

Marine cold seeps and their manifestations: geological control, biogeochemical criteria and environmental conditions

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Abstract Characteristics of cold seeps at different geologic settings are the subject of this review primarily based on results of the Research Consortium SFB 574. Criteria are drawn from examples on the erosive convergent margin off Costa Rica, the accretionary margin off Chile supplemented by examples from the transform margin of the Gulf of Cadiz and the convergent Hikurangi margin off New Zealand. Others are from well-studied passive margins of the Black Sea, the Gulf of Mexico, the eastern Mediterranean Sea and the South China Sea. Seeps at all settings transport water and dissolved compounds to the ocean through the seafloor by different forcing mechanism and from different depths of the submerged geosphere (10s of meters to 10s of km). The compounds sustain oasis-type ecosystems by providing bioactive reductants sulfide, methane and hydrogen. Hereby, the interaction between fluid composition, flux rates and biota results in a diagnostic hydrocarbon–metazoan–microbe–carbonate association; currently, well over 100 active sites are known. The single most important reaction is microbially mediated anaerobic oxidation of methane with secondary reactions involving S-biogeochemistry and carbonate mineral precipitation. Seep fluids and their seafloor manifestations provide clues as to source depth, fluid–sediment/rock interaction during ascent, lifetime and cyclicity of seepage events but less so on the magnitude of return flow. At erosive margins, Cl-depleted and B-enriched fluids from clay dehydration provide criteria for source

depth and temperature. The upward material flow generates mud volcanoes at the seafloor above the projected location of dehydration at depth. At accretionary margins, fluids are derived from more shallow depths by compaction of sediments as they ride on the incoming oceanic plate; they are emitted through thrust faults. At highly sedimented margins, organic-rich and evaporite-containing strata (when present) determine the final fluid composition, by emitting characteristically gas hydrate-derived methane, brine-associated non-methane hydrocarbons or leached elements and their isotopes (Li, $\delta^7\text{Li}$, B, Ba) from host sediments. Smectite–illite transformation and associated Cl-depletion from release of interlayer water is a pervasive process at these margins. Rare earth element pattern in conjunction with redox-sensitive metals retained in seep carbonates indicate whether or not they precipitated in contact with oxic bottom water or suboxic fluids; clear environmental characterization, though, currently remains inconclusive. More deeply sourced fluids as in transform margins may be characterized by their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from interaction with oceanic crustal rocks below. Quantification of flow and reliable estimates of total volatile output from fore-arcs remain a challenge to seep research, as does understanding the role of geologically derived methane in the global methane cycle.

Keywords Seep carbonates · Fore-arc fluids · Global seeps · Biota–carbonate association · Active margin fluids · Passive margin seeps

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Introduction

Transfer from the geosphere to the exosphere (biosphere, hydrosphere, atmosphere) is a fundamental process of the Earth's material recycling. Many sub-cycles and pathways

are active on different timescales and moving different magnitudes of material. Plate boundaries, volcanic arcs and continental margins are the geologic settings that largely determine this transfer process. A unique pathway of material transfer is by seepage of volatile elements and compounds from marine cold seeps and from mud volcanoes when lithic material and fluids are transported together. Geologic settings, biogeochemical reactions and biologic activities are uniquely interconnected to generate the seep products. These come in many shapes and sizes from which environmental conditions, the history and extent of fluid–sediment reactions may be derived. The magnitude of recycled material through seeps is poorly known despite the easily recognizable and mappable seep manifestations. This issue remains a challenge to seep research at subduction zone settings, as does the role of the geologically derived methane in the global carbon cycle (Boetius and Wenzhöfer 2013).

Seeps sustain unique oasis-type ecosystems at the seafloor, here referred to as *the hydrocarbon–metazoan–microbe–carbonate association*. They occur globally along active margins driven by plate convergence and along passive margins by sediment loading and by differential compaction related to vertical tectonics (Fig. 1). Seeps

characteristically flow more slowly than hydrothermal vents and are usually at ambient seafloor temperature, as the terminology implies. More vigorously flowing seeps may show elevated temperatures as may active mud volcanoes. Long-standing objectives of seep studies have been the quantification of water and carbon transfer, characterization of source depth, and the role of seep transport in global element recycling. These were part of the overarching objective of the Research Consortium SFB 574 by the German Science Foundation entitled: “Volatiles and Fluids in Subduction Zones” (Wallmann 2001; Jarrard 2003; Rüpke et al. 2004; Scholl and von Huene 2007; Freundt et al. 2014). Global geologic settings provide an enormous range of depth levels in the Earth’s crust for fluid generation. Seeps range for example from effluents of shallow groundwater aquifers, underlying shelves of a few 10s of meters, to waters expelled through oceanic fore-arcs generated 10s of km below from underlying tectonic plates. On passive margins, the nature and thickness of the accumulating sediment package determine seepage and products variously consisting of mud volcanoes, pockmarks, brine lakes but dominantly of authigenic carbonates. They form above rapidly accumulating, organic-rich sediments, deltaic aprons, hydrocarbon reservoirs or buried evaporites. Return

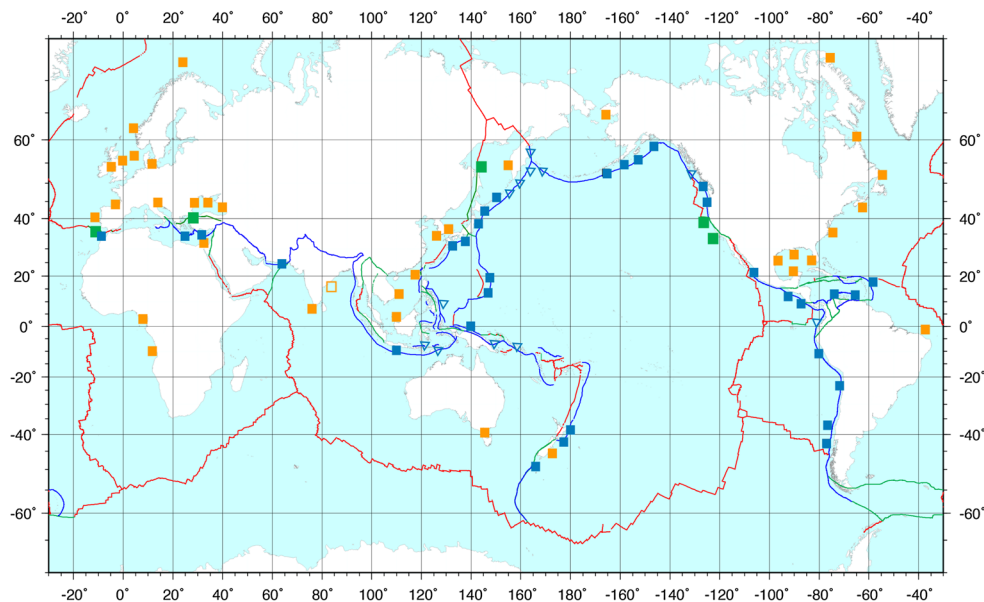


Fig. 1 Global cold seeps. Seep locations with hydrocarbon–metazoan–microbe–carbonate characteristics; active margins sites (blue), passive margin sites incl. groundwater seeps (orange); sites at transform margins (green). Distribution based on first seep location maps by Campbell (2006) with site references. New sites are from Jeong et al. (2004), Loncke et al. (2004), Olu-Le Roy et al. (2004, 2007), Judd et al. (2007), Mastarlerz et al. (2007), Hovland (2007), Han et al. (2008), Sahling et al. (2008), Geli et al. (2008), Hilario and Cunha (2008), Sellanes et al. (2008), Pierre and Fouquet (2007), Niemann et al. (2009), Bayon et al. (2007), Iglesias et al. (2010), Gracia

et al. (2010); dead seep clam site off India (open square) from Collett et al. (2008). Sites based on dredged tube worms (open triangles), mostly at deep-sea trenches, are from Ivanov (1963) prior to recognition that seep communities at plate boundaries are sites of hydrocarbon seepage. Updates of new site locations and descriptions are in: Garcia-Gil and Judd (2007), Bohrmann and Jørgensen (2010), De Batist and Khlystov (2012), Pierre et al. (2014). Maps of global distributions of seep biota can be found in: Krylova and Sahling (2010), German et al. (2011)

flow at active margins is generally more deeply sourced than at passive margins. Characterization cannot be based on margin tectonics alone, however, because reactions with host materials overprint the seep fluid composition during upward flow and the formation of the resulting seep products.

The seep characteristics at different geologic settings are the subject of this review. New knowledge gained is highlighted as it relates to the lifespan of seeps, source depth of fluids, impact of host sediment and characterization of the biogeochemical environment. Speculation on future research concludes the contribution; e.g., reconciling and improving estimates of volatile outflows from fore-arcs, comparing approaches best taken to advance understanding of ancient seeps, and continuing to develop proxies for environmental characterization. The goal is to present a worldwide view of seep studies as currently documented in several special issues (Zhang and Lanoil 2004; Bohrmann and Jørgensen 2010; Roberts and Boland 2010; de Batist and Khlystov 2012; Matsumoto et al. 2011; Pierre et al. 2014 in prep). Whereas most of these report on isolated sites or selected examples of methane seepage, however, the Hikurangi margin project off New Zealand (Greiner et al. 2010) is remarkable as an interdisciplinary approach that brings advanced tools of seep research to a single area. To a degree, this project appears to be a more detailed blue print of the subduction zone input/output objectives at fore-arcs initially addressed by the SFB 574 consortium. The Hikurangi results are compiled from seismic studies, water column characterization, direct ROV observations, seep biology and authigenic carbonates and are here considered—whenever appropriate—together with the SFB 574 results from offshore Costa Rica and southern Chile. In that way, this review provides a reference frame, in some instances going back to and crediting original publications, about the current state-of-the-art of seep research with emphasis on subduction zone settings.

Seeps at active plate margins

Oceanic plate and continental plate convergence

By far, the most frequent and best-studied seafloor seeps worldwide occur at the convergence between oceanic and continental plates and extend from upper continental slopes to deep trenches. Indeed, it was research at global convergent margins that first revealed the uniqueness of seeps and their products resulting from large-scale fluid expulsion by dewatering of sediments (Suess et al. 1985; Kulm et al. 1986; LePichon et al. 1987). The dewatering occurs in response to lateral compression from plate movement. Sediment-laden oceanic plates move underneath less

dense continental plates. Sediments are either scraped off and accreted onto the edge of the overriding plate or are bypassed at its base to become subducted or underplated. Off-scraping and by-passing lead to two types of subduction margins—accretionary and erosive (also referred to as non-accretionary)—typically along the global deep-sea trench system generating seep fluids and products from different depths (Scholl and von Huene 2007; Wannamaker et al. 2009; Moore et al. 2011).

Accretionary margins consist of a series of ridges oriented parallel to the trench axis made up largely of compressed, folded and faulted turbidite or trench-fill deposits (Fig. 2). In landward troughs between the ridges, the fore-arc basins, thick hemi-pelagic sediments are deposited on the slopes. The ridges as well as the basins are the source of seep fluids. Over extended periods of accretion the ridges are increasingly deformed into landward-verging structural packages separated by thrust faults. These packages constitute the accretionary prism. Farther landward they abut the continental framework rock (backstop) that comprises the upper continental plate. The surface of the framework rock continues to accumulate unconformably seaward prograding slope sediments. Where the subduction angle is shallow as off southern Chile, Cascadia or Japan, convergence causes splay faults to develop in the framework rock that drain the upper plate (Moore et al. 2007; Torres et al. 2004, 2009; Geersen et al. 2011; Scholz et al. 2013). Composition and properties of the upper plate framework rock are of vital importance to the behavior of the entire subduction zone, including fluid generation and transport, whether of the accretionary or erosive type.

Where the subduction angle is steep or the surface of the descending oceanic plate is “rough” as off Costa Rica, the base of the upper plate is being eroded and/or experiences underplating of sediments that escaped being scraped off the descending plate thus leading to erosive or non-accretionary margins. According to Scholl and von Huene (2007), 75 % of the global subduction zones are non-accretionary. The underplated sediments constitute the subduction channel, an increasingly recognized site for deep-seated reactions between trapped seawater-derived fluids and seawater-altered oceanic host rocks (van der Straaten et al. 2012). At erosive margins, small accretionary prisms develop near the trench, but most sediments are carried downward with the oceanic plate, thereby removing material from or adding to the underside of the overriding plate. As a consequence, the margin subsides, fractures, and eventually the plate’s edge is destroyed (Fig. 3). The destructive action at the plate’s edge is particularly severe when volcanic seamounts are subducted. These elevated basaltic features, riding on the oceanic crust, arrive at the trench and plough into the continental margin leaving scars and scarps (Ranero and von Huene 2000; Barnes et al.

