

LEON H. CHARNEY SCHOOL OF MARINE SCIENCES בית הספר למדעי הים על שם ליאון צ'רני

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14th International Conference on Gas in Marine Sediments GIMS 14 Haifa, Israel

October 14-20, 2018





ISRAEL Science Foundation







Abstracts for Oral Presentations (alphabetical order)

FORMATION OF SUBMILLIMETER BUBLES AT SHALLOW-WATER BASIN SEDIMENTS NEARBY TECTONIC ACTIVITY AND THEIR POSSIBLE SOURCES

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ABSTRACT

This study is focused on gas seepages at basin sediments distributed on broad areas close to critical tectonic structures, not on small-scale regional fluid and gas release points at the sea bottom. A series of successful laboratory and field experiments have been done for real-time ultrasonic monitoring of bubble escapes and suspended particles in water column, both for anoxic and oxic sediment surfaces. 'Type one bubbles', also known as biogenic gas, were created by bacteria in oxic or anoxic sediment processes. In nature, benthic organisms (e.g. serpulid, tubeworm, tunicate, etc.) are responsible for building of tunnel-type cavities that increases collecting and transportation of biogenic gas. Those cavities means that the complex structure is an enrichment system in generation, accumulation and resource potential of biogenic gas. Second type bubbles created by inert (argon, nitrogen, radon, krypton and xenon) and nobble gases or radioactivity products coming from nearby faults. Another possibility is the "third type bubbles", they also come from faults, but not related to the mantle. They are gas traps at fault surface and have been captured in a short time at shallow waters by vacuum forces occurred during opening and closing of fault fractures. The observations for bubbles and suspended particles will be suitable for the lakes located on the same fault line, like the Sea of Galilee and Dead Sea. In case of any type of stress changes of seafloor thermal features or other precursor tectonic activities, continuous monitoring of bubble size and abundance can be used as an alternative parameter in earthquake prediction, especially in Israel, Jordan and Syria.

A CRITICAL LOOK AT THE COMBINED USE OF SULFUR AND OXYGEN ISOTOPES TO STUDY MICROBIAL METABOLISMS IN METHANE-RICH ENVIRONMENTS

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ABSTRACT

Separating the contributions of anaerobic oxidation of methane and organoclastic sulfate reduction in the overall sedimentary sulfur cycle of marine sediments has benefited from advances in isotope biogeochemistry. Particularly, the coupling of sulfur and oxygen isotopes measured in the residual sulfate pool ($\delta^{18}O_{SO4}$ vs. $\delta^{34}S_{SO4}$). Yet, some important questions remain. Recent works have observed patterns that are inconsistent with previous interpretations. We differentiate the contributions of oxygen and sulfur isotopes to separating the anaerobic oxidation of methane and organoclastic sulfate reduction into three phases; first evidence from conventional high methane vs. low methane sites suggests a clear relationship between oxygen and sulfur isotopes in porewater and the metabolic process taking place. Second, evidence from pure cultures and organic matter rich sites with low levels of methane suggest the signatures of both processes overlap and cannot be differentiated. Third, we take a critical look at the use of oxygen and sulfur isotopes to differentiate metabolic processes (anaerobic oxidation of methane vs. organoclastic sulfate reduction). We identify that it is essential to develop a better understanding of the oxygen kinetic isotope effect, the degree of isotope exchange with sulfur intermediates as well as establishing their relationships with the cell-specific metabolic rates if we are to develop this proxy into a reliable tool to study the sulfur cycle in marine sediments and the geological record.

CONSTRAINTS ON GAS-HYDRATE OCCURENCE IN THE BAY OF BENGAL

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ABSTRACT

We examined environmental magnetic and sedimentological records of four sediment cores retrieved from proven cold seep environment of Krishna-Godavari (K-G) basin, Bay of Bengal. The focus of this study was to decipher the lithological control on gas-hydrate occurences in Bay of Bengal. We identified a uniform and continuous magnetite-rich band extending throughout the K-G basin and appears to be a regional feature. This band comprises of numerous layers of coarse-grained magnetic particles possibly represents multiple-short term events of higher sedimentation. This observation provides clues on significant changes in sedimentation rates and deposition pattern which have taken place in the Bay of Bengal. Based on sediment magnetic signatures, we identified four sedimentary units. In unit-I, high concentration of detrital ferrimagnetic iron minerals give way to progressive diagenetic dissolution of detrital Fe-Ti minerals and precipitation of secondary diagenetic/authigenic minerals with depth as observed in unit- II. The unit-III represents the period of higher sedimentation events. Rock-magnetic and electron microscopic observations confirmed the presence of coarse-grained titanomagnetites in this unit. A close correlation between magnetite concentration and chromium reducible sulfur (CRS) content indicates marked influence of sulfidization on the magnetic record. We further demonstrate that this relationship can be used as a proxy to decipher paleo-H₂S seepage events. We hypothesize that unit-IV was formerly a gas hydrate bearing horizon. The opening of the regional fault system altered the P-T conditions and hydrate started dissociating resulting in upward migration of methane thereby creating a fossil gas hydrate interval in unit-IV.

COLD METHANE SEEPS IN THE LAPTEV SEA: CHARACTERISTICS AND TECTONIC POSITION

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ABSTRACT

Recent investigations have shown that a number of local fields with cold methane seeps exist over the outer shelf of the Laptev Sea. Two of these fields were studied during 69-th Cruise of R/V "Academik Mstislav Keldysh" in August, 2017. These investigations included bathymetric and side-scan sonar mapping, towed video camera observations and bottom sampling. As a result, 38 gas flares were recorded in area of 30 km² indicating the active gas emission. Due to shallow depths of the seep locations (60-70 m) gas bubbles reached the sea surface and were visible from the ship deck. Side-scan sonar images of the gas emission sites correspond to a small light spots, which due to carbonate crusts have stronger backscatter intensity as compared to the surrounding bottom. Sampling and video camera observations showed the presence of symbiotrophic (siboglinids Oligobrachia haakonmosbiensis) and endemic (gastropods Frigidalvania sp. nov.) taxa. At seep sites, the response of the fauna was evident in significantly increased its abundance and biomass as compared to the background. The relief morphology of studied fields suggests the presence of faults striking in the same directions as main tectonic features of the area. These features include the Laptev Sea rift system, mid-oceanic Gakkel Ridge and Khatanga-Lomonosov fracture zone separating the rift system and the ridge. Methane fields are located along the western segment of the Khatanga-Lomonosov fracture zone, which, as evidenced by the structural data is active. This zone and adjoining faults may serve as conduits for gas migration.

LABORATORY STUDIES OF THE GEOPHYSICAL QUANTIFICATION OF SUB-SEAFLOOR GAS IN SEDIMENTS AND RESERVOIR ROCKS

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ABSTRACT

Our ability to image and quantify sub-seafloor gas using geophysical remote sensing is an important prerequisite both for scientific investigations of the natural environment and for application of this knowledge for societal benefit. Topics include sub-seafloor fluid flow, geohazards, hydrate dissociation, oil and gas exploration, CO2 storage, geotechnical engineering, naval defence and so on. To address some of these topics, we have conducted integrated laboratory experimental and theoretical model studies of the effects of gas on elastic wave velocity, attenuation and electrical resistivity in sands and sandstones, including artificial fractures and anisotropic effects. Our philosophy has been to design experiments around specific theoretical predictions or knowledge gaps to gain the necessary insights. This approach has proven successful with studies focussed on offshore hydrocarbon and CO2 storage reservoirs, and seafloor methane hydrates. The laboratory experiments have used various adaptations of an ultrasonic pule-echo system installed inside a triaxial high pressure cell for 5 cm diameter rock samples, for studies of CO2/brine injection, also combined with synthetic silica-cemented sandstone samples with aligned fractures, and of methane hydrate formation in natural sandstone and sand. Using microfocus X-ray computed tomography, we were also able to gain insights into e.g. hydrate/gas formation morphology and its effect on the key geophysical properties listed above. While not exhaustive, our results so far have indicated interesting new possibilities for interpreting seismic and electromagnetic survey data in terms of sub-seafloor gas saturation.

SEQUENTIAL EVOLUTION OF AUTHIGENIC CARBONATE FORMATION IN METHANE SEEPS, EVIDENCE FROM THE ISRAELI SLOPE

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ABSTRACT

Deep-sea authigenic carbonates are an important vet underexplored ultimate sink of carbon. A more rapid pathway for carbonate sequestering is mineralization of organic matter, e.g. through oxidation of methane. Different modes of methane and ionic flux govern the morphology and minerology of the deep-sea carbonate accumulation. The details of these relations are poorly understood. A set of active and paleo-seeps on the Israeli slope presents a unique opportunity to explore the full range of carbon transition modes and morphologies of such authigenic carbonates. A series of ROV dives starting in 2010, revealed a wide range of forms. Notably, in some of the paleo-seeps in steep slope positions the upper portion of the structure was eroded, exposing parts of the underlying structure. Field relations between enhanced bioturbation and autogenic carbonates in the active seep area points to enhancement of infaunal biologic activity in the vicinity of the seep, and formation of the carbonates within the sediment. Ongoing seepage had also resulted in corrosion of the carbonates and release of carbon from mineral from. The spatial distribution and state of the carbonates and bioturbation along the margins reveals multiple seepage activity zones, operating as independent events and potentially at different times. The observations points to the interactions between burrowing organisms, oxidation of methane, and carbon mineralization into calcite and dolomite in the sediment. These interactions potentially govern what portion of the carbon from the methane is maintained in sequestered state in the geosphere, and which part of it returns to the atmosphere/hydrosphere.

EVOLUTION MODEL FOR THE ABSHERON MUD VOLCANO: FROM IN-SITU OBSERVATIONS TO NUMERICAL MODELLING

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ABSTRACT

Research activity on mud volcanoes (MVs), whose morphology has been described since the 19th century, is presently dedicated to increasing the understanding of their underground structure and mud generation mechanisms. An offshore 3-D seismic survey of the Absheron anticline (South Caspian Basin, offshore Azerbaijan) shows an active MV at the seafloor. It is located on the crest of the anticline. Its underground structure is poorly imaged due to the presence of gas-rich sediments. Seafloor bathymetry shows a 4.5 km-diameter mud shield with 5 mud pies, 300 m to 1 km in diameter, distributed at its surface. A 10 km-long mud flow emanated from the western side of the shield through a 100 m wide breach, and is still visible at the seafloor. On seismic sections, older mud flows are imaged, as well as compressional wedges radiating from the volcano. The emplacement of this MV is controlled by a deep thrust and well data reveal the presence of several highly overpressured intervals. Based on seismic interpretation, sediment analysis and well data, we tested both sedimentation-related overpressure as well as gas diffusion as main potential controlling factors on mud generation location. We propose a conceptual evolution model for the emplacement of the mud volcano system: (1) overpressure buildup in the anticline crest in relation to thrust formation and focusing of gas migration through the sedimentary column, (2) hydro-fracturing of gas-saturated and overpressured sediments leading to (3) gas exsolution and mud extrusion to the seabed.

RELATION BETWEEN METHANE CONCENTRATION AND DISSOLVED CARBON FORMS IN SHALLOW SEDIMENTS OF A CONTINENTAL SHELF SEA (BALTIC SEA, GDAŃSK BASIN)

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ABSTRACT

The purpose of the study was to investigate how concentrations of porewater dissolved inorganic and organic carbon (DIC and DOC) change in relation to biogenic methane concentration in shallow sediments of a coastal sea area. The research was conducted based on sediment cores (up to 1.2 m in length) collected in the deepwater area of the southern Baltic Sea (Gdańsk Basin), at two methane and two non-methane stations, in the period from 2014 to 2018. The following parameters were measured: methane, sulfate, dissolved sulfide, ammonium, DIC and DOC in pore waters, as well as δ^{13} C in DIC, and content of organic carbon in sediments. Additionally, the conditions in bottom water were determined (temperature, salinity and dissolved oxygen). The results showed that e.g. (1) DOC concentrations are significantly correlated with methane, (2) DIC and DOC are considerably dependent on each other in the whole examined sediment profile of methane stations, in contrast to the profiles from non-methane sites, and (3) both DIC and DOC fluxes from sediments are higher at stations with methane. Seasonal variations between the correlations were also observed.

This study was financed by the Polish National Science Centre (grant no. UMO-2016/21/B/ST10/02369).

A FRICTIONAL BASED DISCRETE ELEMENT MODEL OF METHANE-HYDRATE SEDIMENTS

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ABSTRACT

Throughout recent decades, considerable efforts have been placed on extracting gas from methane-hydrate sediments, without satisfactory results due to geomechanical issues. To cope with the geotechnical problems, geomechanical characterization of the methane-hydrate sediments is essential. This work presents a Discrete Element Method (DEM) formulation developed for describing the soil and hydrates phases. The microscopic representation of the material allows, unlike average based continuum methods, an insightful investigation into the sediment response, from which macro scale properties can be evaluated. A cohesionless DEM formulation is developed in the current work, following recent discoveries from experimental triaxial tests as well as X-ray microscopic observations of gas hydrate bearing sediments. In the formulation, the hydrate is represented as spherical particles positioned within the sand skeleton in an explicit manner, without any bonding. The suggested configuration can reproduce the hydrate influence on the small strain stiffness, on the maximal deviatoric stress, and on the volumetric dilatancy, as observed in both natural and artificial hydrate-methane samples. A geometrical inter-particle microscopic relation is established and used to reproduce the global macro scale stress-strain response through statistical based calibration.

