

CHAPTER 7

Final discussion

The previous chapters have shown that bubble-releasing seeps occur at different oceanographic and plate-tectonic settings, at different seafloor morphologies, at different water depths, in or outside of the gas-hydrate stability zone. Furthermore, bubble-releasing seeps are often associated with various kinds of chemosynthetic communities and authigenic methane-derived carbonates. Within this chapter an integration and comparison is made of the obtained results and of published data from other seep sites around the world which occur in similar or different geological settings. The comparison and integration allows a better understanding of the controls and the manifestations associated with bubble-releasing seeps.

7.1. Global occurrence of bubble-releasing seeps

Before comparing and integrating the obtained results, an overview is given of bubble-releasing seeps around the world to better assess the similarities and differences between seep sites with regard to their locations, their geological controls and associated subsurface and seafloor manifestations (table 7.1.). Since bubble-releasing seeps form the main subject of this study, only those locations with proven bubble release are listed, be it by visual observations of gas bubbles or by observations of acoustic flares. Locations which are exclusively characterized by indicators of fluid flow or seepage activity, like bacterial mats, chemosynthetic megafauna, MDACs, shallow gas features, etc., are not added to this list. The locations with gas-bubble release are indicated on figure 7.1. The overview given in table 7.1. points out that seep locations occur worldwide in a variety of geological environments at various water depths ranging from coastal areas into the deep ocean basins, where they occur up to water depths of several kilometers. Despite this wide variety of seep locations, the amount of known sites with bubble release is relatively small. But this is probably biased by the restricted ability to find these very small locations at the seafloor. The publication years of the references given in table 7.1. are an indication of how recent and emergent our knowledge is regarding the distribution of bubble-releasing seeps, their controls, and the influence they have on the environment. It is only since the last decade that a more

widespread availability of e.g. ROVs, adapted acoustical methods, etc. allows us to pinpoint bubble-release locations at the seafloor and adequately study seeps and their associated features. This study wants to better understand the geological controls that influence the seep distribution, the seep activity and their associated manifestations.

7.2. Subsurface controls on the distribution of bubble-releasing seeps

Within this section, the main subject of this study is discussed; what are the geological subsurface controls on the distribution of bubble-releasing seeps and on what scale do these controls act. The obtained results are also compared to data from other published seep sites (table 7.1.).

7.2.1. Fluid sources

The fluids released at seeps can have several sources and compositions, however methane is the most common gas released at the seafloor. Methane present in the ocean or lake sediments can have several different origins: microbial, thermogenic, geothermal-volcanic or abiogenic (Judd and Hovland, 2007).

Methane produced in the upper 1000 m below the seafloor is often referred to as shallow gas. It mainly consists of methane which is microbially formed by methanogenesis of

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✓ Location ✓ Tectonic setting	Water depth	✓ Fluid source ✓ Fluid pathway ✓ Fluid type	Features related to seepage	References
Within gas-hydrate stability zone				
✓ Batumi seep area, Black Sea ✓ passive margin	600-890 m	✓ organic-rich shales ✓ faults, diapirs ✓ microbial/thermogenic	gas bubbles, acoustic flares, sampled hydrates, seismic anomalies	(Klaucke et al., 2006; Nikolovska et al., 2008)
✓ Blake Ridge, Atlantic Ocean ✓ passive margin	>2000 m	✓ contourites, gas hydrates ✓ faults, salt diapirs ✓ microbial	gas bubbles, acoustic flares, pockmarks, sampled hydrates, seismic anomalies, chemosynthetic fauna	(Kvenvolden and Dillon, 1981; Holbrook, 2001; Van Dover et al., 2003)
✓ Congo Basin, Atlantic Ocean ✓ passive margin	3200 m	✓ turbiditic fan, gas hydrates ✓ faults, salt diapirs, erosional surfaces, buried chimneys ✓ Microbial/thermogenic	gas bubbles, pockmarks, sampled hydrates, seismic anomalies, chemosynthetic fauna	(Gay et al., 2007; Olu-Le Roy et al., 2007; Sahling et al., 2008)
✓ Dvurechenskiy Mud Volcano area, Black Sea ✓ passive margin	2055 m	✓ organic-rich shales ✓ faults, diapirs, buried chimneys ✓ microbial/thermogenic	gas bubbles, acoustic flares, sampled hydrates, enhanced heat flow, seismic anomalies	(Bohrmann et al., 2003; Greinert et al., 2006; Kutas and Poort, 2008; Feseker et al., 2009)
✓ Gulf of Mexico ✓ passive margin	300-3000 m	✓ carbonate source rocks ✓ faults, salt diapirs ✓ thermogenic/oil/brines	gas bubbles, acoustic flares, sampled hydrates, seismic anomalies, authigenic carbonates, chemosynthetic fauna	(MacDonald et al., 2002; MacDonald et al., 2003; Joye et al., 2004; Solomon et al., 2009)
✓ Håkon Mosby Mud Volcano, Barents Sea ✓ passive margin	1270 m	✓ preglacial biosiliceous oozes ✓ fault, pseudo-mud chamber ✓ microbial/thermogenic	gas bubbles, sampled hydrates, enhanced heat flow, seismic anomalies, chemosynthetic fauna	(Niemann et al., 2006; Jerosch et al., 2007; Perez-Garcia et al., 2009)
✓ Hikurangi accretionary margin, Pacific Ocean ✓ active convergent margin	640-1500 m	✓ accreted marine sediments ✓ faults, stratigraphic conduits ✓ microbial	gas bubbles, acoustic flares, sampled hydrates, enhanced heat flow, seismic anomalies, authigenic carbonate, chemosynthetic fauna	this study, (Lewis and Marshall, 1996; Greinert et al., 2010a; Naudts et al., 2010)
✓ Hydrate Ridge, accretionary margin, Pacific Ocean ✓ active convergent margin	600-840 m	✓ accreted marine sediments, gas hydrates ✓ faults ✓ microbial/thermogenic	gas bubbles, acoustic flares, sampled hydrates, seismic anomalies, authigenic carbonate, chemosynthetic fauna	(Bohrmann et al., 1998; Greinert et al., 2001; Boetius and Suess, 2004; Haeckel et al., 2004)
✓ Lake Baikal, ✓ Rift lake, mud volcanoes	500-1500 m	✓ biosiliceous oozes, gas hydrates ✓ faults, buried chimneys ✓ microbial/thermogenic/oil	gas bubbles, acoustic flares, sampled hydrates, enhanced heat flow, seismic anomalies, authigenic carbonate	(De Batist et al., 2002; Van Rensbergen et al., 2002; Kida et al., 2006; Krylov et al., 2008a)
✓ Makran accretionary margin ✓ active convergent margin	450-2500 m	✓ accreted marine turbidites ✓ faults, mud diapirs ✓ microbial/thermogenic	gas bubbles, acoustic flares, sampled hydrates, tube worms, seismic anomalies, authigenic carbonate, chemosynthetic fauna	(von Rad et al., 1996; von Rad et al., 2000; Judd and Hovland, 2007; Ghosh and Sain, 2008)
✓ Mercator and Darwin Mud Volcano, Gulf of Cadiz, Atlantic Ocean ✓ compressional setting	388-1100 m	✓ marine shales and marls ✓ faults, mud diapirs ✓ microbial/thermogenic/brines	gas, bubbles, seismic anomalies, enhanced heat flow, authigenic carbonate	(Depreiter et al., 2005; Van Rooij et al., 2005)