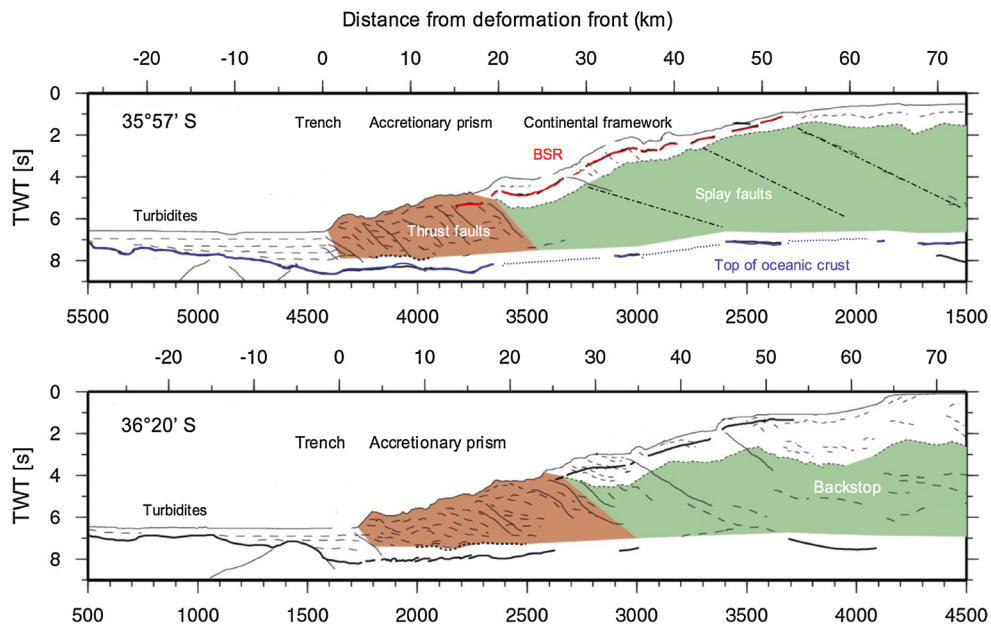


Fig. 2 Accretionary margin. Convergent margin off southern Chile with trench turbidites, accretionary prism, continental framework rock (backstop), and hemi-pelagic sediment cover. Subduction channel between top of oceanic crust and accretionary and continental framework rocks. Fluid escape features are thrust faults separating accretionary ridges, sometimes with basins between them, and splay

faults cutting through the continental framework rocks. Hemi-pelagic sediment cover with well-developed bottom simulating reflector (BSR). Distance in (km) landward and seaward from the deformation front (deep-sea trench); seismic velocity TWT = two-way travel time (s) indicating sediment and rock thicknesses; based on Geersen et al. (2011), Scholz et al. (2013), Reston (pers. com)

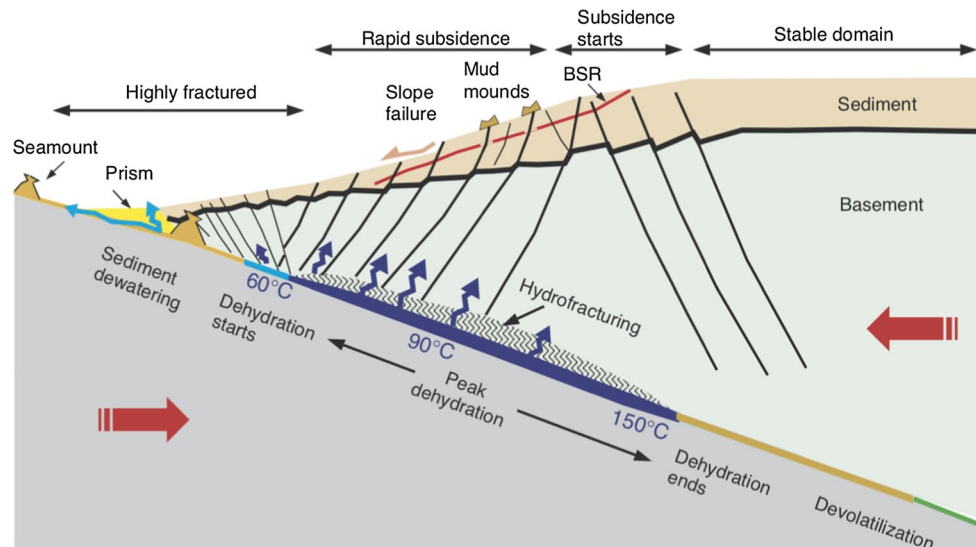


Fig. 3 Erosive margin. Convergent margin off Costa Rica with small accretionary prisms, highly fractured edge of continental plate, region of pronounced subsidence due to removal (erosion) of material from plate underside, and stable continental framework rock; all features covered by seaward prograding hemi-pelagic sediments with well-developed bottom simulating reflector (BSR). Fluid escape features on lower-middle slope are mud volcanoes situated above tempera-

ture–pressure regime of mineral dehydration from top of down-going plate. Fluids and muds are forced upward through deep-reaching fractures. Subducted volcanic seamounts contribute to destruction of overriding plate edge leaving scars, scarps, faults and bulges that facilitate fluid escape; modified from Ranero and von Huene (2000), Ranero et al. (2008)

2010). Ensuing slope failures, faulting and bulging of the sediment strata greatly facilitate fluid escape and seep formation (Mau et al. 2012). Subducted seamounts also pose

a major earthquake hazard. It is near the front where seeps initially form. Farther under the overriding plate, increasing temperatures and higher pressures release mineral-bound

water by dehydration, forcing large amounts of fluids upward through splay faults. Fluids mixed with mud form mud volcanoes and seeps, preferentially aligned above subsurface isotherms consistent with clay mineral dehydration (Ranero et al. 2008; Sahling et al. 2008; Buerk et al. 2010).

Recent drilling into the overriding plate off Costa Rica suggests that the framework rocks, initially thought to be oceanic lithologies derived from the offshore extension of the Caribbean Large Igneous Province (Vannucchi et al. 2006), consist to a significant degree of cemented fore-arc basin sediments (IODP Prelm. Rept., 344; 2013). These lithologies may impart characteristics to the fluids and solids that are transported upward presumably along splay faults imaged as high-amplitude, landward-dipping reflectors that cut through the fore-arc and appear to be offset at the unconformity with the overlying slope sediments (Ranero et al. 2008). These faults drain the deeper part of the margin and focus fluids and sediments to escape and build up the mud volcanoes aligned along the margin.

A significant input of water and volatile elements is through hydration (serpentinization) of the oceanic plate during subduction. Although this had been suspected for some time (Peacock 2001) but not until it was shown that bend-faulting facilitates deep penetration of seawater into the oceanic lithosphere which significantly alters seismic velocities, did it become possible to quantify the degree of serpentinization and hence water input (Ranero et al. 2003; Rüpke et al. 2004; Ivandic et al. 2010). Bend-faulting results from flexure of the oceanic lithosphere causing fractures that reach as deep as the upper mantle. Bend faulting is well-developed off NW Costa Rica and Nicaragua where the old and rigid portion of the Cocos plate that formed at the fast-spreading East Pacific Rise is subducted underneath the Caribbean Plate. Farther southeast off central Costa Rica (Nicoya Peninsula) the slightly younger portion of the Cocos Plate that formed at the Cocos Nazca spreading center is also subject to bend faulting and water intake but less intensive (Fig. 4). Seismic velocity changes of the altered lithosphere indicate that the water intake is substantial and off Nicaragua about 2.5 times larger than off central Costa Rica (van Avendonk et al. 2011).

Other evidence for water intake comes from electrical resistivities derived from magnetotelluric imaging of the margin. Worzewski et al. (2010) showed several domains of increased conductivity indicating the presence of fluids. Two of these coincide with the decrease in seismic velocity and might be of relevance to seep fluids. The first is a conductivity anomaly along the incoming plate related to seawater intake through bend faults and release of water through pores and cracks. Hereby, the release of water is not evident in conductivity changes. The second anomaly occurs at the plate interface and documents increased conductivity presumably related to dehydration of sediments.

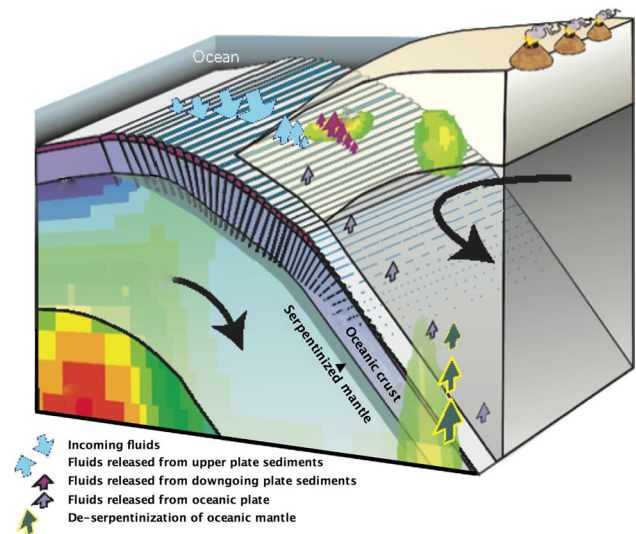


Fig. 4 Serpentinized margin. Prominent bend faulting of incoming Cocos Plate off Nicaragua and NW Costa Rica facilitates deep penetration of seawater into the oceanic lithosphere causing serpentinization of mantle rocks. Water uptake significantly alters seismic velocities and electrical properties. These anomalies indicate several regimes with fluids emitted in the fore-arc: from upper plate sediments (light blue arrows); from dehydration of down-going plate sediments (purple arrows). Deeper anomalies (>30 and 100 km) indicate fluids derived from heating of the mantle wedge and de-serpentinization of the oceanic mantle; these are not emitted in the fore-arc; modified from Worzewski et al. (2010) with information from Ivandic et al. (2010)

Deeper anomalies up to 30 km and 100 km, the authors relate to fluid accumulation derived from heating of the mantle wedge and de-serpentinization of the oceanic mantle, respectively. These anomalies cannot be imaged by seismic nor do they contribute to fore-arc seeps.

Oceanic plate and oceanic plate convergence

Emission of deep-sourced fluids containing abiogenic methane plus traces of non-methane hydrocarbons and hydrogen is observed at the convergence of two oceanic plates in the Mariana fore-arc (Fryer et al. 1995; Mottl et al. 2004). The down-going plate contains little sediment leaving its top to undergo hydration by reacting with seawater at shallow depth to form serpentinite. But as temperature and pressure increase at greater depth, the top of the down-going plate is dehydrated again (de-serpentinization). This may take place as deep as 30 km below the seafloor. The liberated fluids ascend and compound hydration of the overlying oceanic plate. The hydration reactions form serpentine from olivine- and pyroxene-rich crustal rocks. The alteration products are carried upward, along with the excess of fluids, and exit as seeps forming serpentinite mud volcanoes. The abiogenic production of non-methane hydrocarbons (C_2H_6 , C_3H_8 , $n-C_4H_{10}$, $i-C_4H_{10}$ and others) receives much

attention for its far-reaching implications not the least to the origin of life (Prokurowski et al. 2008; Kolesnikov et al. 2009; National Geographic Magazine, June 2013). The area of the southern Mariana Arc including the Challenger Deep and Sirena Deep in the trench, the serpentine mounds and arc volcanoes have been declared in 2009 the Marianas Trench Marine National Monument, administered by the U.S. National Fish and Wildlife Service.

Understanding hydration reactions has been advanced by investigating slow-spreading oceanic ridge segments at which ultramafic rocks are within reach of penetrating seawater and by experimental work of rock–water interactions (Palandri and Reed 2004). On the Mid-Atlantic Ridge, hydrothermal vent fluids from serpentinized oceanic crust form aragonite and calcite chimneys (Ludwig et al. 2006). However, none have been reported so far from serpentinized portions of the oceanic plate entering the subduction zone.

Transform plate boundaries

Transform boundaries generate prolific cold seeps where they crosscut thick sedimentary sequences providing fluid pathways for expulsion along the fault planes. The first cold seep biota and barite precipitates were discovered at the San Clemente transform but mistaken for manifestations at hydrothermal vents of oceanic spreading centers (Lonsdale 1979) and later correctly identified as cold seep products (Torres et al. 2002). At transform boundaries, two plates slide past each other with only horizontal movement between them either threatening earthquakes if they are

locked or facilitating reactions during slow creep if fluids are present. Seeps at transform boundaries have not previously been considered in their own right, but since plate margins are involved, the fault planes reach to great depths and hence a deep-source signal might be expected. Transform faults at continental margins pose earthquake hazards; e.g., San Andreas Fault, Anatolian Fault system, Sakhalin Transform fault, the Queen Charlotte Fault and the Gulf of Cadiz; hence research on gas and fluid seepage and their products—largely in form of authigenic carbonates and methane-rich fluids—has recently focused on such tectonic settings (Shakirov et al. 2004; Geli et al. 2008; Carpenter et al. 2011; Gutscher et al. 2012; Halliday et al. 2008; Barrie et al. 2013).

Seeps at passive continental margins

On passive margins, the variety of geologic settings, the mechanisms of fluid expulsion and the worldwide occurrence of cold seeps are immense (Fig. 5). Pockmarks on shelves and slopes are expressions of seeps fed from submerged aquifers, from overpressured formations containing hydrocarbons and brines, or from rapidly deposited accumulations of water-rich sediments. Hydrocarbon seeps have long guided offshore exploration for oil and gas deposits (Judd and Hovland 2007).

