen, 2003a,b), the study of biology of chemosynthetic communities associated with the seeps (Brooks et al., 1987, 1990; Childress et al., 1986; Fisher et al., 1987; Kennicutt et al., 1985, 1988a,b; MacDonald and Joye, 1997; MacDonald, 1998; MacDonald et al., 1994, 1990a,b; Sassen et al., 1993a,b, 1994a,b, 1998, 1999a,b; Zhang et al., 2002, 2003), and surface gas hydrates (MacDonald et al., 1994; Roberts, 2001; Roberts et al., 1999a,b; Sassen and MacDonald, 1997; Sassen et al., 1993a,b, 1998, 1999a,b; Sassen, 2001, 1999; Lanoil et al., 2001). The study area lies within a broader general area of natural oil and gas seeps encompassing much of the upper continental slope of the Gulf of Mexico (Fig. 1). These natural seeps are closely related geographically, with productive subsurface reservoirs, as shown in Fig. 1 (adapted from Sassen et al., 1993b). A summary of surface and subsurface phenomena associated with the northern Gulf of Mexico gas seeps is shown schematically in Fig. 2. These venting features produce a substantial oil and gas flux into the overlying water column as shown by huge oil slicks over non-oil productive areas described by "MacDonald (1998) and MacDonald et al., (1993, 1996, 2002). The volumes of oil and gas vented to the water column and to the atmosphere are probably substantial, as discussed further in Kvenvolden and Lorenson (2001), Kvenvolden and Rogers (2005) and Judd et al. (2002). The venting also causes significant alterations to subsurface sediments, which can be observed seismically (e.g. Fig. 3 from Hunt, 1996) and in short-term changes in the compositions of oils in reservoirs, as discussed later in this chapter.

The interest of Cornell University and the Woods Hole Oceanographic Institution in this area began with a project to study subsurface migration of oil and gas along the N–S Gulf of Mexico transect, shown in Fig. 4. The most surprising overall conclusion of that study was that long-term dynamic gas migration occurring throughout

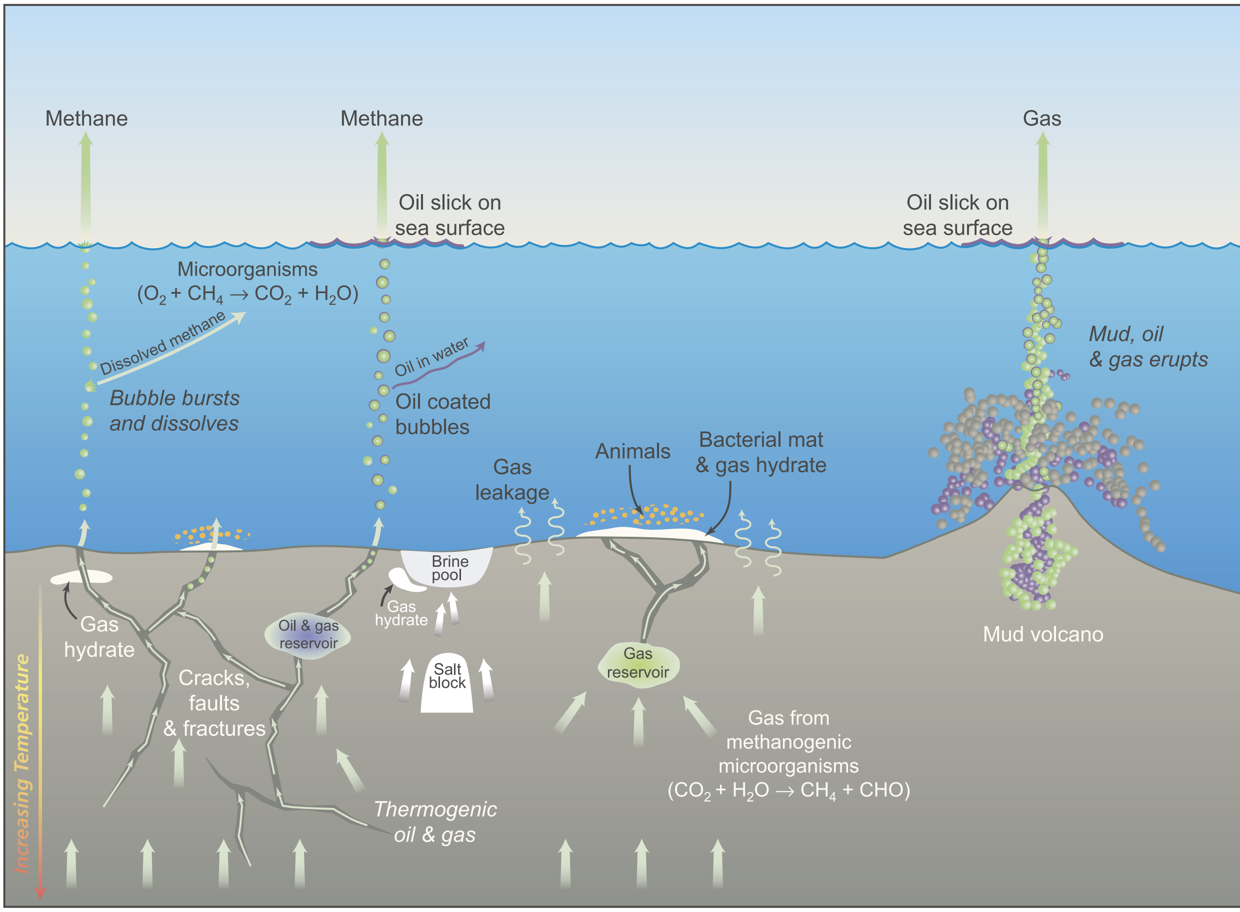

Fig. 2. Summary of all gas seep related processes observed in the vicinity of Green Canyon area in the northern Gulf of Mexico, at the south end of the transect shown in Fig. 1. The processes shown include thermogenic oil and deeper gas generation (to the left) and biogenic methane generation (to the right). Either source of gas can then migrate upward either rapidly through faults and fractures or more slowly by diffusion through sediments into overlying oil and gas reservoirs. In either case, most of the gas bypasses the reservoirs and migrates further upward to the sediment water interface where it can form gas (methane) hydrate deposits (shown in white) or can be vented into the overlying water column. If methane concentrations do not reach saturation, the gas in the dissolved phase is largely biodegraded in the water column. Where sufficient methane is present, gas bubbles form and, if they survive to within 100 m of the surface, can be vented as methane into the atmosphere. In some cases, the bubbles are coated with oil (see Leifer and Boles, this volume). Chemosynthetic communities of animals, shown with pink dots, tend to congregate on surfaces of gas hydrates and within bacterial mats near gas seeps.

the transect had resulted in considerable in-reservoir oil alteration, described in detail later in this chapter. It seemed probable that some of this gas movement must be contemporary and should be detectable as both gas and oil seeps in surface sediments and in the overlying water column. Fortuitously, the southern end of this transect is located at Green Canyon 184, which is adjacent to the intensively studied ‘Bush-Hill’ surface gas and oil seeps and gas hydrate mound; the gas hydrate mound overlies the Jolliet oil field (Fig. 1). Therefore, a relationship between the subsurface transect gas migration and the Green Canyon surface seeps seemed highly likely. Indeed, Brooks et al. (1984) were the first to document the large and vigorous biological communities associated with the seafloor oil and gas seeps at GC184. Subsequently, other surface sediment manifestations of these seeps were described and mapped by various groups as described above. The organisms found in these areas are reminiscent of the prolific chemosynthetic biological communities that are ubiquitous in hydrothermal vent areas (Hessler and Kaharl, 1995).