<ul style="list-style-type: none"> ✓ Nile deep sea fan mud volcanoes, Mediterranean Sea ✓ deep sea fan 	550-2100	<ul style="list-style-type: none"> ✓ deltaic sediments ✓ faults, salt diapirs ✓ microbial/thermogenic/oil/brines 	gas bubbles, acoustic flares, sampled hydrates, tube worms, enhanced heat flow, seismic anomalies, authigenic carbonate, chemosynthetic fauna	(Dupre et al., 2007; Bayon et al., 2009; Huguen et al., 2009; Omoregie et al., 2009; Feseker et al., in press)
<ul style="list-style-type: none"> ✓ northern Cascadia margin, Pacific Ocean ✓ active convergent margin, accretionary prism 	1200-1400 m	<ul style="list-style-type: none"> ✓ accreted marine sediments, hydrates ✓ faults ✓ microbial 	gas bubbles, acoustic flares, sampled hydrates, enhanced heat flow, seismic anomalies, authigenic carbonate, chemosynthetic fauna	(Judd and Hovland, 2007; Riedel et al., in press)
<ul style="list-style-type: none"> ✓ Sea of Marmara ✓ inland sea, pull apart basins 	600-1200 m	<ul style="list-style-type: none"> ✓ deltaic sediments ✓ faults, sandy turbidites ✓ microbial/thermogenic/brines 	gas bubbles, acoustic flares, sampled hydrates, tube worms, seismic anomalies, authigenic carbonate, chemosynthetic fauna	(Gürgey et al., 2005; Géli et al., 2008; Zitter et al., 2008)
<ul style="list-style-type: none"> ✓ Sea of Okhotsk ✓ back-arc basin 	400-1000 m	<ul style="list-style-type: none"> ✓ highly organic-rich sediments ✓ faults ✓ microbial/thermogenic/oil 	acoustic flares, sampled hydrates, seismic anomalies, authigenic carbonate, chemosynthetic fauna	(Greinert et al., 2002b; Ludmann and Wong, 2003; Sahling et al., 2003; Shoji et al., 2005)
Outside of gas-hydrate stability zone				
<ul style="list-style-type: none"> ✓ Adriatic Sea ✓ foreland basin 	80-250 m	<ul style="list-style-type: none"> ✓ Holocene-Pliocene sediments ✓ faults, clay diapirism ✓ microbial/thermogenic 	acoustic flares, pockmarks, seismic anomalies, authigenic carbonate	(Hovland and Curzi, 1989; Conti et al., 2002; Panieri, 2006; Geletti et al., 2008)
<ul style="list-style-type: none"> ✓ Arabian Gulf ✓ rift system 	5-50 m	<ul style="list-style-type: none"> ✓ leaking hydrocarbon reservoirs ✓ erosional surface ✓ thermogenic/oil 	gas bubbles, acoustic flares, pockmarks, seismic anomalies	(Judd and Hovland, 2007)
<ul style="list-style-type: none"> ✓ Bering Sea ✓ active convergent margin 	<200 m	<ul style="list-style-type: none"> ✓ peaty mud ✓ storm-related liquefaction, diffusion ✓ microbial/thermogenic 	acoustic flares, pockmarks, seismic anomalies	(Judd and Hovland, 2007)
<ul style="list-style-type: none"> ✓ Bulgarian shelf, Black Sea ✓ passive margin 	0-20 m	<ul style="list-style-type: none"> ✓ deltaic sediments, sapropels ✓ faults ✓ microbial 	gas bubbles, acoustic flares, seismic anomalies	(Dimitrov, 2002)
<ul style="list-style-type: none"> ✓ Danube canyon, Black Sea ✓ passive margin 	70-400 m	<ul style="list-style-type: none"> ✓ deltaic sediments ✓ faults ✓ microbial 	gas bubbles, acoustic flares, seismic anomalies	(Egorov et al., 1998; Popescu et al., 2004)
<ul style="list-style-type: none"> ✓ Dnepr paleo-delta, Don paleo-delta, Black Sea ✓ passive margin 	66-825 m	<ul style="list-style-type: none"> ✓ deltaic sediments ✓ stratigraphic conduits in association with seals formed by fine-grained and hydrated-bearing sediments ✓ microbial 	gas bubbles, acoustic flares, pockmarks, seismic anomalies, authigenic carbonates, chemosynthetic fauna	this study, (Michaelis et al., 2002; Naudts et al., 2006; Naudts et al., 2008; Naudts et al., 2009)
<ul style="list-style-type: none"> ✓ Eckernförde Bay, Baltic Sea ✓ inland bay 	10-15 m	<ul style="list-style-type: none"> ✓ organic rich mud ✓ glacial outwash sands, diffusion ✓ microbial/fresh-water seepage 	acoustic flares, pockmarks, seismic anomalies, chemosynthetic fauna	(Wever et al., 1998; Judd and Hovland, 2007)

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✓ Eel River Basin, Pacific Ocean ✓ fore-arc basin	<550 m	✓ deltaic sediments ✓ faults, mud diapirs, structural anticlines ✓ microbial/thermogenic	gas bubbles, acoustic flares, pockmarks, seismic anomalies, authigenic carbonates, chemosynthetic	(Orange et al., 2002; Orphan et al., 2004)
✓ Gulf of Cadiz, Atlantic Ocean ✓ compressional setting	300-400 m	✓ deltaic sediments ✓ faults, stratigraphic conduits ✓ microbial	acoustic flares, pockmarks, seismic anomalies	(Baraza and Ercilla, 1996)
✓ Lake Baikal ✓ rift lake	20-340	✓ deltaic sediments, biosiliceous oozes ✓ faults, stratigraphic conduits ✓ microbial/thermogenic	gas bubbles, acoustic flares, pockmarks, seismic anomalies	this study, (Granin and Granina, 2002; Granin et al., in press; Naudts et al., submitted)
✓ Irish Sea ✓ inland sea	66-85 m	✓ coal-bearing rocks, lignites, silts ✓ faults, salt diapirs outcropping source rock ✓ microbial/thermogenic	Acoustic flares, authigenic carbonate, seismic anomalies	(Judd et al., 2007)
✓ North Sea ✓ sag margin	<100-250 m	✓ leaking hydrocarbon reservoirs ✓ salt diapirs, glacial sediments ✓ microbial/thermogenic	gas bubbles, acoustic flares, pockmarks, seismic anomalies, authigenic carbonates, chemosynthetic faun	(Niemann et al., 2005; Hovland, 2007; Judd and Hovland, 2007)
✓ Rias Baixas, Atlantic Ocean ✓ passive margin	10-55 m	✓ deltaic sediments ✓ stratigraphic conduits ✓ microbial	gas bubbles, pockmarks, seismic anomalies	(Garcia-Gil et al., 2002; Iglesias and Garcia-Gil, 2007)
✓ Santa Barbara Channel, Pacific Ocean ✓ fore-arc basin	20-70 m	✓ leaking hydrocarbon reservoirs ✓ faults, structural anticlines ✓ thermogenic/oil	gas bubbles, acoustic flares, seismic anomalies	(Clark et al., 2003; Leifer et al., 2006a)
✓ Skagerrak, Kattegat, Norwegian Sea ✓ passive margin	55-360 m, 10-12 m	✓ leaking hydrocarbon reservoirs, (post-)glacial sediments ✓ faults, clay diapirism, stratigraphic conduits ✓ microbial/thermogenic	acoustic flares, pockmarks, seismic anomalies, authigenic carbonates, chemosynthetic fauna	(Dando et al., 1994; Rise et al., 1999; Judd and Hovland, 2007)
✓ South China Sea ✓ mud volcanoes	<100 m	✓ leaking hydrocarbon reservoirs ✓ mud diapirs, buried chimneys ✓ microbial/thermogenic/oil	gas bubbles, acoustic flares, pockmarks, seismic anomalies	(Judd and Hovland, 2007)
✓ Stockholm Archipelago, Baltic Sea ✓ Inland bay	6-16 m	✓ subducted sediments ✓ faults, stratigraphic conduit ✓ microbial/ thermogenic	gas bubbles, pockmarks	(Judd and Hovland, 2007)
✓ Timor and Arafura Sea, Eastern Indian Ocean ✓ passive margin	40-500 m	✓ leaking hydrocarbon reservoirs, Holocene mud ✓ faults ✓ microbial/thermogenic/oil	acoustic flares, pockmarks, authigenic carbonate, seismic anomalies	(Rollet et al., 2006; Rollet et al., 2009; Logan et al., 2010)
✓ West Spitsbergen continental margin, Barents Sea ✓ passive margin	150-400 m	✓ partially from gas hydrates ✓ stratigraphic conduit in association with seals formed by hydrate-bearing sediments ✓ microbial	acoustic flares	(Westbrook et al., 2009)
✓ Yellow Sea ✓ Inverted extensional basin	80-100 m	✓ deltaic sediments, leaking hydrocarbon reservoirs ✓ mud diapirs, buried chimneys ✓ microbial	acoustic flares, pockmarks, seismic anomalies	(Jeong et al., 2004; Judd and Hovland, 2007)

Table 7.1.

Overview of all known bubble-releasing seep sites in the world with indication of water depth, tectonic setting and associated features.

organic material. This organic material is supplied by river runoff or by sedimentation of plankton, present in the water column. Microbial methane consists mainly of the light carbon isotope ^{12}C and has therefore very low $\delta^{13}\text{C}_{\text{CH}_4}$ values, commonly between -55‰ and -110‰ (Whiticar, 1999). Methanogenesis commonly takes place by CO_2 -reduction, common in marine environments, or by acetate-fermentation, common in freshwater environments (Whiticar, 1999). When organic matter gets buried deep enough to within the oil window, e.g. from 2000 m below surface, where high pressures and temperatures prevail, thermogenic methane (dry gas) can be formed by catagenesis, often in association with crude oil (C_{15+}), condensate ($\text{C}_6\text{-C}_{15}$) and wet gas ($\text{C}_2\text{-C}_5$). Thermogenic methane commonly has $\delta^{13}\text{C}_{\text{CH}_4}$ values between -25‰ and -55‰ (Whiticar, 1999). Catagenesis sources the gas and oil fields produced on many continental margins worldwide. In most cases the source rocks are different from the reservoir rocks; the escape of petroleum from source rocks is called primary migration, and the migration into the reservoirs rocks is referred to as secondary migration. As for the source rocks, the reservoir rocks are also unable to contain and seal off all

hydrocarbon fluids and thus allow further fluid migration towards the seafloor (tertiary migration). In this way the methane seeping into the water column can be mixture of microbial and thermogenic methane with admixtures of higher hydrocarbons. As shown, in table 7.1. tertiary migration seems to be an important source for bubble-releasing seeps worldwide. Abiogenic methane originates from degassing of the earth's mantle, whereas geothermal-volcanic methane is formed by the thermal breakdown of organic hydrocarbons under the influence of volcanic activity (Judd and Hovland, 2007; Etiope, 2009). The importance of the two latter methane sources is still under debate.

Generally, 99% of the gas emitted at bubble-releasing seeps is methane, mainly of a microbial or a microbial-thermogenic origin with small admixtures of higher hydrocarbons (ethane, propane, etc.).

The compositions of the gases released at our study sites are in good agreement with what is observed at other bubble-releasing seeps worldwide. None of the seep sites occur above producible petroleum-bearing sediments, only in the Dnepr paleo-delta seeps occurs in a region with several nearby gas and oil fields (Fig. 2.1.).