Groundwater seepage from sub-seafloor extensions of aquifers has been known since the early days of seafarers. Discharge of sulfide-rich hypersaline water feeding ventlike biological communities was first reported off the

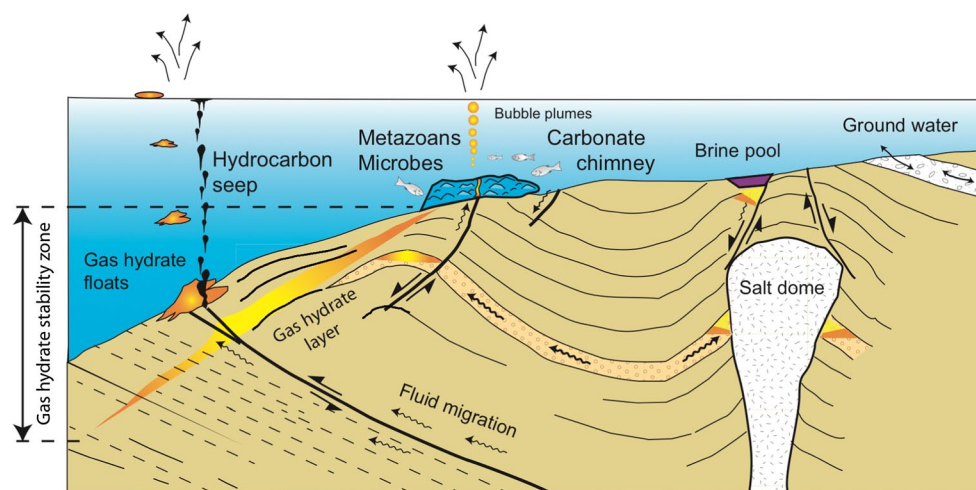


Fig. 5 Passive margin. Geologic settings and the mechanisms of fluid expulsion generate an enormous variety cold seeps ranging from pockmarks on shelves and slopes caused by outflow from submerged aquifers, overpressured formations containing hydrocarbons and brines and rapidly sedimented water-rich sediments in deltas or drift deposits. Carbonate chimneys, asphalt seeps, methane hydrate

mounds, seep fauna and methane plumes in the water column are the ubiquitous manifestations. Methane hydrate rafts—infrequently observed—transfer methane directly from the seafloor to the atmosphere (Pape et al. 2011); modified from Suess and Linke (2006) based on Moore (1999)

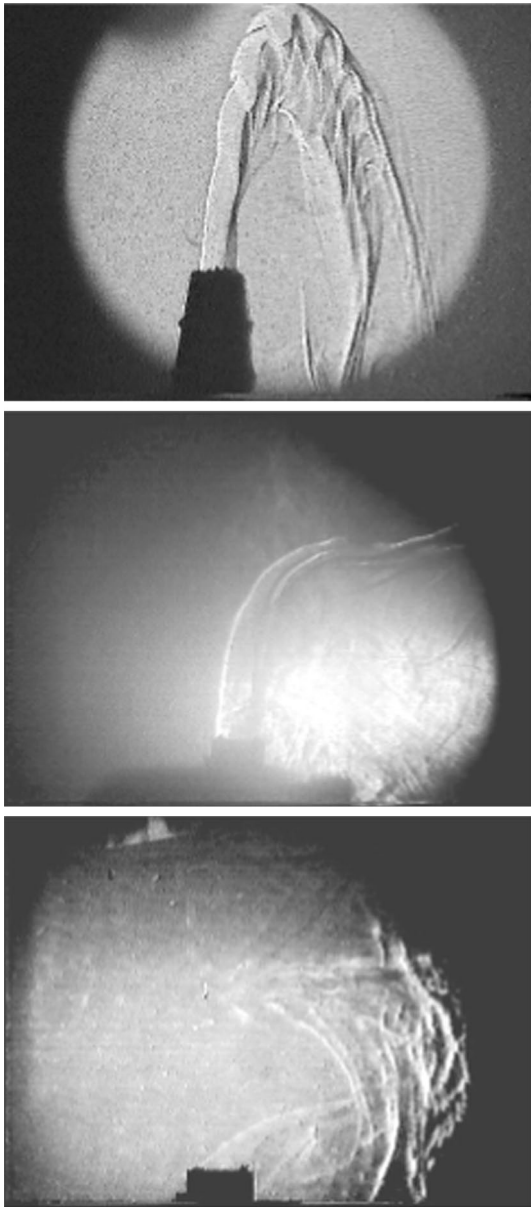


Fig. 6 Seep flow imaged. Visualizing fluid flow from cold seeps based on optical “schlieren” technique that is sensitive to small changes in refractive index from temperature and salinity differences. (*top*) Flume experiment with saline fluid ejected through an opening; diameter of image = 5 cm; (*middle*) channeled fresh water seep at the seafloor (water depth 18 m); (*bottom*) weakly channeled seep fluids at Hydrate Ridge (water 780 m) laterally displaced by bottom current; modified from Suess and Linke (2006) based on Karpen et al. (2004)

Florida Escarpment (Paull et al. 1984). Today groundwater seepage carries pesticides, herbicides and fertilizer residues into shelf waters off coastal areas. Pumping for drinking water depletes groundwater reservoirs and allows seawater to enter or high tidal ranges force it back into the aquifers. The result is widespread salt invasion of groundwater in coastal areas and other problems regarding global

groundwater reservoirs (Gallardo and Marui 2006). Submarine groundwater discharge may be estimated by ^{222}Rn measurements (Peterson et al. 2008).

The driving mechanisms for fluid expulsion at passive margins are: loading by sediment, differential compaction, overpressure and facies changes. Hence, rapidly accumulating water-rich sediments generate seeps and mud volcanoes in deltas, in deep-sea fans and along passive margins as well as in marginal seas. In short, any changes involving different permeabilities of fluid-rich strata, such as ash layers, turbidites, sands and silts (deltas), drift sediments, even buried reefs when intersected by faults, open up pathways for fluid escape. Other driving forces for seepage are free gas movement (buoyancy), hydrological and tidal pumping and thermally driven fluid and gas circulation. Several methods have been used to image fluid flow (Fig. 6; Karpen et al. 2004) and directly measure expulsion rates at seep sites of passive and active margins. Reliability largely depends on the flow rate. Slow rates are estimated by modeling pore water profiles (Hensen et al. 2004; Karaca et al. 2012; many others) and are suited for a method employed by Tryon et al. (2001). High rates are suitable for quantification by flux meters deployed by benthic landers (Linke et al. 2005).

Common seep characteristics at active and passive margins

The type of fluids expelled back into the ocean at accretionary, erosive and transform margins or at passive margins—whether from deep or shallow sources—depends on the thickness and provenance of the sediment column, the rate of sedimentation, the age and cooling history of the subducted plate and the morphology of the moving or stationary plates. Organic-rich and evaporite-containing strata represent end-members of the above spectrum in determining the final seep fluid composition and their recognizable products at the seafloor.

Sedimented margins

The subduction of sedimented oceanic plates provides the first-order input of volatile elements to the Earth’s material recycling (Jarrard 2003; Scholl and von Huene 2007; Freundt et al. 2014). In terms of thickness of the sediment package and its provenance, the sedimented convergent margins are not much different from passive margin. Hence, reactions between fluids and components in hemipelagic passive margin sediments, inside the accretionary prisms, with the backstop rocks and the sediment blanket draped over the margin from shelf depths to the trench, determine the seep fluids, their products and return pathways to the seafloor.

Fluids expelled through seeps at sedimented margins contain the remineralized nutrients (silica, phosphate, ammonia and alkalinity) and hydrogen sulfide, as well as dissolved and free methane from microbial degradation of sedimentary organic matter. Thick sediments often are deposited along continental margins associated with coastal upwelling or otherwise high primary productivity in response to nutrient loading from nearby continents. Such sediments are rich in organic matter, biogenic silica; they accumulate rapidly and thus greatly favor sulfate reduction and methanogenesis of the microbially mediated early diagenetic reaction sequence.

Most sedimented margins generate enough biogenic methane that, when moving upward, exits as dissolved or free gas directly into the bottom water, or alternatively when reaching the methane hydrate zone, is retained in layers of gas hydrate. Whereas free gas ascends through seismically anomalous conduits (acoustic blanket zones; gas chimneys) and forms acoustically detectable plumes in the water column, gas hydrate layers are detected seismically as bottom simulating reflectors (Tinivella and Lodolo 2000). Among the products of seeps emanating from the seafloor the association of biota and authigenic carbonates is by far the most widely encountered “archive” from which source depths, environmental conditions and tectonic settings may be inferred (Liebetrau et al. 2014).

The hydrocarbon–metazoan–microbe–carbonate association

Fluid flow, bioirrigation and bubble-induced mixing at seeps (Sahling et al. 2003; Haeckel et al. 2007) drive the interaction between anaerobic oxidation of methane (AOM), communities of macrobiota and formation of carbonates and sulfides (Fig. 7). Methane, either from subsurface gas hydrate, from ascending bubbles or as dissolved gas, supplies the AOM-consortia that aggregate at different sub-seafloor depths (Reaction 1). The consortia generate hydrogen sulfide that rises and is oxidized either in microbial mats at the surface or by symbionts within the macrofauna, using oxygen or nitrate (Reactions 2a and 2b). When mobile iron is present, the hydrogen sulfide may be fixed as iron sulfides (no such reaction is shown in Fig. 7 but discussed at length by Boetius and Wenzhöfer 2013). Bivalves pump oxygen downward, whereas tubeworms (not shown in Fig. 7) extract hydrogen sulfide through their roots (Freytag et al. 2001). As a consequence of the AOM-activity, calcium carbonate phases precipitate (Reaction 3). Earlier views favored accidental reaction from the byproduct of AOM, now it is thought plausible that the microbial community may actively promote precipitation even of selected mineral phases (Haas et al. 2010; Krause et al. 2012).

Anaerobic oxidation of methane

Subsurface gas hydrates and ascending free methane at seeps provide the C-reservoir for the AOM-consortia that consume interstitial sulfate (Boetius et al. 2000; Orphan et al. 2001; Milucka et al. 2012). The steep gradient of sulfate within the near-surface sediments is a reliable indicator for rapid upward flow of methane-rich seep fluids (Knittel et al. 2003). The subsurface depth of the sulfate–methane interface has become a standard indicator for mapping seep locations and exploring for gas hydrates. Methane usually originates from fermentative decomposition of organic matter or is produced by bacterial CO₂ reduction. In some settings, gas hydrate forms from thermogenic methane that migrates from deeper hydrocarbon reservoirs (Sassen et al. 2004; MacDonald et al. 2004). The sources can readily be distinguished by stable C- and D/H-isotopes of CH₄ (Whiticar 1999).

Gas hydrates form from methane-supersaturated pore fluids at elevated pressure (>60 bar) and low temperature (<4 °C) as exist in the oceans below upper slope depths. Their stability is also influenced by total salinity and presence of other gases in natural systems and by inhibitors and catalysts in technical systems. The top of the natural gas hydrate stability zone (GHSZ) along the global ocean margins is at water depths as shallow as 300 m in Arctic bottom waters and around 750 m in subtropical bottom waters. The base of the GHSZ varies with the water depth and the geothermal gradient and may range from 100s to 1,000s of meters below sea floor. In seep waters, high precision Cl-analyses, coupled with O- and D/H-isotopes of H₂O, may indicate the presence of gas hydrates in the subsurface that may drive seep flow (Matsumoto and Borowski 2000).

Biota and biomarkers

Function, structure and composition of seep biota and AOM-consortia in concert with biomarker are currently a major topic of seep research. The biomarkers are greatly depleted in ¹³C relative to their carbon source and are linked to methanotrophic archaea (Elvert et al. 1999; Hinrichs et al. 1999; Rossel et al. 2008). This may result in isotopic compositions as low as −137 ‰ PDB (e.g., hydroxyarchaeol) depending whether biogenic or thermogenic methane is utilized. The nearly inexhaustible reservoir of methane carbon available to the consortia in seep environments maximizes the kinetic carbon isotope effect. Biomarkers from AOM-consortia are identified from sediments and authigenic carbonates of recent seep sites and increasingly from deposits of ancient seeps (Campbell et al. 2002; Nyman et al. 2010; Yang et al. 2011). So far, the oldest biomarker record was found in 300-million-year-old

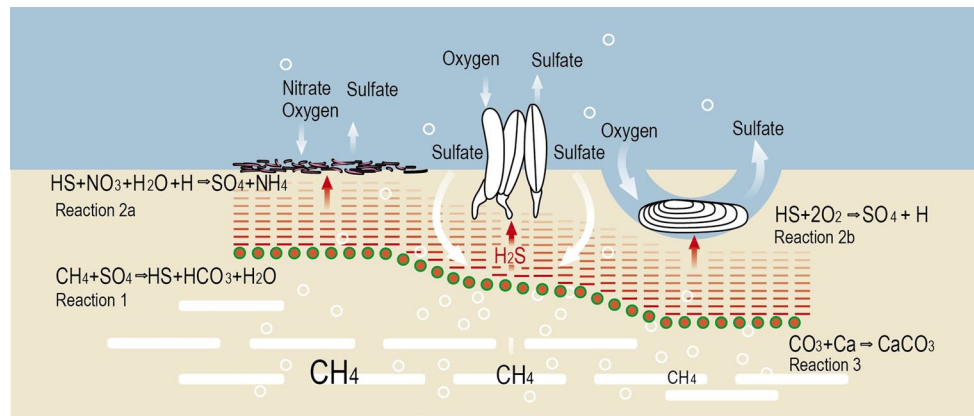


Fig. 7 Anaerobic oxidation of methane. Buried gas hydrates and free gas supply different rates of methane (arrows) to AOM-consortia (red-green circles) concentrated at distinct depths below seafloor. The consortia consume seawater sulfate in oxidizing methane (Reaction 1) producing hydrogen sulfide and bicarbonate; hydrogen sulfide

risks to the sea floor and is oxidized in microbial mats (Reaction 2a) or by macrofauna symbionts (Reaction 2b) using oxygen or nitrate; in the process calcium carbonate precipitates (Reaction 3); from Suess and Linke (2006); see also Sahling et al. (2002) and Boetius and Wenzhöfer (2013)

limestone (Birgel et al. 2008). The library of biomarkers grows steadily (Rossel et al. 2008, 2011). Based on lipid analyses, three distinct AOM-consortia of ANaerobic MEthanotrophic (ANME-1, -2 and -3) archaea and their sulfate-reducing bacterial partners were tentatively identified as environmental indicators that respond to temperature, oxygen and sulfate availability (Rossel et al. 2011).