In the Gulf of Mexico, the primary food source for these seep communities appears to be a complex chemosynthetic community of microorganisms utilizing a coupled process of hydrocarbon (primarily methane) oxidation and sulphate reduction (termed anaerobic oxidation of methane, or AOM), similar to that which has been described at a number of other oceanic methane hydrate and seep sites (e.g. Hinrichs et al., 1999, 2000; Hinrichs and Boetius, 2002; Orphan et al., 2001a,b). An important factor governing how much methane is oxidized at these sites is the rate of methane efflux, which determines the location and type of oxidation taking place. Low rates of methane leakage mean the oxidation is most likely occurring in the sediments and at the expense of sulphate. Product sulphide is then available for the macrofaunal seep communities. High rates of methane seepage will mean that methane

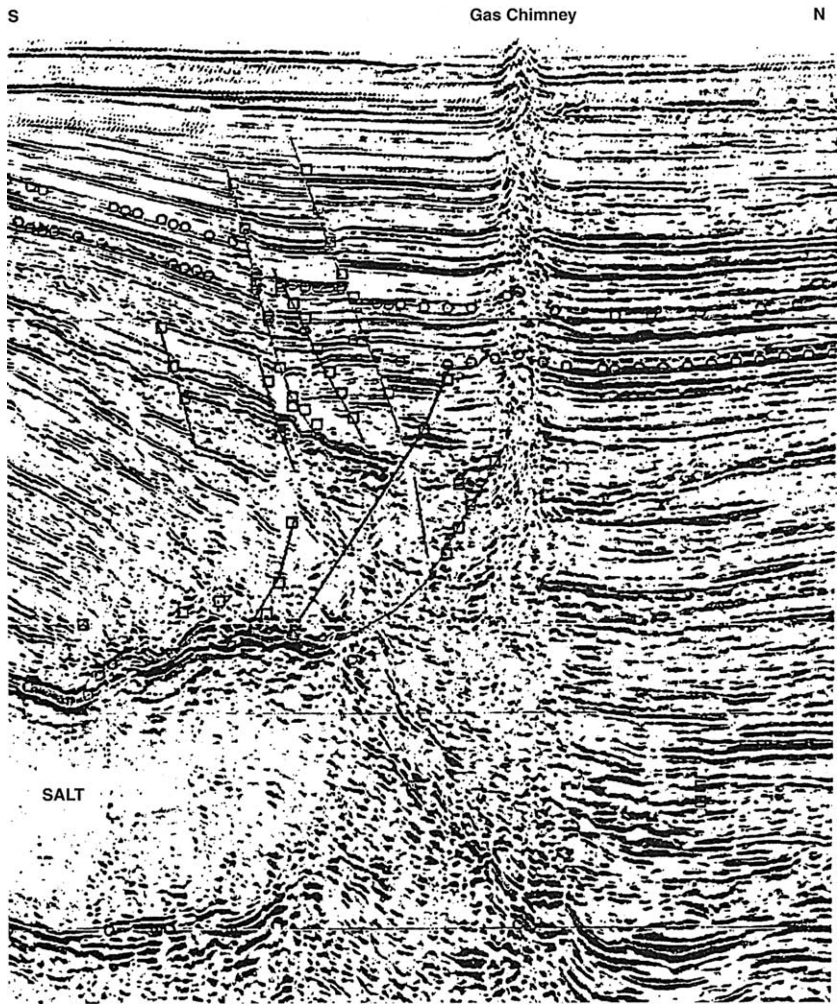

Fig. 3. A three-dimensional seismic profile of a gas chimney rising from depths greater than 15,000 ft (4573 m) up through Plio-Pleistocene sediments in the South Marsh Island area, offshore Louisiana. The gas plume is adjacent to a 7000-ft (2134-m) thick allocthonous Jurassic salt. The straight lines are faults, and the circles and boxes are cross-line interpretations of horizons and faults (from Hunt, 1996).

either forms a hydrate layer, if pressure and temperature conditions are appropriate (Kvenvolden and Rogers, 2005), or that it will reach the water column, where AOM is subordinate, and can be oxidized using oxygen, which yields more energy. In the latter case, macrofaunal seep communities with aerobic methanotrophic symbionts will dominate. For very high methane flux rates, bubble plumes form and carry the methane rapidly up through the water column. If this process allows significant methane ejection into about the top 100 m of the water column, a significant proportion of methane would escape biodegradation and be ejected into the atmosphere via surface air–sea mixing (Broecker and Peng, 1982).

Roberts and Carney (1997) describe three general patterns of seepage: (1) long-term seepage that produces giant carbonate mounds (commonly tens of metres high); (2) ongoing intermediate seepage rates that support extensive biological communities, carbonate crusts, and methane hydrates; and (3) very recent oil and gas ejections that produce huge (often a kilometer or more in diameter) mud volcano craters with no associated living biota. The absence of biota around one of these mud volcanoes is consistent with very recent crater formation. If recovery of biota around these 'cold seeps' after an eruption is analogous to the chemosynthetic communities around the more well-studied hydrothermal vents, then the absence of biota indicates that the mud volcano eruption occurred within the previous year. In one case, foramifera were found in the crater walls on the seafloor, suggesting that venting must have occurred from a depth of at least 15,000 ft (Whelan et al., 2001); this depth is estimated from data of Kohl and Roberts (1994), and seismic data from Coelho (1997). Carbonate associated with the older seeps is derived from degraded petroleum or biogenic gas as shown by light δ^{13}C values (typically −26 to −30‰). U/Th and δ^{14}C dating show that some seeps have been evolving for about the last 1800 years (Aharon et al., 1997). Similar occurrences of xenolithes carried from depth to the surface

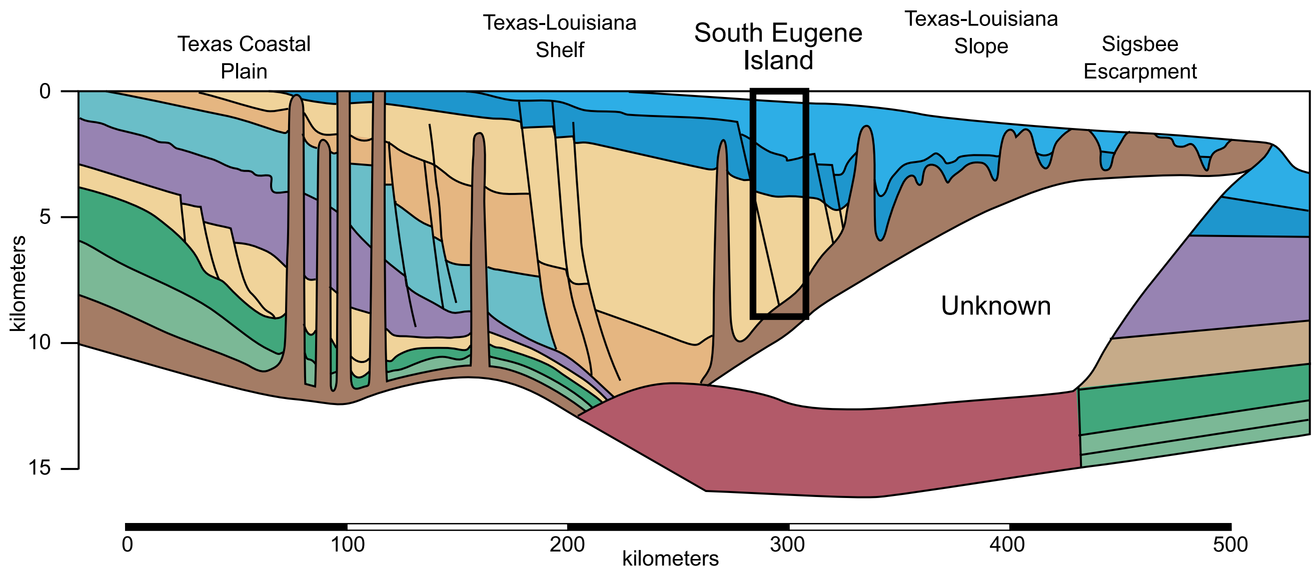

Fig. 4. Generalized subsurface profile of Gulf Coast transect where Miocene and younger sediments overlie salt (brown) and deeper, older 'unknown' formations.

have been described recently for Caribbean Trinidad mud volcanoes (Deville et al., 2003) which lie outside of the Gulf of Mexico in several hundred kilometer long mud volcano and shale diapir zones within the offshore Barbados–Trinidad compressional system.