IDENTIFYING GAS HYDRATE SYSTEMS USING VELOCITY PULL-UPS

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ABSTRACT

Natural gas in marine sediments is easily detectable with seismic data; just a small amount of gas (1-3% of pore volume) significantly affects the bulk moduli and drops the compressional-wave velocity, causing high-amplitude reflections in seismic data. Moreover, within and below gas chimneys pull-down anomalies are often observed because of the low velocity within the chimney relative to the surrounding sediment. Recently, a paper in *Geology* suggested that some high-velocity gas hydrate accumulations may have the opposite effect, a velocity pull-up (VPU). This VPU, which reached up to 0.1 s (~90 m), was observed below high-amplitudes within a turbidite channel complex on the Mississippi Fan in the Gulf of Mexico; the channel complex occurs within the gas hydrate stability zone. The VPU indicates that there is a higher velocity sediment package within the channel relative to surrounding sediments on the fan, which could be caused by high-saturation ($S_h > 40\%$) hydrate. We use logging and core measurements collected from the Deep Sea Drilling Project (DSDP) Leg 96, which drilled three holes above and into the top of the turbidite fan complex in 1983. We combine this data with 2D seismic data to construct velocity models of the Mississippi fan and consider alternate scenarios to explain the VPU, such as overpressured sediments in the surrounding fan causing a velocity contrast with normally compacted sediments in the channel. Preliminary modeling suggests that highsaturation hydrate must be present to explain both the high amplitudes and the VPU observed near DSDP Leg 96.

PORE WATER COLOR IN METHANE-CHARGED SEDIMENT SEQUENCES ON CONTINENTAL SLOPES

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ABSTRACT

Sediment sequences along contiental slopes host enormous amounts of biogenic methane in pore space as dissolved gas, free gas bubbles and gas hydrate. The origin and flow of methane in such systems is known at a basic level. Microbes convert solid organic carbon to carbon dioxide and methane $(2CH_2O \rightarrow CO_2 + CH_4)$, and the methane moves in the time domain via burial, diffusion and advection. However, some key details remain perplexing, especially when one considers that CH₂O is "representative shorthand" for a wide array of complex organic molecules (e.g., carbohydrates, lipids, proteins, and nucleic acids), and conversion to methane involves intermediate reactions. Interestingly, the color of pore waters in all methane-charged sediment sequences drilled to date change over the upper few hundreds of meters, being clear near the seafloor and increasingly whiskey-golden with depth. This "yellowness" can be quantified using a spectrophotometer. For drill sites where this parameter has been measured (ODP Site 1230 Peru Margin; ODP Site 1244 Hydrate Ridge; IODP Sites 1426 and 1427, Japan Sea), profiles are smooth, consistent with diffusion. In general, greater yellowness relates to higher concentrations of dissolved organic carbon (DOC), as well as dissolved inorganic carbon (DIC) and alkalinity. When pore waters are examined at different wavelengths, depth profiles change, suggesting that a suite of dissolved organic molecules, such as humic acids, contributes to yellowness. The color of pore water in methane-charged sequences is likely providing a glimpse at how these systems function beyond the rudimentary level.

FREEZE CORING: SEDIMENT DISTURBANCES

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ABSTRACT

Field studies over the last decades show that sediment in freshwater impoundments can act as an important source of greenhouse gases, like methane and carbon dioxide. Under anaerobic conditions, enhanced mineralisation of organic matter within the sediment favours methane bubble formation. To investigate the influencing sediment parameters and relevance of the emissions, the acquisition of undisturbed sediment samples under near in-situ conditions are required for a wide variety of scientific and engineering studies. Freeze coring is a good way to obtain undisturbed sediment samples of water-saturated and gas-bearing sediment, unaffected by the fast degassing of methane bubbles that may occur after a drop in hydrostatic pressure. In this study we present a new freeze corer, which freezes the sediment inside of a double-walled corer by a strong coolant (mixture of dry-ice and ethanol), which is added into the space between the corer walls. This simple and robust sediment corer was successfully tested in field conditions at Lake Kinneret (Israel), Urft Dam and Lake Olsberg (Germany). Lab and field measurements were carried out to quantify the coring disturbances of the freeze corer, especially how freezing affects the gas and the structure within a sediment core, comparing to a common tube sampler. The obtained cores were scanned with a Dual-Layer X-Ray Computed Tomography (CT) scanner. This new CT techniques allows to obtain both density and atomic number distribution within the sediment core and to visualize coring disturbances.

CARBONATE CRUST FROM A RECENTLY DISCOVERED METHANE SEEP ALONG THE NORTH ATLANTIC CONTINENTAL MARGIN OF THE US: ISOTOPIC CHARACTERIZATION

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ABSTRACT

Authigenic carbonates, which are significant carbon sink, widely occur as carbonate crusts near cold methane seeps at the seafloor. Anaerobic oxidation of methane and sulfate reduction are among the associated microbial metabolisms that increase local alkalinity and cause precipitation of carbonate minerals. Radiometric dating and stable isotope analyses of carbonate crust samples help to evaluate the origin of methane and its seepage history, which could be compared with climate change events in the past. We characterized three samples that were collected at the North Atlantic Continental Margin of the United States (off of New England). Aragonite (66-68 wt%), quartz (25-27 wt%), feldspar (5-7 wt%) were identified with XRD and one sample contained 3-4 wt% of dolomite. Two textural types of aragonite were identified: 1) microcrystalline aragonite groundmass (GM) consisting of fine grey crystals (<1 µm in size) containing equant quartz crystals (>100 µm); 2) aragonite veins and rims around pores consisting of white acicular crystals (AcAr) (up to 100 µm in width). Proportions of Si, Al, (Na+K), Mg, and S determined by LA-ICP-MS in GM suggested occurrence of sub-micron inclusions of alkali feldspar, and potentially pyroxene, Fe oxide, and Fe sulphide which were impossible to avoid with the instrument's spatial resolution (analytical spot with diameter of 40 µm). In contrast AcAr were found to be free of non-carbonate signal. Powdered samples were collected on both textural features (GM and AcAr) using hand drill and New Wave Micromilling device for conducting isotopic analyses, which are pending.

MULTI-SCALE GEOPHYSICAL OBSERVATION OF SEAFLOOR POCKMARKS ALONG THE BASE OF THE SOUTHEASTERN MARGIN OF THE LEVANT

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ABSTRACT

An extensive, autonomous underwater vehicle (AUV) high-resolution geophysical survey, across the continental margin of north central Israel, southeast Mediterranean Sea, discovered a multitude of seafloor pockmarks. These pockmarks are expressed in the AUV bathymetry survey as sets of ~1 m deep, round depressions, with a diameter between ~1 to ~40 m. The majority form tight, on average ~5000 m², clusters. In total, 672 pockmarks-groups were mapped, encompassing 1888 individual pockmarks, distributed over a 5 to 10 km wide and 25 km long belt in ~400m to ~1150m water depths along the base of the continental slope. The AUV subbottom profiles image patches with anomalous high reflectivity ~10 m beneath the pockmark groups, suggesting the presence of focused upward flow of gas from near mudline sub-seafloor levels. The pockmarks area is also imaged by a commercial, depth migrated, 3D seismic reflection volume, within which a sequence of high-amplitude reflections ~200 m to ~400 m beneath the seafloor are seen underlying the seafloor pockmarks area. This sequence is structurally modified by a north trending fault ramp syncline basin and rollover ramp. It thickens and its amplitudes intensifies within the syncline, and thins and pinches out towards the seafloor westwards and northwards. Eastwards, towards the continental slope, it is flexed upwards and then diverges down dip. The entire fault ramp structure is faulted by multiple, conjugate, extensional thin-skinned faults. The structure, sequence of high-amplitude reflections, and faults appear to correlate with the distribution of the seafloor pockmarks. Most of the pockmark clusters are distributed adjacent to the faults, predominantly vertically above where the faults segment and offset the high amplitude reflection surfaces. More so, where these reflections are regionally up warped. We theorize that the high amplitude reflections represent a deformed and faulted multilevel gas-bearing interval, which is pervasively percolating to the surface. Gas is focused by the structure and percolates vertically to the surface where the gas-bearing interval is breached by the faults. Taken together, the relatively simple seafloor pockmarks, the large area of leakage, and no evidence for buried pockmarks in the sub-bottom profiles, suggest that percolation started only relatively recently in geologic time.

UNDERSTANDING STABLE ISOTOPIC FRACTIONATION DURING MICROBIAL METHANOGENESIS

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ABSTRACT

Microbial methane (CH₄) production (methanogenesis) occurs mainly by reducing CO_2 with H₂ (hydrogenotrophy) or by fermenting acetate. Isotopic fractionation during hydrogenotrophic methanogenesis depletes CH₄ of the heavier ¹³C and ²H isotopes. Furthermore, recent advances in analytical methods revealed that biological ¹³CH₃D isotopologue content may deviate significantly from its equilibrium composition. These isotopic signatures are highly variable within both natural and laboratory culture setups and are often used to assess CH4 reservoirs origins and its formation temperature. It is believed the isotope fractionation in multistep enzymatic processes, such as methanogenesis, depend on the reversibility degree of enzymatically catalyzed reactions, and not only on the isotopic equilibrium effects, thus allowing variation to occur. The mechanistic reasons for this phenomenon are not entirely understood. We developed a bio-isotopic model describing the metabolism and isotopic fractionation of stable carbon and hydrogen isotopes and clumped methane isotopologues in hydrogenotrophic methanogenesis. We solved the model using a set of kinetic and thermodynamic parameters under a steady state assumption, yielding the reversibility of each reaction in the pathway. We later predicted the net isotopic fractionation during methanogenesis using a novel set of equilibrium fractionation factors and assigned kinetic fractionation factors. We finally compared our results to previous culture studies of methanogens. Our model can generate the isotopic fractionation trend related to the actual Gibbs free energy of the overall reaction (ΔG_r). We show that kinetic isotope effects (KIE) of the last enzymes in the pathway control isotopic fractionation when ΔG_r tends to zero, and KIE of the upstream enzymes control fractionation in highly negative ΔG_r . Thus our model provides a possible mechanism for the relation of isotope fractionation and ΔG_r of methanogenesis, further elucidating the factors governing the isotopic signature of CH₄ in the environment.

STRUCTURAL EVOLUTION OF ABU GHARADIG BASIN, WESTERN DESERT, EGYPT: IMPLICATION FOR HYDROCARBON EXPLORATION

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ABSTRACT

Discovered in 1969, the Abu Gharadig (AG) Field was the first large hydrocarbon discovery in the Abu Gharadig Basin of the Western Desert of Egypt. Oil production began in 1973, with gas brought into production in 1975. The field produces mainly from upper Cretaceous clastic reservoirs. The AG Basin is an E-W trending intracratonic rift basin, about 330 km long and 50e75 km wide. It was initially formed as a large half graben basin during the Jurassic time in response to Tethyan rifting and continued to subside throughout the Cretaceous time. The half graben was subsequently inverted during the Late Cretaceous as part of the Syrian Arc deformation which affected northern Egypt. The Mid-Basin Arch, the AG Anticline, and the Mubarak High are three NE-SW oriented main inversion anticlines located within the AG Basin and are controlled by inversion of pre-existing Jurassic rift faults. The AG Anticline has an overall NE-SW orientation with a gentle plunge towards the NE and SW. It is locally bounded by two NEeSW-trending inverted faults on the southwest and northeast, accounting for the asymmetry of the anticline. Reverse offset of Cretaceous horizons is obvious at these inverted faults. Fault propagation folding is developed above the tips of the inverted faults at the Late Cretaceous Abu Roash and Khoman Formations. Based on thickness changes and stratigraphic relationships, inversion started during the Santonian time and continued into the Campanian-Maastrichtian. Inversion continued during deposition of the Paleocenee Middle Eocene Apollonia Formation and the Late Eocenee Oligocene Dabaa Formation.

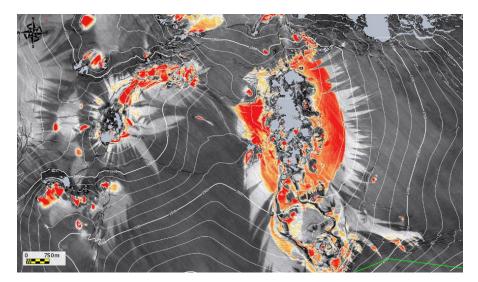
SEISMIC IMAGING OF A FULL METHANE MIGRATION PATHWAY

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ABSTRACT

One processes that may fossilize methane migration is the precipitation of methane-derived carbonates. We report here seismic characterization of linked segments of a fluid migration pathway in a series of gentle compaction-related anticlines and synclines. The amplitude map of one seismic reflection shows a peculiar structure, with positive high-amplitude patches distributed around the heavily pockmarked crest of anticlines; the limits of high amplitudes coincide with isobath lines of their host structures; the patches are surrounded by flower-like features with medium-amplitude spikes extending down radially away from the central patch. A 200 m-deeper reflection shows comparable spikes, but widening downward and converging into synclinal axes. The tips of the downslope-pointing spikes of the upper level lie above the tips of the lower level spikes, suggesting a genetic relationship. The following model is proposed to account for the observed geometry: the lower reflection records deposition of "channels" that originate in mid-slope position and converge towards synclinal axes. Gas migration after some burial follows these channels and accumulates at their tips. Once accumulation exceeds the fracturing threshold of the overlying mudstones, hydrofracturing occurs and gas migrates vertically up to the next carrier bed above. Gas migration and accumulation in this upper level are recorded by carbonate precipitation making the upper level of seismic amplitude anomalies, moderate amplitude for transient conduits and high-amplitude for accumulation at the crest. Pockmarks at anticline crests express final leakage to the seabed and were used by seawater (and sulfates) to percolate down into the layer where precipitation occurred.



FLUID INCLUSIONS – A POTENTIAL TOOL FOR TRACING GAS SOURCES

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ABSTRACT

Hydrocarbon-bearing inclusions in the minerals can provide pointers to hydrocarbon accumulations. A possibility of using gas-bearing inclusions trapped in the minerals in the unexplored areas to obtain some information on gas composition and potential migration directions has been presented on several examples, both on surficial and drilling core samples. The studies were performed in the area of the Western Carpathians and the Polish Lowlands, respectively, the offshore part of the Baltic Sea as well. The age of the rocks studied varies from the Cambrian through Carboniferous, Rotliegend and Zechstein to the Oligocene deposits. Rocks are sandstones, limestones and/or dolomites. Mineralization filling the fractures (quartz, carbonates) has been also concerned. Generally, two types of inclusions are present: (1) aqueous inclusions which contain L and V phases, and (2) hydrocarbon – rich inclusions which sometimes contain a small visible aqueous phase. Under UV light some inclusions show blue fluorescence that points to a presence of heavier hydrocarbons. One phase gas inclusions (methane) either do not fluoresce or, display a dull-blue fluorescence. The consequent studies of fluid inclusions (their content, distribution, micro-thermometric characteristics) combined with more detailed analyses as isotope determinations provide an information on the character of the hydrocarbons in the region, their migration and even the migration directions, the potential sources as well. In the unexplored areas fluid inclusions can be used e.g. for mapping of the regional gas migration, tracing rock source occurrence and for estimation of their maturity at the migration time.