Benthic seep communities are highly visible, persistent and universal indicators for seep activity past and present. The dominant symbiotic taxa are tube worms, clams and mussels whereby different microbial consortia—mostly recognizable as brightly colored mats—provide carbon and energy via AOM. First publications of seep communities invariably noted the similarity of major taxa to those known from hydrothermal vents (Lonsdale 1979; Paull et al. 1984; Suess et al. 1985; Kennicutt et al. 1985). Numerous reviews and case studies since (Sibuet and Olu 1998; Sahling et al. 2002; Levin 2005; Olu-Le Roy et al. 2007; Kiel 2010) summarize vent taxa, document chemoautotrophy, follow energy and carbon flow, establish community structures, propose biogeographical provinces (Sahling et al. 2003; Baco et al. 2010; Zapata-Hernandez et al. 2013) and model interactions between seep fauna and for example microbial consortia (Cordes et al. 2007) or non-symbiotic mega-fauna (Niemann et al. 2013). Noteworthy, tube worms (pogonopherans), initially thought of as indicator organisms for abyssal environments (Ivanov 1963), remained unrecognized as members of the seep fauna until their distribution in deep-sea trenches could be related to convergent plate boundaries (Suess et al. 1985). New chemosynthetic species are continuously discovered at methane seep sites throughout the world (Hilario and Cunha 2008; Sellanes et al. 2008; Warén and Bouchet

2009; Sommer et al. 2009; Krylova and Sahling 2010; Pierre et al. 2014).

Typical members of seep biota from the Cost Rica and the Chile margin are also tubeworms (Fig. 8a, b), clams and mussels (Fig. 8e, f) and microbial mats (Fig. 8c, d). It is quite evident that the former is a sediment-starved environment, whereas the latter is heavily sedimented perhaps affecting the community structure. Zapata-Hernandez et al. (2013) suspect that the seep fauna off southern Chile constitutes a new biogeographical province as does Martin et al. (2010) for seep communities off New Zealand (Hikurangi subduction zone). Niemann et al. (2013) documented intake of AOM-derived food by non-symbiotic fauna (crabs) off Costa Rica based on ^{13}C -depleted fatty acids in stomach and muscle tissue that are identical to those of chemoautotrophic bacteria living there. On the other hand, it is doubtful that significantly ^{13}C -depleted foraminifera tests from seep sites at the Hikurangi margin and elsewhere result from chemoautotrophic intake of seep carbon by living forams. Rather they result from recrystallization of their tests in a ^{13}C -depleted environment (Martin et al. 2010; Torres et al. 2003). Equally, the colonization by cold water corals utilizing carbonate substrates at seep sites off New Zealand seems to be an accidental rather than a chemoautotrophic association (Jones et al. 2010; Liebetrau et al. 2010). A vast data collection with emphasis on chemoautotrophic biota was compiled in connection with the Census of Marine Life. The global effort of researchers from more than 80 nations engaged in a 10-year scientific initiative whereby mid-ocean ridges, hydrothermal vents and cold seeps are accorded special significance (Topics in Geobiology; Kiel 2010).

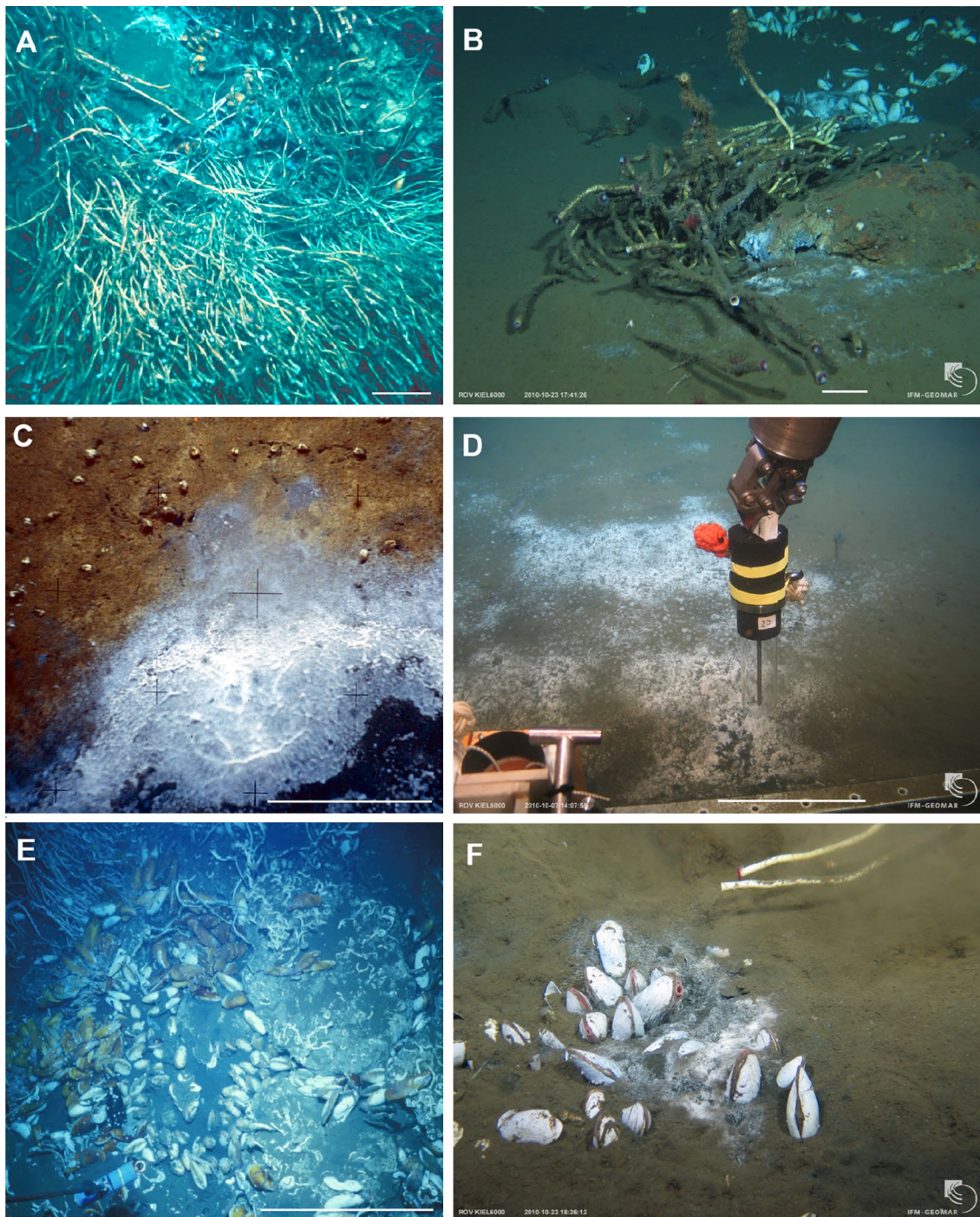


Fig. 8 Seep biota. Seafloor images of typical seep biota from the sedimented Chile accretionary margin (*right*) and the sediment-starved Costa Rica erosive margin (*left*). **a** Proliferous Pogonophora colony from Jaco Scarp off Costa Rica; **b** pogonophora colony on seafloor off Concepcion, Chile; **c** varied microbial mats on seafloor

of Quepos seep, Costa Rica; **d** microbial mat on smooth seafloor off Concepcion; **e** mytilid colonies on carbonates off Costa Rica; **f** vesicomylid colony on seafloor off Concepcion; photographs GEOMAR; Cruise Repts. SO163, Weinrebe and Flüh (2002); M54, Soeding et al. (2003); SO173, Flueh et al. (2004); SO210, Linke (2011)

Authigenic carbonates

A direct consequence of AOM is the precipitation of carbonate minerals. The association of carbonates with gas

emissions, pockmarks and populations of chemosynthetic faunas is among the most widely used criteria to identify seeps. Carbonate buildups (chemoherms; Fig. 9a A, B) reaching several meters above the seafloor are believed to

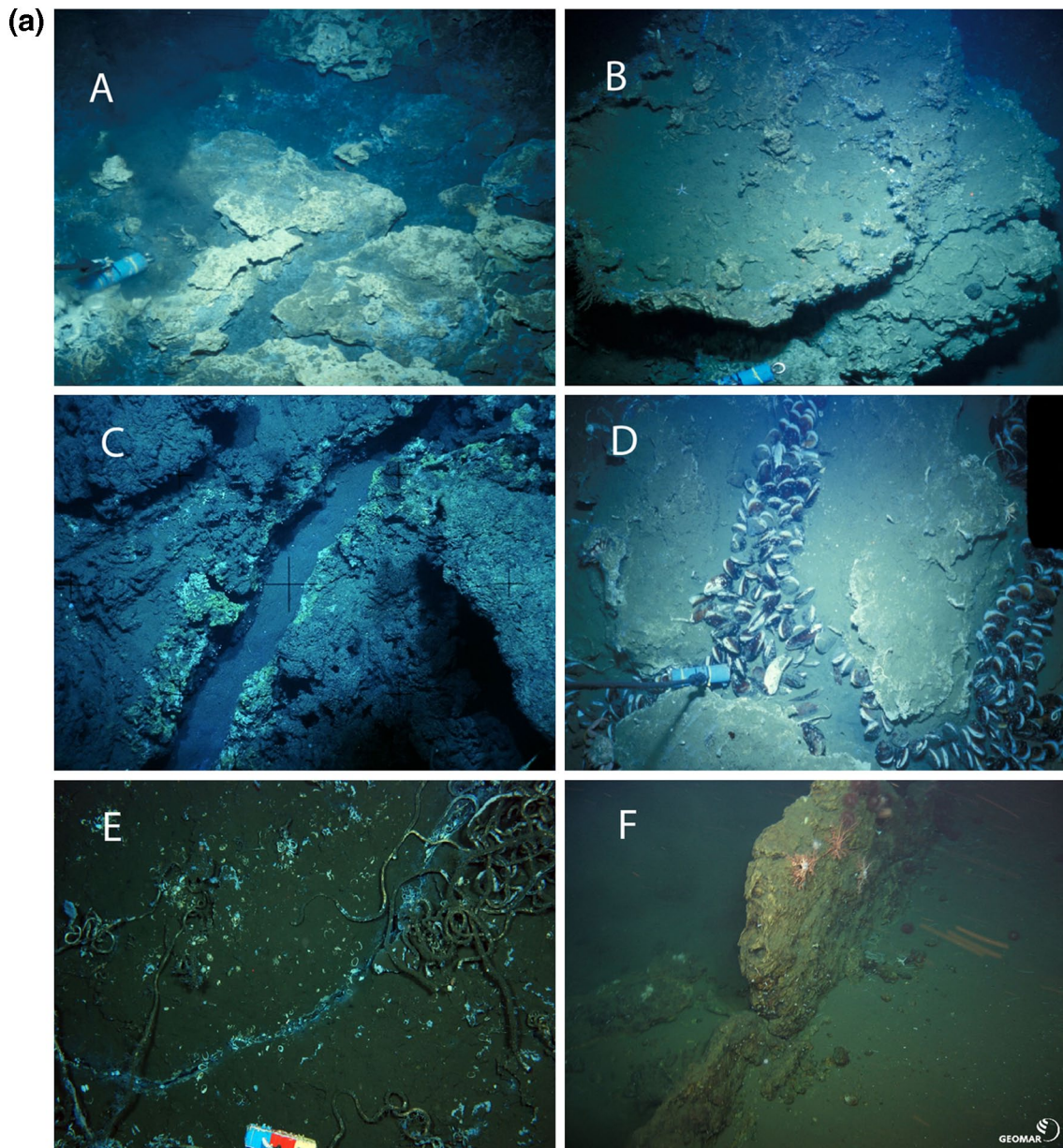


Fig. 9 a Seep carbonate structures. Seafloor images of typical seep carbonates. **A** Fractured block, Costa Rica margin; **B** chemoherm buildup populated by sessile organism, Costa Rica margin; **C** chemoherm buildup with microbial linings, South China Sea; **D** domed and fractured structure atop mud volcano with bivalves, Costa Rica margin; **E** fractured pavement with tube worms and microbial linings, Chile margin; **F** uplifted and eroded block, Chile margin; photographs GEOMAR: Cruise Repts. M54, Soeding et al. (2003); SO173, Flueh et al. (2004); SO177, Suess (2005); SO210, Linke (2011).

form in contact with bottom water (Teichert et al. 2005; Han et al. 2004, 2008; Liebetau et al. 2014). Other formations exist below the seafloor or are uplifted, exhumed and eroded (Fig. 9a D). Typically, chemoherms incorporate shell fragments and have a network of open or cemented fluid channels that can be traced throughout the structure

b Seep carbonate fabric. **A** Intergrowth of gas hydrate (white) and aragonite (yellow) in cemented mud matrix; Cascadia margin; **B** gas hydrate progressively disappears in minutes after recovery due to dissociation; **C** aragonite lining with imprinted gas hydrate fabric after complete dissociation; **D** chemoherm block with sessile organism and open fluid pathways, South China Sea; **E** aragonite linings of voids and open fluid channels; **F** network of open fluid channels in chemoherm block; photographs GEOMAR: Cruise Repts. SO148, Bohrmann et al. (2000); SO177, Suess (2005)

Fig. 9b D–F). Many other shapes and sizes of seep carbonates have been observed, too numerous to detail here. Recent publications note that (e.g., Han et al. 2008; Haas et al. 2010) the seafloor around seeps is often covered by blocky carbonates and fragments, irregular doughnut-shaped, tabular and tubular slabs and concretions with