At the southern end of the N–S transect studied in our work (Figs. 1 and 4), surface and subsurface manifestations of gas and oil movement in the Gulf of Mexico appear to be coupled. For example, gas bubbles are venting at the present time through fractures in a hydrate mound at Bush Hill, GC184, which overlie the Jolliet oil field in the northern Gulf of Mexico. Isotopic evidence shows this gas to be thermogenic and to be the primary gas source for surface gas hydrates found in the area (Sassen et al., 1999a, 2001a,b; Sassen, 2001). Thermogenic gas is the most viable primary chemosynthetic food source for the biological community that overlies the Bush Hill gas hydrate mound (Sassen et al., 1993a,b, 1998; Sassen and MacDonald, 1997; Lanoil et al., 2001; Sassen, 1997), although biogenic gas hydrates also occur (Sassen et al., 2002).

In some areas of the Gulf of Mexico, the results of vigorous gas seepage through subsurface sediments have had a dramatic effect on geophysical data, with seismic signals being smeared to considerable depths (e.g. Fig. 3). This widespread gas seepage may be responsible for the general lack of bottom seismic reflectors in the northern Gulf of Mexico despite the probable widespread occurrence of gas hydrates (e.g. Neurauter and Roberts, 1992, 1994; Roberts et al., 1999a,b; Roberts, 2001; Roberts and Carney, 1997; Milkov and Sassen, 2001a,b; Cooper and Hart, 2003). Slumps and slides on continental slopes are prevalent in many parts of the Gulf of Mexico, particularly in the Mississippi Canyon (e.g. Bouma et al., 1986) and, in some cases, could be triggered by gas. Gas venting, possibly associated with gas hydrates, has been proposed as one possible cause for a massive slide off the North Carolina coast, as discussed later in this chapter.

The Gulf of Mexico upper continental shelf contains many excellent examples of the various phenomena that accompany natural gas seeps in an oil and gas productive area. MacDonald et al. (1993) have published satellite photographs of oil slicks in the Gulf of Mexico that extend for miles over deep water areas where there is currently no oil production. The Gulf of Mexico gas seeps studied most completely to date are comprised primarily of thermogenic gas (Sassen et al., 2001a) although biogenic hydrates and seeps have recently also been reported to be widespread (Sassen et al., 2002). In other parts of the world, biogenic and thermogenic seeps have been described (e.g. Fig. 5). Among the world ocean bottom seeps, the Gulf of Mexico contains an unusually high proportion of thermogenic gas seeps.

3. Summary of effects of ocean bottom gas venting worldwide

The surface and subsurface gas-venting features described above are not unique to the Gulf of Mexico. The phenomena associated with these seafloor gas seepages are often not subtle and have now been observed in a number of areas of the world, as described in recent reviews (Judd, 1997; Hovland and Judd, 1988, 1992; Judd et al., 2002). Some of these areas, indicated on the map in Fig. 5, include the North Sea (Jensen et al., 1992; Judd, 1997; Hovland and Mortensen, 1999; Boe et al., 2000), the Berants Sea (Lammers et al., 1995), the Black Sea (Luth et al., 1999), the Eastern Mediterranean (Charlou et al., 2003),

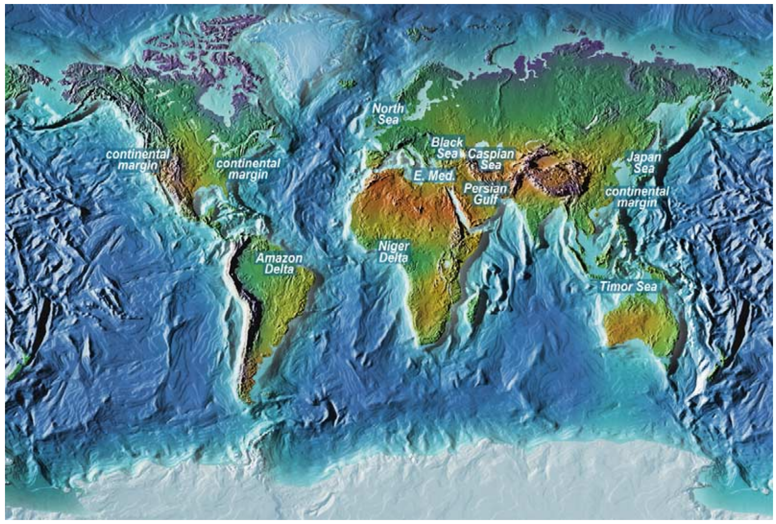

Fig. 5. Mixture of methane hydrates and petroleum accidentally dredged from the sea-bottom in the Canadian Cascadia margin.

the Persian Gulf (Uchupi et al., 1996), the Timor Sea and offshore Australia, (O'Brien et al., this volume), the Niger Delta (Hovland et al., 1997), Penobscot Bay, Maine, USA (Kelley et al., 1994), off western Ireland and north-west Australia (Hovland et al., 1994), and most continental margins (Fader, 1991; Judd et al., 2002; Clennell et al., 2000; Hovland, 2000; Hovland et al., 2001, 2002). The gas sources found for the majority of these areas have been described as containing predominantly biogenic gas (methane δ^{13}C values typically -50 to -65‰ and only traces of C2–C5 components; note, however, that these δ^{13}C ranges are not very diagnostic and could apply equally well to a low maturity thermogenic gas or a partially biodegraded initially very light biogenic gas). In a significant number of cases, both biogenic and thermogenic gas seepage and venting occur, as is the case in the Gulf of Mexico (Milkov and Sassen, 2001a,b, 2003a,b). For example, till very recently, the gas hydrate seeps found along the north western United States subducting Cascadian Margin were thought to be comprised primarily of biogenic gas (Kulm et al., 1986; Whiticar and Hovland, 1995; Carson et al., 1995). However, to the north, more than 1.5 tons of gas hydrates were recently accidentally dredged from the seafloor of the Canadian Cascadian Margin by some very surprised fishermen (Fig. 6). These hydrates were covered with oil, leading to the conclusion that they are associated with thermogenic petroleum and gas deposits.

Venting of this nature often occurs at continental margins and other locations where circulation between gas-containing and open ocean waters is not as restricted as is the case for the Gulf of Mexico (Fig. 5). Comparison of the Gulf of Mexico seeps with seeps worldwide suggests that the latter

Fig. 6. Map of occurrence of some of gas seeps described to date worldwide. New areas of seepage continue to be discovered.

are currently under-appreciated by the scientific community, even though they may be having significant effects on a number of important geological, oceanographic, and atmospheric processes (Judd, 1997; Judd et al., 2002).

Seeps and their fossil manifestations—'pockmarks' in the seafloor—also appear to be ubiquitous in many parts of the ocean floor, particularly in river deltas, which have rapid sedimentation rates, and on continental margins associated with subduction zones (Hovland and Judd, 1988; Hovland et al., 2002; Judd et al., 2002; Clennell et al., 2000). Where water depths are sufficient to provide high pressures and low temperatures, the upward-seeping gas commonly produces gas hydrate deposits at or just below the seafloor (Kvenvolden and Lorenson, 2001; Kvenvolden, 1993; Kvenvolden and Rogers, this volume; Buffett, 2000; Judd et al., 2002). These seafloor gas hydrates are very similar to those occurring in the Gulf of Mexico and are themselves commonly associated with seep gas, disrupted subsurface sediments, and chemosynthetic communities of organisms.

One of the more spectacular results of natural gas seepage are the mud volcanoes in Azerbaijan adjacent to the Caspian Sea (Fig. 7; Hovland and Mortensen, 1999), as well as numerous mud volcanoes on the seafloor of the Caspian Sea (Yusifov and Rabinowitz, 2003; Guliyev, 2003). Seismic evidence suggests that vertical subsurface gas movement to seafloor vents has occurred through narrow sediment 'pipes' from deeper gas sources. Similar vertical seismic and geochemical pipes have been described for North Sea (Løseth et al., 2003) and northeastern Atlantic seafloor gas seeps.