EXTENSIVE METHANE-DERIVED AUTHIGENIC CARBONATE IN THE IRISH SEA FORMED SINCE THE LAST GLACIAL MAXIMUM; GEOLOGICAL AND ENVIRONMENTAL IMPLICATIONS

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ABSTRACT

The 'Croker Carbonate Slabs' is a shallow-water site in the Irish Sea characterised by strong tidal currents, coarse mobile surficial sediments, and extensive methane-derived authigenic carbonates (MDAC). It is underlain by post-glacial sediments sitting unconformably on coal-bearing Carboniferous rocks. Evidence of active gas seepage and the anaerobic oxidation of methane have been observed here at only a few discrete locations. However, recent investigations indicate MDAC is present over an area of at least 20 km² (perhaps as much as 37 km²), occurring as both low relief (<20 cm) and high relief (>20 cm) features, some of the latter forming 'cliffs' >2 m tall. Carbon isotope analyses confirm that the carbonates were derived from methane. Elevated methane concentrations in the waters above the site suggest that contributions to the atmosphere may continue to the present day. As distinct from the surrounding sedimentary seabed, MDAC provides a hard substrate colonised by distinctive and diverse benthic epifaunal communities. These include soft corals, erect filter feeders, sponges, tube worms, anemones, hydroids and Croker Carbonate Slabs has been designated as a Special Areas of Conservation brvozoans. (SAC) under the EC Habitats Directive. to protect the Annex I 'submarine structure formed by leaking gas' feature formed by the MDAC. U-Th dating of aragonite extracted from two samples indicates MDAC formation during the period from approximately 17,000 (+/-5,500 years) to 4,000 (+/- 200 years) years before present, suggesting methane migration from the underlying geological source throughout the Holocene deglaciation.

THERMAL HISTORY OF THE CARBONIFEROUS SANDSTONES OF THE BALTIC SEA AREA (N POLAND)

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ABSTRACT

The research focuses on the Pennsylvanian sandstones from boreholes drilled in the Western Pomerania and the Baltic Sea. They are represented by arenites and wackes, quartz and sublithic. The grains are cemented by matrix and authigenic minerals such as quartz, carbonates, clay minerals and subordinate sulphates. Quartz cement forms overgrowths of authigenic quartz on quartz grains. Measurements of homogenization temperatures of two-phase fluid inclusions in authigenic quartz suggest quartz cementation at temperatures ranging from 58 to113°C. Carbonates are represented mainly by Mn-calcite, dolomite and ankerite and sporadic by calcite and siderite. Homogenization temperatures measured from Mn-calcite and dolomite cements prove their growth within a temperature range of 90-160°C. Authigenic clay minerals are represented mostly by kaolinite, dickite and illite, locally by Fe-chlorite and mixed-layered illitesmectite minerals. Vermiform kaolinite and blocky kaolinite and dickite are observed. Kaolinite/dickite intergrowths are observed what is a proof of kaolinite transformation to dickite which begins above 80°C. The presence of dickite in sediments indicates the temperature about 120°C. The authigenic illite mostly occurs as fibres and needles, forming net structures in the pore space. K-Ar age determinations of the timing of growth of authigenic illite indicate that it began to crystallize from the Upper Permian times - 262±2,0 My to the Middle Jurassic -171,8±1,7 My. The diagenetic illite precipitates at the final stage of diagenesis in temperature of about 100-120°C. K-Ar dating of illite crystallization determines a length of the post-deposition period, when the deposits were permeable for pore fluids, in that - liquids and gaseous hydrocarbons.

CRYSTALLIZATION OF SIDERITES EXTREMELY ENRICHED WITH δ^{13} C ISOTOPE: LAKE BAIKAL, EASTERN SIBERIA

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ABSTRACT

Lake Baikal is the largest and unique freshwater reservoir in the Earth. Its depth reaches a maximal value of 1,642 m (De Batist et al., 2002). Bottom sediments contain numerous focused hydrocarbon fluid discharging zones, often containing gas hydrates with crystallographic structures I and II (e.g. Kida et al., 2006). In Lake Baikal, early diagenetic carbonate formation was long time considered impossible due to the fresh water condition (Knyazeva, 1964; Mizandrontsev, 1975). However, a great number of authigenic siderites (Sapota et al., 2006; Krylov et al., 2008a; 2008b; 2010) and a few rhodochrosites (Krylov et al., 2018) have been found in gas hydrate-bearing structures. The majority of the studied authigenic carbonates had positive δ^{13} C values. Recently, carbonates extremely enriched with a heavy isotope 13 C (up to +36.3‰ VPDB), were found. Normally authigenic carbonates have positive δ^{13} C values in the case of crystallization in the diagenetic zone of methane generation, however these values rarely exceed +20 ‰ VPDB. One place where such unusual authigenic carbonates are found at significant sub-bottom depths is Cascadia continental margin: δ^{13} C up to +37.55% at 150.5 mbsf (Pierre et al., 2009). In the lake Baikal, authigenic siderites with a δ^{13} C value of +36.3‰ were found at sub-bottom depths of only 233 and 240 cm below lake floor. The main task of our report is to explain the conditions for the crystallization of siderites significantly enriched with heavy ¹³C isotope. Research supported by the RFBR grant 16-05-00979.

IRON SPECIES AND SULFUR ISOTOPIC COMPOSITIONS OF AUTHIGENIC PYRITE IN DEEP MARINE SEDIMENTS AT SOUTHERN HYDRATE RIDGE, CASCADIA MARGIN (ODP LEG 204): IMPLICATIONS FOR NON-STEADY-STATE DEPOSITIONAL AND DIAGENETIC PROCESSES

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ABSTRACT

Two accretionary sediment sequences from Sites 1245 and 1252 recovered during Ocean Drilling Program (ODP) Leg 204 at southern Hydrate Ridge were investigated to explore their nonsteady-state depositional and diagenetic history. Five iron species were characterized by a modified sequential extraction procedure that covers almost all iron-bearing minerals in sediment cores, including: (1) iron-bearing carbonates, mainly siderite; (2) ferric (hydr)oxides, probably ferrihydrite and/or lepidocrocite; (3) magnetite; (4) iron-bearing silicates; and (5) pyrite. Downcore distributions of highly reactive iron are relatively invariable, impyling a long-term steady-state history for its accumulation. Pyrite formation seems to be controlled by the limited supply of dissolved sulfide relative to abundant availability of reactive iron. That is also the reason why most samples appear to exhibit an inverse correlation between iron concentrations of pyrite and siderite. Sulfur isotopic compositions of pyrite are very inhomogeneous (-42.4 \sim +16.8‰) with depth, where the δ^{34} S values higher than -20‰ may result from a shallow sulfatemethane transition zone or a rapid deposition event. From early diagenetic pathways of iron and sulfur, we developed two categories of conceptual scenarios based on variations in sedimentation rate and methane flux. The geochemical features similar to those derived from each scenario were searched in the sediment columns and the non-steady-state events behind the scenarios were proved to be consistent with the real observations. These conceptual scenarios may contribute to reconstruction of non-steady-state processes in other research areas.

POCKMARKS, BUBBLES, AND OIL SLICKS FROM AN ACCIDENTAL SEEP IN THE GULF OF MEXICO

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ABSTRACT

Unlike most natural pockmarks, destruction of an energy platform by a mud slide in 2004 designated the exact onset of a discharge that caused excavation of pockmarks of varying sizes. This makes it possible to constrain the timeframe for pockmark formation, but the volume of discharge requires additional measurement. Three of the platform's 35 wells were capable of unassisted flow when the accident occurred. Oil slicks have subsequently been emanating from two well-developed pockmarks, while a number of smaller, inactive pockmarks also appear in sidescan surveys of the site. Aerial photographs of floating oil in MC-20 consistently show a distinctive, linear slick origin. Comparison of a georectified aerial photograph with a site plan of the seafloor wreckage indicates an origin directly over the fallen platform, where persistent discharge has formed two prominent pockmarks. Analysis of 158 synthetic aperture radar (SAR) images collected from 2006 to 2017 show oil slicks with an average area of 9.5 km² (stdev 8.2). Hindcast modeling of oil slick length was be used to estimate surface residence time of 12.3h (stdev 7.57). This is evidence for a discharge rate of 96 barrels per day of oil (18.5 m^3) and a total discharge approaching 500,000 barrels since 2004. More accurate gas to oil ratios will improve understanding of how gas and oil can excavate pockmarks. This site is potentially a natural laboratory for investigating processes related to the discharge of hydrocarbons in the marine environment.

A SHALLOW GAS RESERVOIR SYSTEM DEVELOPED WITHIN BURIED LOBES OF THE NILE DEEP SEA FAN

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ABSTRACT

The eastern deep-sea fan of the Nile, southern Levant basin, is riddled with deep-sea channel and lobe systems. A variety of seepage related features were discovered by us in the southeastern Levant basin at water depths between 1100 to 1300m in the course of ROV expeditions of E/V Nautilus in 2010 and 2011, and EUROFLEETS2 2016 expedition SEMSEEPS onboard R/V Aegaeo. These seeps are associated with bathymetric ridges or channels, pockmarks, carbonate buildups, intense seafloor perturbations and chemosynthetic fauna. A sediments core, collected in one of these seepage sites, portray high concentrations of biogenic methane. The seepage sites and associated phenomena consistently correlate with high amplitude sub-seafloor reflectivity imaged on seismic data across a major part of the Levant. The vertical distribution of this high amplitude reflectivity reveals two principal populations: (1) trending sub-parallel to the seafloor and attributed to shallow gas accumulations beneath the seafloor; and (2) deepening with water depth in correlation with our modeled base hydrates stability, and therefore is attributed to free gas accumulated beneath a scattered hydrates layer. This reflectivity and our modeling suggest the potential presence of natural methane hydrates at water depths >1240m across a substantial part of the basin. The spatial distribution of the first population reveals a multitude of extensive lobes, partly correlated with current seafloor channels, but buried tens of meters beneath them. Active seepage occur where these buried lobes are focused towards and truncated by the seabed. We therefore suggest the presence of a pervasive shallow sub-seafloor gas reservoirs-system within the buried lobes.

PHYSICAL CHARACTERIZATION AND CONTROLS OF GAS IN SHALLOW SEDIMENTS OF THE CONTINENTAL SHELF: THE CASE FOR OFFSHORE HAIFA BAY, ISRAEL

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ABSTRACT

High resolution seismic along the northern Israel continental shelf reveal variable patchy-to-semicontinuous bands of acoustic turbidity underlain by acoustic blanking. Coring affirms that these represent a methane gas front, extending under a ~7x12 km area of the middle to outer continental shelf (water depths of 30-100 m) within the predominantly silt to clay Holocene sedimentary cover. This front is generally subparallel to the seafloor throughout its depth range, with the free gas depth (FGD) varying mostly between ~10-20 msec (~8-16 m). The gas front traverses the sedimentary layering as it preserves its general trend, suggesting a primary biochemical reduction-oxidation control of the FGD. Separating the acoustic turbidity to its specular and scattered components reveal a ~6 m stack of highly reflective layers with randomly scattered diffraction between them. This observation suggests the concentration of gas within more porous layers, and transport of the gas by bubbles fracturing up the finer grain layers in between. When the gas front trend is concordant with the layering, the front is focused and appears to 'climb' up the layering dip. In contrast, when the gas trend crosses the layering, the front becomes diffuse. We suggest that a balance of intergranular invasion versus bubble fracturing controls the upwards gas flow. We find that the second order variations of FGD and termination of the gas front strongly correlate with the morphology of the glacial period erosional surface, underlying the Holocene sediments. This correlation reflects the control of an upward advection from deeper levels. We suggest that our observations reflect the basic controls of shallow gas on continental shelfs worldwide.

IODP PROPOSAL 910: CARBON CYCLING IN METHANE-CHARGED CONTINENTAL MARGIN SEDIMENTS ON THE RIO GRANDE CONE (BRASIL)

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ABSTRACT

Enormous amouts of methane reside in sedimentary pore space on continental margins as dissolved gas, free gas, and gas hydrates. This methane is interesting and important. Beyond the oft-given reasons of a future energy resouce, a modulator of climate change, and a geohazard, methane on continental slopes likely represents a large component of the global carbon cycle. The geoscience community has had difficulites appreciating this aspect, as very evident from modeling studies which indicate no gas in numerous continental slope settings that have abundant gas. Somewhere there are major gaps in knowledge as to how methane in sediment is formed, stored and released over time, There are a range of issues, from how microbes convert organic carbon to methane to how to prperly incorporate temperature with depth. Rio Grande Cone is an extensive area off the southeast coast of Brasil, where generic models predict little methane. Abundant evidence, including prominent BSRs, seafloor pockmarks, chemosynthic communites and shallow cores with gas hydrate specimens, suggest otherwise. Very likely, Rio Grande Cone hosts a large and dynamic methane system in sediment pore space. IODP Proposal 910 aims to drill at least 5 sites using conventional and unconventional techniques coupled with logging to quantify the amount of methane across Rio Grande Fan, and more importantly to understand how and why this methane exists in the time domain with special emphasis on microbial reactions and how the methane couples to the global carbon cycle.