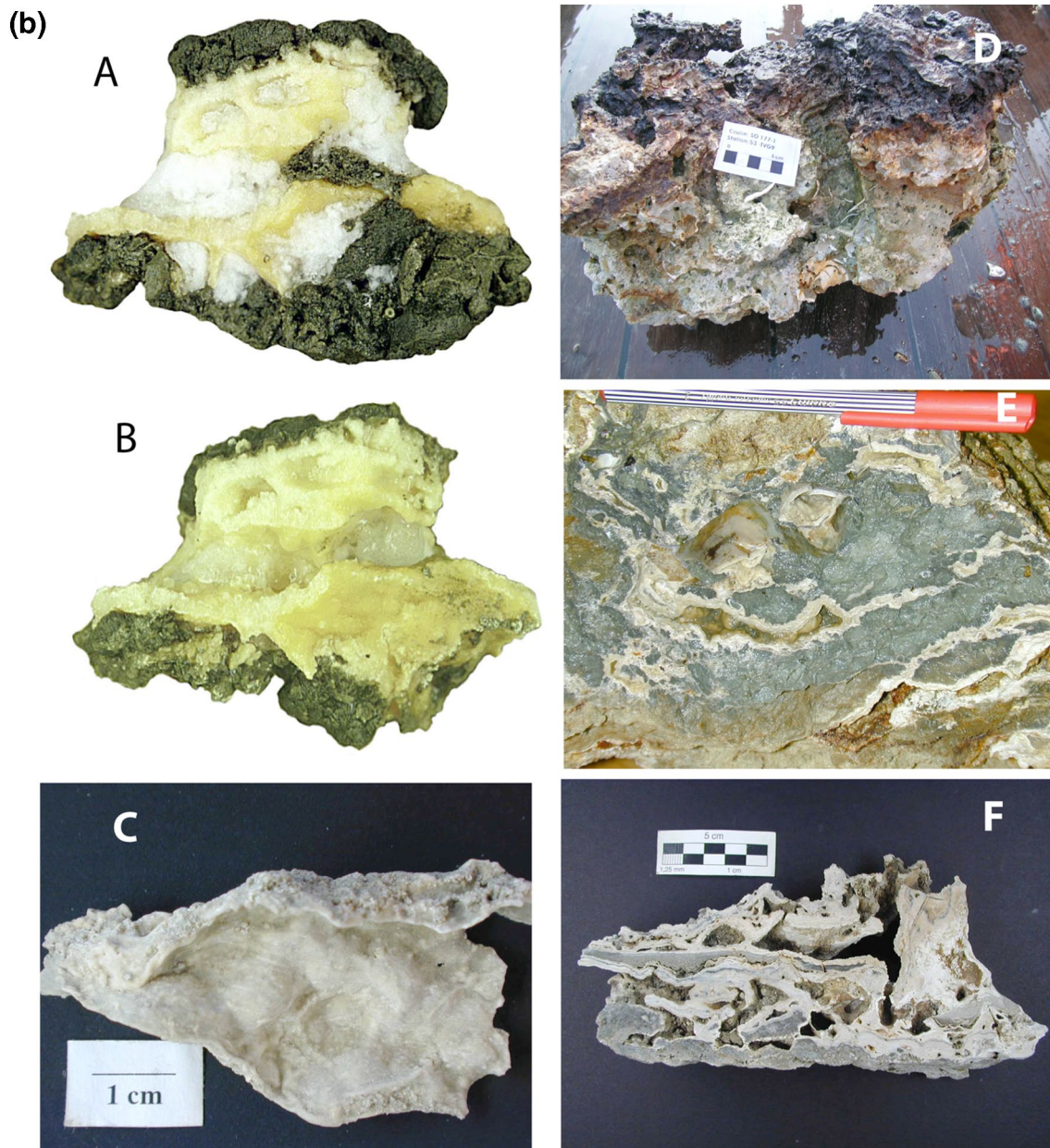


Fig. 9 continued

open or cemented central channels. Some appear to be molds of burrows or linings of fluid channels that formed in the sediment but resemble small chimneys after becoming exhumed by bottom currents. Pure carbonate (aragonite) layers are common that line voids or fill the conduits of near-surface concretions and chemohems (Fig. 9a E, F), whereas concretions deeper in the sediment that are fillings of burrows and molds most often consist of high-Mg-calcites (Han et al. 2008; Haas et al. 2010).

The dominant mineral phases are aragonite, Mg-calcite and (proto)-dolomite, but also Fe- and Mn-carbonates occur. Their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ composition ranges from -60 to

-30 ‰ PDB and $+8$ to $+2$ ‰ PDB, respectively, depending on the C- and O-source, the temperature and the specific mineral phases being formed (Bohrmann et al. 1998; Greinert et al. 2001; Teichert et al. 2005; Han et al. 2014; Mavromatis et al. 2012). Gas hydrate water, clay-dehydration water, glacial seawater and—in rare cases—meteoric water determine the O-isotope make-up, whereas biogenic, thermogenic and abiotic methane carbon, becoming strongly fractionated during AOM, determines the eventual C-isotope signal. The stable isotopes and the mineralogies are robust criteria, along with biomarkers for recognizing ancient seeps.

The characterization by stable C- and O-isotopes and mineralogies of seep carbonates now includes new geochemical, radiochemical and biochemical criteria to constrain absolute and relative ages, redox conditions of their environments of formation, trace elements to indicate sources and/or the types of fluid–sediment/rock interactions. These objectives may best be attained when pore or seep fluids are sampled at active seep sites along with the carbonate lithologies. This is not possible in all cases and—as it turns out—seep carbonates at active sites span a large time range that makes it difficult to assign any fluid or environmental signal to the solid product at any one time. Most promising advances come from lipid biomarker studies of AOM-consortia. Tentatively, the ANME-2/sulfate reducer cluster seems to favor both ambient bottom water temperature and oxygen conditions resulting in predominantly aragonitic phases in calcified mats, whereas the ANME-1 cluster favors elevated temperatures and diminished oxygen contents relative to ambient bottom water resulting in Mg-calcites (Haas et al. 2010; Rossel et al. 2011).

Seep footprint

Massive carbonate caps on mounds and pavements have been mapped as seep manifestations along continental margins. These are often fractured and heavily populated by seep biota attesting to ongoing seep activity (Fig. 9a C–E). Geo-acoustic tools (side-scan sonar, sub-bottom profiler) combined with high-resolution multibeam bathymetry not only serve to identify seep sites but are indispensable for quantification of seep fluxes. The acoustic seep signatures include smooth areas with slightly elevated backscatter intensity that result from high gas content or the presence of near-surface gas hydrates, to rough areas with widespread patches of carbonates at the seafloor thus providing a regional seep footprint as shown for the Costa Rica, Chile and Hikurangi margins (Sahling et al. 2008; Buerk et al. 2010; Klauke et al. 2010, 2012). Ground-truthing by either video observations (Jones et al. 2010), flux measurements (Linke et al. 2005) and modeling of pore water profiles (Hensen et al. 2004; Karaca et al. 2012) provides the database from which to derive seep fluxes and reliably up-scaling as shown in exemplary fashion for the Costa Rica margin (Freundt et al. 2014).

Nowhere does the need for accurate seep flux estimates become more evident than in the recent comparison between global seafloor oxygen consumption related to methane seepage (Boetius and Wenzhöfer 2013). The authors assuming “...a few tens of thousands of active cold seep systems on continental slopes worldwide...” find a significant mismatch between carbon lost from continental slopes globally and the maximum of methane that can be supplied via methanogenesis from within the topmost

1,000 m of Holocene sediments, primarily through seeps. This leads to the suggestion that “...a substantial fraction of the methane at seep systems is sourced from carbon buried kilometers under the seafloor.” Admittedly, a more accurate estimate of global seep fluxes would not erase the mismatch, but the issue of a “deep carbon source” highlights the need for reliable seep flux estimates and up-scaling globally.

Age determination

Foremost among seep research is the age determination of authigenic carbonates. The first published U/Th-ages are from chemoherm samples of the Cascadia subduction zone (Teichert et al. 2003). The authors documented that methane-release events at seep sites largely occurred during low eustatic sea-level stands when lowered hydrostatic pressure falls below the sub-sea formation pressure. This initial interpretation is essentially confirmed as more age determinations become available. Among these are ages from seep carbonates of the Japan Sea going back 65 ky ago with all of six different ages coinciding with low sea levels (Watanabe et al. 2008). A compilation of 41 U/Th-ages (Feng et al. 2010) from the Gulf of Mexico, the Black Sea and the Congo fan shows seep carbonates forming from recent times through the last interglacial. Slightly, more dates fall around the Last Glacial Maximum, but the time span covered by these samples of the Congo fan appears too short for supporting the sea-level mechanism. At the Hikurangi margin, the youngest U/Th-ages measured so far are from several contemporary seeps around $2,100 \pm 100$ years ago (Liebetrau et al. 2010). Here, the geologic setting implies a margin-wide hydrological change controlling seepage.

From the passive margin seeps of the South China Sea, two sets of U/Th-ages have been published of which one (350 ky ago; Tong et al. 2013) coincides with high sea-level stand and another sample (11 ky ago; Han et al. 2014) coincides with rising sea level, whereas all others (16 samples) coincide with low sea-level stands. Other mechanisms have been discussed (Feng et al. 2010; Han et al. 2014) such as warming of bottom water that destabilizes methane hydrate, increase in the sediment loading, salt diapirism or erosion of the seafloor or tectonism at active margins; all of which could force methane from the sediment.

Periods of low sea-level stands do not exclusively favor methane-release events as there is currently—at high sea level—vigorous seepage at large carbonate structures that have had a long history. Recently, Crutchley et al. (2013) have shown by numerical fluid simulations an increase in water–gas fluid accumulation below the base of the gas hydrate stability that underlies a long-lived vigorously seeping carbonate structure, the Pinnacle. This is a >50 m high chemoherm at the Cascadia subduction zone. The site

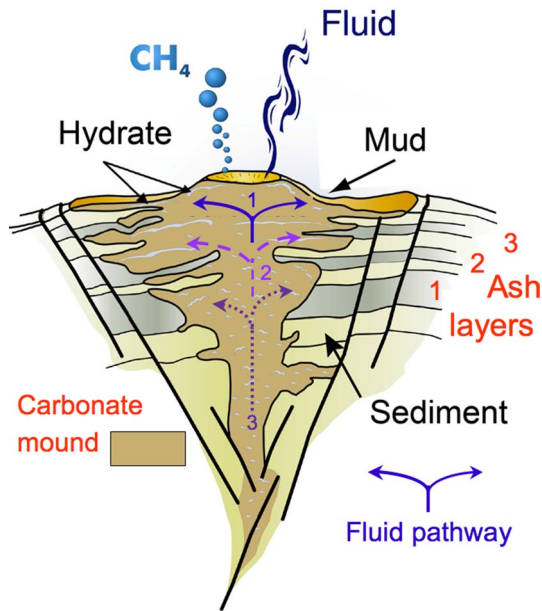


Fig. 10 Generic mud volcano with core of carbonate mound. Mud, methane and fluids are emitting while carbonates and interlayered hydrate form, whereas sediment and ash layers alternate along flanks. A normal sequence of ash layers (1–3) records lifetime and cyclicality of venting. The sequence of carbonate ages (1–3) if reversed (top = older than bottom) results from plugging of fluid pathways; based on Kutterolf et al. (2008) and Liebetrau et al. (2014)

of water–gas fluid accumulation at depth is a distinct lithologic boundary that constricts flow. The resulting overpressure forces methane continuously through a well-defined network of faults to the Pinnacle site regardless of sealevel.

First-of-its-kind investigations of intercalated carbonate and host sediment on flanks of seep structures and of drill cores taken in the centers of mud volcanoes on the Costa Rica margin (Kutterolf et al. 2008; Liebetrau et al. 2014) revealed at first sight unconventional results. The mud volcanoes grew through several active phases with ash layers providing time markers (6, 17, 24.5, 69, 84 ky ago) and carbonates the U/Th-ages (ranging from 5 to 65 ky ago). Ages of the drill core samples through the carbonate cores of the structures showed downward progression of growth instead of upward as the ages of the mounds do with inward growth instead of outward (Liebetrau et al. 2014). Both trends are readily explained by plugging of the fluid pathway with time by authigenic carbonate precipitation. The internal structure of a generic mud volcano with an authigenic carbonate core (Fig. 10) shows intercalated muds and volcanic ash layers that were dated to provide the lifetime and cyclicality of seep activity. The apparently reverse U-/Th-ages result from sequential plugging of older fluid pathways by carbonate precipitation on top of the structure and the younger carbonates forming near the bottom as illustrated in Fig. 10. Though, globally and over

Quaternary times, eustatic sea-level fluctuations are currently favored to control the activity of the numerous less vigorous seeps.

Fluid–sediment interaction

There has been a long-standing and religiously performed analytical procedure on pore water chloride contents with little disagreement about the accuracy by the Deep Sea Drilling Project and its successors. Many 1,000s of interstitial Cl-profiles in drill cores have been established documenting endless deviations—enrichment as well as depletion—relative to seawater chloride. All of these are expressions of fluid–sediment interaction, mostly 100s of meters below the sea floor. In seep settings, these familiar Cl-anomalies along with those of trace constituents are compressed in concentration–depth profiles toward the sediment–water interface by upward fluid flow. Sometimes the anomalous fluids are emitted to the free bottom water where they may or may not be recorded by the hydrocarbon–microbes–metazoan–carbonate association.

Gas hydrate water Much attention has been focused on Cl-anomalies from the release of methane hydrate water. This anomaly is an artifact of sampling as removal of drill cores from in situ temperature and pressures destabilizes gas hydrate phases in the sediment. Coupled with O- and D/H-isotopes of H_2O , the resulting anomalies may be linked to gas hydrates and indeed are widely used to estimate the hydrate saturation of deposits (Matsumoto and Borowski 2000; Haeckel et al. 2004; and many others). Release of hydrate water is restricted to layers at and above the bottom simulating reflector (BSR) diluting the Cl-concentration and increasing the $\delta^{18}O_{H_2O}$ of pore fluids (Fig. 11).

