



# ABSTRACTS

**Ocean Floor Symposium 2022**  
**“Understanding element fluxes – processes and budgets”**

**October 9 - October 12, 2022**  
**at MARUM – Center for Marine Environmental Sciences,**  
**University of Bremen**

## Talks, Overview

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**Alcolombri, Uria**, F. J. Peaudecerf, A. Nissan, J. Słomka, K. S. Lee, Roman Stocker: Unraveling the microscale mechanisms driving particle degradation in the ocean

**Arndt, Sandra**, P. Pika, F. Sales de Freitas, D. Hülse: Regional and Global Patterns of Organic Matter Reactivity and their Influence on Carbon Turnover in Marine Sediments

**Arnosti, Carol**, G. Giljan, S. Brow, C.C. Lloyd, S. Ghobrial, G. Reintjes, R. Amann: The economics of macromolecule degradation in the ocean - a microbial perspective

**Bach, Wolfgang**, L. Schlicht, S. Kasemann, G. Wheat: Crust-seawater exchange in the flanks of mid-ocean ridges (including seamounts)

**Burwicz-Galerie, Ewa**, R. Saman: The influence of temperature-dependent methanogenesis on basin-scale methane emissions from the western Black Sea

**Cannat, Mathilde**: Exploring magmatic controls on hydrothermal fluxes at slow-spreading ridges

**Close, H.G.**, P. K. Wojtal, S. C. Doherty, L. C. Henderson, K. C. Grabb, N. Wallsgrove, C. C. S. Hannides, A. L. Bour, M. D. McCarthy, J. C. Drazen, B. N. Popp: Microbial and metazoan metabolisms leave distinct isotopic traces during degradation of marine particles

**Diehl, Alexander**, W. Bach: An assessment of the global on-axis hydrothermal element fluxes

**Eglinton, Tim, I.**, S. Paradis, H. Gies, N. Haghipour, C. Schnepfer, M. Schwab, E. Bruni: ISODRAPES: Spatial Variability in the Provenance, Vintage and Quality of Organic Carbon accumulating on the Ocean Floor

**Galerie, C.**, N. Lenhardt, O. Rabbal, C. Wiggers, J. Hasenclever, O. Galland, A. Götz, W. Bach, W.-A. Kahl, A. Teske, D. Lizarralde, C. Berndt, T.W. Höfig, and Expedition 385: Scientists Carbon-cycle in sedimentary basins intruded by sills - differing responses and implications from depth to the seafloor

**Kleint, Charlotte**, R. Zitoun, M. Walter, L. Klose, S.M. Chiswell, R. Middag, P. Laan, S. G. Sander, A. Koschinsky: Trace Metal Dynamics in Shallow Hydrothermal Plumes at the Kermadec Arc

**LaRowe, Doug E.**: A global perspective on microbial activity in marine sediments

**Mezri, L.**, J. Garcià-Pintado and M. Pérez-Gussinyé: Tectonic controls on melting and oceanic crust composition at mid-ocean ridges.

**Orcutt, Beth N.**: Impact of geosphere-biosphere interactions at the sediment-basement interface

**Rüpke, Lars**: Hydrothermal circulation at mid-ocean ridges – insights from the joint interpretation of models and data

**Wegener, Gunter**: Anaerobic sediments host an efficient microbial barrier that consumes deep-subsurface-derived oil and gas

## Posters, Overview

---

**Akeerath Mundanatt, Aman,** Silvia Vidal-Melgosa, Jan-Hendrik Hehemann: Algal sulfated fucan: a global carbon sink

**Albers, E.,** A. Gerdes, S. Jöns, W. Bach, C. Beier: Limited duration of carbonate formation in Louisville Seamount basalts revealed by in situ U–Pb dating

**Behrendt, N.,** W. Menapace, R. L. Romer, J. Glodny, G. Bohrmann, A. Witzleb, S. Porrmann, A. Kopf: The Sr-isotope signature of pre-Messinian fluid sources in pore fluids of eastern Mediterranean mud volcanoes

**Bojanova, Diana P.,** Mirna Vazquez-Rosas-Landa, Mojhgana A. Haghnegahdar, Valerie Y. De Anda, Brett J. Baker, Andreas P. Teske, Jeanine L. Ash, Edward D. Young, Douglas E. LaRowe, Jan P. Amend, IODP Expedition 385 Scientists: Well-Hidden Methanogenesis in Deep, Organic-Rich Sediments