Carbonate mounds, or hydrocarbon seep lithoherms similar to those found in the northern Gulf of Mexico

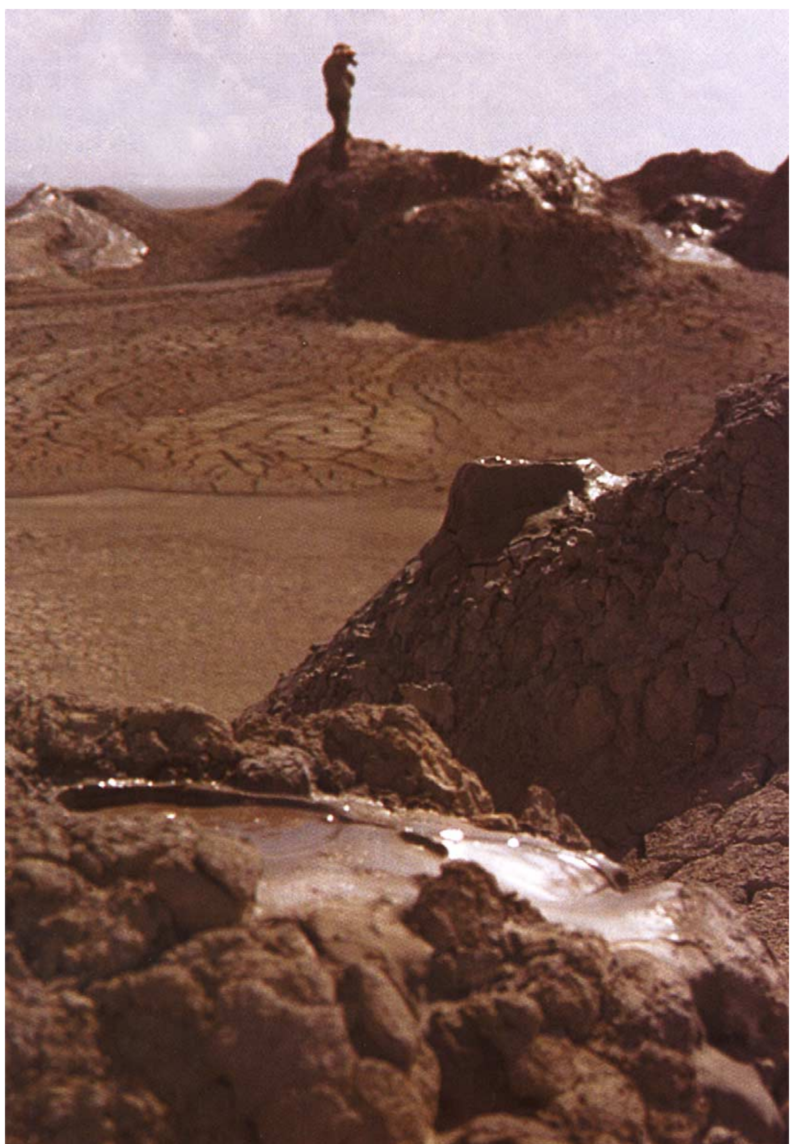

Fig. 7. Gas and water continuously rise up from one of numerous mud volcanoes in Azerbaijan (reproduced from Hovland and Mortensen, 1999).

Fig. 8. North Sea: a violet coral and various sponges living on carbonate mound of the Haltenpipe 'reefs' or hydrocarbon seep lithoherm (from Hovland and Mortensen, 1999).

and described above, are a common feature of 'old' venting areas in other parts of the world as well. For example, carbonate mounds attributable to active oil and gas seepage are very similar to coral reefs in appearance and occur over North Sea reservoirs at a water depth of about 400 m (Fig. 8; Hovland et al., 1998; Hovland and Mortensen, 1999; Hovland and Thomsen, 1997). The North Sea seepage is attributed to venting at the seafloor, where subsurface fractures outcrop at the top of ridges (Fig. 9; Hovland and Mortensen, 1999) in a manner similar to that found at the Bush Hill site in the Gulf of Mexico (Roberts et al., 1989, 1990a; Roberts and Carney, 1997; Roberts, 2001).

Venting through clay layers commonly results in the formation of a pockmarked seafloor as the venting gas is released into the water column (Fig. 9). These 'pockmarks', which were first documented worldwide in a classic book by Hovland and Judd (1988), are attributed to past seafloor venting, as are large subsurface gas chimneys and carbonate hard grounds or mounds on the seafloor similar to those found in the Gulf of Mexico (Roberts et al., 1989, 1990a,b; Roberts and Carney, 1997; Roberts, 2001).

A spectacular ancient example of a seafloor carbonate deposit is shown in Fig. 10 where a huge carbonate mound in the middle of the Sahara desert is attributed to a fossilized gas seep (Wendt et al., 1997). This ancient carbonate mound is believed to have formed initially from seafloor gas seepage at an estimated water depth of 400 m, similar to the present-day water depth of the North Sea coral reef-like mound shown in Fig. 8 which is also thought to be fed from hydrocarbon seepage from the underlying North Sea petroleum reservoirs (Hovland and Mortensen, 1999).

It has been proposed that gas seepage may contribute to slope sediment destabilization leading to the huge underwater mudslides commonly observed on continental slopes (e.g. Tucholke et al., 1977; Thiery et al., 1998; Clennell et al., 2000; Roberts, 2001). A dramatic recent example has been documented on the eastern continental slope off North Carolina (Fig. 11; Driscoll et al., 2000) where methane-rich plumes and hydrates have also been documented (Paull et al., 1995). It has been postulated that the slide (Fig. 11) is large enough to cause a tidal wave if it happened today. Note the small dimples (a and b) at the top of the slope in Fig. 11; these appear to be pockmarks, or depressions, which are commonly caused by fluid discharge (gas or liquid) to the seafloor, similarly to those documented in Hovland and Judd (1988). Scripps and Woods Hole groups have recently mapped methane seepage associated with one of the pockmarks in Fig. 11 (Driscoll and Camilli, unpublished results). More work is required to find out

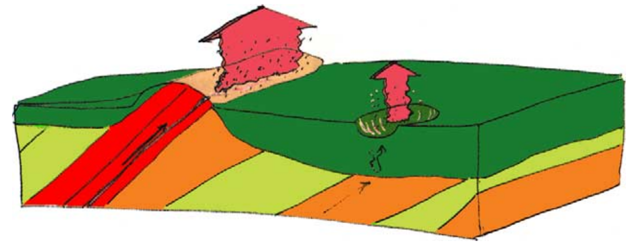

Fig. 9. A sketch suggesting how light hydrocarbons, methane, ethane, and butane (natural gas) seep upward along dipping sedimentary rock layers and through the seafloor in the North Sea Haltenbanken area. Seepage on left occurs through ridge; seepage on right through a layer of clay, causing seafloor pockmark to form (from Hovland and Mortensen, 1999).

Fig. 10. Algerian Sahara: fossilized carbonate mound, a giant coral reef-like structure, previously buried in sand. When living, they existed at estimated depth of about 400 m, similar to Norwegian carbonate 'reefs'. A German expedition found that the carbonate mounds formed along the edge of an extensive sedimentary basin, with large subsurface faults beneath the carbonate mounds. The expedition vehicle can be seen in the foreground (Wendt et al., 1997; from Hovland and Mortensen, 1999).

whether or not sufficient gas is present, and could be vented, to cause a slope failure at this location. An alternative mechanism of slope failure has been proposed by Dugan and Flemings (2000, 2002), which involves sediment compaction, overpressuring, and dewatering possibly enhanced by offshore ground water movement.