SOURCE ROCKS OF THE GERMAN CENTRAL GRABEN – POTENTIAL THERMOGENIC CONTRIBUTION TO SHALLOW GAS ACCUMULATIONS

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ABSTRACT

Within the German Central Graben, the source of shallow gas accumulations in Plio-Pleistocene sediments is still unknown. However, a proportion of thermogenic gas from a deeper source is assumed due to various indications. Geochemical data of the shallow gas field B17 in the Dutch Central Graben are suggestive to a significant thermogenic contribution. The occurrence of gas chimneys on reflection seismic data underneath the shallow gas accumulations indicate fluid migration from a greater depth. Also, the geographically limited appearance of the shallow gas accumulations to the Jurassic graben system may point to formations as a source that were deposited or are preserved only in this area. The purpose of this study is to assess the potential of source rocks in the German Central Graben and to identify the most probable sources of a thermogenic contribution to the shallow gas accumulations. For this reason, prominent source rocks of the Southern North Sea (the Clay Deep Member and the Posidonia Shale Formation) were mapped anew. These and other potential formations from the Upper Triassic to the Lower Cretaceous were integrated into an existing petroleum system model of the Northern German North Sea, which was modified for the new requirements. Results from the petroleum system modeling indicate Middle to Upper Jurassic coal measures of the Central Graben Subgroup as well as Lower Jurassic Aalburg and Sleen Formation as potential sources for thermogenic methane within the shallow gas accumulations of the German Central Graben.

GEOCHEMICAL INVESTIGATION OF GAS FLUXES RELATED TO GAS HYDRATE AND OIL-GAS DEPOSITS IN JAPAN AND OKHOTSK SEAS

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ABSTRACT

From 1988 to 2017 years about 700 gas fluxes were found in the Okhotsk and Japan Seas on the Russian side of its. Quantity gas fluxes every year are grouse. It regularity is very important, because it is connection with seismic activity in the West side Pacific Ocean about from 1988 year and it continues today. In it period to form a new zones faults and active old faults. Gas migrates via faults from interior of Earth to surface. If gas fluxes contents methane, heavy hydrocarbon, gas hydrate to form in sediment in the stable thermodynamic condition of gas hydrate. Gas hydrate in surface sediment in Okhotsk Sea was found in the 17 and Japan Sea 5 areas. Source of methane is deep layers that contain oil-gas on hydrocarbon deposit. It is very important regularity of relationship between methane fluxes, gas hydrate and oil-gas deposit. Investigation of gas hydrate and other geological characteristic in the Okhotsk Sea was provided in frame international projects from 1998 year. These are Russian-Germany (KOMEX, 1998-2004), Russian-Japan-Korea (HAOS, 2003-2006 and SAKHALIN, 2007-2012 and 2013-2017). Thus, complex investigations with international cooperation allow us to discover methane fluxes, gas hydrate and to find much regularity to form and to destroy gas hydrate in the Okhotsk and Japan Seas. There is show that it is present relationship between methane fluxes, gas hydrate and oil-gas deposit.

GAS HYDRATE IN THE ARCTIC: PAST, PRESENT AND FUTURE

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ABSTRACT

Methane is the second most important greenhouse gas after CO₂. It has a short life time, but when integrated over 20 years it has a warming effect over 80 times greater than that of CO₂, triggering very rapid warming. In the Arctic, vast amounts of methane are trapped at shallow depths below the seafloor as gas hydrates, ice-like frozen mixtures of gas and water. Current ocean warming makes these greenhouse gas reservoirs vulnerable to thawing. The Centre for Arctic Gas Hydrate, Environment and Climate (CAGE) is investigating what this could mean for Arctic climate and environment in the future using present day observations and data from the past. The research performed in CAGE will contribute to better understand how methane may affect the marine environment and climate systems in the future. We also study how methane emissions affect living organisms that thrive in methane-rich environments, and in turn how microorganisms affect, and potentially regulate gas emissions from the seabed to the ocean surface. With an everdecreasing Arctic sea ice and increasing ocean warming, these organisms can spread over vast areas. As part of our work, we are quantifying reservoirs of hydrates that represent a potential unconventional energy source, since they store huge quantities of natural gas. In the long run, we could therefore provide important, basic knowledge of natural gas resources that can be the future of energy. This study is funded by CAGE (Centre for Arctic Gas Hydrate, Environment and Climate), Norwegian Research Council grant no. 223259.

DYNAMIC GAS HYDRATE SYSTEMS ON THE NORTHERNHIKURANGI SUBDUCTION MARGIN, NEW ZEALAND

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ABSTRACT

Gas hydrates are susceptible to pressure and temperature changes, in particular near the upper limit of the gas hydrate stability field in the ocean. A number of research expeditions have recently been carried out on the northern Hikurangi Margin east of New Zealand across the updip limit of the hydrate stability field. These expeditions included seismic surveys, heat flow transects and drilling. Results from these surveys show indications that gas hydrates in the study areas are in a transient state, i.e., actively forming or dissociating. In particular, anomalies in thermal gradients suggest that latent heat from ongoing gas hydrate dissociation may act as a buffer to transient advective heat flux. Double-BSRs in the study area are thought to be caused by tectonic uplift leading to depressurization and gas hydrate dissociation. Seismic data show indications of remnant gas hydrate between the two BSRs. This observation is supported by modelling of gas hydrate dissociation during uplift, which suggests gas hydrate dissociation to take place over thousands of years. Our models also emphasize that the response of these shallow gas hydrate systems to glacial-stage changes is highly sensitive to both sealevel changes and changes in bottom-water temperatures. Our findings suggest that near the updip limit of gas hydrate stability, hydrate systems may often be in a transient state leading to on-going hydrate formation or dissociation.

STRESS-DILATANCY BEHAVIOR OF HYDRATE-BEARING SAND

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ABSTRACT

The mechanical behavior of hydrate-bearing sands is affected by the hydrate quantity, hydrate morphology in the pores, soil skeleton characteristics, stress confinement and more. It has been traditionally assumed that bonding exists between hydrate and sand particles, which affects the global sediment strength. However, it is shown here that the mechanical effect of hydrate in the sediment has kinematic rather than cohesive nature, based on comparison of mechanical and visual evidences with cemented sand. The visual analysis includes comparison between microscale X-ray images of sand containing either hydrate or cement agent. The mechanical analysis includes examining drained triaxial test results of hydrate-bearing sands with cemented sand results, using investigation through stress-dilatancy theories. It is concluded that all mentioned hydrate-related effects should be interpreted by their influence on the sediment kinematics, rather than on strength characteristics. For a given kinematic response of hydrate-bearing sand, it is shown that the full mechanical behavior can be described using a single friction parameter.

SALT-DRIVEN EVOLUTION OF A GAS HYDRATE RESERVOIR IN GREEN CANYON, GULF OF MEXICO

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ABSTRACT

The base of the gas hydrate stability zone (GHSZ) is a critical interface, providing a first-order estimate of gas hydrate distribution. Sensitivity to thermobaric conditions makes its detection challenging particularly in the regions with dynamic pressure-temperature regime, such as adjacent to salt bodies. In Green Canyon in the northern Gulf of Mexico (Block GC 955), the existing estimate for the base of the GHSZ is 450 meters below the seafloor, which is 400 m shallower than predicted by gas hydrate stability modeling. We use 3D seismic, log data and heat flow modeling to explain the role of the salt diapir on the observed thin GHSZ in GC 955. We model present day heat flow distribution, which indicates a critical salt-induced temperature anomaly, reaching 8 °C at the reservoir level; this increase in temperature is sufficient to explain the 400 m upward shift of the base of the GHSZ. Our analyses show that overpressure does develop at GC 955, but only within a ~500 m thick sediment section above the salt top, which does not currently affect the pressure field in the GHSZ (~1000 m above salt). Our study confirms that a salt diapir induces a strong localized perturbation of the temperature and pressure regime and thus critically affects the stability of gas hydrates. Based on our results, we propose a generalized evolution mechanism for similar reservoirs, driven by salt-controlled gas hydrate initiation and collapse elsewhere in the world.

CONTROL FACTORS FOR THE DISTRIBUTION OF SEVERAL THOUSAND GAS BUBBLE EMISSIONS DETECTED ALONG THE SOUTHEASTERN SLOPE OF THE CRIMEAN PENINSULA (BLACK SEA)

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ABSTRACT

We investigated the occurrence and distribution of gas bubble emissions in an area of ~1800 km² along the southeastern continental slope of the Crimean peninsula in the Eastern Black Sea basin. About 3500 gas emissions in total were detected in single- and multi-beam echosounder data acquired with the research vessel METEOR during cruise M84/2. Gas emissions occurred with only a few exceptions at depths above the upper limit of the gas hydrate stability zone located at ~700 m, indicating that the formation of gas hydrates in the sediments generally prevents the migration of free gas into the water column. Furthermore, flares were found to be morphologically controlled. In the western province, where the upper continental margin is steep and incised by gullies, flares occurred mainly along ridges. The eastern province, however, is part of the Don-Kuban paleo-fan and characterized by a flat and smoothly sloped margin, which is strongly influenced by mass wasting. Gas emissions in this area were mainly detected aligned along slide scarps of submarine landslides and related sediment failures. Almost all detected flares disappear well below 100 m water depth and any flare reached the sea surface. Although gas bubbles dissolve within the anoxic water body of the Black Sea, they contribute to its methane inventory. The great amount of flares detected at the Don-Kuban paleo-fan in this study as well as other fan systems in previous studies suggest that bubble ebullition is an important pathway in the anoxic carbon cycling system in the Black Sea.

HYDROCARBON SEEPAGE DRIVES HOTSPOTS OF BIOGENIC BURROWING, MICROBIAL DIVERSITY AND ACTIVITY IN THE OLIGOTROPHIC SOUTHEASTERN MEDITERRANEAN

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ABSTRACT

Bacteria and Archaea constitute the largest biomass of benthic deep-sea ecosystems, driving biogeochemical cycles. In the easternmost Levantine basin, which is characterized by high bottom water temperatures and very low downward fluxes of organic carbon, diversity patterns and ecological functions of benthic microbial communities are still largely unknown. In this carbon limited environment, seepage of fossil hydrocarbons fuels chemosynthetic microbial productivity, producing hotspots of biogenic activity, driving autogenesis and forming a unique habitat. In 2016, we revisited pockmarks associated with shallow hydrocarbon deposits at the Palmahim disturbance offshore Israel with the Eurofleets SEMSEEP cruise. In the vicinity of seepage hotspots, we observed extensive biogenic burrowing, unusual for the deep Levantine sediments. Based on this observation, indicative of elevated biologic activity, we hypothesized that the sphere of influence of the chemosynthetic hotspots extends beyond areas of visible bubbling. The production of Bacteria and Archaea in the burrowed sediments was indeed above the very low values measured outside of the seep area and was positively correlated with the occurrence of biogenic burrowing. Sequencing of the 16S rRNA gene amplicons revealed that microbial phylogenetic, and likely functional diversity, were also impacted by nearby methane seepage and biogenic burrowing. Although only trace levels of methane were measured, the occurrence of aerobic methane oxidizers at the sediment surface indicated either cryptic methane cycling or active transport of microorganisms within the sediments. Nitrogen fixation rates in the seep sediments were higher than those in controls, suggesting that excess carbon derived from hydrocarbons can stimulate microbial diazotrophy.

METAL/CA RATIOS IN POCKMARKS AND ADJACENT SEDIMENTS ON THE SW ATLANTIC SLOPE: IMPLICATIONS FOR REDOX POTENTIAL AND MODERN SEEPAGE

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ABSTRACT

Metal/Ca ratios and their corresponding enrichment factors (EFs) in bulk sediment samples collected at a mixed carbonate-siliciclastic continental slope setting with an extensive pockmark field were measured and analysed to find evidence of lateral differences in the redox potential and recent seepage activity inside the pockmarks. The analysed ratios point to metal enrichments that indicate variations in the redox potential inside the pockmarks compared to the adjacent areas, as shown by the Cu/Ca, Ni/Ca and Zn/Ca EFs. Slight but statistically significant differences in the Mg/Ca ratios indicated that the formation of Mg-enriched carbonates within the pockmarks is presently taking place, attesting the maintenance of seepage in the shallow sedimentary column. Recent seepage activity was also confirmed by the upward enrichment of Ba in the sedimentary column. Our study provides direct evidence for pockmark activity and reinforces the need for an extended analysis of the geochemistry of natural seepages on the SW Atlantic margin, an area that has still not been studied in relation to this subject.

GEOCHEMICAL PORE WATER CHARACTERIZATION IN SHORT SEDIMENT CORES WITHIN POCKMARKS, LEVANT CHANNEL AND CORAL SITES AT THE PALMAHIM DISTURBANCE, SE MEDITERRANEAN

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ABSTRACT

The SE Mediterranean continental slope off Israel contain methane related features such as gas seeps, pockmarks and carbonate substrates, mainly across two main disturbances. In this study, we sampled short sediment cores (~40 cm long) in methane related seafloor features at the Palmahim disturbance area, in water depths of 400-1100 m. Geochemical profiles at specific pockmark location showed decrease in dissolved oxygen concentrations at bottom water above the sediment, decrease in nitrate concentration at the upper 20 cm, lower sulfate and methane concentrations than at other sites probably attributed to more intense methane removal. At a shallower water depth (~400m), sites with carbonate rocks, corals and Chemoherms, had close to seawater sulfate concentrations and higher methane concentrations, throughout the sediment core. The results indicate a more intense aerobic and anaerobic respiration processes at the pockmark site compare to the Chemoherms site, with no significant sulfate gradient. This may suggest an active methane flux at sediment layers below the top bioturbated ~40cm.

METHANE BUBBLE ASCENT WITHIN FINE-GRAINED COHESIVE AQUATIC SEDIMENTS: DYNAMICS AND CONTROLLING FACTORS

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ABSTRACT

Migration of buoyant methane bubbles towards sediment-water interface fractures muddy aquatic sediment and may destabilize it. However, despite their importance, bubble rise dynamics and conditions favoring bubble release to the water column remained largely unclear. We use a coupled macroscopic single-bubble mechanical/reaction-transport numerical model to explore bubble ascent towards the sediment-water interface. For the first time, we demonstrate stable and dynamic bubble ascent scenarios. For small effective overburden loads (< 50 kPa), which combine weights of the overlying sediment and water column, two sequential bubble propagation scenarios were observed: (1) Stable fracturing, followed by (2) Dynamic fracturing. Bubbles ascending in the dynamic regime are ultimately released to the water column. In contrast, for higher effective overburden loads ($\geq 50 \ kPa$), only stable bubble propagation was observed. In this pattern the bubble is more sensitive to the ambient field of dissolved methane and may stop at some distance below the sediment-water interface due to solute release caused by local methanotrophy. Retardation of multiple bubbles is usually associated with a gas horizon frequently observed in the field. We demonstrate that bubble migration scenario is managed predominantly by inner bubble pressure that defines methane concentration at the bubble surface and thus solute exchange with ambient porewater. We define overburden load as one of the main controls on bubble solute exchange with surrounding pore waters, in addition to commonly accepted bio-geochemical controls. Our modeling shows an increase in depths of the gas horizon in muddy aquatic sediments with an increase in overburden loads.

