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

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## Abstract

Seep characteristics 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 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 into the ocean 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 (AOM) 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 cyclicality 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 fluid 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 ( $Li/\delta^7Li$ ; Ba) from host-sediments. Smectite-illite tranformation and accociated Cl-depletion from release of interlayer water is a pervasive process at these margins. Rare earth element pattern (REEs) in conjunction with redox-sensitive metals retained in seep carbonates may 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  $^{87}Sr/^{86}Sr$  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 the role of the geologically derived methane in the global methane cycle.

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## 1. 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 time-scales 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 as well from mud volcanos 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. The 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 over-arching objective of the Research Consortium SFB 574 by the German Science Foundation entitled: "*Volatiles and Fluids in Subduction Zones*" (Wallmann 2001; Jarrard 2003; Ruepke et al. 2004; Scholl and von Huene 2007; Freundt et al. this volume). 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 authigenic carbonates. They form above rapidly accumulating, organic-rich sediments, deltaic aprons, hydrocarbon reservoirs or buried evaporites. Return 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, 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 (Bohrmann and Jørgensen 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 (Greinert 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.

## 2. Seeps at active plate margins

### *Oceanic plate – 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). 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 may 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 continent leaving scars and scarps (Ranero and von Huene 2000; Barnes et al. 2010). Ensuing slope failures, faulting and bulging of the sediment strata greatly facilitate fluid escape and seep formation (Mau et al. this volume). 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 volcanos 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 (CLIP; Vannucchi et al. 2006), consist to a significant degree of cemented fore-arc basin type sediments (IODP Prelm. Rept., 344; 2013). These lithologies may impart characteristics to the fluids and solids that are transported upwards presumably along splay-faults imaged as high-amplitude, landward-dipping reflectors that cut through the fore-arc and appear to be off-set 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 volcanos 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; Ruepcke et al. 2004; Ivandic et al. 2011). 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. 3). 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.

5 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 – oceanic plate convergence*

10 Emission of deep-sourced fluids containing abiotic 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 (deserpentinization). This may take place as deep as 30 km below the seafloor. The  
15 liberated fluids ascend and compound hydration of the overlying oceanic plate. The hydration reactions form serpentinite 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 abiotic 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 2009; National Geographic Magazine, June  
20 2013). The area of the southern Mariana Arc including the Challenger Deep and Sirena Deep in the trench, the serpentinite 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  
25 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 serpentinitized oceanic crust form aragonite and calcite chimneys (Ludwig et al. 2006). However, none have been reported so far from serpentinitized portions of the oceanic plate entering the subduction zone.

#### 30 *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 associations at hydrothermal vents of oceanic spreading centres (Lonsdale, 1979) and later correctly identified as cold seep products (Torres et al 2002) At transform boundaries two plates  
35 slide past each other with only horizontal movement between them either threatening earthquakes if they are locked or facilitating reactions during slow creep when 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 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; Géli et al. 2008; Gutscher et al. 2012).

### 5 **3. 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 over-pressured formations containing hydrocarbons and brines, or from rapidly deposited accumulations of water-rich sediments, as in deltas. 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 vent-like biological communities were first reported off the 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 et al. 2006). Submarine groundwater discharge may be estimated by <sup>222</sup>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 volcanos 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, 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 (Karpen et al. 2003) 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 modelling pore water profiles (Hensen et al. 2004; Karaca et al. this volume; 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).

### **4. 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.

#### 4.1 Sedimented margins

The subduction of sedimented oceanic plates provides the first order input of volatile elements to the Earth's material re-cycling (Jarrard 2003; Scholl and von Huene 2007; Freundt et al. this volume). 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 hemi-pelagic 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 sulphide, 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 favour sulphate reduction and methanogenesis of the microbially mediated early diagenetic reaction sequence.

Most sedimented margins generate enough biogenic methane that, when moving upwards, 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 (Tinavella and Lodolo 2000). In the following paragraphs the products of seeps emanating from the seafloor are described of which 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. this volume).

##### *The hydrocarbon-metazoan-microbe-carbonate association*

Fluid flow, bioirrigation and bubble-induced mixing at seeps (Sahling et al. 2003; Haeckel et al. 2007) drives the interaction between anaerobic oxidation of methane (AOM), communities of macro-biota 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. 6 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 (Freitag et al. 2001). As a consequence of the AOM-activity calcium carbonate phases precipitate (Reaction 3). Earlier views favoured 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 sulphate (Boetius et al. 2000; Orphan et al. 2001; Milucka et al. 2012). The steep gradient of sulphate within the near-surface sediments is a reliable indicator for rapid upward flow of methane-rich seep fluids (Knittel et al. 2003). The sub-surface depth of the sulphate-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 CO<sub>2</sub> 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 CH<sub>4</sub> (Whiticar 1999).

Gas hydrate forms 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 starts at water depths as shallow as 300m in Arctic bottom waters and around 750m in subtropical bottom waters. The base of the GHSZ varies with the water depth and the geothermal gradient and may range from 100s to 1000s of meters below sea floor. In seep waters high precision Cl-analyses, coupled with O- and D/H-isotopes of H<sub>2</sub>O 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 <sup>13</sup>C 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 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 visible as brightly colored mats- provide carbon and energy via anaerobic oxidation of methane. 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; Kennicut et al. 1985). Numerous reviews and case studies (Sibuet and Olu,

1998; Sahling et al. 2002; Levin 2005; Olu-Le Roy et al. 2007; Kiel 2010) since 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).  
5 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).

10 Typical members of seep biota from the Cost Rica and the Chile margin are tubeworms (Fig. 8 A and B), clams and mussels (Fig. 8 E and F) and microbial mats (Fig. 8 C and D). It is quite evident that the former is a sediment-starved environment whereas the latter is heavily sedimented perhaps affecting the community structure. Hernandez-Zabata et al. (2013) suspect that the seep fauna off southern Chile constitutes a new biogeographical  
15 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 <sup>13</sup>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 <sup>13</sup>C-depleted foraminifera tests from seep sites at the Hikurangi margin and elsewhere result from chemo-autotrophic intake of seep-carbon by living forams. Rather they  
20 result from recrystallization of their tests in a <sup>13</sup>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-  
25 ocean ridges and vents and seeps are accorded special significance (Topics in Geobiology; S. Kiel, ed, 2010).

### *Authigenic carbonates*

A direct consequence of anaerobic oxidation of methane 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  
30 criteria to identify seeps. Carbonate build-ups (chemoherms; Fig. 9a A and B), reaching several meters above the seafloor are believed to form in contact with bottom water (Teichert et al. 2005; Han et al. 2004; 2008; Liebetrau et al. this volume). Other build-ups 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 Fig. 9b D, E, F). Many other shapes and sizes of seep carbonates have been observed, too  
35 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 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).

5 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. this volume; Mavromatis et al. this volume). 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.

15 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).

### 25 *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, D, E). Geo-acoustic tools (side-scan sonar, sub-bottom profiler) combined with high resolution multi-beam 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. this volume) provide the data base from which to derive seep fluxes and reliably up-scaling as shown in exemplary fashion for the Costa Rica margin (Freundt et al. this volume).

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 1000 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 global up-scaling.

### ***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 exceeds 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 6 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 2100±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. this volume) 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. this volume) such as warming of bottom water that destabilizes methane hydrate, increase of 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 favour methane release events as there is currently—at high sealevel—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 of 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 of water-gas fluid accumulation at depth is a distinct lithologic boundary that constricts flow. The resulting over pressure forces methane continuously through a well-defined network of faults to the Pinnacle site.

A first-of-its-kind investigation of intercalated carbonate and host-sediment on flanks of seep structures and of drill cores taken in the centres of seep structures (mounds) on the Costa Rica margin (Kutterolf et al. 2008; Liebetrau et al. this volume) revealed at first sight unconventional results. The mud volcanos 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 – 65 ky ago). Ages of the drill core samples showed downward progression of growth instead of upward as the ages of the mounds do with inward growth instead of outward. Both trends are readily explained by clogging of the fluid conduits with time by authigenic carbonate precipitation. The internal structure of a generic mud volcano (Fig. 10) shows sediment intercalated (incl. volcanic ash as marker) with muds that were dated to provide the lifetime and cyclicity of seep activity. Though, globally and over Quaternary times, eustatic sea-level fluctuations are currently favoured 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. Since the time of the Deep Sea Drilling Project many 1000s 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 towards 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. The anomaly is an artefact 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<sub>2</sub>O the resulting anomalies may be linked to gas hydrates and indeed is 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  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  of pore fluids (Fig. 11).