4. Gulf of Mexico—subsurface effects of gas movement

The Woods Hole research on the Gulf of Mexico oil and gas seeps began with the finding of rapid (less than 10 year) changes in oil compositions in EI330 oil reservoirs, toward the southern end of the N–S transect in Fig. 1; these changes do not appear to be attributable to production effects (Schumacher, 1993; Whelan, 1997; Whelan et al., 1994, 2001). Further investigation showed that the oils in this stacked reservoir sequence were being altered by upward migration of large volumes of gas in a process cornell workers defined as 'gas washing' (Meulbroek et al., 1998) and envisioned as multiple volumes of gas streaming into and equilibrating with oil in reservoirs (Fig. 12), followed by the gas phase continuing to stream upward. The resulting fractionations of *n*-alkanes observed in these 'gas-washed' oils have been successfully modeled using multiple sequential volumes of gas coming from deeper intervals which equilibrate with the oil, and then continue an upward path into shallower reservoirs (Fig. 12). This process, which was first studied in detail for the EI330 oils (Meulbroek et al., 1998), causes the lowest molecular weight hydrocarbons to be swept out of the oil preferentially and enriched in the moving gas stream so that shallower reservoirs become enriched in progressively lighter hydrocarbons (Fig. 12;

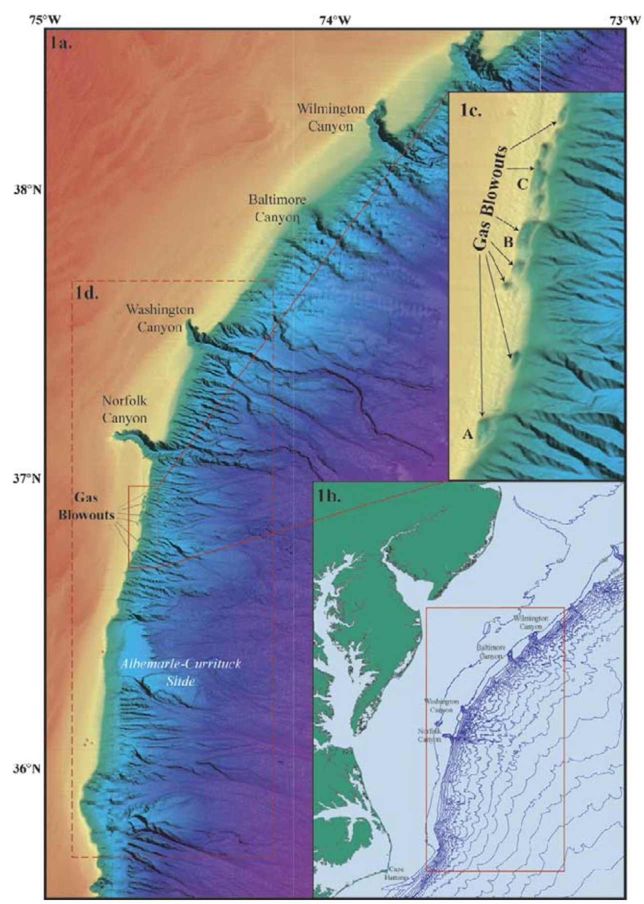

Fig. 11. Massive slide on continental slope, offshore North Carolina. Note pockmarks on upper shelf edge (a and b), which may be indicative of gas seepage at the top of the slope (from Driscoll et al., 2000). Also indicated is a slide/slump (c), postulated to have been triggered by past gas flow. Inset shows location of this area as just one of a number of similar features along US east coast where the potential gas-triggered slides also may be present.

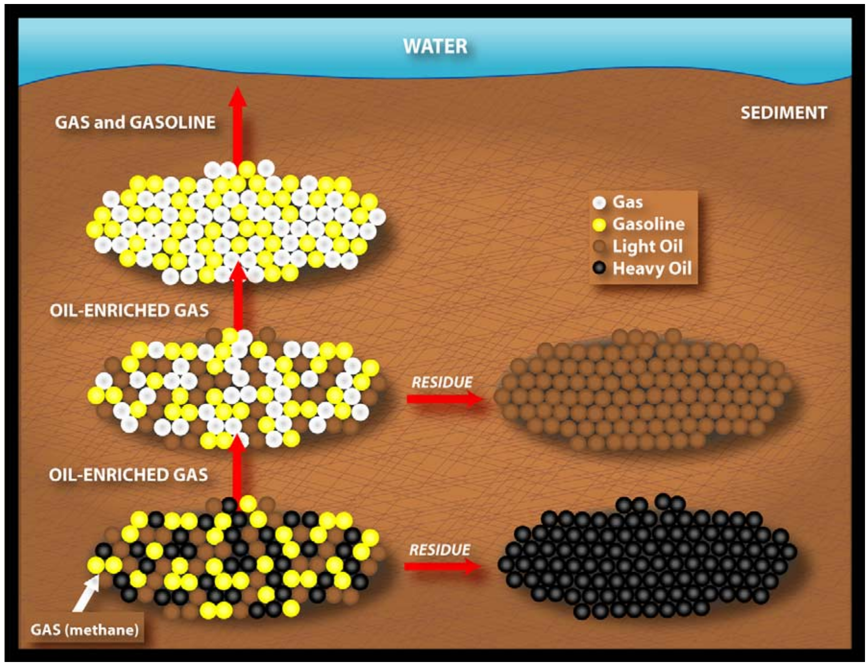

Fig. 12. Schematic diagram of gas washing process.

Losh et al., 2002a,b). Gas washing differs from evaporative fractionation, described by Thompson (1988), which only involves a single stage of gas equilibrating with and separating from oil. Gas washing produces a characteristic hydrocarbon signature different from that produced by water washing—which preferentially removes aromatic hydrocarbons (Hunt, 1996)—and from biodegradation—which preferentially destroys the lowest molecular weight *n*-alkanes first (Palmer, 1994; Whelan et al., 1994, 2001). Meulbroek et al. (1998) demonstrated that gas washing produces, in the absence of these and other complicating factors—including source and oil maturity changes—a characteristic shape for the gas chromatography (GC) homologous *n*-alkane pattern in the oil (Fig. 13). This shape can be used, along with the initial wellhead pressure and temperature conditions in the reservoir, to calculate: (1) the number of volumes of gas which have equilibrated with each oil in the gas washing process; (2) the volume and composition of the oil remaining; and (3) the volume and composition of the oil enriched gas that has moved upward into each overlying reservoir. Losh et al. (2002a) successfully applied a modification of the procedure using only the C_{10+} *n*-alkanes to determine that most oils in the N–S transect shown in Fig. 14 have undergone significant gas washing, with the effect being strongest to the north (30 volumes of gas have washed each volume of oil at Tiger Shoals, the wells furthest to the north) and gradually weakening toward the south (with about 3 volumes of gas having washed EI330 oils toward the south, Fig. 14). There is no evidence that the GC184 oils furthest to the south have experienced any appreciable gas washing.

The relative timing of gas washing and the associated gas movement along the N–S transect in Fig. 4 can be estimated by also considering other processes which might be responsible for these progressive changes in composition, including biodegradation, source changes, and maturity (data from GRI report: Whelan and Eglinton, 2002). Throughout the transect, less mature oil is mixed with more mature gas, as described previously for EI330 (Whelan et al., 1994, 1995 and as discussed at length in Losh and Cathles, 2002). Recent modeling, combined with the organic geochemical data, shows that oil generation probably took place in the Miocene from rocks currently buried directly beneath their present-day Pleistocene reservoirs (Coelho, 1997; Erendi, 2001; Cathles et al., 2004, 2003; Cathles and Losh, 2002). Therefore, oil generation probably occurred considerably before the time of formation of the present-day Pleistocene reservoirs and was initially trapped beneath salt sheets, as shown schematically in Fig. 15.