CATALOGUE OF GAS SEEPS AROUND THE IBERIAN CONTINENTAL MARGIN: ATLANTIC VS. MEDITERRANEAN

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ABSTRACT

A GIS catalogue of gas seeps around the Iberian Margin has been performed for the first time in the framework of the EMODNET-Geology-3 European project. Gas seep-related features include mud volcanoes and pockmarks but also other indicators of seabed fluid venting as the occurrence of methane-derived authigenic carbonates (MDACs) and chemosynthetic fauna hot-spots. The knowledge of these features and their distribution is relevant as they hold specific habitats, they are indicators of the presence of hydrocarbons at depth, they contain fluids rich in methane with a strong greenhouse effect, and they can induce changes in the physic-chemical properties of the sediments, causing instabilities. There are up to now 84 mud volcanoes in the southern Atlantic and Mediterranean margin, clustered into five main fields: 1) The Moroccan field (MF) offshore the Moroccan Atlantic margin; 2) the Guadalquivir Diapiric Ridge (GDR) field located on the southern Atlantic Iberian margin; 3) the TASYO field in the central GoC west off Gibraltar Strait; 4) the Deep Portuguese Margin field (DPMF) in the lower continental slope of the GoC: and (5) the West Alborán Basin (WAB) field (WAB) in the Mediterranean Sea. Gas hydrates have been collected in some mud volcanoes of GoC. In addition, extensive fields of MDAC chimneys and pavements have been identified as product of the anaerobic oxidation of methane (AOM) across the hydrocarbon seepages areas and chemosynthetic hot-spots as beds of Bathymodiulus Mauritanicus at the top of mud volcanoes. Finally, numerous pockmark fields have been detected on multibeam bathymetry and high-resolution seismic profiles across the Iberian continental margin. 198 pockmarks were identified in the Gulf of Cádiz (Atlantic Ocean) and 238 in the western Alborán Basin (Mediterranean Sea). Pockmarks, giant craters and oval depressions have also been identified in the northwestern Atlantic margin (Galicia and Cantabrian margin) and in the Murcia and Balearic Islands in the Western Mediterranean margin.

SEAFLOOR MANIFESTATIONS OF FLUID FLOW TRIGGERED BY SILL-RELATED RESERVOIRS IN OCEANIC-SEDIMENTARY BASINS

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ABSTRACT

Methane, CO₂ and other greenhouses gases associated with sill intrussions in sedimentary basins may have driven catastrophic climate change in the geological past. Modeling of hydrothermal venting based on fossil volcanic sedimentary basins show that overpressure generated by gas release during kerogen breakdown in the sill thermal aureoloe may cause fracture formation. Fluid focusing and overpressure migration above the sill result in vent formation after only few decades. The amount of methane and other gases generated depends on TOC content, the kerogen and the age of the sedimentary sequence. Here we describe the morphological expressions such as mounds, craters and domes related to subsurface sills discovered on the seafloor in deepwater oceanic basins 3,000-5,000 m water depths (e.g. Canary Basin-NE Atlantic and Scan Basin-Scotia Sea, Antarctica). We identify several types of surface manifestations related to evolution of sill intrusions in sedimentary oceanic basins. Therefore, numerous sea-floor mounds discovered on the North Atlantic and Antarctica are are linked to sills intruded in the oceanic sedimentary sequence. In first instance gases (including also mantle-derived volcanic gases) moves upwards through the tips of the sills. Overpressure at its tip form hydro-fractures that can be reach the seafloor forming peripheral vents of mud flows and gases with hydrothermal mineralization. Secondly, methane generated give rise to an overpressure reservoir above the sills deforming progressively the overlying sediments and forming convex reflections and large scale seabed domes. Progressive uplift may elevated mounds in the surface throughout reverse thrusting faults formed on the former hydrofractures at the tip of the sills. Craters identified in the center of some mounds could be response to violent degassing in single events. The occurrence of diagenetic or gas hydrates front under the subseabed, especially in the Antarctica, may complicate the type of surface manifestations of fluid flow forming giant craters or collapses. These expressions of fluid flow show clearly differences with those from derived gas seeps in continental margins such as mud volcanoes or pockmarks. The type of these surface manifestations will be very common as the research activity increase in these huge unexplored oceanic deepwater areas between continental margins and mid-ocean ridges. In addition, sill intrusions increase the possibilities for exploration and discovery of important hydrocarbon reservoirs in oceanic deep-sea basins, and their importance as reservoirs. of methane or other greenhouse gases This research is funded by EXPLO-SEA Project CTM2016-75947-R.

COUPLED METHANE OXIDATION AND DOLOMITE-MAGNESIAN CALCITE DEPOSITION IN CALCAREOUS CHIMNEY STRUCTURES ON THE ISRAELI MEDITERRANEAN SLOPE

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ABSTRACT

ROV dives in the Palmachim Disturbance area, Eastern Mediterranean off shore Israel detected numerous carbonate structures associated with active methane seeps and also inactive ones i.e. palaeo-seeps. They occur in different sizes and show various morphological types and surface features. These structures were video-recorded and some of them were sampled. Among those sampled, the active ones were found to consist of aragonite and calcite whereas the inactive ones consist of calcite and dolomite. One of the largest paleo-seep structures, an inactive conical chimney 20 cm long and 10 cm in maximal diameter, has an irregular upper surface and revealed particularly interesting features. The carbonate mineralogy has a wide range of the proportion of magnesian calcite to dolomite. However, the compositional range of the magnesian calcite is narrow. Sampled aliquots of this chimney structure showed a decreasing trend of bulk $\delta^{13}C$ values -23.0 to -39.9 ‰ (VPDB), when arranged according to their increasing trend in the relative abundance of dolomite to high magnesium calcite. These indicate that the carbon source is dominated by biogenic methane, and reveal a relation between the chemical and isotopic systematics: increase of residual Mg with residual ¹²C. Moreover, these systematic relationships suggest that formation took place in a closed or semi closed system. This means that this carbonate structure formed within the sediment, or that the fluids enclosing the structure during its formation emanated from depth. The δ^{18} O values of the carbonates, 4.7 to 6.2‰ (VPDB) are higher than equilibrium values with seawater, but agree with those derived from clathrates (methane-water). These suggest that the decomposition of the clathrates may have played an important role in the formation of these carbonates.

SEASONAL AND TEMPORAL VARIABILITY OF GAS CONTENT IN SEDIMENT OF LAKE KINNERET, NORTH OF ISRAEL

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ABSTRACT

Shallow gassy aquatic sediments, abundantly found in Israel and worldwide, are a source of major concern for their contribution to destabilization of coastal and marine infrastructure, ecological balance, air pollutions, and global warming. Gas bubbles within sediment change effective sediment properties, including also its geo-acoustic characteristics. Among other characteristics, sound speed is the most sensitive parameters to presence of gas. This study proposes a novel methodology for acoustic sediment characterization. Behavior of reflection coefficient is used for estimations of gas content along off-shore transect and thickness of gassy sediment layer. Study was carried out in the North-Western part of Lake Kinneret, North of Israel. Variations in the free gas content in sediments with water depth obtained using the proposed method shows an agreement with the distribution of organic matter content in and methane fluxes from sediment, both revealed by the preceding studies. Study of seasonal variability of the free gas content shows an agreement in changes in hydrostatic pressure, caused by variations of lake water level. Proposed in this study non-invasive, cost-effective methodology allows a rapid scanning over large areas of aquatic sediments. This method is especially suitable for characterizing gassy sediments and highlighting locations of potential methane emissions. This, in turn, allows a better understanding of methane gas distribution in the upper sediment layer and can be used in monitoring of ecological balance of the region.

TABLE-TOP POCK-MARKS: COUPLING BETWEEN SEEPAGE AND SEDIMENT DEFORMATION

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ABSTRACT

Natural gas is emitted in large quantities from the ocean floor. Many gas seeps originate from oil and gas reservoirs and from methane hydrate deposits, and thus affect, and serve to indicate, energy resources. Hydrocarbon seepage networks often deform the sediment, producing structures like pockmarks, mud volcanoes, and domes. The coupling between seepage and sediment deformation controls the spatially-and temporally variable seepage dynamics, and understanding it is key to using near-surface geochemical methods for basin assessment and prospect evaluation. We present results from table-top experiments that simulate coupled gas seeps and sediment deformation, investigating the underlying mechanisms. In the experiments, air is injected into a reservoir, which is overlaid by a clay seal, both submerged in water. We observe formation of two types of pockmark, depending on the interplay between gas-buoyancy force (i.e. the gas column height or the equivalent gas pressure), confining stress (provided by seal-layer plus water column above) and sediment properties. When the seal layer is thin, yielding is initially elastic, in the form of doming, followed by propagation of cracks and faults through which the gas escapes. When the clay layer is thick it yields in a fluid-like manner, with large gas bubbles ascending, dragging and suspending the clay. A different pock mark morphology evolves in each case.

NEW INSIGHT TOWARD INTERMEDIATES INVOLVED IN IRON-COUPLED ANAEROBIC OXIDATION OF METHANE

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ABSTRACT

The release of methane to the atmosphere from sediments is controlled by its aerobic and anaerobic oxidation. The most common electron acceptor in marine sediments for the anaerobic oxidation of methane (AOM) is sulfate, however, in fresh water lake sediments, where sulfate concentrations are low, iron-oxides can become the dominant electron acceptor. In Lake Kinneret (Sea of Galilee, Israel), microbial iron-coupled AOM was evident, however, the mechanism has been only partly understood, including the intermediates involved species. Molecular data from the lake sediments and previous experiments suggest that several microorganisms take part in this process. Here we present new incubation experiments containing iron oxides, 13C-CH4 and different inhibitors, that were set up to investigate further the potential intermediate species (i.e. nitrate/nitrite) that are produced and their role in the methane oxidation process.

A SENSITIVITY ANALYSIS ON DIFFUSIVE MIGRATION IN GAS HYDRATE RESERVOIR

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ABSTRACT

At some natural gas hydrate sites, for example, the Terrebonne Basin in the northern Gulf of Mexico, gas hydrate is observed at high concentrations in thin sand layers surrounded with hydrate free zones (HFZs) in fine-grained clays. This hydrate distribution pattern was likely related to a short range diffusion mechanism driven by the solubility difference between sand and clay. However, it is not clear which factors most strongly control hydrate saturation in the sand and the thickness of HFZs. To further investigate this scenario, we conducted a sensitivity analysis using a one dimensional numerical model that includes the effects of particular organic carbon (POC) at seafloor, methanogenesis reaction rate $(\lambda\lambda)$, methane solute diffusion (DD), and tortuosity factor (mm) of sediment matrix. Preliminary results show that hydrate formation within a 3-meter sand is very sensitive to POC, reaction rate $\lambda\lambda$ and tortuosity mm, but is not strongly affected by the diffusion factor DD, and that the reaction rate $\lambda\lambda$ has the strongest control among the four variables. A high reaction rate ($\lambda\lambda$ =10-13/s) and a low reaction rate $(\lambda \lambda = 10-14/s)$ with a moderate POC (0.5%) generates gas hydrate saturation of ~35% and ~12% within the sand, surrounded with HFZs of ~4m and ~17m in clays. We will present the full sensitivity analysis and the primary influences on the total amount of methane to better understand the hydrate distribution in the subsurface.

COLD SEEP COMMUNITIES AND COLD WATER CORALS OF THE PALMACHIM DISTURBANCE –BIODIVERSITY HOTSPOTS AT AN EDGE SYSTEM.

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ABSTRACT

The Palmachim Disturbance is a 15 km wide feature on the Israeli shelf. The initial exploration by the E/V Nautilus in 2010 revealed a unique biological hotspot, which was visited on three additional expeditions since. Using geophysical surveys, remotely operated vehicles, and a boxcorer, we have explored the Palmachim Disturbance discovering two distinct biological communities - thriving cold water coral communities (CWC) growing on seep related authigenic carbonate rocks at 500-800 meters depth, and chemosynthetic assemblages at 900-1150 meters depth. Collected specimen were identified, genetically barcoded and analyzed using compound specific stable isotope ratio (CSIA). Carbon stable isotope ratios in amino acids showed methanotrophic activity at the base of the food chain, indicating active methane seepage, this was the first time this method was used to find evidence for active gas seepage. Active seeps provide energy for primary production via chemosynthetic production feeding the local biological communities. Seeps generate authigenic carbonates facilitated by microbial activity which provide substrate for cold water corals, which may settle once the seeps become inactive. These discoveries shed new light on the biogeography of endangered cold water corals and seep communities, and the relations between them. The discovery of CWC communities at the southeastern Levant, which is both extremely warm and nutrient deprived, has expanded the temperature and depth range of many of the discovered biological species. Both habitats provide new biodiversity records in the south eastern Levant Sea, including species new to science.