Seep carbonates being precipitated during AOM are another sink of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  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 ( $\delta^{13}\text{C} = -40$  to  $-54$  ‰ PDB) of this intergrowth (Fig. 9b A and 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 temperatures, the Mg-calcite –the older phase-- was enriched in  $\delta^{18}\text{O}$  by about +1 ‰ PDB. This is attributed to gas hydrate water in the precipitating fluid. Hydrate water may be enriched in  $^{18}\text{O}$  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”  $^{18}\text{O}$  from hydrate waters to

carbonates. The term “clathrite” 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 of “heavy”  $\delta^{18}\text{O}$ -values of seep carbonates as sourced by methane hydrate. Currently, too 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) because  
5 there are other sources of “heavy” water being emitted at seeps (Dählmann et al. 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  
10 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 McKiernann 2009). Incomplete dehydration changes 18Å- to 15Å-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  
15 (Torres et al. 2004) show progressive freshening attributable to increased compaction and smectite-illite transformation (Fig. 12). Sites at the accretionary prism (1245-1247) show Cl-dilution at 150 m below seafloor and above the BSR depth from dissociation of gas hydrate.

The  $\delta\text{D}$  (-32‰ SMOW) and  $\delta^{18}\text{O}$  (+10‰ SMOW) of interlayer water differs significantly from seawater as  
20 determined from deeply buried strata of mud volcanos (Dählman et al. 2003). These isotope characteristics affect the pore water  $\delta\text{D}$  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 volcanos) off Costa Rica  
25 and the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  isotope-ratios of seep water are 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 1000s 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 volcanos but is rarely examined in detail.

30 Lithium, a widely used tracer of water–sediment interactions, has been investigated experimentally for temperatures between 70°-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 the temperature. Hence authigenic smectites may be efficient Li-sinks and,  
35 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 volcanos 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 ( $>200^{\circ}\text{C}$ ; Scholz et al. 2009). This attests to the fluid signal acquired 1000s 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. Release of radiogenic strontium (high  $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7149$ ) from terrigenous sediment to pore- and seep-fluids represent one end-member component and low radiogenic strontium (low  $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7029$ ) from the oceanic crust and basalt the other. Both end-members are affected –through time- by changing seawater strontium (Quaternary [high]  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7091$ ; 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 ( $^{87}\text{Sr}/^{86}\text{Sr}$  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) towards hydrothermal exchange (underlying oceanic crust) with distance. By extension, outside the accretionary prism, largely basement-derived 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 recently been recognized as impacting pore water compositions (Aloisi et al. 2004; 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 data sets of REE pattern and trace metals (V, U, Mo) available from seep carbonates 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<sub>2</sub>. 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) indicate a deep-sourced signal. Whereas Bayon et al. (2011) emphasize that REEs emitted by seep fluids are scavenged by Fe-Mn-oxihydroxides and that authigenic precipitates do not record any REE-signal other than that of seawater based on εNd-values. This appears to be the case for oxic environments whereas anoxic or sub-oxic conditions prevail at more active seeps.

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#### **4.2 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 volcanos, 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.

25

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 upwards 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. These are important provinces of oil and gas exploration and of classical hydrocarbon seep studies (MacDonald et al. 1990; Sassen et al. 2004).

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The Messinian salt underlying the Mediterranean Sea affects fluid movement in the Nile deep-sea fan (Loncke et al. 2006). Seeps, mud volcanos, methane plumes, carbonates and microbes have been reported there (Dupré et al. 2007; Gontharet et al. 2007; Feseker et al. 2010). Two prominent mud volcanos (>50 km in diameter) with high temperatures (>>50° 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. They appear moderately to highly active (Feseker et al. 2010).

Quite similar features have been recorded for the Hakon Mosby mud volcano on the slope of the Barents Sea with a >300 k year 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 Hakon Mosby mud volcano (Feseker et al 2009).

This is different in the eastern Mediterranean Sea. Along the subduction zone -the Mediterranean Ridge- 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). Here 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 (2000-3000 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 et al. 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; Leon 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 is 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 volcanos at 1000-2300 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 with state-of-the-art pressure coring technology 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 towards a fully passive 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. this volume) 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 attention so far.

### **5. 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  $^{18}\text{O}$ -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<sub>2</sub>-reduction is abundant at serpentinitization-driven seeps as are Archaea thriving at pH-values of >12 (Mottl et al. 2003).

Mud volcanos 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 volcanos 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 systems. As with seep fluids, however, and with mud volcanos 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 Anatolian fault system (Cremière et al. 2012), initially thought to be unique to transform settings (Suess 2010), are now thought to originate from non-detrital barite. Barium associated with biogenic opal is well known of these marginal basins of high biological productivity. Barium would be mobilized by dissolution from detritus in sulphate-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. 2004).

Tentatively though, two criteria may have emerged for transform fault seepage: (1) <sup>87</sup>Sr/<sup>86</sup>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 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.

## 6. 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 modelled emission rates at seep sites and up-scaling (Wallmann et al. 2006; Hensen et al. 2004; Ranero et al. 2008; Freundt et al. this volume; Karaca et al. this volume).

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 up-scaled seepage rates from direct measurements. To improve this situation modelled 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  $<10^{-3}$  to  $>10^2 \text{ cm} \cdot \text{y}^{-1}$ . A geo-acoustic technique, GasQuant, based on the backscatter intensity of bubbles, scans escaping plumes horizontally at the sea floor and integrates bubble-spectra for total gas fluxes (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  $\text{CO}_2$  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 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 well. 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 bio-signature extraction procedures introduced (Leefmann et al. 2008).

Abundant structures of suspected fossilized microbes are present in seep carbonates. Among these are filamentous, rod-shaped, cylindrical, spindle- and dumb-bell shaped bodies and rice-shaped grains that await identification

(Peckmann et al. 2004; Han et al. 2008; Cremiere 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 sulphate-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 sediments, such fluids may maintain high pH-values, and Mg-, Ca- and aqueous SiO<sub>2</sub>-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 the hydrothermal sites. The most likely site for emission of such fluids is at trench-outer rise, usually quite deep (>4000m), 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. 2011). 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 CO<sub>2</sub>-sink. This would complement estimates of CO<sub>2</sub> sequestered in onshore ophiolite massifs and ultramafic intrusions as well as offshore slow-spreading ridge segments and magmatic fore-arcs as currently debated (Keleman 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 conditions (Whiticar and Suess 1998). This characterization does not strictly hold, as other environments of ikaite formation have been identified (Burchardt 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  $-1\pm 1^{\circ}\text{C}$  (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  $\delta^{18}\text{O}$  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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### References

- 20 Aloisi G, Wallmann K, Drews M, Bohrmann G (2004) Evidence for the submarine weathering of silicate minerals in Black Sea sediments: possible implications for the marine Li and B cycles. *Geochem Geophys Geosyst* 5, Q04007 doi:10.1029/2003GC000639
- 25 Aloisi G, Pierre C, Rouchy C, Foucher JP, Woodside J, The MEDINAUT Scientific Party (2000) Methane-related authigenic carbonates of eastern Mediterranean Sea mud volcanoes and their possible relation to gas hydrate destabilisation. *Earth Planet Sci Lett* 184:321–338
- Aloisi G, Wallmann K, Bollwerk SM, Derkachev A, Bohrmann G, Suess E (2004) The effect of dissolved barium on biogeochemical processes at cold seeps. *Geochim Cosmochim Acta* 68 (8):1735-1748
- 30 Baco AR, Rowden AA, Levin LA, Smith CR and Bowden DA (2010) Initial characterization of cold seep faunal communities on the New Zealand Hikurangi margin. *Mar Geol* 272:251-259
- Barnes PM, Lamarche G, Bialas J, Henrys S, Pecher I, Netzeband GL, Greinert J, Mountjoy JJ, Pedley K and Crutchley G (2010) Tectonic and geological framework for gas hydrates and cold seeps on the Hikurangi subduction margin, New Zealand. *Mar Geology* 272:26-48
- 35 Bayon G, Birot D, Ruffine L, Caprais JC, Ponzevera E, Bollinger C, Donval JP, Charlou JL, Voisset M, Grimaud S (2011) Evidence for intense REE scavenging at cold seeps from the Niger Delta margin. *Earth Planet Sci Lett* 312 (3-4):443-452
- Bayon G, Pierre C, Etoubleau J, Voisset M, Cauquil E, Marsset T, Sultan N, Le Drezen E, Fouquet Y (2007) Sr/Ca and Mg/Ca ratios in Niger Delta sediments: Implications for authigenic carbonate genesis in cold seep environments. *Mar Geol* 241:93-109
- 40 Birgel D, Himmler T, Freiwald A, Peckmann J (2008) A new constraint on the antiquity of anaerobic oxidation of methane: Late Pennsylvanian seep limestones from southern Namibia. *Geology* 36:543-546
- Boetius A and Wenzhöfer F (2013) Seafloor oxygen consumption fuelled by methane from cold seeps. *Nature Geoscience* 6:725-734 doi:10.1038/NGEO1926
- 45 Boetius A, Ravensschlag K, Schubert CJ, Rickert D, Widdel F, Gieseke A, Amann R, Jørgensen BB, Witte U, Pfannkuche O (2000) A marine consortium apparently mediating anaerobic oxidation of methane. *Nature* 407:623–626