**Bourceau, P.,** M. Rubin-Blum, E. Kröber, H. Gruber Vodicka, C. Borowski, M. Liebeke, N. Dubilier: Similar but different: Comparative analyses of symbiotic and free-living methane-oxidizing bacteria (*Methyloprofundus*) from hydrothermal vents and cold seeps

Brünjes, J., M. Seidel, T. Dittmar, J. Niggemann, **F. Schubotz:** Natural asphalt seeps are potential sources for recalcitrant oceanic dissolved organic sulfur and dissolved black carbon

**Buck-Wiese, Hagen,** Mona A. Andskog, Nguyen P. Nguyen, Margot Bligh, Eero Asmala, Silvia Vidal-Melgosa, Manuel Liebeke, Camilla Gustafsson, and Jan-Hendrik Hehemann: Brown algae inject fucoidan carbon into the ocean

**Chen, Jie,** Jean-Arthur Olive, Mathilde Cannat: Beyond Spreading Rate: Controls on the Thermal Regime of Mid-Ocean Ridges

Evans, Thomas W., Weimin Liu, Gesine Mollenhauer, Marcus Elvert, Karin A. Zonneveld, Kai-Uwe Hinrichs, **Hendrik Grotheer:** Untargeted mapping of polar organic compounds in suspended particulate organic matter off Cape Blanc, NW Africa

**Flintrop, C.M.,** B. Glemser, A. Rogge, F. Koch, J. Balaguer, C. Völkner, I. Peeken, L. Eggers, S. Trimborn, M.H. Iversen: Impact of phytoplankton composition on aggregate formation and carbon export in the southern Weddell Sea

**Freitas, F.S.,** K. H. Hendry, C. März, S. Arndt: Organic matter degradation in Arctic shelf sediments: controls and feedbacks on organic carbon burial, nutrient fluxes, and benthic carbonate chemistry

**García-Pintado, J.,** M. Pérez-Gussinyé, L. Mezri, W. Bach, L. Rüpke: One million years of interplay between tectonics and hydrothermal activity in a rifting ocean basin

**Groninga, Janina,** Jenny Wendt, Lars Wörmer, Gunter Wegener, Andreas Teske and Kai-Uwe Hinrichs: High-resolution insight into microbial community zonation in hydrothermal sediments via mass spectrometry imaging of intact polar lipids

**Hansen, Christian T.,** Frederike K. Wilckens, Melissa Schwarz, Simone A. Kasemann, Wolfgang Bach: Dissecting the intricate Mg systematics during hydrothermal basalt glass alteration – insight from experiments at 70, 150 and 250°C (40 MPa)

**Holtappels, M.**, G. Gomez, Z. Zhu, H. Waska, B. Wei, H. Grotheer, S. Henkel, G. Mollenhauer, S. Kasten, T. Dittmar: Iron and DOM transformations in coastal sands

**Klose, L.**, D. Garbe-Schönberg, A. Koschinsky: Dissolved As, Sb, Tl, Pb, Ag, Cd and Co in hydrothermal vent fluids from the Atlantic, Indian and Pacific Ocean

**Kremin, I.**, Z. Guo, L. Rüpke: The effect of permeability on the pressure regime in 2D outcrop-to-outcrop submarine hydrothermal flow models

**Kürzinger, Victoria**, Alexander Diehl, Samuel I. Pereira, Harald Strauss, Gerhard Bohrmann, Wolfgang Bach: Sulfur formation in the Kemp Caldera hydrothermal system

**Kumawat, P.**, F. Schubotz, W. Bach, E. Albers: Characterizing chemosynthetic microbial communities in abyssal serpentinites: a lipid biomarker approach

Lalk, E., **T. Pape**, D.S. Gruen, N. Kaul, J.S. Karolewski, G. Bohrmann, S. Ono: Clumped methane isotopologue-based temperature estimates for sources of methane in submarine gas hydrates

**Lefebvre, Alice**, Tilmann Schwenk, Renée Bernhard, Elda Miramontes: Towards an investigation of the transport of particles along and across the Irish continental shelf – hydroacoustic measurements during MSM107