SULFUR ISOTOPE VARIATIONS OF COARSE-GRAINED AUTHIGENIC PYRITE IN GAS HYDRATE-BEARING SEDIMENTS AND THEIR IMPLICATIONS FOR ANAEROBIC OXIDATION OF METHANE

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ABSTRACT

Larger silt-sized (> 63 μ m) grains of authigenic pyrite observed in gas hydrate-bearing sediments exhibit various morphological features, mainly in the forms of rod, tube, and infilling of foraminifer tests. But their origins and associations to anaerobic oxidation of methane (AOM) remain controversial. During early diagenesis, it is normally considered that dissolved sulfide becomes more enriched in ³⁴S as pore water sulfate is consumed with progressive burial in the sulfate reduction zone, and finally reaches maximum sulfur isotopic compositions in the sulfatemethane transition (SMT) zone where AOM occurs. Sulfur isotopes of dissolved sulfide at each depth enter pyrite so that pyrite becomes more enriched in ³⁴S with increasing depth, and thus the isotopically heaviest pyrite occurs in the SMT zone. This means that sulfur isotopic composition can reflect the order and associations of pyrite formation, with later formed, AOM related pyrite heavier in ³⁴S than the earlier formed one. In this study, we characterized various forms of coarse-grained pyrite in the Hydrate Ridge and Kaoping Slope sediments and compared their sulfur isotopic compositions. From this, the origins and growth histories of different sizes and forms of pyrite were developed, and then a detail discussion of their relationships to AOM was further given.

HYDROCARBON GASES OF THE BOTTOM SEDIMENTS IN THE TATAR STRAIT, SEA OF JAPAN, RUSSIA

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ABSTRACT

Systematic gas-geochemical studies of bottom sediments of the Tatar Strait, Sea of Japan were initiated by POI FEB RAS within the framework of the Russian-Korean-Japanese project «Sakhalin Slope Gas Hydrate» (SSGH) in 2012. During this project, four marine expeditions (2012-2015) were carried out at the R/V "Academik M.A. Lavrentyev" in the southern part of the Tatar Strait. As a result of these studies, local accumulations of gas hydrates, gas-geochemical anomalies in sediments, gas flares areas, mainly along the southwestern shelf and the slope of Sakhalin Island, were discovered for the first time. In 2017, during the expedition on the R/V "Academik Oparin" in the southern part of the Tatar Strait, areal gas-geochemical survey of bottom sediments was conducted for the first time. In total, 66 bottom sediment sampling stations were completed, with gravity coring up to 350 cm below seafloor surface. The average step between sampling stations was about 20 km. The spatial distribution of hydrocarbon gases (HCG) is conducted. Areas with an abnormal HCG content in the sediments are identified, the regional background is specified, and possible sources of hydrocarbon gases are determined. It is established that in the South Tatar sedimentary basin a zonal gas geochemical field with an increased level of hydrocarbon gases concentrations is widespread, a combination of which indicates the existence a hydrocarbon generation vast source. The reported study was funded by Russian Foundation for Basic Research (RFBR) according to the research project № 18-35-00047.

Abstracts for Poster Presentations (alphabetical order)

BURROWS AT SEAFLOOR METHANE SEEPAGE SITES AND THEIR ROLE IN FLUID MIGRATION

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ABSTRACT

Enhanced bioturbation is commonly observed at methane seepage sites, and have been associated with intense burrowing. It has been suggested that these burrows serve as fluid migration pathways channelizing fluids towards centers of authigenic carbonates precipitation, which our study aims to elucidate. This study is based on the 2016 Eurofleets2 SEMSEEP combined ROV survey and coring campaign onboard RV Aegaeo offshore Israel. In this project, 12 box cores were collected, 7 of them in methane gas seep areas. CT scans were performed on one sub-core from each box core, allowing the morphological characterization and quantification of the burrows. A comparison between cores taken form seepage areas with cores from non-seepage areas was conducted. The preliminary results evidence a prominent network of burrows (some of them interconnected) in cores close to active gas seepage foci, in contrast to generally smaller and shorter burrows found in the other sites. Moreover, the burrows' length, width and depth appear to correlate with the seepage intensity, as judged from ROV video footage. Authigenic carbonate fragments and burrowing fauna were found within the core sections collected in the gas seepage areas. A new reaction-transport diagenetic model, under construction, aims to study correlation between bio-irrigation intensity, flow rate, dissolved methane and sulfate contents, and the subsurface carbonate precipitation depth in the system.

AUTHIGENIC MAGNETITE IN DEEP MARINE SEDIMENTS

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ABSTRACT

Magnetite is a semi-conductive iron-oxide mineral that contains both ferrous and ferric iron and has the ability to record the earth magnetic field components. Magnetite crystals can be produced chemically in volcanic and metamorphic rocks, or biologically as intra-cellular crystals by magnetotactic bacteria or as an extra-cellular by-product of dissimilatory iron reduction (so called authigenic magnetite). Due to its mixed-valent structure, magnetite can serve also as an electron acceptor in the dissimilatory anaerobic respiration process. Recently we observed unexpected microbial iron reduction below its traditional zone in the deep methanogenic zone in Mediterranean continental shelf sediment. In this study, we explore the association between this iron reduction and the production or consumption of authigenic magnetite through geochemical and magnetic tools. Pore-water chemistry and magnetostratigraphic profiles from Mediterranean continental shelf sediment show a peak of maximum magnetite concentrations, bulk low field (χ_{lf}) , frequency dependent susceptibility (χ fd) Natural Remanence Magnetization (NRM) and Anhysteresis Remanence Magnetization (ARM) intensities at the same depth of the increase of ferrous iron. This suggests that authigenic magnetite is precipitated during the microbial iron reduction process and that this authigenic magnetite has the ability to affect the magnetic field signal.

THE SUITABILITY OF GEOLOGICAL CO₂ STORAGE IN THE ZOHAR STRUCTURE (ARAD AREA)

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ABSTRACT

One of the proposed ways to reduce anthropogenic CO_2 emissions to the atmosphere is carbon capture and storage (CCS). In this technique, CO_2 is separated and captured from large stationary sources, transported to the storage site and injected into suitable storage formations, typically saline aquifers. The main goals of the current research are to characterize and evaluate the potential of the Zohar and Kidod Formations (top of the Jurassic saline aquifer and base of its overlaying aquitard, respectively), for deep geological CO₂ storage in the Zohar structure (northeastern Negev). The Zohar Formation in this area has been previously used as a natural gas reservoir that became diluted with time. The petrophysical properties of this formation were therefore characterized by porosity, permeability and density measurements. The current study, however, also examines the petrophysical properties of the sealing unit (Kidod). The study comprises of high resolution petrological and petrophysical measurements that have been carried out on cores taken from boreholes in the research area. As the Zohar Formation is characterized by fractures, the research also focuses on structural study of outcrops to evaluate possible structural damage, for better evaluation of sequestration potential and as a base for future modeling. Spatial interpolation methods used to estimate the geological storage capacity, estimated 70 Mt CO₂ considering effective CO₂ saturation of 60% in the Zohar Structure only. MICP test for Kidod Formation resulted in capillary pressure breakthrough value larger than 3000 psi and a typical pore throat size smaller than 0.01µm, meaning CO₂ column can fill the entire reservoir without leakages through the cap rock.

THE INFLUENCE OF METHANE OCCURRENCE ON THE IRON SPECIATION IN THE SEDIMENTS OF THE SOUTHERN BALTIC (GDAŃSK BASIN)

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ABSTRACT

Our aim was to characterize iron speciation in the sediments of the Gdańsk Basin (S Baltic Sea) at sites differing in methane presence. We collected sediment cores in the period 2015-2017, at three sites, one where methane was absent and two where it was found. We distinguished six iron species: carbonate-associated (FeCARB); easily reducible oxides (with the two most reactive forms ferrihydrite and lepidocrocite) (FeOX1); reducible oxides including goethite, hematite (FeOX2) as well as magnetite (FeMAG); poorly reactive sheet silicate (FePRS) and pyrite. Their concentration was measured using the sequential extraction. We also determined concentration of total iron (FeT) and methane in sediment. Additionally, we measured concentration of the following compounds in pore waters: iron(III) (FeII), iron(II) (FeII), hydrogen sulphide (H2S) and sulphate (SO4 2-). The iron species varied in concentration both between sites and along the sediment profile. We found FeCARB and FePRS to be dominating and determined the lowest concentration for FeMAG. Our results show that anaerobic methane oxidation governs the iron speciation in sediments of the Gdańsk Basin. This study was financed by the Polish National Science Centre (Project no. UMO2013/11/B/ST10/00322 and UMO-2016/21/B/ST10/02369).

RELATION BETWEEN METHANE CONCENTRATION AND DISSOLVED CARBON FORMS IN SHALLOW SEDIMENTS OF A CONTINENTAL SHELF SEA (BALTIC SEA, GDAŃSK BASIN)

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ABSTRACT

The purpose of the study was to investigate how concentrations of porewater dissolved inorganic and organic carbon (DIC and DOC) change in relation to biogenic methane concentration in shallow sediments of a coastal sea area. The research was conducted based on sediment cores (up to 1.2 m in length) collected in the deepwater area of the southern Baltic Sea (Gdańsk Basin), at two methane and two non-methane stations, in the period from 2014 to 2018. The following parameters were measured: methane, sulfate, dissolved sulfide, ammonium, DIC and DOC in pore waters, and content of organic matter (as LOI) in sediments. Additionally, the conditions in bottom water were determined (temperature, salinity and dissolved oxygen). The results showed that e.g. (1) DOC concentrations are significantly correlated with methane, (2) DIC and DOC are considerably dependent on each other in the whole examined sediment profile of methane stations, in contrast to the profiles from non-methane sites, and (3) both DIC and DOC fluxes from sediments are higher at stations with methane. Seasonal variations between the correlations were also observed. The obtained data confirmed that dissolved carbon concentrations in pore waters are significantly higher in shallow sediments dominated by methane production, and lower DIC:DOC ratio corresponds to higher concentration of methane in sediments. This study was financed by the Polish National Science Centre (grant no. UMO-2016/21/B/ST10/02369)

FLUID ORIGIN AND SPATIAL VARIATION IN FLUID TRANSPORT AND BIOGEOCHEMICAL PROCESSES AT A SUBMARINE MUD VOLCANO OFFSHORE TAIWAN

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ABSTRACT

In order to determine the fluid source and spatial heterogeneity of fluid transport and biogeochemical processes across submarine mud volcanoes in accretionary prism, sediment cores distributed along a transect of the TY1 mud volcano offshore southwestern Taiwan were acquired, and analyzed for their geochemical characteristics. The analyses yielded increasing δ^{18} O values (up to +7 ‰) and decreasing δ^{2} H values (down to -20 ‰) with depth at crater sites. Geochemistry profiles showed significantly decrease in Cl⁻, Br⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, and sulfate but increase in ammonium, Li⁺, B, hydrocarbons, and total alkalinity (TA) with depth. These data combined with estimates of equilibrium temperatures based on Na/Li geothermometer indicate that the observed geochemical patterns could be attributed to a mixing between seawater and deep-rooted with enriched ¹⁸O, Li, B, and methane at 74 to 104 °C and fluids derived from smectite dehydration. Numerical modeling indicates that the generated fluids ascend to the seafloor at a rate of 2.0 to 5.0 cm yr⁻¹ at crater sites but diffuse at hillside sites. Correspondingly, rates of anaerobic methanotrophy also decrease from 25.9 mmol m⁻² yr⁻¹ at crater sites to 8.92 mmol m⁻² yr⁻¹ at slope sites and nearly negligible at hillside sites while both rates of sulfate reduction and methanogenesis are minor. The difference in rate suggests the change of fluid transport from advection at crate sites to diffusion at the hill bottom. Such contrasting fluid transport across the transect of a mud volcano modulates the activities of anaerobic methanotrophy.

RECONSTRUCTION OF PAST METHANE RELEASE EVENTS IN THE ARCTIC RECORDED BY BENTHIC FORAMINIFERAL STABLE ISOTOPES FROM THE VESTNESA RIDGE (WESTERN SVALBARD).

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ABSTRACT

Natural modern and past methane seepage episodes have been identified along the Vestnesa Ridge (west of Svalbard, 79°N). Several active pockmarks emitting methane (1200 m water depth) were targeted during the drilling campaign MSM57/1 R/V MARIA S. MERIAN in 2016 in order to investigate active pockmarks and reconstruct paleo-methane emissions. In this study, we present new results on MeBo drilling cores collected in a pockmark still active and which has been estimated active over the Quaternary. Stable isotopes (δ^{13} C and δ^{18} O) measured on benthic and planktonic foraminiferal tests were used to investigate the chronology of the past methane emissions. The faunal distribution was also investigated for the first time in a million year-record in the Fram Strait. We used results from 2 cores in one of the most active pockmark in the Vestnesa Ridge and we compared these results with 1 reference core collected out of the pockmarks. Foraminiferal assemblages and isotopes revealed strong environmental changes related to the different glacial and interglacial periods. Negative excursions of δ^{13} C is a clear evidence of strong methane emissions, occurring at several times over the last 2 Ma. These events are correlated with increase of the δ^{18} O suggesting a gas hydrate dissociation, as a source of methane seepage. Some negative excursions revealed the precipitation of authigenic carbonate in the ancient sulfate-methane transition zone. These results confirm the methane seepages over the quaternary on the Vestnesa Ridge and the chronology of these events indicates the control processes of gas hydrate dissociation in the Arctic.

IN SITU QUANTIFICATION OF GAS BUBBLES FLUX AT GC600 HYDROCARBON SEEPS IN THE NORTHERN GULF OF MEXICO

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ABSTRACT

Natural cold seeps in the marine environment are important sources of methane and other greenhouse gases to the ocean and atmosphere (Judd and Hovland, 2007). Accurate quantification of methane flux at hydrocarbon seeps is therefore necessary to evaluate their influence on the global methane budget and climate change. A deep-sea high definition video time lapse camera was used to observe the gaseous and oily bubbles released through partially exposed deposits of gas hydrate. The bubble size and release rate and the temporal variability in bubble releases has been determined. Image processing techniques was used to determine the bubble type (oily, mixed, and gaseous), size distribution, release rate, and temporal variations. A semi-automatic bubble counting algorithm was developed to analyze bubble count and release rates from video data. The seep at GC600 released a mixture of oily and gaseous bubbles with an average diameter of 3.0 mm at a rate of 85 bubbles×s⁻¹. The bubbles flux released form mega plume 2 is $0.0086-0.036L\times s^{-1}$. However, the bubbles release rate was not correlated with tidal effects rather than with pore activation (Johansen et al, 2017). The method of in situ gas flux quantification may provide new solutions to evaluate the impact of seeping methane in marine settings.