Seep carbonates being precipitated during AOM are another sink of $\delta^{18}O_{H_2O}$ from hydrate water. This was first shown in an aragonite–Mg–calcite intergrowth retrieved from seeps at the Cascadia convergent margin (Bohrmann et al. 1998). The C-isotope ratio ($\delta^{13}C = -40$ to -54 ‰ PDB) of this intergrowth (Fig. 9b A, B) identifies both mineral phases as being derived from biogenic methane. As the aragonite—the younger phase—was shown to have formed in equilibrium with ambient bottom water temperature, the Mg–calcite—the older phase—was enriched in $\delta^{18}O$ by about $+1$ ‰ PDB. This is attributed to gas hydrate water in the precipitating fluid. Hydrate water may be enriched in ^{18}O of up to 3.5 ‰ PDB (Maekawa 2004). The lining of the carbonates in contact with the hydrate images the hydrate morphology (Fig. 9b C) and further supports the transfer of “heavy” ^{18}O from hydrate waters to carbonates. The term “clathrate” was proposed for this type of rock, invoking “clathrate” the family of water-caged gases. The name did not stick but what stuck is the interpretation

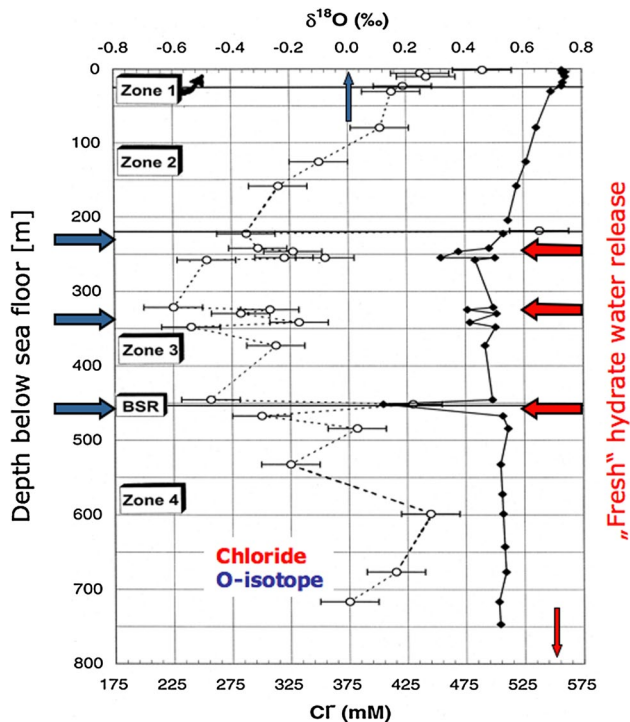


Fig. 11 Hydrate water in pore fluids. Well-known artifact of dissociating gas hydrates in drill cores by warming after retrieval; release of hydrate water dilutes Cl-concentration and increases $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of pore fluids; from Matsumoto and Borowski (2000)

of “heavy” $\delta^{18}\text{O}$ -values of seep carbonates as sourced by methane hydrate. Currently, many reports of “heavy” $\delta^{18}\text{O}$ -values of seep carbonates are linked to methane hydrates in the subsurface (Tong et al. 2013; Lu et al. 2005; Han et al. 2004; Matsumoto 1989) although there are other sources of “heavy” water being emitted at seeps (Dählmann and de Lange 2003; Hensen et al. 2004).

Clay dehydration Trioctahedral clays (smectite group) lose interlayer water in three steps to form illite responding to temperatures and pressures that prevail at the plate interface in subduction zones (80–120 °C). This was experimentally shown by Colten-Bradley (1987) and since by many others. Depending on the percentage of smectites, dehydration generates considerable amounts of fresh water, affecting interstitial chloride contents (Saffer and McKiernan 2009). Incomplete dehydration changes 18 Å- to 15 Å-smectite by releasing water without forming illite. The expression of clay-dehydration either at complete or incomplete conversion to illite is evident on a large scale in Cl-dilution of pore fluids of accretionary margins. For example, data from ten drill sites across the Cascadia subduction zone (Torres et al. 2004) show progressive freshening attributable to increased compaction and smectite–illite transformation (Fig. 12). Sites at the accretionary prism (Stations 1245–1247) show

Cl-dilution at 150 m below seafloor and above the BSR depth from dissociation of gas hydrate.

The δD (−32 ‰ SMOW) and $\delta^{18}\text{O}$ (+10 ‰ SMOW) of interlayer water differ significantly from those of seawater as determined for deeply buried strata of mud volcanoes (Dählmann and de Lange 2003). These isotope characteristics affect the pore water δD and $\delta^{18}\text{O}$ upon dehydration. In addition, trace elements sorbed in the interlayer space or external clay surfaces are also affected by clay dehydration as for example with boron and lithium.

Significant boron enrichment with diluted Cl-contents in pore fluids from seep sites (mud volcanoes) off Costa Rica and the δD and $\delta^{18}\text{O}$ isotope ratios of seep water is attributed to clay dehydration (Fig. 13; Hensen et al. 2004). The desorption of boron from smectites is temperature dependent (complete at 100 °C), and thus, for the first time, it was established that fluids originate 1,000s of meters below the seafloor—preserving a signal of sediment–fluid interaction—and transport it through the backstop rocks of the overriding plate (Ranero et al. 2008). The transport is facilitated and in concert with lithic material that constitutes the mud volcanoes but is rarely examined in detail.

Lithium, a widely used tracer of water–sediment interactions, has been investigated experimentally for temperatures between 70 and 150 °C. This range prevails at the plate interface of subducting margins (Decarreau et al. 2012). In smectites, magnesium is replaced by lithium in the octahedral layer (hectorite, swinfordite). This reaction is favored by increased Li-content of the fluid and increased temperature. Hence, authigenic smectites may be efficient Li-sinks, and equally, dehydration of Li-smectites is expected to be a source of lithium. Scholz et al. (2009, 2010) established a widely applicable relationship between Li-content and $\delta^7\text{Li}$ for fluid–sediment interaction (Fig. 14). This relationship is based on a large dataset of pore fluids from different diagenetic regimes involving different host sediments. Basically, it characterizes the following regimes: (1) low- and (2) high-temperature diagenesis and (3) ridge-crest and (4) sediment-hosted hydrothermal systems. Significantly, seep fluids associated with mud volcanoes of the Mediterranean Ridge and the Gulf of Cadiz show characteristics of the high-temperature regime, those of the Gulf of Cadiz even of fluid–sediment interaction at hydrothermal regimes (>200 °C; Scholz et al. 2009). This attests to the fluid signal acquired 1,000s of meters below the seafloor; e.g., release of Li at high temperatures and uptake during illitization of smectite. Seep fluids from mud extrusions of the Nile delta and the Central American subduction zone exhibit characteristics related to provenance; in the one case, weathered low Li-sediments are delivered and in the other high-Li-volcano clastics.

Strontium and its $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio provide another set of signals related to fluid–sediment and rock interaction.

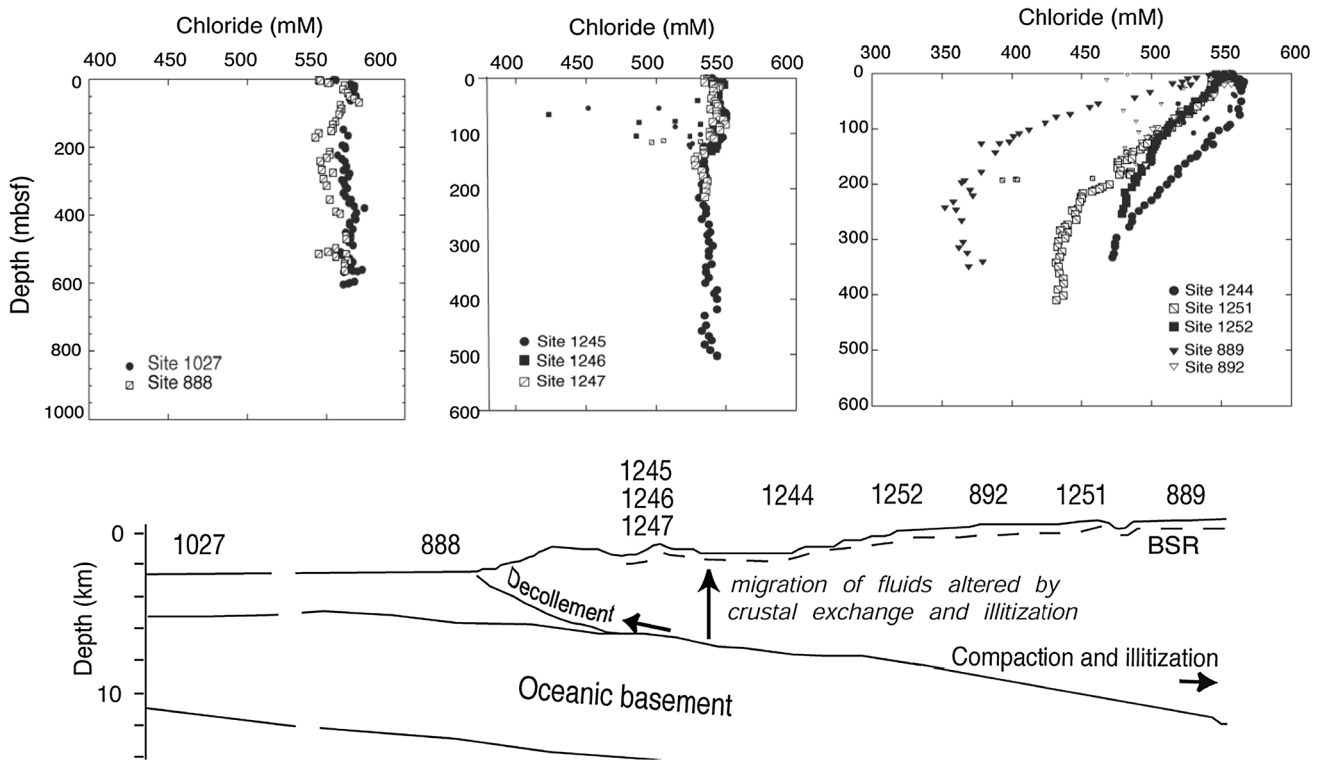


Fig. 12 Clay dehydration. Chloride dilution in pore fluids of accretionary margins from deformation toward continental framework rock is observed worldwide in ODP-drill sites. Data from ten sites across the Cascadia margin show progressive freshening attrib-

uted to increased compaction and smectite–illite transformation. Sites at the accretionary prism (Stations 1245–1247) show Cl-dilution <150 m below seafloor and >BSR depth from dissociation of gas hydrate; modified from Torres et al. (2004)

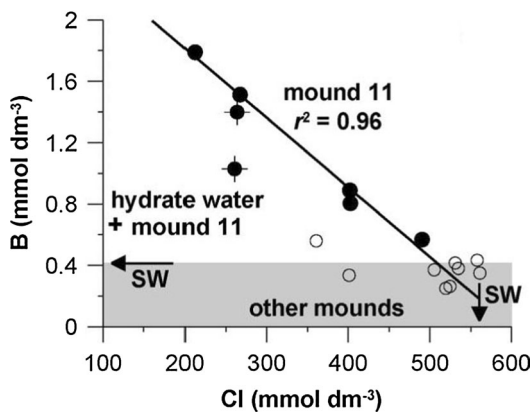


Fig. 13 Boron as tracer for clay-dehydration water. Seeping of clay-dehydration water from active mud volcanoes off Costa Rica with B-enrichment and strong Cl-dilution; release of hydrate water as cause for Cl-dilution is excluded and temperature of dehydration (~85 °C) derived from $\delta^{18}O_{H_2O}$ and δD_{H_2O} (not shown here). SW = concentration in seawater; modified from Hensen et al. (2004)

basalt the other. Both end-members are affected –through time- by changing seawater strontium (Quaternary [high] $^{87}Sr/^{86}Sr = 0.7091$; Cretaceous/Jurassic [low] = 0.7068 (Burke et al. 1982). As boron and lithium provide better temperature records of interaction, authigenesis and dehydration, strontium seems better suited as source indicator. This is true for seep fluids from the oceanic basement and volcanic clastics. Continental volcanics contain a small proportion of radiogenic strontium ($^{87}Sr/^{86}Sr$ from 0.7072 to 0.7082).

Seep and pore fluids from mud volcanoes across the Gulf of Cadiz (Scholz et al. 2009) record the evolution from high radiogenic strontium leached from terrigenous clays of the accretionary prism located close to land (eastern Gulf of Cadiz) to basement-derived fluids farther away at the margin of the prism (western Gulf of Cadiz; Fig. 15). Remarkably, one set of mud volcanoes is located along the northern branch of a transform fault system that crosses the accretionary prism from E–W and the other set located along a southern branch. Both sets show coincident progressive change from continental runoff (sediments of the accretionary prism) toward hydrothermal exchange (underlying oceanic crust) with distance. By extension, outside the accretionary prism, largely basement-derived

Release of radiogenic strontium (high $^{87}Sr/^{86}Sr \sim 0.7149$) from terrigenous sediment to pore and seep fluids represent one end-member component and low radiogenic strontium (low $^{87}Sr/^{86}Sr \sim 0.7029$) from the oceanic crust and

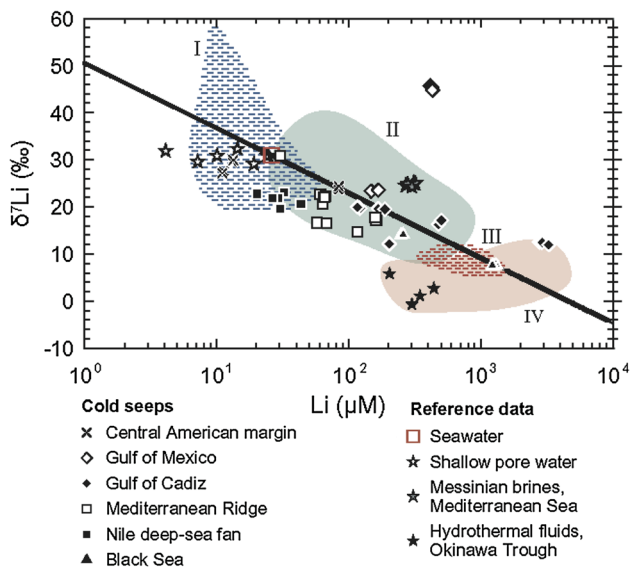


Fig. 14 Lithium tracer for fluid–sediment reactions. Based on reference data of Li and $\delta^7\text{Li}$ relationships (partially listed in the legend), several domains of fluid–sediment interaction are evident: (I) low-temperature diagenesis, (II) high-temperature diagenesis, (III) ridge-crust hydrothermal systems and (IV) sediment-hosted hydrothermal systems. Superimposed seep fluids from convergent, transform and passive margins show such source signals or differing signals depending on host sediments; modified from Scholz et al. (2010)

fluids are to be expected. The injection of basement fluid is likely driven by strike-slip motion and simultaneous thrusting along deep-rooted faults of the African–Eurasian plate boundary (Gutscher et al. 2012).