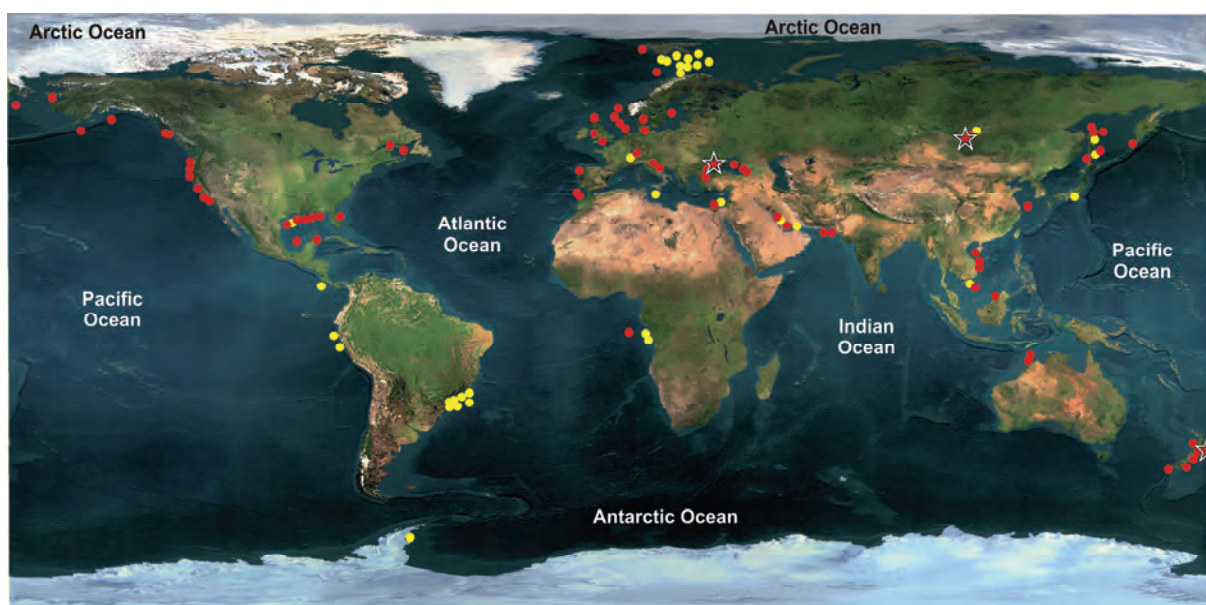


Figure 7.1. The locations of our study areas (indicated by white stars) within the worldwide distribution of bubble-releasing seeps (red dots) and gas seepage indicators (bacterial mats, authigenic carbonates, ice streamthroughs, etc.) (yellow dots). Where seeps as well as the seep indicators are present; they are indicated by red dots (after Judd and Hovland, 2007).

For the Dnepr paleo-delta (Black Sea), gas samples were taken with the submersible JAGO in October 2004 (as part of the EC-funded METROL project) at the -92 m seep site, directly at the seafloor. The initial gas composition of the bubbles was almost pure methane (80 to 90 %) of presumed microbial origin as indicated by the $\delta^{13}\text{C}_{\text{CH}_4}$ values (-62‰ to -68‰) (McGinnis et al., 2006). A similar observation was made for the -200 m seep site, as indicated by the $\delta^{13}\text{C}_{\text{CH}_4}$ values (-62‰ and -68‰) (Michaelis et al., 2002). Within these areas, gas-bearing layers have been seismically mapped up to a depth of 30 m below the seafloor. Thus gas generation in sediment layers occurs at least at 30 m subsurface depth (Fig. 3.9.). Measurements of the natural radiocarbon content of the methane ($^{14}\text{C}_{\text{CH}_4}$) show that most of it derives from radiocarbon-free sources (5.02 ± 0.4 pMC, 24 ka) (Kessler et al., 2006). The released methane is thus assumed to represent a mixture of methane generated in organic-rich deltaic sediments deposited during various sealevel lowstands along the Dnepr paleo-delta and upward migrating radiocarbon-free methane from deeper strata. The most recent sealevel lowstands occurred at 9-10 ka ^{14}C B.P (Ivanova et al., 2007). For the -600 m seep site, heat-flow measurements and helium isotopes indicate a deeper source, originating from 200-300 m subsurface depth with a crustal helium overprint (Poort et al., 2007; Holzner et al., 2008).

At the Hikurangi Margin (SW Pacific), water samples taken at Faure Site and LM-3 obtained during ROV dives have $\delta^{13}\text{C}_{\text{CH}_4}$ values between -66 ‰ and -67 ‰, indicative of a microbial methane source (Faure et al., 2010). These values are very similar to the ones measured at e.g. Hydrate Ridge, another example of an accretionary margin with bubble-releasing seeps within the GHSZ (Heeschen et al., 2005). For both Faure Site and LM-3 no higher hydrocarbons were detected (Faure et al., 2010). Barnes et al. (2010) suggest that the substrate of exposed Cretaceous and Paleogene rocks or an eroded cover sequence of Miocene-Pliocene age acts as sources for the observed seeps and possible gas hydrates at the Rock Garden area. There is no indication that gas hydrates in the Rock Garden area are sources

for the observed seepage. It rather seems that conduits through the GHSZ source the seeps from below the GHSZ (Crutchley et al., 2010; Crutchley et al., in press).

At the Posolsky Bank (Lake Baikal), gas samples from seeps were analyzed by Kalmychkov et al. (2006). They obtained a $\delta^{13}\text{C}_{\text{CH}_4}$ value of -66.6‰, with a C_1/C_{2+} ratio of 118, indicating a microbial-thermogenic origin for the released gasses. Organic matter in Lake Baikal comes from the input of the Selenga River and from primary production of phytoplankton (Vykhristyuk, 1980). Based on the seismic data, the gas-bearing layer feeding the seeps could be traced to below the BGHSZ. This indicates, together with the shallow depth occurrence of the seeps, that these seeps are not directly fed by the hydrates (Fig. 6.7.). The microbial-thermogenic origin also supports this assumption. The real thermogenic source could however not be determined. Sediment thickness in the SBB reaches up to 7.5 km and could therefore favor thermogenic methane production.

The previous paragraphs have shown that the released gas in the study areas has different sources and different compositions, albeit minor differences (Fig. 7.2.). The difference in source sediment and the nature of the associated fluids is strongly related to the present and past sedimentary environments of the seep areas. The tectonic setting partially determines the sedimentary environment but is rather a minor and indirect factor in relation to the fluid source and composition. Even though the three studied areas have the potential and established prove of thermogenic hydrocarbon production, none of the observed seeps have a clear thermogenic source, but rather a primarily microbial origin with merely a minor admixture of higher hydrocarbons. This conclusion can be made for a lot of the seep sites summarized in table 7.1. Regarding the overwhelming abundance of bubble-releasing seeps in the Dnepr paleo-delta (Black Sea), semi-enclosed (anoxic) basins with a high input of organic material can provide an enormous source for seepage (chapter 2-4). Other possible interesting anoxic basins to study seeps sites could be the anoxic Cariaco and Gotland Basins. Despite both having strong indications for shallow gas, no bubble-releasing

seeps have been observed until now (Piker et al., 1998; Wakeham et al., 2004).

7.2.2. Fluid migration modes, triggers and rates

First of all, it has to be stated that the 'normal' advective and diffusive flow of fluids, respectively related to pressure differences (Darcy's Law) or concentration differences (Fick's Law of diffusion), occurs everywhere and is a rather slow process (mm/yr) (Berndt, 2005; Judd and Hovland, 2007). This is related to the low solubility of gases (e.g. methane: 35 mg/l) and to the low permeability of normal marine sediments (10^{-8} - 10^{-9} m²) (Judd and Hovland, 2007). It is only where fluid flow is focused, e.g. through permeable sandy layers (permeability: 10^{-2} - 10^{-5} m²) or through cracks (permeability: 10^{-4} - 10^{-8} m²), that advective fluid flow rates become much higher provided an excess of pressure at the depth. In this case the 'cubic law' and Poiseuille's Law come into play (Judd and Hovland, 2007). The occurrence of focused fluid flow can be witnessed, since it 'visibly' affects the geosphere, biosphere, hydrosphere and atmosphere. The studied release of bubbles into the water column, and the associated free gas migration through the sediment, is an ultimate example of focused fluid flow.

Focused fluid flow, which is often a result of compaction, is strongly depended on the sedimentation rate, the lithology and the stratigraphy (Berndt, 2005). Focused fluid flow will, for example, not occur in continuous sandy deposits because of its high permeability and hydraulic conductivity which leads to heterogeneous fluid flow. It is only where fluid flow is impeded by low-permeability stratigraphic horizons (e.g. clayey sediments with a permeability of 10^{-10} - 10^{-12} m², gas hydrates with a permeability 10^{-10} - 10^{-18} m²) or by structural features (e.g. faults) that focused fluid can occur (Judd and Hovland, 2007).

In general, focused fluid migration through sediments has mainly two possible driving forces that can act separately or in combination; overpressure and buoyancy. Overpressure is generated at depth in location where pore pressure rises above hydrostatic pressure and

approaches lithostatic pressure due to the increased compression and decreased permeability of sedimentary layers as a result of high sedimentation rates and/or tectonic loading (Judd and Hovland, 2007). In general, tectonic stress reaches values between 10-100 MPa, whereas hydrostatic pressure has a value of 10 MPa/km and lithostatic pressure reaches values of 20-30 MPa/km. These values indicate that tectonic stress can have a major impact on focused fluid flow and lead to overpressure situation in relatively shallow sediments, i.e. upper kilometers (Judd and Hovland, 2007). Therefore typical indications for overpressure and sediment underconsolidation, e.g. formations of subsurface diapirs or seabed mud volcanoes, can be found in tectonically active regions (Judd and Hovland, 2007; and references therein). Overpressure also occurs without the presence of tectonic loading, but due to sediment loading or in relation to gas hydrates (see section 7.2.3.).