- Bohrmann G, Greinert J, Suess E, Torres ME (1998) Authigenic carbonates from the Cascadia subduction zone and their relation to gas hydrate stability. *Geology* 26:647–650
- Bohrmann G, Linke P, Suess E, Pfannkuche O (eds) (2000) RV SONNE Cruise Report SO143, TECFLUX-I GEOMAR Report 93, 217 pp
- 5 Bohrmann G, Ivanov MK et al (2003) Mud volcanoes and gas hydrates in the Black Sea: new data from Dvurechenskii and Odessa mud volcanoes. *Geo-Mar Lett* 23 (3-4):239-249
- Bohrmann G, Jørgensen BB, (eds), (2010) Proc 9th Intl. Conf. Gas in Marine Sediments Bremen, Germany. *Geo-Mar Lett* SI 30(3/4)
- 10 Buchardt B, Seaman P, Stockmann G, Vous M, Wilken U, Duwel L, Kristiansen A, Jenner C, Whitticar MJ, Kristensen RM, Petersen GH, and Thorbjorn L (1997) Submarine columns of ikaite tufa. *Nature* 390:129–130
- Buerk D, Klaucke I, Sahling H, Weinrebe W (2011) Morpho-acoustic variability of cold seeps on the continental slope offshore Nicaragua: Result of fluid flow interaction with sedimentary processes. *Mar Geol* 275:53–65
- 15 Burke WH, Denison RE, Hetherington EA, Koepnick RB, Nelson HF, Otto JB (1982) Variation of seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  throughout Phanerozoic time. *Geology* 10:516-519
- Camerlenghi A, MB Cita, Della Vedova, M, Fusi N, Mirabile LG, Pellis G (1995) Geophysical evidence for mud diapirism on the Mediterranean Ridge accretionary complex, *Mar. Geophys. Res.* 17:115-141
- Campbell KA (2006) Hydrocarbon seep and hydrothermal vent palaeo-environments: Past developments and future research directions. *Palaeogeogr Palaeoclimat Palaeoecol* 232:362-407
- 20 Campbell KA, Farmer JD, DeMarais D (2002) Ancient hydrocarbon seeps from the Mesozoic convergent margin of California: carbonate geochemistry, fluids and paleoenvironment. *Geofluids* 2:63-94
- Carpenter BM, Marone C, and Saffer DM (2011) Weakness of the San Andreas Fault revealed by samples from the active fault zone. *Nature Geoscience* 4:251-254
- 25 Chan LH, Kastner M (2000) Lithium isotope compositions of pore fluids and sediments in the Costa Rica subduction zone: implications for fluid processes and sediment contribution in the arc volcanoes. *Earth Planet Sci Lett* 183:275-290
- Chen D, Huang Y, Yuan X, Cathles III LM (2005) Seep carbonates and preserved methane oxidizing bacteria and sulfur reducing bacteria fossils suggest recent gas venting on the seafloor in the northeastern South China. *Mar Petrol Geol* 22:613-621
- 30 Collett T et al (2008) Indian continental margin gas hydrate prospects: Results of the Indian national gas hydrate program (NGHP) Exp. 01. Proc. 6<sup>th</sup> Internatl. Conf. Gas Hydrates, Vancouver BC, Canada July 6-10; <https://circle.ubc.ca/handle/2429/1022>
- Colten-Bradley VA (1987) Role of pressure in smectite dehydration: Effects on geopressure and smectite to illite transformation. *Am Assoc Petrol Geol, Bull* 71:1414–1427
- 35 Cordes EE, Carney SL, Hourdez S, Carney, R, Brooks JM and Fisher CR (2007) Cold seeps of the deep Gulf of Mexico: Community structure and biogeographic comparisons to Atlantic and Caribbean seep communities. *Deep-Sea Res I* 54:637–653
- 40 Crémère A, Pierre C, Blanc-Valleron MM, Zitter T, Cagatay MN, Henry P (2012) Methane-derived authigenic carbonates along the North Anatolian fault system in the Sea of Marmara (Turkey). *Deep-Sea Res I* 66:114–130
- Crutchley GJ, Berndt C, Geiger S, Klaeschen D, Papenberg C, Klaucke I, Hornbach MJ, Bangs NLB and Maier C (2013) Drivers of focused fluid flow and methane seepage at south Hydrate Ridge, offshore Oregon, USA. *Geology* 41:551-554
- 45 Dählmann A, and de Lange G (2003) Fluid-sediment interactions at eastern Mediterranean mud volcanoes: A stable isotope study from ODP Leg 160. *Earth Planet Sci Lett* 212:377-391
- De Batist M, Khlystov O, (eds). (2012) Proc 10th Intl. Conf. Gas in Marine Sediments. Listvyanka, Russia. *Geo-Mar Lett* SI 32(5/6)
- 50 Decarreau AN, Vigier N, Pálková H, Petita S, Vieillarda P, Fontainea C (2012) Partitioning of lithium between smectite and solution: An experimental approach. *Geochim Cosmochim Acta* 85:314–325
- Dupré S, Woodside J, Foucher JP, de Lange G, Mascle J, Boetius A, Mastalerz V, Stادنiskaia A, Ondréas H, Huguen C, Harmégnies F, Gontharet S, Loncke L, Deville HEN, Omoregie E, Roy KOL, Fiala-Medioni A, Dählmann A, Caprais JC, Prinzhofer A, Sibuet M, Pierre C, Damste JS, NAUTINIL Scientific Party (2007) Seafloor geological studies above active gas chimneys off Egypt (Central Nile Deep Sea Fan). *Deep Sea Res* 54:1146-1172
- 55

- Elvert M, Suess E, and Whiticar M (1999) Anaerobic methane oxidation associated with marine gas hydrates. Superlight C-isotopes from saturated and unsaturated C<sub>20</sub> and C<sub>25</sub> irregular isoprenoids. *Naturwissenschaften* 86:295-300
- 5 Feng D, Roberts HH, Cheng H, Peckmann J, Bohrmann G, Edwards RL, Chen D (2010) U/Th dating of cold-seep carbonates: An initial comparison. *Deep-Sea Res II* 57:2055–2060
- Feseker T, Brown K, Blanchet C, Scholz F, Nuzzo M, Reitz A, Schmidt M and Hensen C (2010) Active mud volcanoes on the upper slope of the western Nile deep-sea fan - first results from the P362/2 cruise of R/V Poseidon *Geo-Mar Lett* 30 (3/4):169-186
- 10 Flueh ER, Suess E, Soeding E (eds) (2004) Cruise Report SO173/1 and SO173/3+4 Subduction II. GEOMAR-Report 115, 491
- Foucher JP, Dupré S, Scalabrin C, Feseker T, Harmegnien F and Nouzé H (2010) Changes in seabed morphology, mud temperature and free gas venting at the Hakon Mosby mud volcano, offshore northern Norway, over the time period 2003-2006. *Geo-Mar Lett* 30 (3-4):157-167
- 15 Freundt A, Grevemeyer I, Rabbel W et al (2014) Volatile (H<sub>2</sub>O, CO<sub>2</sub>, Cl, S) budget of the Central American subduction zone. *Int J Earth Sci* (this volume)
- Freytag JK, Girguis PR, Bergquist DC, Andras JP, Childress JJ, Fisher CR (2001) A paradox resolved: Sulfide acquisition by roots of seep tubeworms sustains net chemoautotrophy. *Proc Nat Acad Sci* 98:13408-13413
- Fryer P, Mottl M, Johnson L, Haggerty L, Phipps S, Maekawa H (1995) Serpentine bodies in the forearc of Western Pacific convergent margins: Origin and associated fluids. In Taylor B, Natland J (eds) *Active Margins and Marginal Basins of the Western Pacific*. Amer Geophys Union, Geophysical Monogr 88:259-279
- 20 Furlé E, Hilton DR, Brown KM, and Tryon MD (2009) Helium systematics of cold seep fluids at Monterey Bay, California, USA: Temporal variations and mantle contributions. *Geochem Geophys Geosystems* 10 (8) Q08013, doi:10.1029/2009GC002557
- Gallardo AH, Marui A (2006) Submarine groundwater discharge: An outlook of recent advances and current knowledge. *Geo-Mar Lett* 26:102-113
- 25 Garcia-Gil S, Judd A (2007) Gas in marine sediments VIII: An introduction to the Vigo conference of the shallow gas group. *Geo-Mar Lett* 27:71-74
- Ge L, Jiang S. Y, Swennen R, et al. (2010) Chemical environment of cold seep carbonate formation on the northern continental slope of South China Sea: Evidence from trace and rare earth element geochemistry. *Mar Geol* 277(1-4):21-30
- 30 Geersen J, Behrmann JH, Völker D, Krastel S, Ranero CR, Diaz-Naveas J, and Weinrebe W (2011) Active tectonics of the South Chilean marine fore arc (35°S–40°S) *Tectonics* 30 doi:10.1029/2010TC002777
- Geli L, Henry P, Zitter T, MARNAUT Scientific Party (2008) Gas emissions and active tectonics within the submerged section of the North Anatolian Fault zone in the Sea of Marmara. *Earth Planet Sci Lett* 274:34–39
- 35 German CR, Ramirez-Llodra E, Baker MC, Tyler PA, and ChEss Scientific Steering Committee (2011) Deep-Water chemosynthetic ecosystem research during the Census of Marine Life Decade and beyond: A proposed deep-ocean road map. *PLOS One* 6 (8) e23259
- Gontharet S, Pierre C, Blanc-Valleron MM, Rouchy JM, Fouquet Y, Bayon G, Foucher JP, Woodside J, Mascle J et al (2007) Nature and origin of diagenetic carbonate crusts and concretions from mud volcanoes and pockmarks of the Nile deep-sea fan (eastern Mediterranean Sea). *Deep-Sea Res II* 54:1292-1311
- 40 Gracia A, Rangel-Buitrago N, Sellanes J (2010) Evidences of the Presence of Methane Seeps in the Colombian Caribbean Sea. EGU General Assembly, Vienna, p.3632
- Greinert J (2008) Monitoring temporal variability of bubble release at seeps: The hydroacoustic swath system GasQuant. *J Geophys Res* 113: DOI:10.1029/2007JC004704
- 45 Greinert J, Artemov, Y, Egorov V, De Batist M, McGinnis D (2006) 1300-m-high rising bubbles from mud volcanoes at 2080m in the Black Sea: hydroacoustic characteristics and temporal variability. *Earth Planet Sci Lett* 244:1-15
- Greinert J, Bialas J, Lewis K and Suess E, (eds) (2010) Methane seeps at the Hikurangi Margin, New Zealand. *Mar Geol*, 272; doi:10.1016/j.margeo.2010.02.018.
- 50 Greinert J, Bohrmann G, Suess E (2001) Gas hydrate-associated carbonates and methane venting at Hydrate Ridge: Classification, distribution and origin of authigenic lithologies. In: C. Paull and W. Dillon (eds.) *Natural Gas Hydrates: Occurrence, Distribution, and Detection*, Washington, American Geophysical Union, Monogr 124: 99-113.
- 55 Greinert J, Bollwerk SM, Derkachev A, Bohrmann G, Suess E (2002) Massive barite deposits and carbonate mineralization in the Derugin Basin, Sea of Okhotsk: Precipitation processes at cold seep sites. *Earth Planet Sci Lett* 203:165-180