Reference

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THE MICROBIAL SIGNATURE OF ANAEROBIC OXIDATION OF METHANE (AOM) COUPLED TO IRON OXIDES IN FRESH WATER SEDIMENTS

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ABSTRACT

Methane (CH₄) is a greenhouse gas that is 20 times more potent then carbon dioxide. Over 70% of this natural gas emission is attributed to freshwater systems and over 50% of the methane produced in these environments is oxidized by microorganisms under anaerobic conditions, thus making it a central process that controls the natural release of methane from aqueous systems. In freshwater systems, which are depleted in sulfate, iron and manganese become significant electron acceptors. The existence of methane oxidation by iron oxides has been shown in lake Kinneret, but its mechanism and the involved microorganisms remain largely a mystery. This research focuses on quantifying changes in the microbial characterises of Lake Kinneret deep methanogenic zone over time through sediment incubation experiment with different inhibitors. The microbial characterization includes the identity of the microorganism and the presence and expression of specific functional genes that might be involve in the process. All these parameters are evaluated on DNA and RNA samples that are extracted from the sediment and show the existence of AOM in geochemical measurements.

STABLE CARBON, NITROGEN AND SULFUR ISOTOPES IN ORGANIC FRACTIONS OF SEEP CARBONATES

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ABSTRACT

Sulfate-driven anaerobic oxidation of methane (AOM) supports chemosynthesis-based communities and limits the release of methane from marine sediments. This process promotes the formation of carbonates close to the seafloor along continental margins. The geochemical characteristics of the carbonate minerals of these rocks are increasingly understood, questions remain about the geochemical characteristics of the non-carbonate fractions. Here, we report stable carbon, nitrogen and sulfur isotope patterns in non-carbonate fractions of seep carbonates. The authigenic carbonates were collected from three modern seep provinces (Black Sea, Gulf of Mexico, and South China Sea) and three ancient seep deposits (Marmorito, northern Italy, Miocene; SR4 deposit of the Lincoln Creek Formation and Whiskey Creek, western Washington, USA, Eocene to Oligocene). The δ^{13} C values of non-carbonate fractions range from ~-25% to -80‰ VPDB. These values indicate that fossil methane mixed with varying amounts of pelagic organic matter is the dominant source of carbon in these fractions. The relatively small offset between the δ^{34} S signatures of the non-carbonate fractions and the respective sulfide minerals suggests that locally produced hydrogen sulfide is the main source of sulfur in seep environments. The δ^{15} N values of the non-carbonate fractions are generally lower than the corresponding values of deep-sea sediments, suggesting that organic nitrogen is mostly of a local origin. This study reveals the potential of using δ^{13} C, δ^{15} N, δ^{34} S values to discern seep and non-seep deposits.

MAGNETIC TRACING OF PALEO-SULPHATE METHANE TRANSITION ZONE (SMTZ) IN COLD SEEP ENVIRONMENT OF KRISHNA-GODAVARI (K-G) BASIN, BAY OF BENGAL, INDIA.

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ABSTRACT

Greigite (Fe₃S₄) is a widely distributed meta-stable ferrimagnetic iron-sulfide mineral forming authigenically in sulfide rich sedimentary environments as precursor to pyrite. The present study focuses on magnetic tracing of diagnetically formed magnetic iron sulfides in gas hydrate proven region to gain insights into the variability of paleo-methane fluxes and occurrences of cold seeps in Krishna-Godavari (K-G), Basin Bay of Bengal. A high resolution rockmagnetic and microscopic analysis were carried out on a sediment core from a proven cold seep environment of Krishna-Godavari (KG) Basin. We identified a magnetically enhanced zone which is occurring within the sediment depth of 17 - 23 mbsf below the present-day SMTZ in the K-G offshore basin. This sediment interval is dominated by fine grained superparamagnetic (SP) sized ferrimagnetic iron sulphides minerals (Greigite) as indicated by high SIRM/k and fd (%). We believe that this zone is formed as a result of intense anaerobic oxidation of methane (AOM) processes fuelled by high methane supply. SEM-EDS and TEM analysis on the magnetic separates from this interval showed following features: (i) SP sized ferrimagnetic inclusions of magnetite, pyrite and greigite within matrix of host siliceous grain formed during sediment authigenesis (ii) crystals of fine-grained magnetite probably produced as a result of extracellular mineral precipitation by magnetotactic bacteria (MTBs). We propose that limited supply of hydrogen sulphide and presence of residual iron resulted in the formation and preservation of greigite in that sediment interval. We believe that the sufficiently high fluxes of methane provided the required geochemical condition for the precipitation of greigite in the proximity of SMTZ depth. Our work demonstrates that the magnetic tool can be used to identify the paleo-SMTZs positions and better constrain geochemical environment created by sub-surface gas hydrates in marine sedimentary systems.

LIPID BIOMARKER PATTERNS OF AUTHIGENIC CARBONATES REVEAL FLUID COMPOSITION AND SEEPAGE INTENSITY AT HAIMA COLD SEEP, SOUTH CHINA SEA

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ABSTRACT

Authigenic carbonates retrieved from sites ROV1 and ROV2 of the Haima hydrocarbon seeps of the South China Sea at approximately 1390 m water depth were studied using lipid biomarker analyses. Abundant molecular fossils of anaerobic methane oxidizing archaea (ANME) and sulfate-reducing bacteria (SRB) with strong ¹³C-depletions (δ^{13} C values as low as -126‰), in combination with low $\delta^{13}C_{carbonate}$ values (-42.7% to -36.8%), provide evidence that anaerobic oxidation of methane (AOM) was the major process driving the precipitation of the studied seep carbonates. The extremely low δ^{13} C values of archaeal biomarkers confirm that biogenic methane was the main carbon source, but the seepage of accessory crude oil is also suggested by the presence of an unresolved complex mixture in the hydrocarbon fractions. A suite of ¹³C-depleted biomarkers indicate the predominance of ANME-1/DSS consortia at both sites, which indicates that the studied carbonates formed during low to medium methane flux. Somewhat higher contents of archaeal biomarkers and their stronger ¹³C-depletion at site ROV2 reflect at least temporarily higher seepage intensities than at site ROV1. Abundant bacterial dialkyl glycerol diethers (DAGEs), revealing a large offset of their δ^{13} C values compared to SRB-derived terminally branched fatty acids, were possibly produced by distinct SRB species other than members of the DSS cluster. The encountered hopanoids are attributed to aerobic methanotrophic bacteria based on their moderate ¹³C-depletion. The application of molecular fossils in combination with their compound-specific isotope signatures is an efficient tool to reconstruct the composition of seepage fluids and seepage intensities.

METHANE BUBBLE DYNAMICS AND PREFERENTIAL RELEASE UNDER PERIODIC WAVE LOADING

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ABSTRACT

Preferential methane ebullition is often observed at low tides and waves in marine and lacustrine settings. Under these conditions, hydrostatic pressure drops is suggested to induce fracturing of muddy sediments by rising bubbles and their release to the water column. In this study methane bubble dynamics is modelled under different kinds of periodic water loadings, characterized by variable wave period, T, and wave amplitude, A. Our preliminary results demonstrate that under the high-frequency waves (e.g. T=11 s) and A=0.5 m, associated, for instance, with surface waves, in the shallow water environment (e.g. 0.5 m water column height) bubble propagates upward ~7 cm in the dynamic regime. It may eventually be released to the water column if thickness of sediment above the gas horizon is smaller than 7 cm. In contrast, in a much deeper water environment (e.g. 10 m water column height) bubble propagates in the stable regime ~ 7 mm only, while under 50 m water column height, it remaines in place. Comparison to the bubble with conserved mass, reveals that fast hydrostatic pressure drop in the frequent waves plays a dominant role in the bubble dynamics, compared to the less important role of the solute transport component. Alternatively, under the lower-frequency (e.g. internal) waves (e.g. T=4 hr, A=0.5m), under 50 m water column height, the difference between the dynamics of the real bubble and that with conserved mass is significant. In the former case bubble propagation is driven by a competition between a slow decrease in the hydrostatic pressure, and a bubble solute exchange with an ambient field of solute. The relative contribution of the latter becomes much more significant than that in a case of high- frequency waves.

CHARACTERISTICS AND FORMATION MECHANISMS OF SEEPAGE FEATURES IN THE SE OF THE LEVANT BASIN: INSIGHTS FROM 3D SEISMIC DATA

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ABSTRACT

Detailed interpretation of high resolution 3D seismic data from the southeastern section of the Levant Basin (offshore Israel) has allowed the identification of seabed pockmarks as circular to sub-circular depressions in water depths of 1000 to 1300 m. These pockmarks are associated with sub-seabed high amplitude seismic reflections typical of shallow gas accumulations within Quaternary sediments. Despite the fact that the origin and mechanisms behind the formation of these pockmarks remain unclear, we reveal that the features represent important perturbations in the seafloor and may have implications for understanding basin evolution. In this study, pockmarks may be divided into two different classes (1 and 2) based on their (a) acoustic characteristics, (b) morphology and distribution. Class-1 pockmarks are irregular large seabed depressions with basal bright spots and sub-seabed seismic chimneys (acoustic imprints of highly focused, cross-stratal fluid plumbing). These pockmarks which show a spatial correlation with subsurface faults are well documented in a compressional zone within the toe of the Palmachim disturbance. Class-2 pockmarks however, have a regular-subtle form, u or v shapes in crosssection and dominate the western half of the study area where they are spatially associated with the Nile deep sea fan, plus a few occurrences in the eastern domain. They show no associated seismic chimneys and have little or no apparent bright spot at their base. In addition to large scale faulting which likely facilitated km-scale fluid migration to form class 1 pockmarks, seismic data suggests hydro-fracturing after reservoir pressure build-up as a possible mechanism involved in the formation of the two classes of pockmarks. Pockmarks and shallow gas occurrences in this area may serve as important evidence for the presence of a deep hydrocarbon system coupled with a previously unexplored shallow reservoir system. It is important that effective predrilling/pre-infrastructure installation shallow hazard analysis in this area takes these features into consideration as results will have impacts on drilling and installation decisions.

GEOCHEMISTRY OF BARIUM IN SEDIMENTS OF SOUTH CHINA SEA: IMPLICATIONS FOR BA_{EX}/S RATIO TO INFER THE TEMPORAL VARIATION OF METHANE FLUX

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ABSTRACT

The accumulation of excess barium (Baex; Total Barium-Barium associated with terrigenous material) in marine sediments is thought a robust proxy for marine biological productivity. However, application of Ba_{ex} as a proxy for export productivity is limited due to the uncertainty in parameters that controlling barite preservation in sediments and detrital inputs of aluminosilicate minerals. To investigate the factors that control the barite preservation in marine sediments and its potential for indication of methane flux, surface and subsurface sediments in the well-characterized seep areas from the South China Sea were collected. Content of TOC, TS, major and trace element were obtained to examine the influence of methane seepage and organic carbon mineralization. Our results suggest that Ba preservation may be compromised in some geological conditions. For example, under suboxic conditions as revealed by high authigenic uranium (U) content as a result of high organic matter, Ba preservation may be reduced. Moreover, during intense methane seepage, aerobic methane oxidation may occur that will reduce the bottom water oxygen, which in turn will reduce Baex content. However, change of Baex content is not expected but accompanied by high sufur content, when methane flux is small because the sulfate methane transition zone located at the depth of sediment. The proxy, Baex/S ratio in sediments, proposed in this study could be used as an indicator of temporal variation of methane flux. Acknowledgment: Funding was provided by the NSF of China (Grants: 41373085 and 41422602).

THE MECHANISM OF METHANE GAS MIGRATION THROUGH THE GAS HYDRATE STABILITY ZONE: INSIGHTS FROM NUMERICAL SIMULATIONS

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ABSTRACT

Free gas migration through the gas hydrate stability zone (GHSZ) and subsequent gas seepage at the seabed are characteristic features in marine gas hydrate provinces worldwide. The biogenic or thermogenic gas is typically transported along faults from deeper sediment strata to the GHSZ. Several mechanisms have been proposed to explain free gas transport through the GHSZ. While inhibition of hydrate formation by elevated salinities and temperatures have been addressed previously in studies simulating unfocused, area-wide upward advection of gas, which is not adequately supported by field observations, the role of focused gas flow through chimney-like structures has been underappreciated in this context. Our simulations suggest that gas migration through the GHSZ is, fundamentally, a result of methane gas supply in excess of its consumption by hydrate formation. The required high gas flux is driven by local overpressure, built up from gas accumulating below the base of the GHSZ that fractures the overburden when exceeding a critical pressure, thereby creating the chimney-like migration pathway. Initially rapid hydrate formation raises the temperature in the chimney structure, thereby facilitating further gas transport through the GHSZ. As a consequence, high hydrate saturations form preferentially close to the seafloor, where temperatures drop to bottom water values, producing a prominent subsurface salinity peak. Over time, hydrates form at a lower rate throughout the chimney structure, while initial temperature elevation and salinity peak dissipate. Thus, our simulations suggest that the near-surface salinity peak and elevated temperatures are a result of transient high-flux gas migration through the GHSZ.

IN-SUIT MEASUREMENT OF DISSOLVED CH4, CO2, H2S CONCENTRATION AND δ^{13} Cch4, δ^{13} Cco2 IN DEEP SEA OCEAN FOR GAS HYDRATION EXPLORATION

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ABSTRACT

Real-time in-situ quantitative measurement of the dissolved methane in water is important for the gas hydrate mineral exploration, and environmental issue caused by methane seepage of natural hydrocarbon seeps or anthropogenic development of gas hydrate. In particular, measurement of the carbon isotopic composition (δ^{13} C) can offer a better understanding of nature of sources, fluxes and bio geochemical cycling processes of carbon. For this purpose, we are developing an in-situ analyzer capable of δ^{13} C_{CH4}, δ^{13} C_{CO2}, and H₂S measurement in the deep ocean. Membrane gas/liquid separation and off-axis integrated cavity output spectroscopy(ICOS) techniques are used in our analyzer. Firstly, Seawater is pumped by a submersible pump and flow through a sediment water filter to prevent clogging and protect the membrane. The sample gas including methane, carbon dioxide, hydrogen sulfide, water vapor and other gas is extracted from water by the high-pressure membrane gas/liquid exchange module. Then water vapor is removed by a Nafion dryer from sample gas to reduce the interference of water vapor to gas analysis. At last, the sample gas is transfer to the analysis cavity by a vacuum pump and analyzed by off-axis integrated cavity output spectroscopy(ICOS). Concentration and isotopic ratio data is acquired by spectra analysis and corrected by reference gas.