Another important driving force for fluid migration is buoyancy, which acts where the concentration of gas dissolved in pore waters exceeds its solubility and free-gas bubbles form. The formation of free gas lowers the bulk density of a sediment body and can lead to a density inversion. In this way, buoyancy can lead to migration of sediments (whether or not initiated by overpressure) or instigates migration of pore waters containing microscopic bubbles even without the mobilization of sediments or makes bubbles rise through the sediments without the mobilization of sediments or pore waters.

The most effect way of gas to migrate through the sediments occurs in association with sediment mobilization. Whenever sediment mobilizations doesn't occur, the migration of gas through sediments is most effective by the movement of bubbles through the sediment pore spaces (Saunders et al., 1999). Depending on the grain size of the host sediment and the composition of the gas, bubble diameters can be too large in comparison with the pore spaces to facilitate bubble movement. Unless an overpressure situation is created, the gas can only migrate through the sediment by diffusive flow out of the bubble into the pore water. Where the space between the sediment grains

allows it, bubbles can form again. In this manner a chain of bubbles gets established that allows movement of gas through the sediments (Judd and Hovland, 2007).

For our studied seep areas, seismic data show a clear linkage between the presence of free gas in the subsurface and the release of bubbles into the water column, generally without clear indications for overpressure (e.g. subsurface deformation, strong thermal anomalies, mud volcanism, etc.). This suggests a mainly buoyancy-driven free gas migration in the upper sedimentary layers (Figs. 2.4., and 6.7.). At some locations however, buoyancy-driven fluid flow seems to occur in association with or is initiated by overpressure. Possible indication for overpressure forcing in our study areas are: i) the occurrences of submarine landslides near Faure Site (Hikurangi Margin) (Fig. 5.2.) and in the Dnepr paleo-delta at the -600 m seep site (Black Sea) (Figs. 3.5. and 3.11.); ii) the focused migration of free gas through the GHSZ at Faure Site and LM-3 (Hikurangi Margin) (Fig. 5.2.) (see section 7.2.3.) (Crutchley et al., 2010; Crutchley et al., in press); iii) breaching of the impermeable sediment cover on sedimentary ridges in the Dnepr paleo-delta (Fig. 3.10) (see section 7.2.4.). The presence of overpressure in an accretionary margin, like the Hikurangi Margin is often due to tectonic loading (Judd and Hovland, 2007). The Hikurangi accretionary prism is not an exception with overpressure reaching near-lithostatic pressure at about 2 km depth in near-shore and on-shore oil wells (Sibson and Rowland, 2003). The accretion and subduction cause significant dewatering, which is linked to the seep sites observed onshore and offshore (Lewis and Marshall, 1996; Barnes et al., 2010).

While buoyancy and overpressure are the main driving forces of fluid flow, in some cases additional triggers, such as earthquakes, can lead to enhanced fluid flow. This can lead to the release of bubbles at the seafloor due to enhanced fluid pressure, due to the reactivation of faults or by causing submarine landslides (Hovland et al., 2002; Kuscu et al., 2005; Judd and Hovland, 2007; Géli et al., 2008). Other environmental changes, like pressure changes by tides, by current changes or by storm waves are also known to regulate fluid flow and seep

activity (see chapter 5) (Boles et al., 2001; Hovland et al., 2002; Torres et al., 2002; Judd and Hovland, 2007).

Lake Baikal and the Hikurangi Margin are seismically very active regions, nevertheless no direct relation between earthquakes and seepage has been established during our observations. But this doesn't rule out that seepage and fluid flow are always unrelated to earthquakes in these areas. For the seeps off New Zealand, there are strong indications that the seep activity is related to tides (Linke et al., 2010). In Lake Baikal and in the Black Sea there are no strong tidal variations, and thus seep activity can't be related to tides in these areas. In the Black Sea, strong current changes were observed by ADCP measurements, but no relation with seep activity was established (CRIMEA Project Team, 2006).

The fluid rates at which fluids can move through the sediments can strongly differ, depending on the observed fluid-flow system (i.e. with or without mobilization of sediments) and on the activity during the time of observation. Mud volcanoes, for example, are often characterized by repetitive fluid-flow activity with high flow rates. They are also associated with high thermal gradients which affect the stability of gas hydrates and results in enhanced fluid flow and in the release of bubbles into the water column (table 7.1.) (see section 7.2.3.). Fluid-flow rates of up to 4 m/year have been measured just below the seabed at the Håkon Mosby mud volcano, whereas at the Dvurechenskiy mud volcano fluid rates were less significant at 0.25 m/year at the center of the mud volcano (Aloisi et al., 2004; Feseker et al., 2008). The release of bubbles has been observed at both mud volcanoes, and seems to be independent of the release of other fluids, all or not associated with sediment movement or mud expulsions (table 7.1.) (Greinert et al., 2006; Sauter et al., 2006). The flux rates given here clearly represent a rather dormant period in the activity of the mud volcano without very active mud expulsions. Fluid rates related to the movement of free gas through the sediments have been measured for e.g. Hydrate Ridge, where rates varied between 0 to 10 m/year (Tryon et al., 2002).

For our study areas no subsurface fluid flow

rates were measured. Based on the relation between subsurface fluid flow rates and bubble-release rates in other areas, the bubble-release rates determined in our study areas can be used as an indication for the local fluid flow rates (table 5.1.). For the Håkon Mosby mud volcano for example, bubble release leads to methane flow rates of 4.8-21.6 mol/minute. At Hydrate Ridge flow rates were estimated to vary between 2.6-13 mol/minute. In our study areas, visual observations indicated methane flow rates of 0.2-7 mol/minute for Faure Site, whereas in the Dnepr paleo-delta flow rates of only 0.03 mol/minute were measured. This shows that at Faure Site, subsurface fluid flow rates are probably in the same order as at Hydrate Ridge. This indicates that at similar tectonic and sedimentary settings, comparable fluid flow systems with similar driving forces occur. In this case, an accretionary prism where probably overpressure is the main driving force allowing fluid flow through the GHSZ and bubble-release at the seafloor. Methane flow rates in the Dnepr paleo-delta point toward much lower subsurface fluid flow rates. This could indicate that the different tectonic and sedimentary environment of the Dnepr paleo-delta is associated with a different kind of fluid flow system with different driving forces. Buoyancy is probably the main driving force in the Dnepr paleo-delta, leading to lower fluid flow rates and more widespread occurrence of seeps (i.e. thousands) (Fig. 7.2.). Whereas, on the Hikurangi Margin, fluid flow rates are high and the number of seep sites is limited (i.e. dozens), as a result of enhanced focused fluid flow (Fig. 7.2.). The latter is probably related to the presence of hydrates and the associated overpressure; hydrates limit the widespread occurrence of seeps and overpressure only leads to seepage where fluid flow is highly focused and passage through the GHSZ is possible.

For the Posolsky Bank, no fluid flow rates or bubble-release rates are known. But visual observations of bubbles reaching the lake surface and the relatively high amount of seeps occurring in a small and well-defined area indicate that fluid flow is probably relatively high (Fig. 6.5.). Fluid flow rates at the Posolsky Bank are probably higher than in the Dnepr paleo-delta and lower than in the Hikurangi

Margin. This again shows that tectonic and sedimentary settings are associated with a particular fluid flow system that leads to different fluid flow focusing and fluid flow rates (Fig. 7.2.).

This section shows that fluid migration modes, rates and triggers differ in the different study areas and are strongly related to the geological setting of the studied area (Fig. 7.2.). The sedimentary environment and stratigraphic buildup of the study areas plays a major role, not only by providing adequate fluid sources (see section 7.2.1.), but also by providing stratigraphic conduits and seals that focus fluid flow. Conduits and seals can also be provided by structural features like faults, etc. (table 7.1.), but for our study areas stratigraphic conduits and seals are the most common (see section 7.2.3.-7.2.4.). With regard to the driving forces for focused fluid flow, buoyancy seems to be omnipresent in the shallow subsurface of all our study areas. But buoyancy-driven fluid flow sometimes occurs in association with overpressure leading to more enhanced focused fluid flow. Overpressure in our study areas is mainly related to stratigraphic seals, e.g. impermeable fine-grained or hydrate-bearing sediments, as was stated for buoyancy. This is also the case for an active tectonic environment as the Hikurangi Margin (see section 7.2.3.) (Crutchley et al., in press). This indicates that overpressure at gas-hydrate-bearing accretionary margins is not only related to tectonic loading with associated dewatering, but is also related to the sedimentary environment and associated stratigraphic buildup. The variety of driving forces, the complexity of the stratigraphy and the seismic activity makes accretionary prisms very interesting geological settings to study seeps with regard to driving forces and to fluid flow triggers. On the other hand, the amount of seeps detected in the Dnepr paleo-delta (Black Sea) is far greater than the amount of seeps detected on the Hikurangi Margin or any other accretionary prism, again pointing to the Black Sea as a unique seep environment. Concerning migration rates, tectonically active compressional systems associated with strong overpressure indicated by active mud volcanism and -diapirism are