**Lloyd, Chad C.**, Sarah Brown, John Paul Balmonte, Adrienne Hoarfrost, Sherif Ghobrial, Carol Arnosti: Particle-associated bacteria produce a versatile collection of extracellular enzymes throughout the Western North Atlantic

**Nadolsky, C.**, A. Höfken, T. von Dobeneck, S. Kasten: Signatures and Proportions of Lithogenic, Hydrothermal and Authigenic Mineral Fractions in Ridge Flank Sediments of the East Pacific Rise

**Paradis, Sarah**, Tim Eglinton: Geospatial characterization of organic carbon in continental margin sediments worldwide

**Roza, Surya Eldo V.**, Gerard J. M. Versteegh, Gerhard Fischer, Karin A. F. Zonneveld: Particulate organic matter export flux and ecosystem change in the Cape Blanc upwelling region during the last 18 years reflected by dinoflagellate cysts: a sediment trap study

Ruben, M., H. Marchant, M. Wietz, T. Gentz, **G. Mollenhauer**: Quantifying fossil carbon utilization and release from eroding permafrost coastlines – results from an incubation experiment

**Samant, Rohit**, Gunter Wegener, Ewa Burwicz-Galerie: Role of temperature on the seafloor methane emission estimates in the Western Black Sea basin

**Seidel, Michael**, Leonie Jaeger, Hendrik Grotheer, Jutta Niggemann, Philipp Böning, Gesine Mollenhauer, Thorsten Dittmar: Dissolved organic matter cycling in the coastal upwelling zone off Cap Blanc, Mauritania

Türke, Andreas, **Maren Walter**, Christian Mertens, Wolfgang Bach, Chris German, Jürgen Sültenfuß, Patrick Monien, Koichi Nakamura, Simon Prause, Alexander Diehl, Antje Boetius: Fluxes and properties of in the proximal hydrothermal plume at the Aurora vent field, Gakkel Ridge, Arctic Ocean

**Versteegh, G.,** E. Tessin, K. Zonneveld: Different micro-FTIR derived molecular characteristics of particular organic matter represented by dinoflagellate cysts with diverse sensibility to preservation

**Wilckens, Frederike K.,** Christian T. Hansen, Wolfgang Bach, Simone A. Kasemann: The Mg conundrum of the Kermadec Arc – new insights from Mg isotopes

**Wildberger, A.,** S. Paradis, T.I. Eglinton: Tackling geomorphological heterogeneity: a comparison of predictors and modelling approaches to assess the distribution of sedimentary organic carbon in submarine canyons

**Zabel, M.,** R. N. Glud, H. Sanei, M. Elvert, T. Pape, P.-C. Chuang, E. Okuma, P. Geprägs, M. Kölling: High carbon mineralization rates in subseafloor hadal sediments - Result of frequent mass wasting

**Zhu, Qing-Zeng,** Xiuran Yin, Michael W. Friedrich, Marcus Elvert, Kai-Uwe Hinrichs, Jack J. Middelburg: Secondary production and priming effect reshape the organic matter composition in marine sediments

**Zonneveld, K.,** H. Grotheer, G. Versteegh: Dinoflagellate cysts production, excystment and transport in the upwelling off Cape Blanc (NW Africa).

## **List of Abstracts: Talks**

### **Unraveling the microscale mechanisms driving particle degradation in the ocean**

**U. Alcolombri<sup>1</sup>, F J. Peaudecerf<sup>1</sup>, A. Nissan<sup>1</sup>, J. Słomka<sup>1</sup>, K S. Lee<sup>1</sup> and Roman Stocker<sup>1</sup>**

<sup>1</sup>Swiss Federal Institute of Technology (ETHZ), Dept. of Civil, Environmental and Geomatic Engineering, Zurich, Switzerland.