Submarine silicate weathering Reactions of poorly weathered sediments with pore fluids in continental margin sediments has been recognized as impacting pore water compositions (Aloisi et al. 2004a; Wallmann et al. 2008; Scholz et al. 2013). Hereby, submarine silicate weathering continues to form smectitic phases from cations, alkalinity and silica. In the process, water is taken up and increases the chloride content of the pore fluids. Although no such Cl-enriched fluids have been observed seeping from the seafloor above the accretionary prism off central Chile or other margins, the authors (Scholz et al. 2013) argue that water uptake by smectite formation and water release by smectite–illite transformation might compensate each other to a degree that makes documentation difficult. At this point, it should be recognized that continued submarine silicate weathering is an important post-depositional process that is probably more prevalent in buried continental margin pore fluids as it is in seep fluids emitted at the seafloor along margins.

Redox conditions The few datasets of REE pattern and trace metals (V, U, Mo) available from seep carbonates

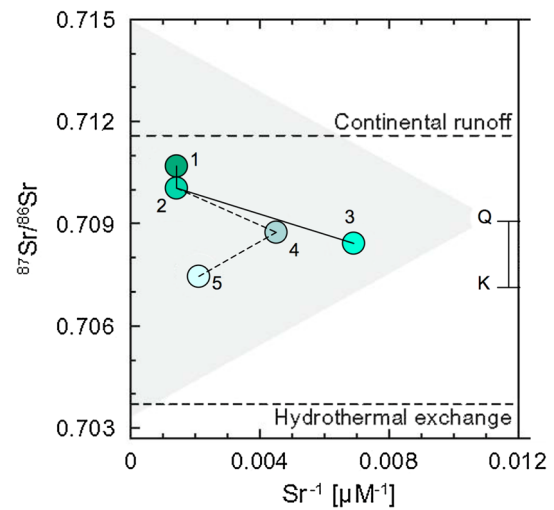
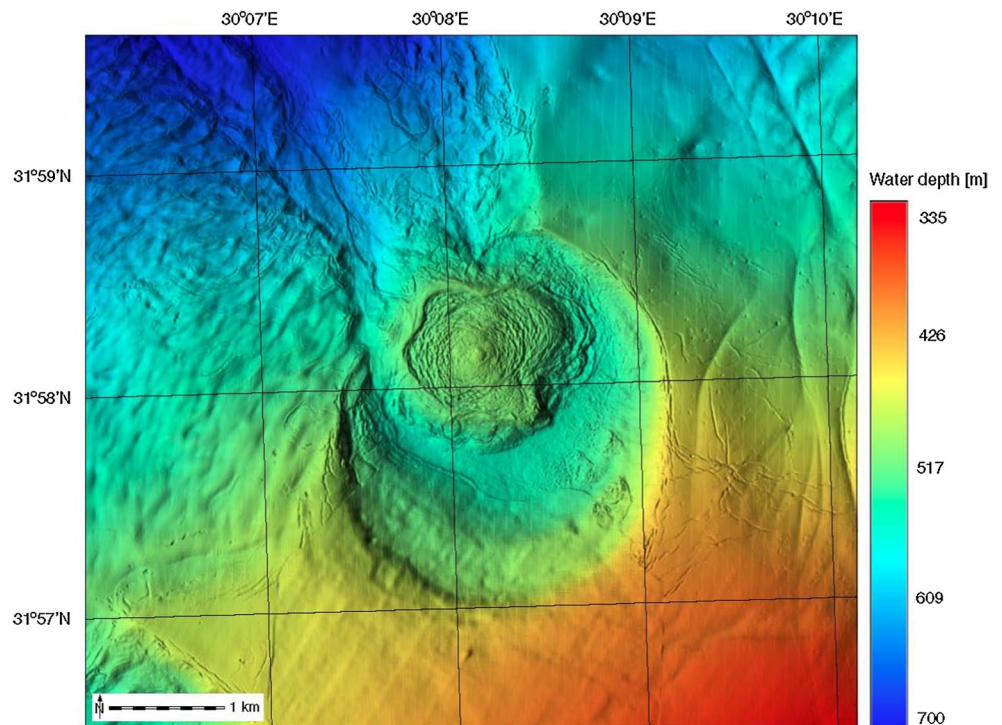


Fig. 15 Strontium tracer for deep fluids. Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ relationship in seep and pore fluids from mud volcanoes in the Gulf of Cadiz. Mud volcanoes #1–3 are located along a northern transform fault that crosses the accretionary prism from E–W and mud volcanoes #1, 4–5 are located along a southern transform fault. Both show progressive change from continental runoff (sediments of the accretionary prism) toward hydrothermal exchange (underlying oceanic crust) with distance. Such signals in seep fluids may be regarded as criteria for transform fault systems. Sr-isotopic characteristics for current (Q = Quaternary) and past (K = Cretaceous) seawater; modified from Scholz et al. (2009)

might be used as redox indicators (Ge et al. 2010; Himmler et al. 2010; Rongemaille et al. 2011; Bayon et al. 2011). The basis for interpreting trace metal and REE patterns is that these elements have multiple oxidation states and that a transition may be accompanied by a change in solubility in seawater, hence fixation of insoluble species during seep carbonate precipitation; e.g., for Ce as CeO_2 . Samples from passive margin settings exhibit a range in Ce-anomaly pattern [=log (Ce/Ce*) between 1.19 (oxic environment) and <1 (anoxic environment) tentatively assigning redox conditions during seep carbonate formation. In some cases, the V, Mo and U concentrations (e.g., U = highly insoluble under anoxic conditions) vary in accordance with the Ce-anomalies. Overall though, the redox characterization at present seems weak or inconclusive as several authors point to the need for improved extraction procedures to reduce contamination, better knowledge about REE-partitioning among the carbonate phases, and advantage of micro-scale determination [laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)] to detect changes in formation fluid from which the carbonates precipitated (Rongemaille et al. 2011; Himmler et al. 2010). Though some promising criteria have emerged in that aragonite more faithfully preserves fluid REE pattern at bottom water conditions and that strong enrichment of the MREE pattern (normalized to Post-Archaean Australian Shale) indicates a deep-sourced signal,

Fig. 16 Nile deep-sea fan. Shaded bathymetric map of the North Alex Mud Volcano with mud ponding, breached crater rim and outflow structures; modified from Feseker et al. (2010); map DTM courtesy BP Ltd)



whereas Bayon et al. (2011) emphasize that REEs emitted by seep fluids are scavenged by Fe–Mn-oxhydroxides and that authigenic precipitates do not record any REE-signal other than that of seawater based on ϵNd values. In contrast, a significant step in understanding REE pattern comes from pore waters of cold seep sediments from Hydrate Ridge (Himmler et al. 2013). High total dissolved REEs seem to become mobilized from remineralization of organic matter in the active AOM-depth interval. Here, formation of carbonates consumes calcium and REEs, which highlights the great potential to constrain environmental conditions from REEs in seep carbonates.

Unique seep settings

Among the geologic settings that generate seeps are those that accumulate organic-rich sediments in basins, in deltas, and those that are underlain by evaporites and hydrocarbon reservoirs. They provide unique characteristics expressed in mud volcanoes, pockmarks, brine lakes and—as with all seep settings—in authigenic carbonates. The Gulf of Mexico, the eastern Mediterranean Sea including the Nile deep-sea fan, the Black Sea, the South China Sea and the deltas of the rivers Congo, Niger and Mississippi all have been extensively investigated. Focus of the most recent investigation is the Atlantic coast off North America.

Seeps associated with evaporites are generated from underlying salt strata where loading by sediments causes salt to flow forming salt domes and salt ridges. Hereby,

low-density and low-viscosity salts escape the pressure of overburden by flowing upward. Salt domes push through the overlying strata, dragging them upward thereby developing faults along their flanks. This facilitates migration of fluids and in most cases liquid hydrocarbons. The tops of salt domes, near the seafloor, often dissolve away by circulating seawater and collapse. The result is large pockmarks, resembling the circumference of the underlying salt dome. Some contain brine pools and significant amounts of non-methane hydrocarbons including asphalt (MacDonald et al. 2004). The shelves and slopes surrounding the Gulf of Mexico contain such seeps and pockmarks related to salt tectonics as does the seafloor of the slope off Yucatan and have been the sites of extensive investigation (Roberts and Boland 2010). These are important provinces of oil and gas exploration and of classical hydrocarbon seep studies (MacDonald et al. 1990; Sassen et al. 2004).

The Messinian salt underlying the Mediterranean Sea affects fluid movement in the Nile deep-sea fan (Loncke et al. 2006). Seeps, mud volcanoes, methane plumes, carbonates and microbes have been reported there (Dupré et al. 2007; Gontharet et al. 2007; Feseker et al. 2010). Two prominent mud volcanoes (>50 km in diameter) with high temperatures ($\geq 50^\circ$ a few meters below seafloor) extrude muds and fluid, strongly depleted interstitial chloride and contain thermogenic gases (Figs. 16, 17). The mud surface appears wrinkled with ponding and outflow structures where the rim is breached. Currently they appear to be moderately to highly active (Feseker et al. 2010).

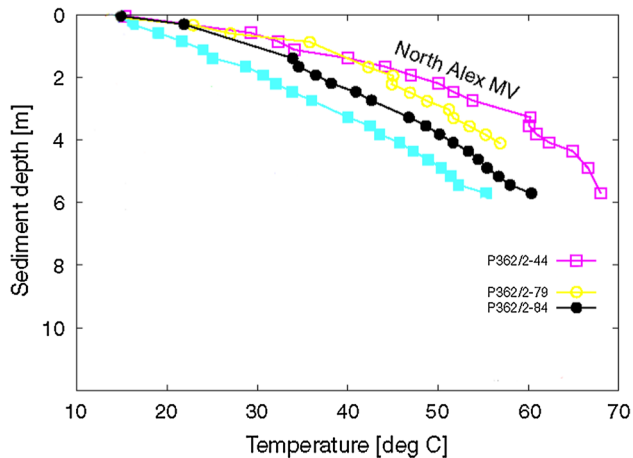


Fig. 17 Mud volcano near-surface temperature. In situ sediment temperature profiles from the center of North Alex Mud Volcano; strong increase to >60 °C attests to strong activity and mud extrusion from depth; modified from Feseker et al. (2010)

Quite similar features have been recorded for the Håkon Mosby mud volcano on the slope of the Barents Sea with a >300 ky history of extrusion (Perez-Garcia et al. 2009). Ongoing activity has produced flow structures inside the crater evident in subtle morphological changes recorded by high-resolution seabed mapping over a 3-year period (Foucher et al. 2010). Even though large amounts of hydrocarbon gasses are emitted, the elevated mud temperature of currently active mounds prevent gas hydrates from forming entirely—as with those on the Nile deep sea—or only around the margins where temperatures are low as with Håkon Mosby mud volcano (Feseker et al. 2008).

This is different along the subduction zone of the eastern Mediterranean Sea—the Mediterranean Ridge. Here at the intersection of the Hellenic and Cyprus arcs lies the Anaximander Mountain region, the Olimpi area of mud volcanoes (Limonov et al. 1996; Aloisi et al. 2000; Pape et al. 2010) with extensive gas hydrate and brine lakes (Westbrook and Reston 2002). The driving mechanism for seepage and mud extrusion is the convergence of the African and Eurasian plates whereby the Messinian evaporites impart their composition on the hydrocarbon–metazoan–microbe–carbonate association (Olu-Le Roy et al. 2004; Pancost et al. 2000). Most noteworthy are brine pools at the seafloor (2,000–3,000 m) at the western part of the accretionary wedge where the morphology is controlled by convergent tectonic (Camerlenghi et al. 1995). The brines are at or close to saturation with respect to chlorides of sodium, magnesium and potassium (Fig. 18). The composition varies significantly between adjacent pools and depends on the depths within the salt sequence from which the fluid is generated (Westbrook and MEDRIF Consortium 1995).

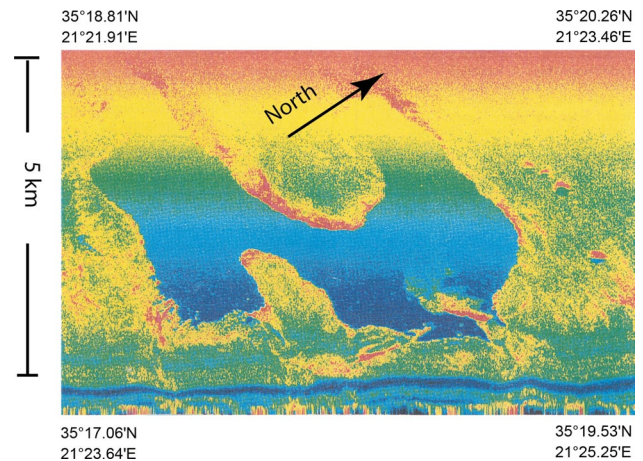


Fig. 18 L'Atalante brine lake. False-color side-scan sonar image shows horse shoe-shaped brine lake on the Mediterranean Ridge; modified from Suess and Linke (2006) based on Westbrook and MEDRIF Consortium (1995)

In the Gulf of Cadiz, an accretionary wedge partially underlain by evaporites and cut by a transform fault system combine to generate complex expressions of seepage and mud extrusion (Gutscher et al. 2012; León et al. 2012). Few of the mounds are currently active, harbor seep biota (Sommer et al. 2009) and are thought to experience thermal pulses and injection of brine (Haffert et al. 2013). The composition and source of fluids and muds are controlled by terrigenous continental characteristics in the landward part of the complex changing to oceanic crustal characteristics seaward (Hensen et al. 2007). Fluid–sediment and rock interactions convincingly document this trend (Scholz et al. 2009).