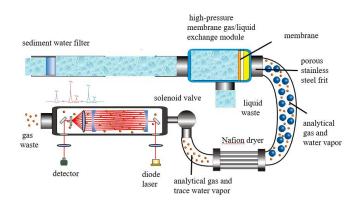


Fig.1. Schematic diagram of in-situ analyzer

We will use the analyzer acquire a higher temporal and spatial resolution in the hydrate region to analysis the gas source of hydrate, anaerobic oxidation of methane from hydrate dissociation, and CO₂-hydrate for CH₄-hydrate exchange.

SULFUR AND IRON BIOGEOCHEMISTRY IN THE LARGEST MANGROVE FOREST ON EARTH: TRACKING THE CARBON CYCLE IN SEDIMENTS OF THE INDIAN SUNDARBANS

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ABSTRACT

Mangroves are highly productive, carbon-rich coastal ecosystems found throughout the tropics and subtropics. Although it has been shown that mangrove sediments can be a source for the greenhouse gas methane, the specific biogeochemical processes by which carbon is exported and transformed in the sediments are still poorly understood. In this project, we propose to take sediment cores in the mangrove forests of the Indian Sundarbans (West Bengal, India) to produce a comprehensive dataset of the concentrations and stable isotope compositions of the biogeochemically relevant chemical species involved in carbon-iron-sulfur cycling. The Sundarbans in India and Bangladesh are the largest continuous mangrove forest on Earth and therefore play an important role in the global mangrove methane budget. Microbial sulfate reduction (MSR) in sediments constrains the spatial location of methanogenesis and sulfatedriven anaerobic oxidation of methane (AOM), and dissolved iron and iron oxides can sequester and re-oxidize reduced sulfur, respectively, thereby indirectly affecting methane dynamics. To track these processes in the mangrove sediments, we will take down-core measurements of the concentrations of dissolved inorganic carbon (DIC), SO₄²⁻, H₂S, Fe²⁺, and CH₄. In the solid-phase we will take down-core measurements of total organic carbon (TOC), total organic nitrogen (TON), acid volatile sulfides (AVS), and chromium reducible sulfur (CRS). Finally, we will measure the following stable isotope ratios: δ^{13} CDIC, CH4, TOC, δ^{34} SSO4, H2S, AVS, CRS, and δ^{18} OSO4. Overall, this integrated dataset will provide a better understanding of how carbon-sulfur-iron cycling controls methane production and consumption in the Sundarbans and other mangrove systems.

AUTHIGENIC CARBONATE FORMATION FROM ACTIVE METHANE SEEP OFFSHORE SOUTHWESTERN TAIWAN

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ABSTRACT

In this study, we selected seven authigenic carbonates retrieved from the seafloor at two cold seep sites (Yong-An Ridge and Good Weather Ridge) and one mud volcano site (96 Mud Volcano Group) offshore southwestern Taiwan. In order to constrain the formation of authigenic carbonates, we measured the mineralogy, stable isotopic compositions, elemental geochemistry and radiogenic isotopic compositions. The mineralogy results show that the carbonates are dominated by dolomite for Yong-An Ridge and Mg-calcite for Good Weather Ridge and 96 Mud Volcano Group. δ^{13} C data of authigenic carbonates, ranging from -36 ~ -47‰, are lighter than but heavier than seawater value of 0‰ and total organic carbon δ^{13} C (δ^{13} CToC) data of -23‰. The observations suggest anaerobic oxidation of methane (AOM) is a predominant factor on carbonate precipitation. REE data show that elevated REE concentrations with middle REE enriched patterns, indicating reduction of Fe-oxides release abundant REEs in anoxic sediments. ⁸⁷Sr/⁸⁶Sr ratios from 0.709284–0.709588 display more radiogenic values than modern seawater value of 0.709175, indicating fluid sources are influenced by water-rock interaction.

MULTIPATH STRUCTURE OF THE SOUND FIELD IN ACOUSTIC SENSING OF GAS-SATURATED SEDIMENTS AND DATA PROCESSING

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ABSTRACT

Basis of remote acoustic sensing for upper sedimentary layer characterization is estimation of angular-frequency dependence of the reflection coefficient from the sea floor. Main problem in this approach is multiple reflections of sound signal from the seafloor and sea surface, which interfere with each other. As a result, structure of sound field at the receiving system (single hydrophone or array of hydrophones) is very complex. In addition, natural sources of sound (e.g. surface breaking waves and sea animals) and human-made sources of sound (e.g. vessels, onshore and offshore structures) produce sound noise at wide range of frequencies. In this work, specific data processing is developed and applied for the system of a single sound source and receiving array for the short range (up to 300 m) sound propagation in Lake Kinneret (depth up to 40 m). Chirp signal in the wide frequency band was radiated. Signals recorded by the vertical line array were cross-correlated with radiated signal replica to obtain pulse response. Reflection coefficient was estimated by spectral analysis and comparison of the direct and reflected pulses.

GAS HYDRATE DISSOCIATION EVENT AND ITS RELATIONSHIP WIHT SUBMARINE SLIDE IN DONGSHA AREA OF NORTHERN SOUTH CHIINA SES

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ABSTRACT

Dongsha area is a critical gas hydrate area of the northern South China Sea, and the submarine slide is extensively developed on its slope. In this paper, the sedimentological particle size, species characteristic and stable isotope of benthic foraminifera in the core 973-4 and 973-5 respectively recovered from the middle of the slope and the flat area at the base were analyzed. The results of the distinctly negative of δ^{13} C values and the heavier of δ^{18} O values in both cores in the Last Glacial period suggested that there were persistent gas hydrate dissociation events in the Dongsha area during this period. The phenomenon of δ^{13} C negative was gradually disappeared and the δ^{18} O values decreased since the Last Deglacial indicated that gas hydrate dissociation were prevented because of global sea level rise. In the core 974, obvious submarine slide deposits only occurred in 440-600 cm according to Last Glacial Maximum and the number of *Uvigerina* spp. and *Bulimina* spp. sharply increased in this position, which implied the submarine slide was probably caused by the intense methane release event induced by the descending sea level in Last Glacial Maximum period. A smaller scale submarine slide was also recorded in core 973-5, but the deposition time was later than that of core 973-4.

USING GEOCHEMICAL CHARACTERISTICS OF SEDIMENT TO INFER METHANE SEEPAGE DYNAMICS: A CASE STUDY FROM HAIMA COLD SEEPS OF THE SOUTH CHINA SEA

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ABSTRACT

Cold seeps are extensively developed close to the seafloor along continental margins worldwide (Suess, 2014). The dominant biogeochemical processes at cold seeps are the anaerobic oxidation of methane via sulfate reduction, which significantly impact the global carbon and sulfur cycles. It has been shown that the intensities of seepage are highly variable with time and space (Dickens, 2001; Peckmann and Thiel, 2004). However, questions remain about the establishing of geochemical markers for methane seepages. In order to constrain the methane seepage dynamics, multiple sedimentary records were obtained for three piston gravity cores (QDN-14A, ODN-14B, and ODN-31) from the Haima seep of the South China Sea (SCS). Three methane release events (MRE) were identified, which occur at about 260-300 cm (MRE 1), 380-420 cm (MRE 2) and 480-520 cm (MRE 3), respectively. Indicator used to constrain the record of seepage through the cores are low $\delta^{13}C_{TIC}$ values and high TS content for MRE 1, high TS and CRS contents for MRE 2 and high $\delta^{34}S_{acid-insoluble}$ and $\delta^{34}S_{CRS}$ values for MRE 3. The mechanisms for the presence or absence of these geochemical indicators are not known. It is suggested that the variations of methane flux over time and duration of the MRE is the most probably reason, which need to be confirmed in the future. Overall, our results suggest that sedimentary carbon and sulfur and their isotopes are useful for better understanding of the seepage dynamics over time.

IMAGING P- AND S-WAVE VELOCITY STRUCTURES IN HYDRATE BEARING SEDIMENTS ALONG THREE OBS PROFILES, OFF SOUTHWEST TAIWAN

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ABSTRACT

In order to advance our understanding of the marine slope instability of hydrate-bearing sediments in the offshore southwestern Taiwan, P-waves and S-waves seismic data generated by P-S conversion on reflection from air-gun shots recorded from three multi-component Ocean Bottom Seismometer (OBS) surveys were used to construct two-dimensional velocity models. One of the investigated profile lies above a structural high of the Yuan-An ridge, proposed as a high priority drilling site for gas hydrate investigations off southwest Taiwan. The locations of the OBSs were determined to high accuracy by an inversion based on the shot traveltimes. Traveltime inversion and forward modeling of seismic data result in general trends P-wave and S-wave velocities of sediments. Beneath the Yuan-An ridge, P-wave and S-wave velocities are high beneath topographic high which might represent a series of thrust-cored anticlines develop in the accretionary wedge. In addition, P-wave velocities of the sea floor are about ~1.58 km/s, increasing to the bottom simulating reflectors (BSR), reaching values of about ~2 km/s. Below it, a low velocity layer (1.62-1.74 km/s) is observed, which indicates the presence free gas in the sedimentary layer. S-wave velocities of the sediments over the entire section range from 0.3 to ~0.6 km/s. Significant lateral velocity variations were found beneath the eastern flank of the Yuan-An ridge, probably represents thrust faults that extend from seafloor to hydrate-bearing layer. We suggest that the BSR has been disturbed by the thrust faults and any further displacement associated with thrust uplift could potentially trigger failures in the study area.

MEASUREMENTS OF THE DISSOCIATION CONDITIONS OF METHANE HYDRATE IN THE PRESENCE OF ADDITIVES AT ELEVATED PRESSURES

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ABSTRACT

Besides the traditional fossil fuel energies, gas hydrates are considered as the emerging energy source. Gas hydrates are ice-like solid that consist of water and guest molecules such as methane or carbon dioxide. In practical applications, additives are used to increase or decrease the stable phase ranges of gas hydrates for natural gas exploration or carbon dioxide sequestration. The thermodynamic phase equilibrium data for gas hydrates with additives are essentially required for engineering process simulation and design. This study reports the equilibrium conditions for the dissociation of methane hydrates in the presence of additives such as 2,5-dihydrofuran, cyclopentanol, acetamide and 1,3-dioxane. Various concentrations of additives in aqueous and brine solutions were experimentally measured using an isochoric method. The hydrate-liquid water-vapor (H-L_w-V) three-phase equilibrium temperatures and pressures for methane hydrates were determined for pressures ranging from 6 to 13 MPa. For the addition of 2,5-dihydrofuran, cyclopentanol and 1,3-dioxane, promotion effect for methane hydrate formation is observed. The greatest promotion effects for the additive of 2,5-dihydrofuran is approximately 13 K. Acetamide additive, however, shows an inhibition effect up to 8.7 K. The structures of gas hydrates with additives were also determined using the Clausius-Clapeyron equation for methane hydrates with various additives. The explanation of the hydrate structures and the promotion or inhibition effect is discussed.

DETERMINATION OF THE PHASE EQUILIBRIUM AND KINECTIC DATA FOR THE FORMATION OF CARBON DIOXIDE HYDRATE WITH ADDITIVES

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ABSTRACT

Gas hydrates are ice-like solids that consist of gas (guest) and water (host) molecules. The water molecules construct the framework of clathrate structures through H-bonding while the cavities are occupied by gas molecules. Recently, carbon dioxide capture and storage receive great attention. Besides the ocean and geological storage, carbon dioxide can also be stored in the form of hydrate. The basic phase equilibrium data for carbon dioxide with proper amount of additives to reach the appropriate temperature and pressure region for storage is always required. This study reports the dissociation temperatures and pressures of carbon dioxide hydrate with various additives at several concentrations. The experiments were carried out in a high pressure cell using the isochoric temperature cycling method. The reported phase diagrams are useful for engineering process design. These data are also useful for trapping carbon dioxide as hydrate during methane hydrate extraction. This study presents the phase equilibrium data for carbon dioxide hydrate with several additive compounds such as tetrabutylammonium hydroxide, 2,5dihydrofuran, and urea. The tetrabutylammonium hydroxide acts as a promoter for carbon dioxide hydrate formation. Its promotion effect is up to 11 K. The structures of carbon dioxide hydrates with various additives are also investigated. With the tetrabutylammonium hydroxide additive, the carbon dioxide hydrate shows an interesting semi-clathrate structure. The kinetic data, such as the induction time with urea additive, are also reported.

PAST METHANE EMISSIONS AT THE STORFJORDRENNA GAS HYDRATE-BEARING MOUNDS

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ABSTRACT

We investigated gas hydrate-bearing mounds that were recently discovered in the northern Barents Sea, south of the Svalbard archipelago (ca. 380m water depth). These mounds are ~10m high and ~500m wide, gas hydrates were recovered at different sediment depths (40, 70, and 120cm), and we observed release of methane bubbles from some mounds during video and echo sounder surveys. Herein, we report the results of isotopic investigation of calcitic foraminifera and lipid biomarkers of microbial communities mediating the Anaerobic Oxidation of Methane (AOM) in sediments to infer the past methane emissions in the area. Sediment cores were recovered from two mounds: Pingo 3 is active showing release of methane bubbles and containd gas hydrate, while the other mound, Pingo 5 is inactive with no evidence of present-day methane ebullition or gas hydrate in the sediments. At both pingos we used δ^{13} C of calcitic foraminifera and AOM lipid biomarkers to infer the past sulfate methane transition zones. We found several past SMTZs in the investigated cores in both pingos, and further infer the methane flux history using Ba/Ti ratio from XRF. We found out that the active pingo 3 experienced increasing methane flux whereas the inactive pingo 5 was more active in the past that experienced decreasing methane flux for a long time, most likely due to the gas reservoir is depleted or the conduit closed.