The influence of source changes is considered to be minimal. Hopane and sterane biomarkers are remarkably similar for the shallower shelf oils to the north (SMI9) and the deeper water oils at the south (GC184,) even though there appears to be an enhanced contribution from younger Eocene oils to the north and older Cretaceous and Jurrassic oils to the south. Many of the oils to the north of the transect appear to be mixed with Tertiary sourced oil, as shown by slightly higher amounts of dibenzothiophene/phenanthrene which increases in oils to the south of the transect (Fig. 16a). Increases in this ratio are indicative of an increased source input from higher sulphur more marine kerogens (Hughes et al., 1995). In addition, the proportion of oleanane, diagnostic of input from source rocks containing higher plant input, simultaneously increases to the north

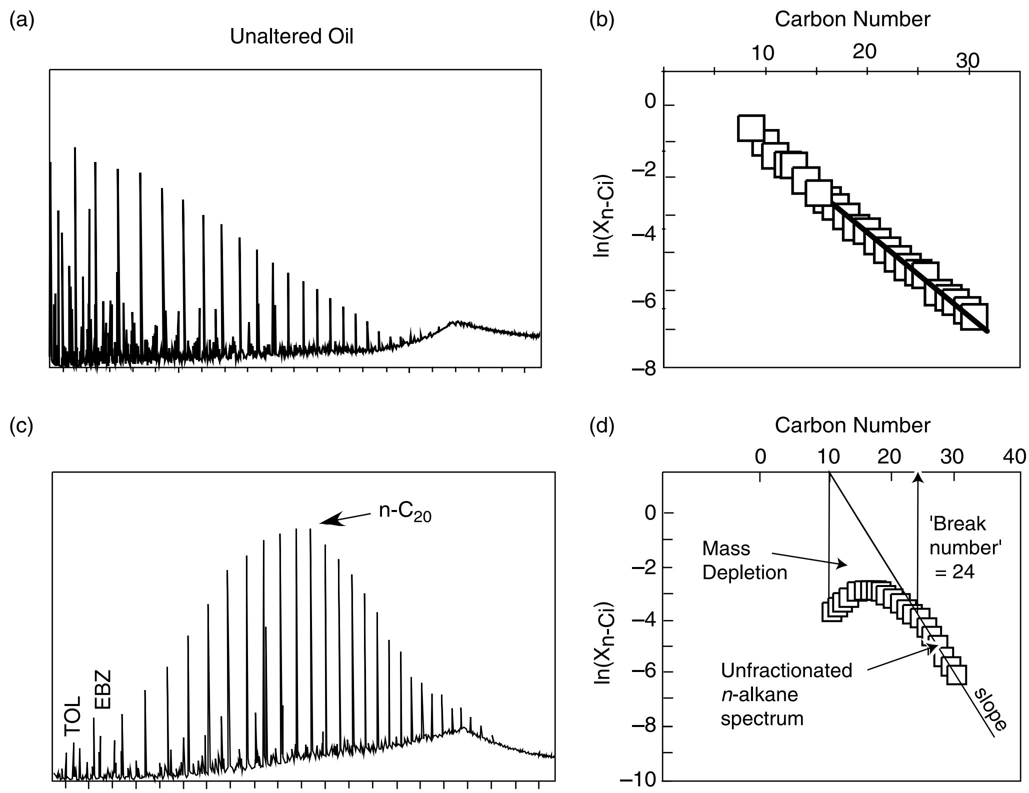

Fig. 13. (a) Typical C_{10+} *n*-alkane pattern for Gulf Coast oil that has not undergone gas washing. (b) The relative amount of each *n*-alkane decreases exponentially with increasing carbon number (from Losh et al., 2002a,b). (c) Same as (a), for oil that has experienced gas washing (from Losh et al., 2002a). (d) Relative amount of each *n*-alkane versus carbon number for oil in (c). The break number, slope, and mass depletion are used to estimate the number of volumes of gas which have 'washed' a particular volume of oil.

(not shown) as would be expected if sourced from the shallower terrigenous Tertiary rocks in this area, but not from the older and more marine Jurassic and Cretaceous rocks. A similar trend results when the ratio of oleanane to C_{30} hopane is plotted (not shown). 30ββ Hopane is commonly used as a marker for input of marine organic matter (Peters and Moldowan, 1993).

The differences in most biomarkers are quantitatively minor, even though they are useful for distinguishing at least two different oil families. IRGCMS analyses of individual C7–C10 components (Fig. 16b) also reveal two end members of a series. SMI9 oils are statistically distinct from GC184 oils (Fig. 16b). This similarity in source of a majority of oils in the transect probably originates from the predominant generation from marine sourced kerogen.

Evidence for the geologically dynamic nature of reservoirs within the transect is reflected in the highly variable *n*-alkane hydrocarbon fluid compositions throughout the transect, with different sands producing a variety of admixtures of gas, condensate, and oil. In addition, at EI330 low molecular weight, highly biodegradable compounds (i.e. light *i*-alkanes) are commonly superimposed over the 'hump'—or unresolved complex mixture (UCM)—of a typical biodegraded oil background (Whelan et al., 1994, 2001). This pattern is very common throughout the transect and also occurs widely throughout the Gulf Coast and has been observed in other areas as well (e.g. Dzou and Hughes, 1993; Holba et al., 1996; Curiale and Bromley, 1996a,b). Many of the oils at the southern end of our transect are similar to the EI-330 oils in having the lightest and most volatile—and the most highly biodegradable—*n*-alkanes as the most predominant C_3–C_{10} hydrocarbon fraction. This pattern of unbiodegraded *n*-alkanes being superimposed over a biodegraded background is interpreted as indicating continuous replenishment of the very rapidly biodegraded *n*-alkane fraction by continuous upward streaming of lighter oil components by the gas washing process. In any petroleum reservoir having a temperature of less than 60 °C, and in some cases up to 80 °C, as well as the proper nutrients, anaerobic biodegradation is probably a ubiquitous and ongoing process. Therefore, the presence of unbiodegraded oil occurring together with a biodegraded background has been attributed to extant hydrocarbon injection occurring on time scales of less than the rates of biodegradation—typically weeks to a few years under in situ reservoir conditions at higher pressures (Jannasch and Taylor, 1984; Rueter et al., 1994; Stetter et al., 1993; Gibson, 1984; Singer and Finnerty, 1984). Anaerobic sulphate reducing microbes of a moderately thermophilic nature (60 °C) have been isolated. These consortia utilize *n*-alkanes from C_6 to C_{16} as substrates (Rueter et al., 1994) with the best growth occurring in the C_8–C_{12} range. This is

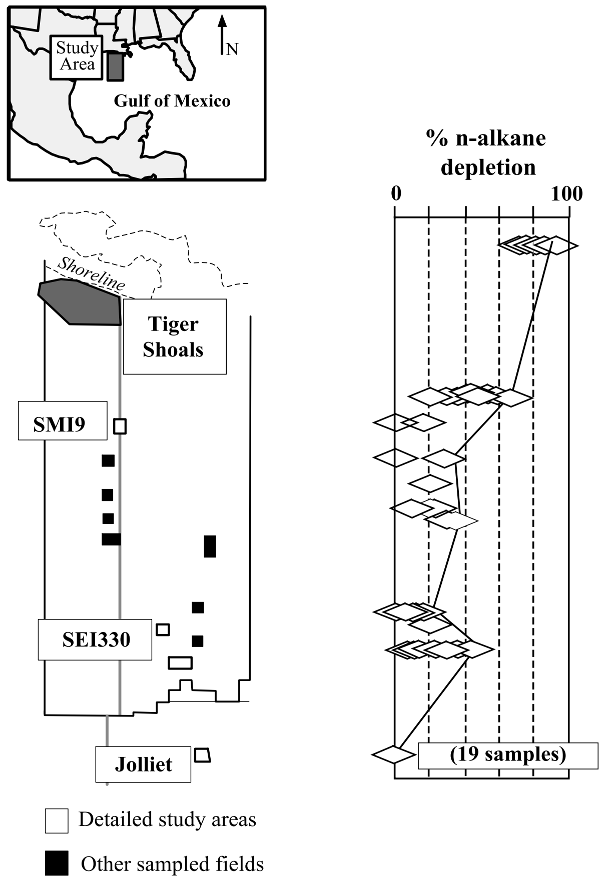

Fig. 14. Percent of C_{10+} depletion for Gulf Coast oils in study transect indicated in Figs. 1 and 4 assuming that maturity and origin for all oils is the same as is the case for these oils (see text).

the carbon range that is commonly the most depleted in partially biodegraded Gulf Coast oils (Whelan et al., 2001). A recent review of biological activity in deep subsurface petroleum reservoirs proposes that the rate of supply of nutrients is a critical control on the rate of petroleum biodegradation in these deep reservoirs (Head et al., 2003).

Losh et al. (2002a) conclude that the GC184 oils have not yet been appreciably altered by gas washing. However, these oils do show the co-occurrence of degraded and non-degraded *n*-alkanes within the same reservoir, suggesting active light hydrocarbon movement (Whelan and Eglinton, unpublished data).

The overall scenario that is developing is of rapid and recent upward movement of thermogenic hydrocarbons, which first preferentially alter oils in shallow reservoirs and are then vented through the sediment–water interface to produce the characteristic seep features discussed previously and summarized in Fig. 2.