- Greinert J, Derkachev A (2004) Glendonites and methane-derived Mg-calcites in the Sea of Okhotsk, eastern Siberia: Implications of a venting-related ikaite/glendonite formation: *Mar Geol* 204:129–144
- Gutscher MA, Dominguez S, Westbrook GK, Le Roy P, Rosas F, Duarte CD, Terrinha P, Miranda JM, Graindorge D, Gailler A, Sallares V, Bartolome R (2012) The Gibraltar subduction: A decade of new geophysical data. *Tectonophysics* 574/576:72-91
- 5 Haas A, Peckmann J, Elvert M, Sahling H and Bohrmann G (2010) Patterns of carbonate authigenesis at the Kouilou pockmarks on the Congo deep-sea fan. *Mar Geol* 268:129-136
- Haeckel M, Boudreau BP, Wallmann K (2007) Bubble-induced porewater mixing: a 3-D model for deep porewater irrigation. *Geochim Cosmochim Acta* 71:5135-5154
- 10 Haeckel M, Suess E, Wallmann K, Rickert D (2004) Rising methane gas-bubbles form massive hydrate layers at the seafloor. *Geochim Cosmochim Acta* 68:4335-4345
- Haffert L, Haeckel M, Liebetrau V, Berndt C, Hensen C, Nuzzo M, Reitz A, Scholz F, Schönfeld J, Perez-Garcia C, Weise SW (2013) Fluid evolution and authigenic mineral paragenesis related to salt diapirism – The Mercator mud volcano in the Gulf of Cadiz. *Geochim Cosmochim Acta* 106:261-286
- 15 Han X, Suess E, Liebetrau V, Eisenhauer A, Huang YY (2014) Methane release events and environmental conditions at the upper continental slope of the South China Sea: constraints from seep carbonates. *Int J Earth Sci* (this volume)
- Han X, Suess E, Huang Y, Wu N, Bohrmann G, Su X, Eisenhauer A, Rehder G, Fang Y (2008) Jiulong methane reef: Microbial mediation of seep carbonates in the South China Sea. *Mar Geol* 249:243-256
- 20 Han X, Suess E, Sahling H, Wallmann K (2004) Fluid venting activity on the Costa Rica margin: New results from authigenic carbonates. *Int J Earth Sci* 93:596-611
- Heeschen KU, Haeckel M, Klauke I, Ivanov MK, Bohrmann G (2011) Quantifying in-situ gas hydrates at active seep sites in the eastern Black Sea using pressure coring technique. *Biogeosciences* 8:3555-3565
- 25 Hensen C, Nuzzo M, Hornibrook E, Pinheiro LM, Bock B, Magalhaes VH, Brückmann W (2007) Sources of mud volcano fluids in the Gulf of Cadiz—indications for hydrothermal imprint. *Geochim Cosmochim Acta* 71:1232-1248
- Hensen C, Wallmann K, Schmidt M, Ranero CR, Suess E (2004) Fluid expulsion related to mud extrusion off Costa Rica—A window to the subducting slab. *Geology* 32:201-204
- 30 Hilario A, Cunha, MR (2008) On some frenulate species (Annelida: Polychaeta: Siboglinidae) from mud volcanoes in the Gulf of Cadiz (NE Atlantic). *Scientia Marina* 72(2):361-371
- Himmler T, Bach W, Bohrmann G, Peckmann J (2010) Rare earth elements in authigenic methane-seep carbonates as tracers for fluid composition during early diagenesis. *Chem Geol* 277:126-136
- Hinrichs KU, Hayes JM, Sylva SPO, Brewer PG, DeLong EF (1999) Methane-consuming archaeobacteria in marine sediments. *Nature* 398 802-805
- 35 Hovland M (2007) Discovery of prolific natural methane seeps at Gullfaks, northern North Sea. *Geo Mar Lett* 27:197-201
- Huang C-Y, Chien C-W, Zhao M-X, Li H-C, Iizuka Y (2006) Geological study of active cold seeps in the syn-collision accretionary prism Kaoping slope off SW Taiwan, Terr. Atmos. Ocean. Sci. 17 (4) 679-702
- 40 Iglesias J, Ercilla G, García-Gil S, Judd AG (2010) Pockforms: an evaluation of pockmark-like seabed features on the Landes Plateau, Bay of Biscay. *Geo-Mar Lett.* 30:207–219
- IODP Prelim. Rept. Expedition 344 Scientists (2013) Costa Rica Seismogenesis Project, Program A Stage 2 (CRISP-A2): sampling and quantifying lithologic inputs and fluid inputs and outputs of the seismogenic zone. Prel. Rept, 344; doi:10.2204/iodp.pr.344
- 45 Ivandic M, Grevemeyer I, Bialas J, Petersen CP (2010) Serpentinization in the trench-outer rise region offshore of Nicaragua: constraints from seismic refraction and wide-angle data. *Geophys. J. Int.* (2010) 180, 1253–1264
- Ivanov AV (1963) Pogonophora. *Publ Consultants Bureau, New York* 477
- Jansen JHF, Woensdregt CF, Kooistra MJ, van de Gaast SJ (1987) Ikaite pseudomorphs in the Zaire deep-sea fan: An intermediate between calcite and porous calcite: *Geology* 15:245–248
- 50 Jarrard RD (2003) Subduction fluxes of water, carbon dioxide, chlorine, and potassium, *Geochem. Geophys. Geosyst.* 4(5) 8905; doi:10.1029/2002GC000392.
- Jeong KS, Cho JH, Kim SR, Hyun S, Tsunogai U (2004) Geophysical and geochemical observations on actively seeping hydrocarbon gases on the south-eastern Yellow Sea continental shelf. *Geo-Mar Lett* 24:53-62
- Jones AT, Greinert J, Bowden DA, Klauke I, Petersen CJ, Netzeband GL and Weinrebe W (2010) Acoustic and visual characterization of methane-rich seabed seeps at Omakere Ridge on the Hikurangi Margin, New Zealand. *Mar Geol* 272:154-169
- 55 Judd AG, Croker P, Tizzard L (2007) Extensive methane-derived authigenic carbonates in the Irish Sea. *Geo Mar Lett* 27:259-267