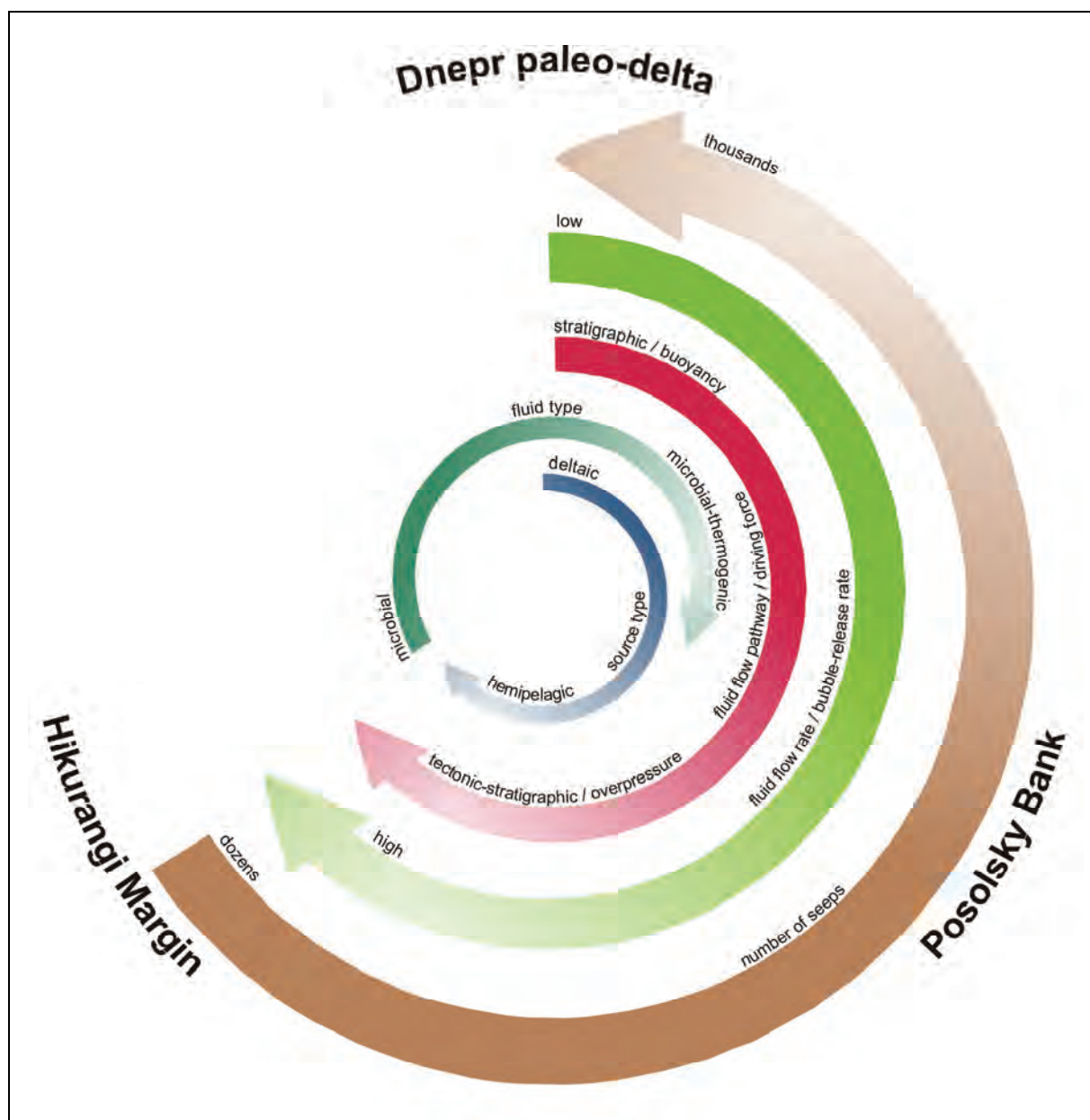


Figure 7.2. Overview of the fluid sources, the fluid types, the fluid pathways, the fluid flow rates and the numbers of seeps for the three study areas, shown relatively to each other as indicated by the arrows. The figure shows that the Hikurangi accretionary margin and the Dnepr paleo-delta are the two end-members for most fluid flow characteristics.

probably most interesting study areas.

In conclusion, the differences between our study areas indicate that fluid flow and bubble-release is primarily dependent on the sedimentary and stratigraphic environment. However, as was stated for fluid sources, the sedimentary environment and stratigraphic buildup is partially determined by the tectonic setting that therefore also influences the fluid migration mode and rates. That the tectonic

setting does play a role is also indicated by the absence of seeps in the GHSZ of the Dnepr paleo-delta and the presence of seeps in the GHSZ of the Hikurangi Margin (see section 7.2.3.). Overpressure generated below the GHSZ, solely by the presence of gas hydrates, doesn't lead to fluid flow through the GHSZ as can be witnessed in the Dnepr paleo-delta. It is only where the tectonic setting enhances the overpressure due to tectonic loading and an

excess of fluids that fluid flow through the GHSZ occurs. The latter is demonstrated in the Hikurangi Margin and many other accretionary convergent margins (see section 7.2.3.).

7.2.3. Fluid migration within the gas-hydrate stability zone

With regard to the water depth, a division is made between seeps occurring within and seeps occurring outside of the theoretical gas-hydrate stability zone. The overview given in table 7.1. clearly shows that gas hydrates have been sampled at all seep sites occurring within the gas-hydrate stability zone, independent of the geological or tectonic setting. A large amount of these seeps occur at mud volcanoes in a compressional tectonic setting, or at accretionary prisms at active convergent margins, or in areas with diapiric sediment or salt movement. Often these deep seep sites correspond to locations with enhanced heat flow, indicating an upward flow of warmer fluids and/or sediments that affect the stability of hydrates present in the sediment. Deep bubble-releasing seeps can be sourced by these destabilized hydrates or by free gas that is able to migrate through the GHSZ at certain locations. This can also be the case for areas where saline fluids migrate towards the seabed.

Migration of free gas through the GHSZ is also witnessed at locations where gas hydrates should be thermodynamically stable given the temperature, the pressure and the presence of pore water with normal salinities, e.g. the Gulf of Mexico, the Cascadia Margin, Blake Ridge, Congo Basin, the Hikurangi Margin (Brooks et al., 1994; Tryon et al., 1999; Taylor et al., 2000; Gorman et al., 2002; Wood et al., 2002; Gay et al., 2007; Crutchley et al., 2010). Several mechanisms are proposed for the migration of free gas through the GHSZ. Torres et al. (2004) suggested that free gas can move freely through the GHSZ as long as the bubble pressure exceeds the overburden stress caused by the sediment load, resulting only in massive hydrate formation close to the seafloor as is observed at Hydrate Ridge and in the Congo Basin (Sahling et al., 2008). Flemings et al. (2003) suggest for Blake Ridge that rather the formation of massive

hydrate layers at greater subsurface depth leads to overpressure generated by the build-up of free gas reservoirs beneath a low-permeable gas-hydrate cemented sediment layer. If the gas pressure of the gas reservoir exceeds the pressure exerted by the sediments above, a temporal conduit can be made allowing migrations of free gas through the GHSZ and the release of gas bubble into the water column. A high gas flux associated with rapid hydrate formation can lead to a depletion of pore water resulting in a high salinity of the residual pore waters or the formation of hydrate-coated veins that prevent interaction with the surrounding pore waters (Clennell et al., 1999; Flemings et al., 2003; Pecher et al., 2010). In both cases, further formation of hydrates may be impeded and this would allow the migration of free gas through the GHSZ. Alternatively, Ginsburg and Soloviev (1997) suggested that a diffusion barrier caused by a hydrate film at the gas-water interface may allow the free gas to migrate through the GHSZ.

Our study provides some interesting insights regarding the influence gas hydrate have on the migration of free gas through the GHSZ and on the associated distribution of seeps. Probably the most revealing observation is the almost complete absence of seeps in the GHSZ of the Dnepr paleo-delta, even though seismic data clearly indicated the presence of free gas in the sediments (Figs. 2.8. and 3.8.). The seismic data also show BSRs that indicate the presence of hydrates and free gas in the subsurface. Seismic inversion revealed that there is $38 \pm 10\%$ hydrate in the pore space at BSR depth, where the porosity is 57% (Zillmer et al., 2005). For the Dnepr paleo-delta it seems to be clear that gas hydrates present in the sediments act as a buffer for upward migrating free gas and prevent the release of gas bubbles at the seafloor. Bubble-releasing seeps are only observed within the GHSZ of the Dnepr paleo-delta where the activity of a mud volcano allows to surpass this effective hydrate buffer (Kruglyakova et al., 2004). This almost complete absence of seeps within the GHSZ also suggests that the above proposed mechanisms for free gas migration through the GHSZ are not present or are unsuccessful in the Dnepr paleo-delta. For example, overpressure-related seepage that is

not related to mud volcanism, as is seen on many accretionary margins, doesn't seem to be effective in the Dnepr paleo-delta. This is true for the whole Black Sea, where bubble-releasing seeps occur exclusively outside of the GHSZ and only above mud volcanoes inside the GHSZ (Fig. 1.7.). The only exception is the Batumi seep area offshore Georgia, where seeps occur at gas hydrate-bearing circular structures associated with authigenic carbonates indicating focused fluid flow but without the presence of any mud extrusions or positive relief. Seepage at the Batumi seep area seems to be related to underlying mud diapirs which can however sometimes be precursors of mud volcanism (Klaucke et al., 2006).

Notwithstanding the different, geological and tectonic settings of the Black Sea and Lake Baikal, the seep distribution and the role of hydrates seems to be very similar. As for the Black Sea, bubble-releasing seeps in Lake Baikal's GHSZ are almost exclusively found at mud volcanoes, in spite of the widespread occurrence of active faults within the Baikal Basins (Figs. 1.7. and 1.11.) (Granin et al., in press). Within the Posolsky Bank study area free gas is observed on seismic recordings within the GHSZ and hydrates have been sampled by a submersible at the southwestern fault scarp of the Posolsky Bank (Figs. 6.3. and 6.7.). The absence of seeps in the GHSZ of the Posolsky study area and in Lake Baikal (excluding mud volcanoes) indicates that gas hydrates act as a seal for the upward migration of free gas and the release of free gas in the water column, as was observed in the Black Sea. The only differences between the Dnepr paleo-delta and the Posolsky Bank study area is that the seeps at the Posolsky Bank are partially sourced by gas coming from below the BGHSZ. Whereas in the Dnepr paleo-delta there are no indications that gas from below the BGHSZ is migrating along the sediment layers and is being released outside of the GHSZ (Figs. 2.8. and 3.8.). The geometry and the layering of the Posolsky Bank are probably a unique example allowing gas escape from below the BGHSZ without having to pass through the GHSZ. The only other known example are the seeps studied along the West Spitsbergen continental margin (Westbrook et al., 2009).