The sinking of organic particles to the ocean depths is the main driving force of the biological pump, the process responsible for the export of more than 50 Gt of fixed CO<sub>2</sub> annually and one of the major fluxes in the oceans' carbon cycle. Yet, the mechanisms determining the magnitude of the pump remain poorly understood, limiting our ability to predict this carbon flux in future ocean scenarios. Current ocean models assume that the biological pump is governed by the competition between sinking speed and degradation rate, with the two processes independent from one another. In this talk, I will demonstrate that contrary to this paradigm, sinking itself is a primary determinant of the rate at which bacteria enzymatically degrade particles in the ocean. By combining video microscopy and microfluidic experiments to directly observe and quantify bacterial degradation of individual organic particles in flow, I will show that even modest sinking speeds of 8 meters per day enhance degradation rates more than 10-fold. I will further discuss the molecular mechanism behind the sinking-enhanced degradation, as well as possible ways by which bacteria can slow the sinking of particles. Finally, using the results obtained from a mathematical model, I will show that the flow associated with sinking is a major contributor to the observed magnitude of the vertical carbon flux in the ocean, and will outline major open questions in the field.

# Regional and Global Patterns of Organic Matter Reactivity and their Influence on Carbon Turnover in Marine Sediments

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The degradation of organic matter (OM) in marine sediments is key to understanding carbon cycling in the past, present, and future. While the potential controls on OM reactivity are increasingly well understood, their relative significance and the way in which they interact to control OM reactivity remains difficult to quantify. As a consequence, no framework currently exists to predict OM reactivity, and thus OM degradation dynamics, in global marine sediments.

In an attempt to address this knowledge gap, we inversely fit a 1D early diagenetic model to 14 sets of organic carbon and sulfate depth profiles and 392 diffusive oxygen uptake (DOU) measurements. Our analysis shows that OM reactivity is highly variable and a function of the whole depositional environment. Nevertheless, clear regional patterns in reactivity emerge. High reactivity is associated with conditions that either reduce exposure to pelagic degradation (phytodetrital aggregates, fronts, mesoscale eddies, ice edge effects, gravity driven mass flow) or directly limit pelagic degradation (oxygen minimum zones, low temperature), while low reactivity is associated with conditions that enhance the exposure to degradation (remoteness from continental margins, slow sinking and deep water). Based on our results we derive a first global map of benthic OM reactivity. This map is then used to drive a global diagenetic model with the aim of establishing global organic carbon budgets and benthic-pelagic exchange fluxes.

## **The economics of macromolecule degradation in the ocean - a microbial perspective**

**C. Arnosti<sup>1</sup>, G. Giljan<sup>2</sup>, S. Brown<sup>3</sup>, C.C. Lloyd<sup>1</sup>, S. Ghobrial<sup>1</sup>, G. Reintjes<sup>2</sup>, R. Amann<sup>2</sup>**

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Heterotrophic microbial communities process much of the organic matter in the ocean; they rework and respire components of sinking particles, and in sediments act as the final filter before organic matter is buried on geologic timescales. Despite the importance of the processes they carry out, our understanding of the tools and strategies microbes use to transform complex organic matter is still lacking. In particular, the economics of extracellular enzymes – the tools used to initiate processing of high molecular weight substrates – are incompletely understood. Ecological theory considers extracellular enzyme production via a cost-benefit analysis: investments of C, N, and energy into enzymes that are released into the environment must pay off, even though some of the resulting hydrolysate may be lost to scavenging bacteria. Our discovery that some marine bacteria use a ‘selfish’ uptake mechanism, in which a substrate is bound, initially hydrolyzed, and transported into the cell with little to no loss of hydrolysis products to the external environment, changes the terms of this equation. We recently found that selfish bacteria are active throughout the water column of the ocean, and especially in the bathypelagic, they process complex substrates that are otherwise not hydrolyzed. Selfish strategies clearly pay off under a wide range of environmental conditions, and should be included in our measurements and models of organic matter processing in the ocean.



## Crust-seawater exchange in the flanks of mid-ocean ridges

Wolfgang Bach<sup>1,2</sup>, Lucy Schlicht<sup>1</sup>, Simone Kasemann<sup>1,2</sup>, Geoff Wheat<sup>3</sup>