- Judd AG, Hovland M (2007) *Submarine Fluid Flow, the Impact on Geology, Biology, and the Marine Environment*. Cambridge University Press 475pp.
- Karaca D, Schleicher T, Hensen C, Linke P, Wallmann K (2013) Quantification of methane emission from bacterial mat sites at Quepos slide offshore Costa Rica. *Int J Earth Sci* (this volume)
- 5 Karpen V, Thomsen L, Suess E (2004) A new 'schlieren' technique application for fluid flow visualization at cold seep sites. *Mar Geol* 204:145–59
- Kasten S, K. Nöthen K, Hensen C, Spieß V, Blumenberg M, Schneider RR (2012) Gas hydrate decomposition recorded by authigenic barite at pockmark sites of the northern Congo Fan. *Geo-Mar. Lett.* doi: 10.1007/s00367-012-0288-9
- 10 Kelemen PB, Matter J, Streit EE, Rudge JF, Curry WB, Blusztajn J (2011) Rates and mechanisms of mineral carbonation in peridotite: Natural processes and recipes for enhanced, in situ CO<sub>2</sub> capture and storage. *Annu. Rev. Earth Planet. Sci.* 39:545–76
- Kennicutt, MC et al (1985) Vent-type taxa in a hydrocarbon seep region on the Louisiana slope. *Nature* 317, 351–353
- 15 Kiel S (2009) Global hydrocarbon seep-carbonate precipitation correlates with deep-water temperatures and eustatic sea-level fluctuations since the Late Jurassic. *Terra Nova* 21:279-284
- Kiel S (ed) 2010: *The Vent and Seep Biota: Aspects from Microbiology to Ecosystems*. Vol. 33 *Topics in Geobiology*, Springer Heidelberg
- 20 Klaucke I, Weinrebe W, Petersen CJ and Bowden D (2010) Temporal variability of gas seeps offshore New Zealand: Multi-frequency geoaoustic imaging of the Wairarapa area, Hikurangi margin. *Mar Geol* 272:49-58
- Klaucke I, Weinrebe W, Linke P, Klaeschen D, Bialas J (2012) Sidescan sonar imagery of widespread fossil and active cold seeps along the central Chilean continental margin *Geo-Mar Lett*, 32:489-499
- Knittel K, Boetius A, Lemke A, Eilers H, Lochte K, Pfannkuche O, Linke P (2003) Activity, distribution, and diversity of sulfate reducers and other bacteria in sediments above gas hydrate (Cascadia margin, Oregon). *Geomicrobiol J* 20:269-294 doi: 10.1080/01490450390241008
- 25 Koleshnikov A, Kutcherov VG, Goncharov AF (2009) Methane-derived hydrocarbons produced under upper-mantle conditions. *Nature Geoscience* 2:566 - 570
- Krause S, Liebetrau V, Gorb S, Sanchez-Roman M, McKenzie JA, Treude T (2012) Microbial nucleation of Mg-rich dolomite in exopolymeric substances under anoxic modern seawater salinity: New insight into an old enigma *Geology*, 40 (7) 587-590
- 30 Krylova EM, Sahling H (2010) Vesicomidae (Bivalvia): current taxonomy and distribution. *PLoS ONE* 5 (4) e9957
- Kulm LD, Suess E, Moore JC, Carson B, Lewis BT, Ritger SD, Kadko DC, Thornburg TM, Embley RW, Rugh WD, Massoth GJ, Langseth MG, Cochrane GR, Scamman RL (1986) Oregon subduction zone: Venting, fauna, and carbonates. *Science* 231:561–566
- 35 Kutterolf S, Liebetrau V, Mörz T, Freundt A, Hammerich T, Garbe-Schönberg CD (2008) Lifetime and cyclicity of fluid venting at forearc mound structures determined by tephrostratigraphy and radiometric dating of authigenic carbonates *Geology*, 36 (9) 707-710
- Leefmann T, Bauermeister J, Kronz A, Liebetrau J, Reitner J, Thiel V (2008) Minutized biosignature analysis reveals implications for the formation of cold seep carbonates at Hydrate Ridge (off Oregon USA). *Biogeosciences* 5:731-738
- 40 León R, Somoza L, Medialdea T et al (2012) New discoveries of mud volcanoes on the Moroccan Atlantic continental margin (Gulf of Cádiz): morpho-structural characterization. *Geo-Mar Lett* 32:473-488
- LePichon X, Ilyami T, Boulegue J, Charvet J et al (1987) Nankai trough and Zenisu ridge: A deep-sea submersible survey. *Earth Planet Sci Lett* 83 (181):285-299
- 45 Levin LA (2005) Ecology of cold seep ecosystems: interactions of fauna with flow, chemistry and microbes. *Oceanogr. Mar. Biol. Annu. Rev.* 43, 1–46
- Liebetrau V, Augustin N, Kutterolf S, Schmidt M, Eisenhauer A, Garbe-Schönberg D, Weinrebe W (2014) Authigenic carbonate archives of mound and slide related fluid venting at the Central American Forearc: Geochemical and mineralogical insights. *Int J Earth Sci* (this volume)
- 50 Liebetrau V, Eisenhauer A and Linke P (2010) Cold seep carbonates and associated cold-water corals at the Hikurangi Margin, New Zealand: New insights into fluid pathways, growth structures and geochronology. *Mar Geol* 272:307-318
- Limonov AF, Woodside JM, Cita MB, Ivanov MK (1996) The Mediterranean Ridge and related mud diapirism: a background. *Mar Geol* 132:7–19
- 55 Lin AT, Liu C-S, Lin C-C, Schnurle P, G.-Yu. Chen, W.-Z. Liao, Teng L-S, Chuang H-J, Wu M-S (2008) Tectonic features associated with the overriding of an accretionary wedge on top of a rifted continental margin: An example from Taiwan. *Mar Geol* 255:186-203

- Linke P, (ed) (2011) FS SONNE Fahrtbericht / Cruise Report SO-210 ChiFlux. IFM-GEOMAR Report; pp. 112; ISSN Nr. 1614-6298
- Linke P, Wallmann K, Suess E, Hensen C, Rehder G (2005) In situ benthic fluxes from an intermittently active mud volcano at the Costa Rica convergent margin. *Earth Planet Sci Lett* 235:79-95
- 5 Loncke L, Gaullier V, Mascle J, Vendeville B, Camera L (2006) The Nile deep-sea fan: an example of interacting sedimentation, salt tectonics, and inherited subsalt paleotopographic features. *Mar. Petr. Geol.* 23:297-315
- Lonsdale P (1979) A deep-sea hydrothermal site on a strike-slip fault. *Nature* 281:531–534
- Lu H-F, Liu J, Chen F, Liao Z-L, Sun X-M, Su X., (2005) Mineralogy and stable isotope composition of authigenic carbonates in bottom sediments in the offshore area of southwest Taiwan, South China Sea, evidence for gas hydrate occurrence. *Earth Science Frontiers* 12 (3) 268-276
- 10 Ludwig KA, Kelley DS, Butterfield DA, Nelson BK, Früh-Green G (2006) Formation and evolution of carbonate chimneys at the Lost City hydrothermal field. *Geochim Cosmochim Acta* 70:3625-3645
- MacDonald IR et al (2004) Asphalt volcanism and chemosynthetic life in the Campeche Knolls, Gulf of Mexico. *Science* 304, 999–1002
- 15 MacDonald IR, Reilly JF, Guinasso jr NL, Brooks JM, Carney RS, Bryant WA, Bright TJ (1990) Chemosynthetic mussels at a brine-filled pockmark in the northern Gulf of Mexico. *Science* 248:1096-1099
- Maekawa T (2004) Experimental study on isotopic fractionation in water during gas hydrate formation. *Geochemical Journal* 38:129-138
- Martin RA, Nesbitt EA and Campbell KA (2010) The effects of anaerobic methane oxidation on benthic foraminiferal assemblages and stable isotopes on the Hikurangi Margin of eastern New Zealand. *Mar Geol* 272:270-284
- 20 Mastarlerz V, de Lange GJ, Dählmann A, Feseker T (2007) Active venting at the Isis mud volcano, offshore Egypt: Origin and migration of hydrocarbons. *Chem Geol* 246:87-106
- Matsumoto R, 1989. Isotopically heavy oxygen-containing siderite derived from the decomposition of methane hydrate. *Geology* 17:707–711
- 25 Matsumoto R, Borowski WS (2000) Gas hydrate estimates from newly determined oxygen isotopic fractionation  $a_{GH-1W}$  and  $\delta^{18}O$  anomalies of the interstitial waters: Leg 164, Blake Ridge.. In: Paull, C.K., Matsumoto, R., Wallace, P.J., and Dillon, W.P. (eds) *Proc. ODP Sci Res* 164:59-66
- Matsumoto R, Riedel M, Lin S, Ryu BJ, Sain K, Lu H; eds. (2011) Occurrence and exploration of gas hydrate in the marginal seas and continental margin of the Asia, India and Oceania region. *Marine and Petroleum Geology* 28 (10):1751-1986
- 30 Mau S, Rehder G, Sahling H, Schleicher T, Linke P (2012) Seepage of methane at Jaco Scar, a slide caused by seamount subduction offshore Costa Rica. *Int J Earth Sci*; doi:10.1007/s00531-012-0822-z (this volume)
- Mavromatis V, Botz R, Schmidt M, Liebetrau V, Hensen C (2013) Formation of carbonate concretions in surface sediments of two mud mounds offshore Costa Rica: A stable isotope study. *Int J Earth Sci* (this volume)
- 35 Mazzini A, Ivanov MK, Nermoen A, Bahr A, Bohrmann G, Svensen H, Planke S (2008) Complex plumbing systems in the near subsurface: Geometries of authigenic carbonates from Dolgovskoy Mound (Black Sea) constrained by analogue experiments. *Marine and Petroleum Geology* 25:457–472
- McQuay EL, Torres ME, Collier RW, Huh C, McManus J (2008) Contribution of cold seep barite to the barium geochemical budget of a marginal basin. *Deep Sea Res* 55:801-811
- 40 Milucka J, Ferdelman TG, Polerecky L, Franzke D, Wegener G, Schmid M, Lieberwirth I, Wagner M, Widdel F, Kuypers MMM (2012) Zero-valent sulphur is a key intermediate in marine methane oxidation. *Nature* 491:541-546
- Moore CJ (1999) Seeps give a peek into plumbing. *Am Assoc Petrol Geol, Expl* 99:22-23
- 45 Moore GF, Bangs NL, Taira A, Kuramoto S, Pangborn E, Tobin HJ (2007), Three-dimensional splay fault geometry and implications for tsunami generation, *Science*, 318:1128-1131
- Moore GF, Saffer D, Studer M, Costa Pisani P (2011) Structural restoration of thrusts at the toe of the Nankai Trough accretionary prism off Shikoku Island, Japan: Implications for dewatering processes, *Geochem. Geophys. Geosyst.* 12, Q0AD12; doi:10.1029/2010GC003453
- 50 Mottl MJ, Komor SC, Fryer P, Moyer CL (2003) Deep-slab fluids fuel extremophilic Archaea on a Mariana forearc serpentinite mud volcano: Ocean Drilling Program Leg 195. *Geochem Geophys Geosyst* 4:9009; doi:10.1029/2003GC000588
- Mottl MJ, Wheat CG, Fryer P, Gharib J, Martin JB (2004) Chemistry of springs across the Mariana forearc shows progressive devolatilization of the subducting plate. *Geochim Cosmochim Acta* 68:4915-4933
- 55 Naudts L, Greinert J, Artemov Y, Staelens P, Poort J, Van Rensbergen P, De Batist M (2006) Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea. *Mar Geol* 227:177-199