A preliminary working model of oil–gas generation–migration consistent with both the surface and subsurface geochemical modeling, as well as observational data throughout the transect, gives a very dynamic picture of the gas and oil movement, which has caused significant alteration of the oils to the north and is just beginning to affect the oils toward the south. After initial filling of deeper reservoirs beneath a salt layer, further rapid sediment deposition caused the salt to flow, thereby forming holes in the salt and enabling trapped oil to migrate rapidly upward through these holes and into the overlying productive reservoirs (Fig. 15). This process is probably still in progress at the present time in southern portions of the transect, including EI330 and GC184 (Erendi, 2001; Sassen et al., 2001a,b; Cathles, 2004). This scenario is consistent with the maturity data for the transect which show an overall gradual change from more mature to the north (SMI9, MPI-1 = 1.1) to less mature in the south (GC184, MPI-1 = 0.9, Fig. 16). Superimposed on this general trend are 'hot spots' of higher maturity oil which are possibly interpreted as indicating zones of higher heating where kerogen and oils were, until very recently, trapped beneath salt in deeper sediments.

5. Relation of surface and subsurface gas migration in the Gulf of Mexico

The most general and surprising conclusion of our research on oils and gases in the Gulf of Mexico N–S transect has been the rapid and dynamic nature of the whole oil–gas generation–migration system in this area. This pervasive gas movement at various times and various places, both over geologic time and continuing up to the present time, directly affects the style of seepage overlying various parts of the transect. The extensive and older gas migration system to the north has given rise to the isotopically light carbonate pavements and mounds on the seafloor across much of the continental shelf. The sediments overlying EI330 at the shelf edge also contain carbonate pavements and apparent signs of active chemosynthetic communities fed by underlying gas. At the southern end of the transect, GC184 reservoirs do not yet show evidence of alteration of oils in reservoirs, but do show strong evidence of active present-day gas migration through surface sediments. This gives rise to gas bubble venting though fractures, surface sediment gas hydrates, chemosynthetic biological communities, and mud craters and volcanoes, as discussed previously.

Similar observations have been made at a number of other seafloor hydrate deposits, including some in much deeper water, such as the Cascadian Margin (Suess et al., 2001). These observations suggest a very dynamic gas flow system in some cases where gas hydrates are only the ephimeral manifestation of a much larger gas flow system, as previously proposed by Dickens (1999, 2001a,b). At the Bush Hill GC184 site, Chen and Cathles (2003) compared the size of present-day hydrate deposits with the calculated rate of gas delivery using basin and fluid flow modeling. It was concluded that gas is being actively delivered to the hydrate at the present time and that 90% of this gas is being actively vented to the ocean, while only 10% is trapped in the hydrate. Data of Sassen et al. (2001a) were used to show

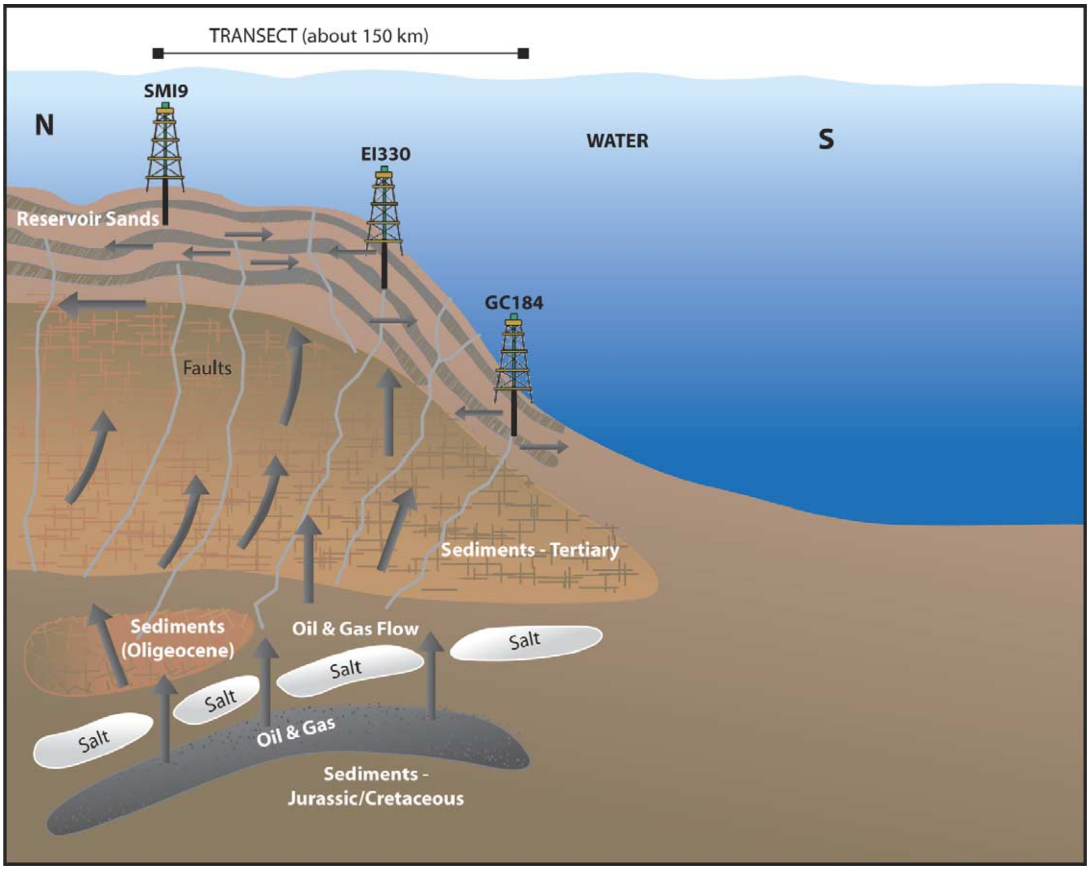

Fig. 15. Gulf Coast transect: general schematic diagram of subsurface oil and gas flow consistent with geochemical, geological, and fluid flow modeling (Whelan and Eglinton, 2001).

that isotopic properties of the upward streaming gas and of the gas hydrate are identical, making separate gas sources for the hydrate and venting methane unlikely.

6. Can surface seeps be used to explore for subsurface oil? Perspective from a mass balance point of view

The results described above suggest a potentially substantial difficulty in using surface seeps to explore for subsurface oil; a large ubiquitous 'background' of gas seepage moving continuously through the subsurface may, in some areas, make utilization of seeps in exploration very confusing. In the absence of ancillary geochemical, geological, and geophysical data, the presence of this background gas makes difficult the determination of when and how a surface gas seep is related to an economic subsurface petroleum accumulation. The magnitude of the problem can be appreciated by considering that, worldwide, less than 2% of generated gas and oil is ever found in a producible reservoir. Of the remainder, about half is vented into the ocean, while the other half remains in the subsurface (Whelan et al., 2001, estimated using data from Hunt, 1996). Modelling in the area of the Gulf of Mexico shown in Fig. 14 indicates that less than 30% of the generated hydrocarbons are retained in the subsurface in this area (Cathles, 2004). A significant portion of this 'non-reservoir' gas may be available for the processes described here that require a continuous gas stream, including gas washing of oils, gas venting through surface sediments, gas hydrate formation, and the feeding of chemosynthetic biological communities.

Where is all this gas coming from? We suggest that ubiquitous thermogenic and biogenic methane generation processes, which occur in most organic carbon-containing sediments worldwide, are responsible. Thermogenic methane generation is ubiquitous in sediments having as little as 0.5% total organic carbon and which are exposed to temperatures of 80 °C and higher (Hunt, 1996). Similarly, methanogenesis (or anaerobic biogenic methane generation) is almost ubiquitous in sediments having as little as 0.3% total organic carbon and has been observed to sub-bottom depths of at least 800 m sub-bottom (Parkes et al., 1994). Two important and abundant starting materials for both processes, kerogen—comprising the bulk of the TOC pool of most sediments—and carbonate carbon, represent two of the largest carbon pools on earth (Kvenvolden, 1993). Therefore, it would not be surprising if some portion of this 'background' gas generation and migration is confusing our interpretations of surface seep data.