The only study area with a clear observation

of fluid migration through the GHSZ that results in the release of bubbles into the water column is Rock Garden (LM-3 and Faure Site) (Fig. 5.2.). Numerous authors suggest that overpressure at the BGHSZ caused by rising bubbles or gas pockets allows the migration of fluids through the GHSZ at the Rock Garden seep sites (Pecher et al., 2005; Faure et al., 2006; Barnes et al., 2010; Crutchley et al., 2010; Crutchley et al., in press). Our study doesn't provide any data that sustains or contradicts these suggestions. But as was postulated in section 7.2.2., the overpressure generated at Rock Garden, and probably at a lot of hydrate-bearing accretionary prisms, is associated with the tectonic setting in combination with the sedimentary and stratigraphic buildup (i.e. presence of hydrates). Furthermore, Crutchley et al. (2010) show that for Faure Site migration through the GHSZ occurs along tilted permeable layers whereas at LM-3 faults control the fluid flow through the GHSZ (Fig. 5.12.). Our data and interpretation show that the difference in depth of LM-3 (-908 m) and Faure Site (-659 m) and the associated thickness of the underlying GHSZ (respectively 300 m and 35 m) has a strong influence on the bubble release and the seep environment (carbonates, fauna, etc.) at both seep sites. Crutchley et al. (in press) explains how a shallower BGHSZ is more strongly influenced by overpressure caused by underlying gas pockets allowing temporal migration of free gas through the GHSZ. The latter clearly shows up as strong differences in bubble release at LM-3 and Faure Site, as well as in the present seep fauna and authigenic carbonates (Fig. 5.12.). Overpressure can also have caused the submarine landslide at the Faure Site, changing and focusing fluid migration pathways towards the present bubble-releasing sites as was observed at the Dnepr paleo-delta and other seep sites in the world (Orange and Breen, 1992; Eichhubl et al., 2000; Kuscu et al., 2005).

This study has shown that gas hydrates play an important role in controlling the activity of bubble-releasing seeps, their distribution and associated manifestations on a basin-wide scale (Dnepr paleo-delta) and on smaller scales (Hikurangi Margin). The study of the seeps in the Dnepr paleo-delta clearly showed that gas hydrates can be regarded as buffers for upward

rising fluids, preventing bubble release at the seafloor. This was often suggested but never shown on such a scale. The Lake Baikal study also indicated gas hydrates as buffers, but the unique geometry and build-up of the Posolsky Bank allowed gas to escape from below the BGHSZ without migrating through the GHSZ. Whereas at the Hikurangi Margin the overpressure typically associated with accretionary prisms allowed the migration of free gas through the GHSZ. In none of the studied areas gas hydrates have been inferred as direct sources for the released methane.

7.2.4. Fluid migration outside of the gas-hydrate stability zone

Fluid migration outside of the gas-hydrate stability zone, i.e. shallower water depths or greater subsurface depths, can be controlled by various types of conduits or seals which are also present in the GHSZ, but are often obscured by the presence of gas hydrates. Most important factors controlling fluid flow are overlying sediment layers (permeability, porosity, continuity, heterogeneity, etc.), the stratigraphic buildup of sedimentary strata, mud diapirs and the presence of (active) faults (see section 7.2.5.) (Judd and Hovland, 2007).

For the Dnepr paleo-delta, migration of gas in the upper 200 m is mainly controlled by stratigraphic and sedimentary factors, as revealed by the behavior of the gas front visible on high-resolution seismic reflection data (Figs. 3.6., 3.7. and 3.10.-3.12.). Along-strata and across-strata free gas migration seems to be important in the cut-and-fill delta deposits on the shelf and in stacked channel-levees on the continental slope. Near the seabed the occurrence of an overall-present fine-grained impermeable sediment cover, with a thickness up to 25 m, focuses fluids upslope to the margins of e.g. canyons or submarine landslides, where the cover is thinner or absent. These are the locations where free gas is released in the water column (Figs. 3.6. and 3.10-3.12.). On the shelf, filled paleo-channels and authigenic carbonates control and alter fluid migration pathways and lead to well-defined seep distributions on meter to kilometer scales (Figs.

3.6., 4.4. and 4.11.). At morphological highs, such as sediment ridges, gas generally accumulates near the top of the ridge, where overpressure or density inversion leads to breaching of the overlying stratigraphic cover and to bubble release (Figs. 3.10. and 3.12.). The available seismic data provides no evidence for the existence of faults which could act as conduits for upward fluid migration in the shallow subsurface of the Dnepr paleo-delta. However where faults were observed they were not related to bubble-releasing seeps. This does not rule out that deeper structures may be present. Structural pathways may be provided by: the large West-Crimean fault, diapiric structures on the slope, a normal fault along the shelf edge, and possible faults buried under channel-levee systems perpendicular to the slope at 300 m to 600 m below the seafloor (Lüdmann et al., 2004). Only for the -600 m seep site, helium isotopes indicate that the released gasses are possibly influenced by fluid advection from depth, possibly along deep-rooted faults (Fig. 3.13.) (Holzner et al., 2008). At this site, seismic data however indicates that the focusing and release of free gas at the seafloor is probably related and controlled by the underlying channel-levee systems (Fig. 3.7.), in a similar way as was observed in the Congo Basin (Gay et al., 2007). At the margin of the gas-hydrate stability zone, gas-hydrate recycling caused by paleoclimate-related temperature and pressure changes may also be a source for gas seeps although no direct evidence for this was observed (Poort et al., 2005). Gas-hydrate destabilization could however have led to sliding of submarine sediments, resulting in new release paths for gas seepage (Fig. 3.11.).

As was already indicated in section 7.2.3., the controls on seepage in the Posolsky Bank study area are very similar to the ones in the Dnepr paleo-delta, i.e. stratigraphic and sedimentary controls (Figs. 6.7. and 6.10.). However across-strata migration seems to be almost absent at the Posolsky Bank where mainly focusing along the tilted sedimentary strata occurs. This focusing is probably a result of the angle and continuity of the layers and the presence of an overlying continuous fine-grained sediment layer that acts as a seal (Fig. 6.10.). Gas release into the water column occurs where the gas-bearing

strata get cut off by a large fault, and not by erosional features like canyons or submarine landslides as observed in the Dnepr paleo-delta (Figs. 3.13. and 6.10.). The co-occurrence of the Posolsky Fault and the seeps could suggest that the fault acts as a conduit for fluid flow and seepage. However integration of the data counters this suggestion. Remarkable is the similarity of the controls on fluid flow and seep distribution between the Dnepr paleo-delta and the Posolsky Bank, notwithstanding the complete different geological setting (paleo-delta vs. tilted fault block) and the difference in tectonic activity between both settings.

On the Hikurangi Margin fluid migration below the GHSZ is mostly controlled by NW-dipping layers at LM-3 and by a permeability contrast at the BGHSZ at Faure Site (Crutchley et al., 2010). This implies that there is a difference in control of fluid migration for both seep sites, below as well as above the BGHSZ (see section 7.2.3.).

7.2.5. Faults versus sediments; which is the primary conduit/seal related to bubble-releasing seeps?

The previous two sections have shown that there are a lot of different controls on fluid migration in the shallow subsurface that lead to bubble release at the seafloor. However, these different controls are often not consistent with what could be expected from the geological and tectonic setting. Often it is a combination of sedimentary- and fault-controlled fluid flow even within a same area or at different subsurface depths below a certain seep site. For the Rock Garden seep sites on the Hikurangi Margin (Faure Site and LM-3), Crutchley et al (2010) showed that fluid migration can differ depending on the observed subsurface interval allowing sedimentary strata and faults to act as conduits for a same seep site (Fig. 5.12.). Gay et al.(2007) came to similar conclusions for the Congo Fan. At LM-3, for example, fluid flow below the GHSZ is stratigraphic-controlled by NW-dipping layers, whereas in the GHSZ fluid flow occurs along faults and by across-strata migration near the seafloor. The formation of MDACs and the activity of (seep) fauna near the

seafloor at LM-3 act as an additional control on fluid flow and seep distribution (see section 7.3.1. and 7.3.2.). This change of migration mechanism is not fixed with depth or related to a certain driving force. Crutchley et al. (2010) show that the control of fluid flow below Faure Site is mainly stratigraphic-controlled, in as well as below the GHSZ. The type of fluid flow control is rather dependent on the local stratigraphic and structural setting below a seep site, even within a same study area. The example above indicates that it is very hard to predict whether sedimentary- or fault-controlled fluid flow occurs at a certain geological or tectonic setting, or at a certain depth interval

For our study areas, an integration was made of high-resolution seismic data with detailed and high amounts of seep-location data and other relevant datasets in order to understand the subsurface controls and the distribution of seeps. Variations in grain-size distribution and the consequent changes in permeability of the sediments in the upper hundreds of meters, all or not influenced by the presence of gas hydrates, seems to be the major control on fluid migration, on seep distribution and on seep activity, and this on meter to basin scale. This differs strongly from the general view that faults act as the primary conduit at most cold seep sites (Judd and Hovland, 2007; and references therein). We can't argue about the deep subsurface controls in our study areas since we don't always have the deep low-resolution seismic data. At the seafloor, often alignments of seeps were observed on different scales (Figs. 3.6., 3.10., 3.11., 4.1. and 5.9.). Without the integration of different high-resolution datasets these alignments could have been interpreted as related to underlying faults, although they are related to stratigraphic and sedimentary controls. It is clear that there is not a straightforward answer to the question raised in the title of this section; however our study indicates that stratigraphic and sedimentary factors in the shallow subsurface are probably very important for the distribution of bubble-releasing seeps (Fig. 7.3.). This conclusion can be extended to numerous other seep areas, since it is based on the study of seeps in three completely different geological settings.