- Niemann H, Fischer D, Graffe D, Knittel K, Montiel A, Heilmayer O, Nöthen K, Pape T, Kasten S, Bohrmann G, Boetius A, Gutt J (2009) Biogeochemistry of a low-activity cold seep in the Larsen B area, western Weddell Sea, Antarctica. *Biogeosciences* 6, 2383-2395
- 5 Niemann H, Linke P, Knittel K, MacPherson E, Boetius A, Brückmann W, Larvik G, Wallmann K, Schacht U, Omoregie E, Hiltons D, Brown K, Rehder, G (2013) Methane-carbon flow into the benthic food web at cold seeps – a case study from the Costa Rica subduction zone. *PLOS One* 8 (10) e74894
- Nyman SL, Nelson CS, Campbell KA (2010) Miocene tubular concretions in East Coast Basin, New Zealand: Analogue for the subsurface plumbing of cold seeps. *Mar Geol* 272:319
- 10 Olu-Le Roy K, Caprais J, Fifis A, Fabri M, Galeron J, Budzinsky H, Le Menach K, Khripounoff A, Ondreas H, Sibuet M (2007) Cold-seep assemblages on a giant pockmark off West Africa: spatial patterns and environmental control. *Marine Ecology* 28:115-130
- Olu-Le Roy K, Sibuet M, Fiala-Médioni A, Gofas S, Salas C, Mariotti A, Foucher JP, Woodside J (2004) Cold seep communities in the deep eastern Mediterranean Sea: composition, symbiosis and spatial distribution on mud volcanoes. *Deep-Sea Res I* 51:1915-1936
- 15 Orphan VJ, House CH, Hinrichs KU, McKeegan KD, DeLong EF (2001) Methane-consuming archaea revealed by directly coupled isotopic and phylogenetic analysis. *Science* 293:484– 487
- Palandri JL, Reed MD (2004) Geochemical models of metasomatism in ultramafic systems: Serpentinization, rodingitization, and sea floor carbonate chimney precipitation. *Geochim Cosmochim Acta* 68 (5) 1115-1133
- 20 Pancost RD, Sinninghe Damsté JS, de Lint S, van der Maarel MJEC, Gottschal JC, and The Medinaut Shipboard Scientific Party (2000) Biomarker evidence for widespread anaerobic methane oxidation in Mediterranean sediments by a consortium of methanogenic Archaea and Bacteria. *Appl. Environ. Microbiol.* 66 (3) 1126-1132
- Pape T, Bahr A, Klapp SA, Abegg F, Bohrmann G (2011): High-intensity gas seepage causes rafting of shallow gas hydrates in the southeastern Black Sea. *Earth Planet Sci Lett* 307:35-46
- 25 Pape T, Kasten S, Zabel M, A Bahr, Abegg F, Hohnberg H-J, Bohrmann G (2010) Gas hydrates in shallow deposits of the Amsterdam mud volcano, Anaximander Mountains, northeastern Mediterranean Sea. *Geo-Marine Lett.* 30:187-206
- Paull CK, Becker B, Commeau R, Freeman-Lynde RP, Neumann C, Corso WP, Golubic S, Hook JE, Sikes E, Curry J (1984) Biological communities at the Florida Escarpment resemble hydrothermal vent taxa. *Science* 226:965-967
- 30 Peacock SM, 2001. Are the lower planes of double seismic zones caused by serpentine dehydration in subducting oceanic mantle? *Geology* 29:299–302.
- Peckmann J, Reimer A, Luth U, Luth C, Hansen BT, Heinicke C, Hoefs J, Reitner J (2001) Methane-derived carbonates and authigenic pyrite from the northwestern Black Sea. *Mar Geol* 177, 129-150
- 35 Peckmann J, Thiel V, Reitner J, Taviani M, Aharon P, Michaelis W (2004) A microbial mat of a large sulfur bacterium preserved in a Miocene methane-seep limestone. *Geomicrobiol J* 21:247-255
- Perez-García C, Feseker T, Mienert J, Berndt C (2009) The Håkon Mosby mud volcano: 330 000 years of focused fluid flow activity at the SW Barents Sea slope *Mar Geol*, 262 (1/4) 105-115
- 40 Peterson RN, Burnett WC, Taniguchi M, Chen J, Santos IR, Ishitobi T (2008) Radon and radium isotope assessment of submarine groundwater discharge in the Yellow River delta, China. *J. Geophys. Res.* 113; doi:10.1029/2008JC004776
- Pierre C, Fouquet Y (2007) Authigenic carbonates from methane seeps of the Congo deep-sea fan. *Geo-Mar Lett* 27(2/4):249–257.
- Pierre C, Mascle J, Imbert P; (eds) (2014) Contributions from the 11<sup>th</sup> Inter Conf on Gas in Marine Sediments, Nice 2011, *Geo-Mar Lett* 34 (2/3)
- 45 Prokurowski G et al (2008) Abiogenic hydrocarbon production at Lost City hydrothermal field. *Science* 319: 604–607
- Ranero C R, von Huene R (2000) Subduction erosion along the Middle America convergent margin. *Nature* 404: 748-752
- 50 Ranero CR, Grevemeyer I, Sahling H, Barckhausen U, Hensen C, Wallmann K, Weinrebe W, Vannucchi P, von Huene R, McIntosh K (2008) Hydrogeological system of erosional convergent margins and its influence on tectonics and interplate seismogenesis. *Geochem Geophys Geosys* 9 (3) doi:10.1029/2007GC001679
- Ranero CR, Phipps Morgan J, McIntosh K., Reichert C (2003) Bending, faulting, and mantle serpentinization at the Middle America Trench. *Nature* 425:367–373
- 55 Ranero CR, von Huene R (2000) Subduction erosion along the Middle America convergent margin. *Nature* 404:748-752
- Rickaby REM, Shaw S, Bennitt G, Kennedy H, Zabel M, Lennie A (2006) Potential of ikaite to record the evolution