The Black Sea has been accorded special effort in ongoing seep studies for its anoxic, methane-rich water column below about 100 m and its thick, up to 16 km, organic-rich sediments (Bohrmann et al. 2003; Mazzini et al. 2008). Over 2000 seeps were mapped off Romania and the Ukraine (Naudts et al. 2006). The sites are concentrated at the shelf-slope break extending to about 725 m water depth. In the sub-seafloor below that water depth, the stability limit of methane hydrates has been projected from the bottom water temperature and the geothermal gradient implying that above 725 m gaseous methane escapes into the bottom water and below, methane is retained as hydrate. The seep province continues off the Crimean Peninsula where in the eastern basin, gas hydrates, methane plumes in the water column and mud volcanoes at 1,000–2,300 m depth were discovered (Greinert et al. 2006). Still farther east at the margin off Georgia, extensive methane seepage is found in the Batumi area where state-of-the-art pressure coring technology was used to quantify methane emissions and subsurface gas hydrate (Pape et al. 2011; Heeschen

et al. 2011). Throughout the Black Sea authigenic carbonates of many morphologies and compositions are associated with the seep provinces although seep macrofauna appears to be absent. Instead, microbial communities, mats and microbial reefs abound (Peckmann et al. 2001; Treude et al. 2007). Several new discoveries of seeps and ongoing research from other known sites on passive margins are likely to expand the criteria for characterizing the hydrocarbon–metazoan–microbe–carbonate association.

In the South China Sea, basin-wide seep activity is concentrated in active and passive margin settings. Along the accretionary prism that results from plate subduction at the Manila Trench off Taiwan Island, methane seeps are common (Huang et al. 2006; Lin et al. 2008; Schnürle et al. 2011). The westward transition toward a fully passive margin setting reveals equally active seeps (Suess 2005). Their manifestations are largely authigenic carbonates with biomarkers, REEs, U/Th-ages and carbonate mineralogies having all been investigated in detail (Chen et al. 2005; Lu et al. 2005; Han et al. 2008). The timing of methane-release events primarily during low sealevel stands (Feng et al. 2010; Tong et al. 2013; Han et al. 2014) and the possible recording of oxic or anoxic conditions during carbonate precipitation are currently under discussion (Ge et al. 2010). Other finds are reported from the Congo deep-sea fan (Kasten et al. 2012) with research on authigenic carbonates and associated biota in progress (Pierre et al. 2014).

A most recent survey of the water column and the seafloor along the Atlantic margin off North America with an advanced multibeam sonar system aboard the NOAA ship *Okeanos Explorer* showed methane plumes in 40 locations (NOAA ref. 2013). The subsequent Deepwater Canyons 2013 Expedition (NOAA-OER/BOEM/USGS) documented all manifestations of cold seepage of which the images of “creepy crawlies” attracted the most media attention so far.

Seep characteristics from erosive and transform margins

No previous attempts are known for characterizing the seep fluids emitted at erosive and transform margins in their own right, although some specific properties stand out. As higher temperatures and pressures and portions of the down-going plate are involved, mineral-bound water from opal or clays, and elements susceptible to mobilization under these conditions are added to the upward flow. Mineral-bound water dilutes the salinity of the seep fluid. It is characteristically ^{18}O -enriched and contains mobilized elements as boron and lithium (Chan and Kastner 2000; Dählmann and de Lange 2003; Hensen et al. 2004; Scholz et al. 2010).

At still higher pressures and temperatures, serpentinization sets in. During these reactions, methane is formed from reduction of oceanic carbon dioxide by hydrogen which in turn is released from common olivine reacting with seawater. Basically, the dissolution of mixed Mg-, Ca-silicates containing Fe (fosterite, enstatite, fayalite) initially results in high-pH waters forming cations and aqueous silica. These in turn react to form suites of serpentinite minerals (chrysotile, serpentine), hematite and molecular hydrogen. Further reactions, e.g., of hydrogen with dissolved carbonate ions of seawater form abiotic hydrocarbons largely methane and of high-pH waters with seawater form authigenic carbonates. Free hydrogen that is not consumed by CO_2 reduction is abundant at serpentinization-driven seeps as are archaea thriving at pH values of >12 (Mottl et al. 2003).

Mud volcanoes are seafloor manifestations of deep-sourced seeps on erosive margins. At the Mariana Fore-Arc and the Costa Rica margin, they are aligned above sub-seafloor isotherms (Mottl et al. 2004; Ranero and von Huene 2000; Ranero et al. 2008). Hence, their geochemical and isotope characteristics provide good evidence for depths and temperature of fluid generation. Not just fluids are expelled at mud volcanoes but also solids from the conduit walls. Unfortunately, studying these lithic products is not fully taken advantage of. Besides establishing the stratigraphy and composition through which fluids pass, the material may also transport microbial life from the deep biosphere to the seafloor.

Fluids from transform margins are derived from great depth because steeply dipping and deep-reaching fault planes are common for transform fault systems. As with seep fluids, however, and with mud volcanoes in any tectonic setting the nature and provenance of the sediment sequence through which the fluids ascend will impart their characteristics to the fluids and thus mask any deep-source signal. The pore and seep fluids from the North Anatolian Transform in the Marmara Sea have a brackish water source among others and have experienced a diversity of reactions (Zitter et al. 2008; Tryon et al. 2010) with no clear transform fault indicator. Fluids from the Gulf of Cadiz that ascend through evaporites are clearly characterized by their halite, gypsum and late-stage evaporite salt contributions (Hensen et al. 2007; Haffert et al. 2013). Barium in fluids and barites from the Derugin Basin (Sakhalin Transform system; Greinert et al. 2002) the San Clemente Fault (San Andrea Transform system; Torres et al. 2002; McQuay et al. 2008) as well as among the precipitates from the North Aantolian fault system (Crémier et al. 2012), initially thought to be unique to transform settings (Suess 2010), are now thought to originate from non-detrital biogenic barite. Barium associated with biogenic opal is well known of these marginal basins of high biological productivity. Barium would be

mobilized by dissolution from biological detritus in sulfate-free pore waters and emitted by seep fluids. Such a mechanism had been suggested for barites at seeps along the Peru subduction and the Sakhalin transform fault (Torres et al. 1996; Aloisi et al. 2004b).

Tentatively though, two criteria may have emerged for transform fault seepage: (1) $^{87}\text{Sr}/^{86}\text{Sr}$ in fluids from the interaction with the underlying oceanic plate (Scholz et al. 2009) and (2) neo-formation of smectite recovered at depth from the sliding surfaces of the San Andrea Fault zone (Carpenter et al. 2011). Currently, it is difficult to envision that neo-formation of smectite may have any relevance to seeps, yet the sorely neglected studies of lithic material ejected from mud volcanoes may prove successful if the newly formed smectite in question may be differentiated from detrital smectite.

Some significant and speculative issues

Budgets of volatile emissions from seeps and retention of carbon as authigenic carbonates

Several approaches are in use to estimate the water output from the subducting sediment packages at convergent margins. One depends on porosity reduction and rate of subduction to yield water loss with distance from the deformation front (Saffer 2003; Moore et al. 2011). The other is based on measured and/or modeled emission rates at seep sites and up-scaling (Wallmann et al. 2006; Hensen et al. 2004; Ranero et al. 2008; Freundt et al. 2014; Karaca et al. 2012).

Restored structural sections that partition total shortening into fault slip and volume loss yield dewatering rates of $\sim 10 \text{ km}^3 \text{ Ma}^{-1}$ per km of length as shown for the Nankai subduction zone (Moore et al. 2011); this approach appears attractive. However, according to the authors, it does not include the water loss from soft sediments during initial accretion, which might be the reason for discrepancies with seepage rates up-scaled from direct measurements. To improve this situation modeled flow rates from pore water profiles, bubble and fluid escape from seepage and the degree of biological methane oxidation (benthic filter) need to be better quantified. Deep-sea landers equipped with flux meters deployed at single sites (Tryon et al. 2001; Linke et al. 2005; Fürli et al. 2009) have recorded flow rates between $<10^{-3}$ and $>10^2 \text{ cm year}^{-1}$. A geo-acoustic technique, GasQuant, based on the backscatter intensity of bubbles, horizontal scans of escaping plumes at the sea floor and integration of bubble spectra provides total gas flux estimates (Greinert 2008; Schneider von Deimling et al. 2011). These techniques combined with characterizing seep footprints should be refined and results compared to and harmonized with those from the geophysical approach.

Finally, if the biota at the seafloor and in the water column consume methane aerobically, the carbon is largely added as CO_2 to the seawater. If they consume methane anaerobically (AOM), the carbon is retained as authigenic carbonates (Treude 2012). Partitioning the methane-C sink from biological oxidation between seawater bicarbonate and mineral carbonate is a scientific challenge that has not been addressed as of today. The high apparent seafloor oxygen consumption and the apparently insufficient methane-carbon supply (Boetius and Wenzhöfer 2013) more than highlights the need for accurate budgeting.

Fossilization of microbial structures involved in AOM

Documentation of microbial activity from ancient seeps is progressing rapidly. The geologic time scale for seep activity is steadily being pushed back, with ancient plate boundaries and passive margins being recognized as characteristic settings (Campbell et al. 2002; Kiel 2009, 2010). Sediment fabric and organic geochemistry of geological material will continue to yield sites of ancient seeps. The concern over contamination of geological samples is not as serious as with recent material since microbial bodies are fully encased in the carbonate matrix that formed during AOM. Likewise, preparatory work in isolating biomarkers from authigenic carbonates ascertains contamination-free samples such as the miniaturized biosignature extraction procedures introduced recently (Leefmann et al. 2008).

Abundant structures of suspected fossilized microbes are present in seep carbonates. Among these are filamentous, rod-shaped, cylindrical, spindle- and dumbbell-shaped bodies and rice-shaped grains that await identification (Peckmann et al. 2004; Han et al. 2008; Crémère et al. 2012). Fossilized bodies, resembling microbial morphologies and consisting wholly of AOM-carbonates, e.g., aragonite, high-Mg-calcite, and dolomite grains, and their biomarkers will provide considerable new knowledge. A breakthrough in this approach is that sulfate-reducing bacteria are able to directly form dolomite grains via a selective biofilm that actively alters the Mg/Ca ratio (Krause et al. 2012).

Elusive carbonates from serpentinization at subducting margins

If the return flow pathway of fluids released from serpentinization of the down-going oceanic plate is directly into bottom waters instead of through thick fore-arc sediments, such fluids may maintain high-pH values, Mg-, Ca-, and aqueous SiO_2 -contents from dissolution of the ultramafic crustal minerals. Mixing at the slightly more acidic pH of seawater and with dissolved inorganic carbonate species (DIC) would result in carbonate mineral precipitation analogous to those chimneys formed from the products of serpentinized

oceanic crust at hydrothermal sites. The most likely site for emission of such fluids is at the trench-outer rise, usually quite deep (>4,000 m) such that carbonate formations might have escaped detection so far. Geophysical methods constrain the trench-outer rise offshore Nicaragua as a region underlain by serpentinized and highly fractured oceanic plate (Ivandic et al. 2010). A search there for subduction zone chimneys along with molecular hydrogen emissions would be a scientific objective for future convergent margin studies. Its relevance is seen in that the hypothetical carbonates could represent a hitherto unrecognized global CO₂-sink. This would complement estimates of CO₂ sequestered in onshore ophiolite massifs and ultramafic intrusions as well as offshore slow-spreading ridge segments and magmatic fore-arcs as currently debated (Kelemen et al. 2011).

Far-out option for reconstructing paleo-seawater from seep products

Pseudomorphs of carbonates after ikaite, an authigenic 6-hydrated calcium carbonate frequently found in the geologic record as well as in seep settings, has long been associated with polar environments (Whiticar and Suess 1998). This characterization does not strictly hold, as other environments of ikaite formation have been identified (Buchardt et al. 1997; Jansen et al. 1987), although generally a cold water environment seems to be favored (Schubert et al. 1997). Crude attempts to glean information on the temperature of formation from O-isotopes of ikaite, recovered from the Bransfield Strait and the Sea of Okhotsk (both at bottom water temperatures around freezing) yielded temperatures of -1 ± 1 °C (Suess et al. 1981; Greinert and Derkachev 2004). Thereby, the isotopic composition of the seawater from the Okhotsk Sea site was diluted by meteoric water, and more importantly, it remained unclear why calcium carbonate hexahydrate (ikaite) should behave like anhydrous calcite with regard to O-isotope fractionation. Experimental work on synthetic ikaites (Rickaby et al. 2006) showed that the crystal water of the hydrated carbonate phase preserves the original $\delta^{18}\text{O}$ of the precipitating water and the authors suggest its potential usefulness as proxy for ancient seawater. As $\delta^{18}\text{O}(\text{sw})$ is a crucial factor for calculating the temperature of formation from the O-isotopes, a search for hydrated authigenic carbonates among the seep products might yield surprising results. Ikaites are rarely preserved from seep sites; however, gas hydrates are ubiquitous. Much work has been done on hydrate water of methane hydrates, unfortunately—as of now—no clear relationship has emerged between the $\delta^{18}\text{O}$ of the precipitating fluid and the water retained in the clathrate structure (Maekawa 2004) that might be used as a proxy for ancient seawater.

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