7.3. Seafloor manifestations associated with bubble-releasing seeps

Bubble-releasing seeps are often associated with a multitude of seafloor manifestations which can be recognized even when seeps are not actively emitting bubbles into the water column. The three main types are: chemosynthetic communities, methane-derived authigenic carbonates and fluid-flow related seafloor morphologies. The presence of these seep indicators implies focused fluid flow and seepage but therefore not always seepage with bubble release. Only acoustic or visual observations can determine whether certain seep indicators are indeed associated with bubble-releasing seeps. The composition of fluids released can alter the biological and MDAC manifestations at a seeps site, seafloor morphology is however independent of the fluid composition.

7.3.1. Chemosynthetic communities

Chemosynthetic communities are probably the most striking and thus the most recognizable seepage indicators since they occur very localized and often strongly differ from other seafloor communities. Chemosynthetic communities thrive on diffusively released methane and sulfide which are available at seep sites and thus not directly on the methane that is present in bubbles. These communities are believed to be the base of complete chemosynthetic food web where higher non-chemosynthetic organisms feed on chemosynthetic lower organisms (Judd and Hovland, 2007). Microbes are the foundation for chemosynthetic communities. They live in the sediments or are present as endosymbionts in seep megafauna. The main microbial groups involved are sulfate-reducing bacteria (SRB) and methanotrophic archaea that utilize methane and sulfate dissolved in the pore waters. This process is known as the anaerobic oxidation of methane (AOM) which results in the release of hydrogen sulfide and bicarbonate (Boetius et al., 2000). AOM and the associated chemosynthetic

communities utilize most of the methane available at seep sites and can therefore be seen as an effective benthic filter (Boetius and Suess, 2004; Sommer et al., 2006). It is only where this seabed utilization of methane can't account for the entire methane flux or where fluid migration is highly focused that bubble release can occur.

In the Dnepr paleo-delta, two different chemosynthetic communities were observed: white bacterial mats at the -100 m seep site and black-pink bacterial mats covering up to 4-meter-high carbonate buildups at the -200 m seep site (Figs. 4.7. and 4.8.) (Michaelis et al., 2002; Blumenberg et al., 2004; Kruger et al., 2008). Whereas the bacterial-covered buildups are clearly associated with bubble release, the bacterial mats in the -100 m seep site show an inverse proportional relationship between the extent of the bacterial mats and the distribution and activity of the bubble-releasing seeps (see chapter 4). At the -100 m seep sites, methane-derived authigenic carbonates block fluid flow and bubble release whereas at the -200 m seep site the buildups are prolongations of the fluid-flow pathways. The occurrence of these two types of chemosynthetic communities and the chimney-like buildups is strongly related to the water depth and presence of anoxic water masses below -145 m in the Black Sea.

At the Hikurangi Margin, no bacterial mats were found at Faure Site and LM-3. They were, however, found at other seep sites at the Hikurangi Margin (Greinert et al., 2010a). As discussed in chapter 5, the difference in seep fauna observed at Faure Site and LM-3 is related to the difference in fluid release mode. At Faure Site, methane emission occurs mainly by bubble-release and only living ampheretid polychaetes were found. At LM-3 where methane is mainly released diffusively, living *Bathymodiolus* sp mussels and *Lamellibrachia* sp. tubeworms were observed on top of a carbonate platform. As for Faure Site, living ampheretid polychaetes were found near the bubble-releasing seeps at LM-3. These polychaetes are regarded as ecosystem engineers that facilitate the transition from a soft sediment environment with mainly bubble release to a hard substrate seep environment with associated fauna where AOM and diffusive methane transport prevail (Sommer et al., 2010;

Thurber et al., 2010). At both sites, high abundances of shells from dead *Calypptogena* sp. were found. We explained the difference in methane release and seep environment (chemosynthetic fauna and authigenic carbonates) by the depth of the underlying hydrate occurrence and the different tectonic histories of both sites (chapter 5).

At the Posolsky Bank, large bacterial mats were found near the hydrate site on the Posolsky Fault scarp during submersible observations (Oleg Khlystov, personal communication). Besides this, chemosynthetic fauna in Lake Baikal is mainly limited to microbial communities which can be found at gas-hydrate-bearing mud volcanoes, oil seeps and hydrothermal vents (Shubenkova et al., 2005; Namsaraev et al., 2006; Pavlova et al., 2008).

In the different study areas we observed a variety of chemosynthetic communities in completely different environments (anoxic, freshwater and sea water) and at different water depths ranging from -84 m to -908 m. For the Dnepr paleo-delta and Hikurangi margin, seep fauna's were indicative for locating the bubble-release sites even though bubble-release was more important where seep fauna was less abundant (see section 7.3.2.). For both study areas the water depth is an important factor controlling fluid flow, bubble release and the type of associated chemosynthetic fauna.

7.3.2. Methane-derived authigenic carbonates

Methane-derived carbonates (MDACs) are in most cases a result of AOM and are often formed by cemented seafloor sediments. Common carbonate minerals in these cements are high-magnesium calcite, aragonite and dolomite formed by Ca and/or Mg and the bicarbonate resulting from AOM present in the pore waters or bottom waters. Since they result from AOM, the carbonates are ^{13}C -depleted with $\delta^{13}\text{C}_{\text{CH}_4}$ values generally ranging from -60 to -20 ‰ (von Rad et al., 1996; Peckmann et al., 2001; Greinert et al., 2002a; Luff et al., 2005; Judd and Hovland, 2007). Other well-known MDACs are barites (Torres et al., 1996; Greinert et al.,

2002b). MDACs occur in several forms (chimneys, plates, crusts, etc.). Their presence in the fossil record indicates that seepage and AOM were already important in earlier geological times (Luth et al., 1999; Díaz-del-Río et al., 2003; De Boever et al., 2006a; Judd and Hovland, 2007; Campbell et al., 2008).

In the Dnepr-paleo delta several MDACs are present at water depths ranging from -86 to -700 m. The carbonates occur often in association with bacterial mats and are ^{13}C -depleted with $\delta^{13}\text{C}_{\text{CH}_4}$ values generally ranging from -25.5 to -41.‰ (Fig. 4.7.) (Luth et al., 1999; Peckmann et al., 2001; Michaelis et al., 2002; Gulin et al., 2003; Reitner et al., 2005; CRIMEA Project Team, 2006). At the -100 m seep site, the MDACs are plate-like or form small buildups that are often covered by sediments (Fig. 4.7.). These MDACs control the locations of bubble-releasing seeps by clogging up, and eventually sealing, fluid pathways (chapter 4). This self-sealing process of seeps was previously suggested by Hovland (2002) for seeps in the North Sea. At the deeper seep sites, MDACs are present as chimney-like buildups which focus bubble release. These carbonate buildups are unique in the world due to anoxic water column of the Black Sea below -145 m water depth. Carbonate chimneys are normally formed within the anoxic environment present in the sediments and not within the water column (Díaz-del-Río et al., 2003; De Boever et al., 2006b). Peckmann et al. (2001) dated the carbonates from the -200 m seep site and concluded that the chimneys are made up from methane with an age of 19 ka BP. The real upper age limit of the microbial tower-like structures is given by the limnic-marine transition of the Black Sea and the subsequent development of a permanent anoxic water body about 8 ka BP ago (Pape et al., 2008). The presence of the MDACs indicates that seepage is long-lived at the Dnepr paleo-delta.

At the Hikurangi Margin, MDACs are present as a relatively large carbonate platform associated with live seep mega fauna at LM-3 and several smaller platforms without live seep megafauna near Faure Site. Carbonates from LM-3 had a $\delta^{13}\text{C}_{\text{CH}_4}$ value of -36.49 ‰ indicating the AOM-related formation of the MDACs (Campbell et al., 2010). As was observed in the

Dnepr paleo-delta, the carbonate platform at LM-3 focuses and relocates bubble-releasing seeps to an area just next to the area affected by massive carbonate precipitation. Near the bubble-releasing seeps of Faure Site, however, no MDACs were observed. This is remarkable for the Hikurangi Margin where most seep sites are associated with large carbonate structures, suggesting a longtime seepage history at this accretionary prism (Greinert et al., 2010a). The absence of MDACs indicates that seepage at Faure Site is rather recent, probably related to the presence of a submarine landslide.

At the Posolsky Bank, no sampling of carbonates was undertaken or observed. However, small MDACs do occur in Lake Baikal, notwithstanding the sulfate-poor freshwater environment. MDACs (siderites) have been sampled at several mud volcanoes where they occur in association with gas hydrates and are formed due to aceticlastic methanogenesis (Krylov et al., 2008a; Krylov et al., 2008b).

MDACs have been observed in the same water depth range as the chemosynthetic communities (-84 m to -908 m). Besides the visual observations, MDACs can be easily localized based on backscatter data from multibeam and side-scan sonar recordings making them strong seep indicators (chapter 4) (Greinert et al., 2010a). MDACs control the location and activity of bubble-releasing seeps, and therefore their presence doesn't always indicate active seepage. Vast occurrences of MDACs do, however, indicate that seepage is/was active over longer periods. Highly focused fluid flow can however also inhibit AOM and the formation of MDACs and chemosynthetic communities.