- of oceanic  $\delta^{18}\text{O}$ . *Geology* 34:497-500
- Rongemaille E, Bayon G, Pierre C, Bollinger C, Chu NC, Fouquet Y, Riboulot V, Voisset M (2011) Rare earth elements in cold seep carbonates from the Niger delta. *Chem Geol* 286:196-206
- 5 Rossel PE, Elvert M, Ramette A, Boetius A and Hinrichs K-U (2011) Factors controlling the distribution of anaerobic methanotrophic communities in marine environments: Evidence from intact polar membrane lipids. *Geochim Cosmochim Acta* 75:164-184
- Rossel PE, Lipp JS, Fredricks HF, Arnds J, Boetius A, Elvert M, Henrichs KU (2008) Intact polar lipids of anaerobic methanotrophic archaea and associated bacteria. *Organic Geochemistry* 39:992-999
- 10 Rüpke LH, Phipps-Morgan J, Hort M, Connolly JAD (2004) Serpentine and the subduction zone water cycle. *Earth Planet Sci Lett* 223:17-34
- Saffer DM (2003) Pore pressure development and progressive dewatering in underthrust sediments at the Costa Rican subduction margin: Comparison with Northern Barbados and Nankai. *J Geophys Res* 108 B5; doi:10.1029/2002JB001787
- 15 Saffer DM, McKiernan AW (2009) Evaluation of in situ smectite dehydration as a pore water freshening mechanism in the Nankai Trough, offshore southwest Japan. *Geochim Geophys Geosys* 10 (2); doi:10.1029/2008GC002226
- Sahling H, Galkin SV, Salyuk A, Greinert J, Foerstel H, Piepenburg D, Suess E (2003) Depth-related structure and ecological significance of cold-seep communities. A case study from the Sea of Okhotsk. *Deep Sea Res* 50:1391-1409
- 20 Sahling H, Masson DG, Ranero CR, Hühnerbach V, Weinrebe W, Klauke I, Bürk D, Brückmann W, Suess E (2008) Fluid seepage at the continental margin offshore Costa Rica and southern Nicaragua. *Geochem Geophys Geosys* 9 (5); doi:10.1029/2008GC001978
- Sahling H, Rickert D, Lee RW, Linke P, Suess E (2002) Macrofaunal community structure and sulfide flux at gas hydrate deposits from the Cascadia convergent margin; NE Pacific. *Mar Ecol Progr Ser* 231:121-138
- 25 Sassen R, Roberts HH, Carney R, Milkov A, DeFreitas DA, Lanoil B, and Zhang CL (2004) Free hydrocarbon gas, gas hydrate and authigenic minerals in chemosynthetic communities of the northern Gulf of Mexico continental slope: relation to microbial process. *Chem Geol* 205 195-217
- Schneider von Deimling J, Rehder G, Greinert J, McGinnis DF, Boetius A, Linke P (2011) Quantification of seep-related methane gas emissions at Tommeliten, North Sea. *Cont Shelf Res* 31:867–878
- 30 Schnürle P, Liu C-S, Lin A-T, Lin S (2011) Structural controls on the formation of BSR over a diapiric anticline from a dense MCS survey offshore southwestern Taiwan. *Mar Petrol Geol* 28 (10):1932-1942
- Scholl DV, von Huene R (2007) Crustal recycling at modern subduction zones applied to the past—issues of growth and preservation of continental basement crust, mantle geochemistry, and supercontinent reconstruction. *Geol Soc of America, Mem* 200:9-32
- 35 Scholl DW, von Huene R (2007) Crustal recycling at modern subduction zones applied to the past— Issues of growth and preservation of continental basement crust, mantle geochemistry, and supercontinent reconstruction. *Geol. Soc. America, Memoir* 200:9-32
- Scholz F, Hensen C, de Lange GJ, Haeckel M, Liebetrau V, Meixner A, Reitz A, Romer RL (2010) Lithium isotope geochemistry of marine pore waters – Insights from cold seep fluids. *Geochim Cosmochim Acta* 74:3459-3457
- 40 Scholz F, Hensen C, Reitz A, Romer RL, Liebetrau V, Meixner A, Weise SM, Haeckel M (2009) Isotopic evidence ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^7\text{Li}$ ) for alteration of the oceanic crust at deep-rooted mud volcanoes in the Gulf of Cadiz, NE Atlantic Ocean. *Geochim Cosmochim Acta* 73:5444–5459
- Scholz F, Hensen C, Schmidt M, Geersen J (2013) Submarine weathering of silicate minerals and the extent of pore water freshening at active continental margins. *Geochim Cosmochim Acta* 100:200-216
- 45 Schubert CJ, Nürnberg D, Scheele N, Pauer F, Kriews M (1997)  $^{13}\text{C}$  depletion in ikaite crystals: Evidence for methane release from the Siberian shelves? *Geo-Mar Lett* 17:169–175
- Sellanes J, Quiroga E, Neira C (2008) Megafauna community structure and trophic relationships at the recently discovered Concepcion Methane Seep Area, Chile  $\sim 36^\circ\text{S}$ . *ICES Journal of Marine Science Advance Access*; doi:10.1093/icesjms/fsn099
- 50 Shakirov R, Obzhirov A, Suess E, Salyuk A, Biebow N (2004) Mud volcanoes and gas vents in the Okhotsk Sea area. *Geo-Mari Lett* 24:140-140
- Sibuet M, Olu K (1998) Biogeography, biodiversity and fluid dependence of deep-sea cold-seep communities at active and passive margins. *Deep Sea Res Part II* 45:517-567
- 55 Soeding E, Wallmann K, Suess E, Flueh ER (eds) (2003) Cruise Report M54/2+3: Fluids and Subduction Costa Rica 2002. *GEOMAR-Report* 111; 336 pp
- Sommer S, Linke P, Pfannkuche O, Schleicher T, Schneider von Deimling J, Reitz A, Haeckel M, Flögel S, Hensen

- C (2009) Seabed methane emissions and the habitat of frenulate tubeworms on the Captain Arutyunov mud volcano (Gulf of Cadiz). *Mar Ecol Progr Ser* 382:69-86
- Suess E (2010) Marine cold seeps. In: Timmis, Kenneth N. (ed). *Handbook of Hydrocarbon and Lipid Microbiology*, vol. 1; part 3:187-203; Springer Heidelberg; doi:10.1007/978-3-540-77587-4\_12
- 5 Suess E (ed) (2005) RV SONNE 177; South China Sea continental margin: geological methane budget and environmental effects of methane emissions and gas hydrates. IFM-GEOMAR Report 04;doi 10.3289/ifm-geomar\_rep\_4\_2005
- Suess E, Balzer W, Hesse KF, Müller PJ, Ungerer CA, Wefer G (1981) CaCO<sub>3</sub>-hexahydrate from organic-rich sediments of the Antarctic shelf: Precursors of glendonites. *Science* 216:1128-1131
- 10 Suess E, Carson B, Ritger SD, Moore JC, Jones ML, Kulm LD, Cochran GR (1985) Biological communities at vent sites along the subduction zone off Oregon. *Biol Soc Washington Bull* 6:475-484
- Suess E, Linke P (2006). *Der Ozean unter dem Meeresboden – Kalte Quellen als Oasen der Tiefsee*. In: G. Wefer (editor) *Expedition Erde*, 2 nd Ed, 88-101.
- 15 Teichert BMA, Bohrmann G, Suess E (2005) Chemoheterms on Hydrate Ridge - Unique microbially-mediated carbonate build-ups growing into the water column. *Palaeogeogr Palaeoclimatol Palaeoecol* 227:67-85
- Teichert BMA, Eisenhauer A, Bohrmann G, Haase-Schramm A, Bock B, Linke P (2003) U/Th systematics and ages of authigenic carbonates from Hydrate Ridge, Cascadia Margin: Recorders of fluid flow variations. *Geochim Cosmochim Acta* 67(20):3845-3857
- 20 Tinivella U, Lodolo E, (2000) The Blake Ridge bottom-simulating reflector transect: tomographic velocity field and theoretical model to estimate methane hydrate quantities. In: Paull CK, Matsumoto R, Wallace PJ, Dillon WP (eds) *Proc ODP, Sci Results* 164:273-281; doi:10.2973/odp.proc.sr.164.237.2000
- Tong H, Feng D, Cheng H, et al. (2013) Authigenic carbonates from seeps on the northern continental slope of the South China Sea: New insights into fluid sources and geochronology. *Mar Petrol Geol.* 43:260-271
- 25 Torres ME, Bohrmann G, Suess E (1996) Authigenic barites and fluxes of barium associated with fluid seeps in the Peru subduction zone. *Earth Planet Sci Lett* 144:469-481
- Torres ME, McManus J, Huh C-A (2002) Fluid seepage along the San Clemente Fault scarp: basin-wide impact on barium cycling. *Earth Planet Sci Lett* 203:181-194
- Torres ME, Embley RW, Merle SG, Tréhu AM, Collier RW, Suess E, Heeschen KU (2009) Methane sources feeding cold seeps on the shelf and upper continental slope off central Oregon, USA, *Geochem Geophys Geosys* 10 (11):Q11003, doi:10.1029/2009GC002518
- 30 Torres ME, Mix AC, Kinports K, Haley B, Klinkhammer G, McManus J, DeAngelis MA (2003) Is methane venting at the seafloor recorded by  $\delta^{13}\text{C}$  of benthic foraminifera shells? *Paleoceanography* 18 (3) doi:10.1029/2002PA000824
- Torres ME, Teichert BMA, Trehu AM, Borowski W, Tomaru H (2004) Relationship of pore water freshening to accretionary processes in the Cascadia margin: Fluid sources and gas hydrate abundance. *Geophys Res Lett* 31:L22305; doi:10.1029/2004GL021219
- 35 Treude T (2012) Biogeochemical reactions in marine sediments underlying anoxic water bodies. In: A.V. Altenbach, J.M. Bernhard and J. Seckbach (eds) *Anoxia: Evidence for Eucaryote survival and paleontological strategies*. Series: Cellular Origin, Life in Extreme Habitats and Astrobiology 21:17-38
- 40 Treude T, Orphan V, Knittel K et al (2007) Consumption of methane and CO<sub>2</sub> by methanotrophic microbial mats from gas seeps of the anoxic Black Sea. *Appl Environ Microbiol* 73:2271–2283
- Tryon MD, Brown K, Dorman L, Sauter E (2001) A new benthic aqueous flux meter for very low to moderate discharge rates, *Deep Sea Res I* 48(9):2121–2146
- 45 Tryon MD, Henry P, Cagatay MN, Zitter TAC, Geli L, Gasperini L, Burnard P, Bourlange S, Grall C (2010) Pore fluid chemistry of the North Anatolian Fault Zone in the Sea of Marmara: A diversity of sources and processes. *Geochem Geophys Geosys* 11:1-22
- van Avendonk HJA, Holbrook WS, Lizarralde D, Denyer P (2011) Structure and serpentinitization of the subducting Cocos plate offshore Nicaragua and Costa Rica. *Geochem Geophys Geosys* 12 (6); doi:10.1029/2011GC003592
- 50 van der Straaten F, Halama R, John T, Schenk V, Hauff F, Andersen N (2012) Tracing the effects of high-pressure metasomatic fluids and seawater alteration in blueschist-facies overprinted eclogites: Implications for subduction channel processes. *Chem Geol* 292-293 (2012) 69–87
- Vannucchi P, Fisher DM, Bier S and Gardner TW (2006) From seamount accretion to tectonic erosion: formation of Osa mélange and the effects of Cocos Ridge subduction in southern Costa Rica. *Tectonics* 25(4):TC2004; doi:10.1029/2005TC001855
- 55 Wallmann K (2001) The geological water cycle and the evolution of marine  $\delta^{18}\text{O}$  values. *Geochim Cosmochim Acta* 65:2469-2485