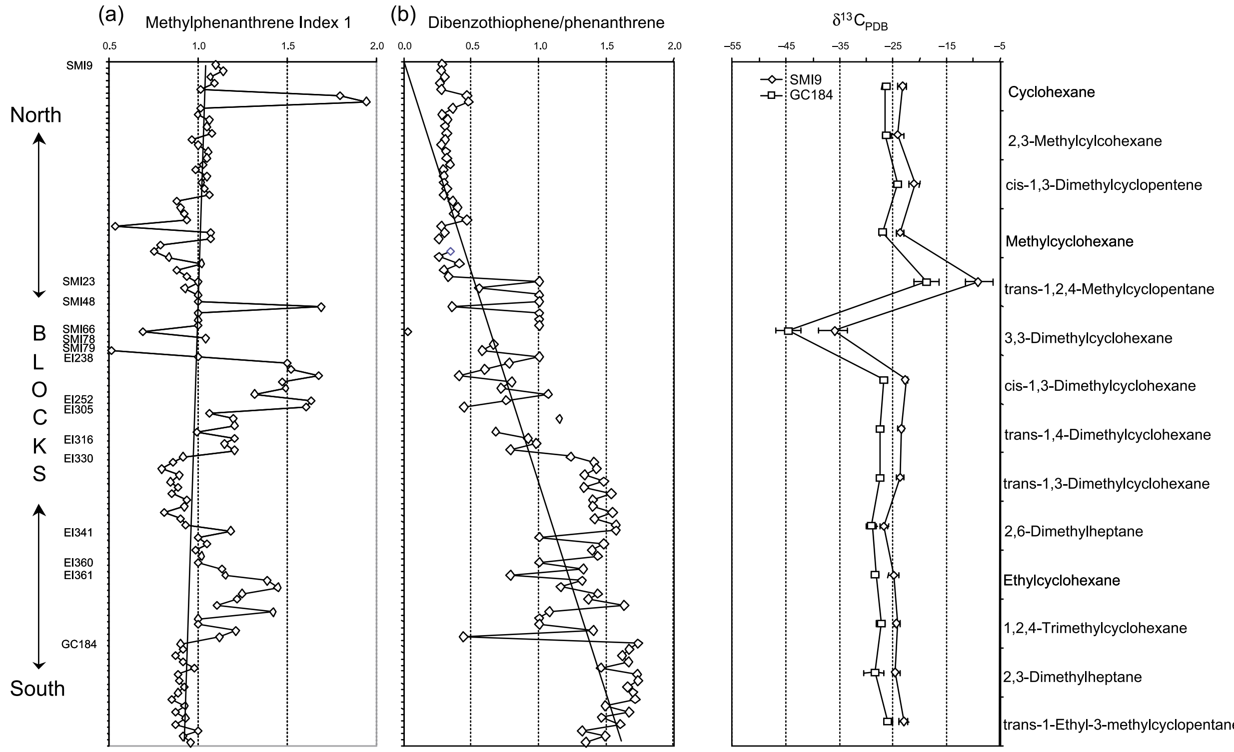

Fig. 16. Gulf Coast transect oil source and maturity indicators for wells toward the north, SMI9, and proceeding to GC184, furthest to the south. Each point indicates data for one well in the transect. (a) Methyl Phenanthrene Index I, a maturity indicator as defined by Radke (1988). Note the general slight increase in maturity of oils to the north with anomalous zones of higher maturity: these are 'hot spots' occurring at a number of EI wells in the center of the transect. These hot spots are postulated to represent upward injection of more mature oils from deeper sections through holes in overlying salt layers. Also shown is a source indicator, dibenzothiophene to phananthrene, which tends to increase with increasing marine (that is marine carbonate or siliceous ooze, non-clay mineral) source contribution (Hughes et al., 1995). This ratio increases toward the south of the transect indicating a larger marine source contribution to southern-most wells. (b) IRGCMS results for suite of C6 and C7 hydrocarbons. The average δ^{13}C values and standard deviations are shown for oils from seven wells from the northern-most SMI9 field and eight wells from the southern-most GC184 field.

In dynamic gas migration systems such as that described here for the Gulf of Mexico transect, an actively charging economic reservoir could be confused for an old leaky non-economic one. The specific seafloor manifestations of seepage described above can help in distinguishing these two possibilities. Furthermore, if the gas streams which carry underlying oil components upward are widespread, then it may be possible to utilize the complex seep hydrocarbon signatures in much smarter ways than has previously been possible.

The research presented here suggests a general way that molecular hydrocarbon seep data could be used to gain a more quantitative picture of gas flow through the subsurface using procedures similar to those described here for elucidating the degree of subsurface gas washing (Figs. 13 and 14).

In conclusion, surface seeps are not a 'magic bullet' for petroleum exploration. Their full potential can only be realized if individual compounds in seeps can be separated and quantitated, and their signatures distinguished from those of sediments surrounding the seeps. In addition, diagnostic molecular seep information related to subsurface accumulations must be interpreted in the broader context of all available geochemical, geological, geophysical, oceanographic, and atmospheric data available for a particular area. The first step might be to use seep data together with initial geophysical and well data to determine whether or not a particular 'petroleum system' is relatively closed, as is currently generally assumed, or if it is more of a moving stream similar to that envisioned for the Gulf of Mexico transect gases in Figs. 2 and 15. This distinction is important in deciding whether a seep represents an actively charging economic reservoir, an old leaky non-productive reservoir, or some other state lying between these two extremes.

7. Conclusions

Evidence for the dynamic nature of gas movement in both surface and subsurface sediments through a N–S transect in the northern Gulf of Mexico has been presented. Some of the effects discussed include:

- gas hydrates
- gas bubble streams issuing through fractures and faults in the seafloor, even in deep water

- pockmarks and craters in the seafloor
- mud volcanoes
- carbonate pavements
- large oil slicks that cover large areas of the ocean having no oil production
- prolific chemosynthetic communities of organisms supported by hydrocarbons and sulphur as the primary food sources
- evidence of massive disruption of subsurface sediments
- alteration of some subsurface oils and gases on short time scales
- significant alteration of oils in reservoirs by upward gas movement and gas washing

These processes are not confined to the Gulf of Mexico; examples are presented to show that similar phenomena occur in many areas worldwide with new ocean bottom seep areas continuing to be discovered. These processes may be so widespread that they lead to confusion in the utilization of surface seeps to explore for subsurface economic petroleum accumulations. A review of these processes as they occur in the Gulf of Mexico is presented, along with a discussion of the close inter-relationship of seeping gas and its associated biota, gas flow through and around petroleum reservoirs, gas hydrates, and observations of ocean-floor seep associated biota.

The general relationship between the nature of the surface seep features and the relative amount and timing of gas movement through subsurface oils is described for a N–S transect in the northern Gulf of Mexico. Large volumes of gas can be involved; as much as 30 times the oil volume was estimated for some reservoirs in the transect. The degree of gas washing appears to be reflected in the general nature of gas seep features in surface sediments overlying these reservoirs. The reservoirs to the north which have experienced the most gas washing are overlain by carbonate pavements characteristic of older 'fossil' seeps, while complex chemosynthetic communities, surface gas seeps, and active gas bubble discharge areas increase gradually to the south, reaching a peak over the southernmost Green Canyon reservoirs which currently show little or no evidence of alteration of reservoir oils by gas washing. It is proposed that these features of present-day gas seepage overlying Green Canyon reservoirs are diagnostic of a much earlier stage of gas generation and movement, possibly diagnostic of active present-day reservoir charging.

It is suggested that the relationship between surface seep oils and subsurface petroleum plumbing within this N–S transect in the northern Gulf of Mexico, far from being an anomaly, can serve as a natural laboratory for other seep–reservoir systems worldwide. Future work should focus on utilizing the quantitative geochemical data from specific organic compounds in the seep—along with the geology, geophysics, and biology—in order to gain more information about the nature of any of the underlying reservoirs with respect to oil quality, timing of reservoir filling, and probable degree of alteration by gas washing, water washing, and biodegradation.

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