7.3.3. Seafloor morphology

In some cases bubble-releasing seeps occur at typical seafloor morphologies. The most common are seafloor depressions known as pockmarks or cone-shaped seafloor highs related to mud volcanism. Pockmarks are believed to be formed by blow-outs due to overpressure generated by gas trapped underneath an impermeable cohesive sealing layer. Mud volcanoes are formed by

overpressured fluid and mud rising from great depths that extrude at the seafloor. (Judd and Hovland, 2007). Notwithstanding that both morphologies are very characteristic they are not always associated with bubble release. Acoustic and visual observations are needed to confirm if these features are actively bubbling. In the Dnepr paleo-delta, bubble-releasing seeps occur at several seafloor morphologies: pockmarks, sedimentary ridges, scarps of submarine landslides and canyons (Figs. 3.5.-3.6. and 3.10.-3.12.). Probably only the pockmarks are a direct result of fluid flow and seepage. Whether they are formed by blow-outs is rather doubtful. Perhaps they are formed by the entrainment of sediment grains by bubbles over long time spans. The presence of MDACs in the deep pockmarks indicates such a longtime seepage. Visual observations at Faure Site clearly show that bubbles are capable of forming seafloor depressions by entrainment of sediment grains (Fig. 5.10.). The submarine landslides present in the Dnepr paleo-delta and near Faure Site are probably also related to fluid flow and/or seepage (Figs. 3.11. and 5.2.) (Pecher et al., 2005; Crutchley et al., in press). Whether in both cases bubble release was the cause or is rather the result of the mass movement is unclear. In the Dnepr paleo-delta, canyons are typically associated with bubble release. As for the submarine landslides, erosion of an impermeable cover exposes gas-bearing layers and leads to seepage. The formation and location of a canyon can be strongly controlled by fluid flow and seepage (Popescu et al., 2004). Furthermore, the alignment of seeps on the crests of sedimentary ridges is very common in the Dnepr paleo-delta, but such alignments are hardly observed anywhere else (Figs. 3.10. and 3.12.). This is maybe due to our detailed echosounder coverage and resulting seeps distribution. The presence of an impermeable top layer and the tendency of fluids to migrate towards the highest location in permeable reservoirs is probably the cause of this alignment. Whether overpressure helped to breach the cover layer at the crest of the ridges or whether the presence of MDACs have enhanced the ridge morphology is not clear.

As mentioned in the previous paragraph the seeps at Faure Site are associated with a

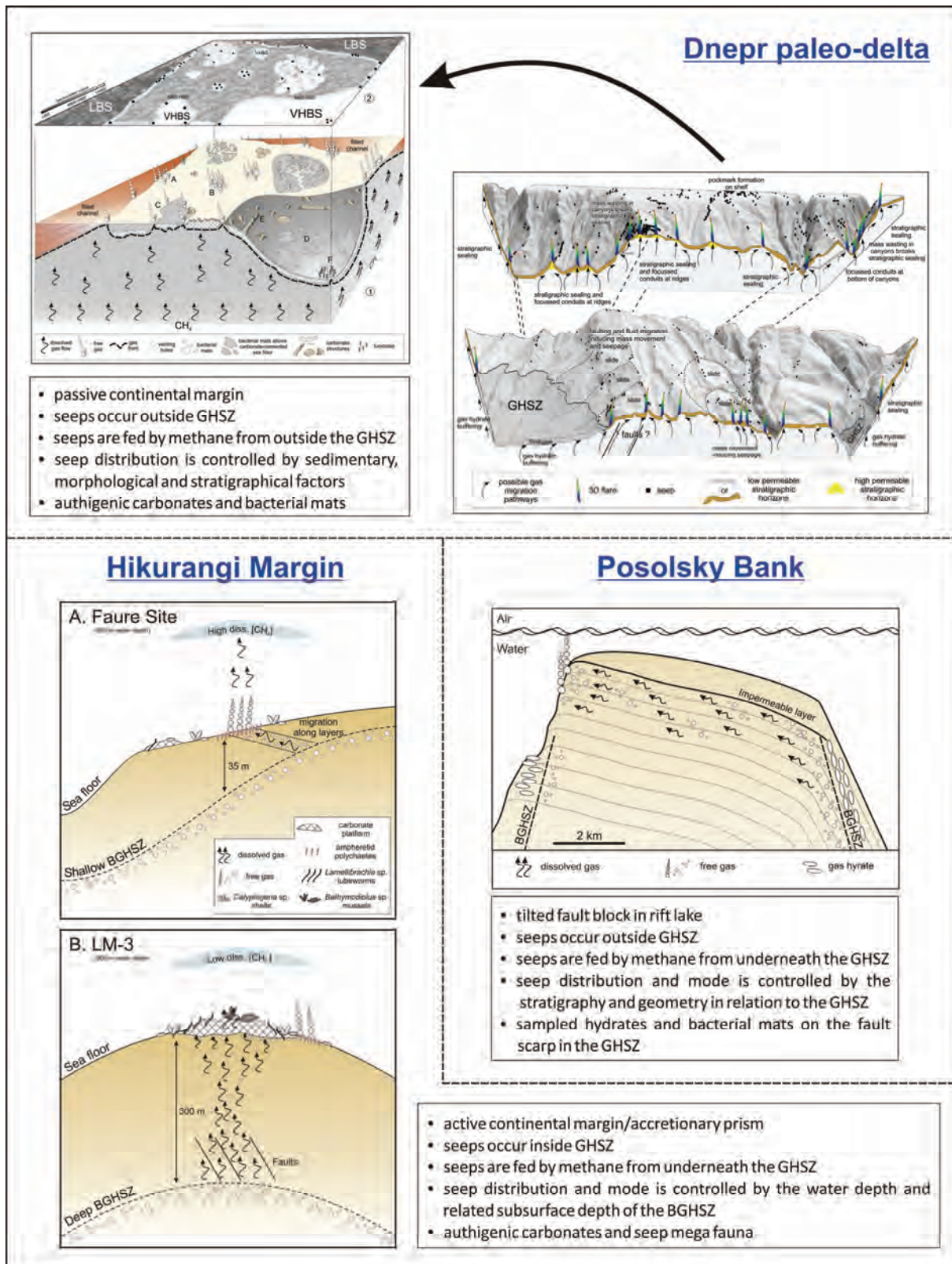


Figure 7.3. Overview of the models explaining fluid flow, the distribution of seeps and the associated seafloor/lake floor manifestations for the different study areas.

submarine landslide and with very small pockmarks formed by bubble release. At LM-3, no small-scale change in seafloor morphology is present at the seep site except for the presence of the carbonate platform. On a larger scale, seepage at Rock Garden and at the Hikurangi Margin is located on the crests of thrust-faulted ridges on the mid slope of the accretionary prism (Barnes et al., 2010).

At the Posolsky Bank, seeps occur where a major fault cuts off gas-bearing strata, whereas for the Dnepr paleo-delta and Faure site erosional features expose gas-bearing layers. Fault scarps seem to be the main seep location in the Posolsky Bank study area. One local pockmark was also observed at a fault scarp; however no bubble release was observed (Fig. 6.3.).

The previous has shown that seeps tend to occur at certain seafloor morphologies, but those seafloor morphologies are not always associated or caused by fluid flow or bubble release. Pockmarks are probably the most indicative for present or past seepage activity. However, in our study areas, the amount of pockmarks is rather small. Whether this is due to sediment type or fluid-flow activity is unclear. Locations where subsurface layers are exposed due to erosion or fault activity are particularly interesting to be associated with bubble-releasing seeps.

7.4. Fate of methane released at bubble-releasing seeps

Although it was not one of the main goals of this study, the fate of the methane released at bubble-releasing seeps is one of the key questions behind the conducted seep research and can therefore not be omitted from this discussion. Within the CRIMEA project (Black Sea), the main goal was to study and quantify the transfer of methane to the atmosphere emitted from bubble-releasing seeps. Several publications resulting from this project explained the mechanism controlling the release of methane from the seafloor, into the water

column and potentially into the atmosphere (Durisch-Kaiser et al., 2005; Schmale et al., 2005; Greinert et al., 2006; Kourtidis et al., 2006; McGinnis et al., 2006; Schubert et al., 2006; Greinert, 2008; Greinert and McGinnis, 2009; Greinert et al., 2010b; Schmale et al., 2010). The main conclusion is that bubble-releasing seeps are only active over short periods, e.g. Faure Site (see table 5.1.), and are only effective in transferring methane into the atmosphere in shallow water depths (< 100 m). Even in these shallow water depths the resulting flux is rather limited. It is only where a widespread massive constant release of gas bubbles occurs, e.g. from destabilizing gas hydrates or from mud volcanoes, that bubble plumes can form and enable the release of significant volumes of methane into the atmosphere and influence regional atmospheric methane concentrations. In case of the mud volcanoes the duration of such outbursts is rather limited in time and thus less significant. Our observations at Faure Site also showed that bubble release is very transient and is controlled by different factors on different time scales (see section 5.5.2.). It seems that only very shallow and very active seeps, e.g. Coil Oil Point seeps, significantly contribute to atmospheric methane (Leifer et al., 2006b). Solomon et al. (2009) indicated however that deep oily seeps or seeps releasing large bubbles can have an important influence on atmospheric methane concentrations. It is clear that much more research needs to be conducted to understand the release of methane from bubble-releasing seeps. One of the main target study areas should be the shallow Arctic Shelf, where rapidly warming bottom waters are potentially affecting gas-hydrate stability and cause the thawing of permafrost. The release of the possible vast amounts of methane stored in the sediments and the shallow water depth could lead to enormous fluxes of methane into the atmosphere and could affect atmospheric methane concentrations and global climate in the near future (Shakhova and Semiletov, 2007; Greinert et al., 2010b).

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