- Wallmann K, Aloisi G, Haeckel M, Tishchenko P, Pavlova G, Greinert J, Kutterolf S, Eisenhauer A (2008) Silicate weathering in anoxic marine sediments. *Geochim Cosmochim Acta* 72:2895-2918
- Wallmann K, Drews M, Aloisi G, Bohrmann G (2006) Methane discharge into the Black Sea and the global ocean via fluid flow through submarine mud volcanoes. *Earth Planet Sci Lett* 205:181-194
- 5 Wannamaker TG, Caldwell GR, Jiracek V, Maris GJ, Hill Y, Ogawa H, Bibby M, Bennie L, Heise W (2009) Fluid and deformation regime of an advancing subduction system at Marlborough, New Zealand. *Nature* 460:733-736
- Warén A, Bouchet P (2009) New gastropods from deep-sea hydrocarbon seeps off West Africa. *Deep-Sea Res II* 56:2326-2349
- 10 Watanabe Y, Nakai S, Hiruta A, Matsumoto R, Yoshida K (2008) U-Th dating of carbonate nodules from methane seeps off Joetsu, Eastern Margin of Japan Sea. *Earth Planet Sci Lett* 272(1-2):89-96
- Weinrebe W, Flüh ER (eds) (2002) FS/RV SONNE Cruise Report SO163 SUBDUCTION I; GEOMAR Report 106, 531 pp
- Westbrook GH, Reston TJ (2002) The accretionary complex of the Mediterranean Ridge: Tectonics, fluid flow and the formation of brine lakes - an introduction. *Mar Geol* 186:1-8
- 15 Westbrook GK and MEDRIF Consortium (1995) Three brine lakes discovered in the seafloor of the Eastern Mediterranean. *EOS Trans. American Geophysical Union* 76:313-318
- Whiticar MJ (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem Geol* 161 291-314
- 20 Whiticar MJ, Suess E (1998) The cold carbonate connection between Mono Lake, California and the Bransfield Strait, Antarctica. *Aquatic Geochem* 4:429-454
- Worzewski T, Jegen M, Kopp H, Brasse H Taylor WT (2010) Magnetotelluric image of the fluid cycle in the Costa Rican subduction zone. *Nature Geoscience* 4:108-111
- 25 Yang JY, Chung K-H, Jin Y-K, Shin K-H (2011) Characterizing lipid biomarkers in methanotrophic communities of gas hydrate-bearing sediments in the Sea of Okhotsk. *Marine and Petroleum Geology* 28 (10):1884-1898
- Zapata-Hernandez G, Sellanes X, Thurber A R, Levin L A, Chazalon F and Linke P (2013) New insights on the trophic ecology of bathyal communities from the methane seep area of Concepcion, Chile (~36° S). *Marine Ecology* doi:10.1111/maec.12-51
- 30 Zhang CL, Lanoil B (eds) (2004) Geomicrobiology and biogeochemistry of gas hydrates and hydrocarbon seeps. *Chem Geol* 205(3/4)
- Zitter TAC, Henry P, Aloisi G, Delaygue G, Cagatay MN, Mercier de Lepinay B, Al-Samir M, Fornacciari F, Tesmer M, Pekdeger A, Wallmann K, Lericolais G (2008) Cold seeps along the main Marmara Fault in the Sea of Marmara (Turkey). *Deep-Sea Res I* 55:552-570

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### Figure captions

- 40 **Fig. 1** Global 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 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
- 45 (2007); Niemann et al. (2009); Bayon et al. (2007); Iglesias (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. Up-dates of new site locations and descriptions are in: Zhang and Lanoil (eds 2004), Garcia-Gil and Judd (eds, 2007); Bohrmann and Jørgensen (eds 2010); Pierre et al. (eds 2014). Maps of global distributions
- 50 of seep biota can be found in: Krylova and Sahling (2010); German (2011).

**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 covered by seaward prograding hemi-pelagic sediments with well-developed bottom simulating reflector (BSR). Fluid escape features on lower-middle slope are mud volcanos situated above temperature-pressure regime of mineral dehydration from top of down-going plate. Fluids and muds are forced upward through hydrofractures. 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

**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 km 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 Worzweski et al. (2010) with information from Ivandic et al. (2010)

**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, over-pressured 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. (A) Flume experiment with saline fluid ejected through an opening; diameter of image = 5 cm; (B) channeled fresh water seep at the seafloor (water depth 18 m); (C) 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)

**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 sulphate in oxidizing methane (Reaction 1) producing hydrogen sulphide and bicarbonate; hydrogen sulphide rises to the sea floor and is oxidized in microbial mats (Reaction 2a) or by macro-fauna 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).

**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) Prolific Pogonophora colony from Jaco Scarp off Costa Rica; (B) Pogonophora colony on seafloor off Conception, Chile; ; (C) Varied microbial mats on seafloor of Quepos Seeps, Costa Rica; (D) Microbial mat on smooth seafloor off Conception; (E) Mytilid colonies on carbonates off Costa Rica; (F) Vesicomid colony on seafloor off Conception; photos GEOMAR; Cruise Repts. SO163, Weinrebe and Flüh (2002); M54, Soeding et al. (2003); SO173, Flueh et al. (2004); SO210, Linke (2011)

**Fig 9a** Seep carbonate structures. Seafloor images of typical seep carbonates. (A) Fractured block, Costa Rica margin; (B) Chemoherm build-up populated by sessile organism, Costa Rica margin; (C) Chemoherm build-up 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; photos GEOMAR: Cruise Repts. M54, Soeding et al. (2003); SO173, Flueh et al. (2004); SO177, Suess (2005); SO210, Linke (2011)

**Fig. 9b** 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; photos GEOMAR: Cruise Repts. SO148, Bohrmann et al (2000); SO177, Suess (2005)

**Fig. 10** Generic mud volcano. Active mud volcano emitting methane and mud, interlayered hydrate, sediment and mud alternate along flanks recording lifetime and cyclicity of venting activity; based on Kutterolf et al. (2008).

**Fig. 11** Hydrate water in pore fluids. Well-known artefact 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)

**Fig. 12** Clay dehydration. Chloride dilution in pore fluids of accretionary margins from deformation front towards continental framework rock is observed worldwide in ODP-drill sites. Data from 10 sites across the Cascadia margin show progressive freshening attributed to increased compaction and smectite-illite transformation. Sites at the

accretionary prism (1245-1247) show Cl-dilution <150 m below seafloor and > BSR depth from dissociation of gas hydrate; modified from Torres et al. (2004)

5 **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  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $dD_{\text{H}_2\text{O}}$  (not shown here). SW = concentration in seawater; modified from Hensen et al. (2004)

10 **Fig. 14** Lithium tracer for fluid-sediment reactions. Based on reference data of Li and  $d^7\text{Li}$  relationships (partially listed in the legend) several domains of fluid-sediment interaction are evident: (I) low-temperature diagenesis, (II) high-temperature diagenesis, (III) ridge-crest 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).

15 **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) towards hydrothermal exchange (underlying oceanic crust) with distance. Such signals in seep fluids may be regarded as criteria for transform fault systems. Sr-  
20 isotopic characteristics for current (Q = Quaternary) and past (K = Cretaceous) seawater; modified from Scholz et al. (2009)

**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)

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

30 **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 et al. (1995)

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**Figures 1 -18**

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