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The chemical and isotopic composition of seawater is strongly affected by exchange processes in ridge-flank hydrothermal systems (RFHS), which are responsible for >80% of the advective marine heat flux. RFHS related geochemical fluxes across the seabed are poorly constrained. Recent sampling of fluids from off-axis springs and from aquifer waters within the ridge flank crust has provided new constraints that we will present at the workshop. We focus on Li, because the data provide a clear picture. The  $\delta^7\text{Li}$  of the open oceans ( $\sim 31 \text{ ‰}$ ) differs markedly from the  $\delta^7\text{Li}$  of the continental runoff ( $\sim 16.5 \text{ ‰}$ ), requiring the uptake of  $^6\text{Li}$  by low-temperature interaction between seafloor and seawater. Dorado Outcrop, a basaltic edifice on 18 to 23 Ma old crust of the Cocos Plate, issues  $12.5^\circ\text{C}$  warm fluids and represents the first sampled RFHS that is typical of much of the global flux. The end-member fluid of Dorado Outcrop is depleted in Li ( $25.0 \pm 0.3 \mu\text{mol Li kg}^{-1}$  (1sd)) and enriched in  $\delta^7\text{Li}$  ( $31.9 \pm 0.2 \text{ ‰}$  (2sd)) relative to bottom seawater ( $26.2 \pm 0.3 \mu\text{mol Li kg}^{-1}$  (1sd),  $31.2 \pm 0.2 \text{ ‰}$  (2sd)). If these changes in Li concentration and isotopic composition are combined with a temperature increase in the Dorado aquifer of  $13^\circ\text{C}$  and a global ridge flank heat flow of 8TW, we find that RFHS can explain 7 to 27 % of the observed shift in seawater composition (i.e., 31 ‰ vs. 16.5 ‰). We estimate a Li flux of  $5.8 \times 10^9 \text{ mol Li yr}^{-1}$  which corresponds to 58 to 73 % of the continental runoff. The potential role of RFHS in the oceanic budgets of other elements, namely Mg, Sr and U, are also discussed in the presentation. The uncertainties here are still very large; more sampling of crustal fluids from drill holes in the ocean crust is dearly needed.

# **The influence of temperature-dependent methanogenesis on basin-scale methane emissions from the western Black Sea**

**Ewa Burwicz-Galerne<sup>1</sup>, Rohit Samant<sup>2</sup>**

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<sup>2</sup>University of Bremen, Bremen, Germany

In our study, we use a large-scale 3D basin model of the western Black Sea to quantify the amounts and rates of biogenic and thermogenic methane fluxes within the sediments as well as the seafloor methane emissions. The model construction is based on over one hundred interpreted seismic horizons repopulated with more than forty sedimentary layers of complex lithological and facies distribution. The deepest and the oldest central part of the basin (98 Ma) is located at the depth of about seventeen kilometres. Well known organic-rich Oligocene-Early Miocene Maykopian facies provide high petroleum potential to form thermogenic methane. However, our results show that due to mostly premature state of these Maykopian source rocks, the majority of methane generated in the Black Sea basin manifests its clear biogenic origin. To investigate in detail the potential variability of generated biogenic methane amounts, we have performed multiple numerical simulations using various temperature-dependent kinetic rates of organic matter degradation. Precisely, we tested numerous temperature limits of microbial methanogenesis ranging from 40 to 120 deg. C. On a basin-scale, it lead to significant differences in methane generation, migration and capture in a form of natural gas hydrate deposits. Our results highlight the importance of spatio-temporal temperature changes on microbial communities and their abilities to produce light hydrocarbon components throughout the basin history.

# Exploring magmatic controls on hydrothermal fluxes at slow-spreading ridges

Mathilde Cannat<sup>1</sup>

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Estimating hydrothermal fluxes at mid-ocean ridges (MORs) is relevant both in terms of heat transfer and the thermal state of the axial lithosphere, and in terms of chemical fluxes from the solid Earth to the oceans. MOR hydrothermal systems, however, are complex and their activity varies over relatively short time scales. This is particularly the case for slow spreading MORs, where three distinct types of hydrothermal vent fields have been recognized: basalt (Lucky Strike-type) or ultramafic (Rainbow-type) hosted black smoker vent fields, and ultramafic hosted alkaline vent fields (Lost City-type). Black smoker vents have very high fluid fluxes, extracting a lot of heat, and in the case of Rainbow-type fields, resulting from high rates of serpentinization in the substratum. Lost City-type vents by contrast have very low fluid and heat fluxes. This presentation explores the links between hydrothermal heat and chemical fluxes at slow-spreading MORs, and the flux and depth of emplacement of magma in the axial lithosphere. It builds on published and on-going works that address the time-integrated heat loss at the scale of the ridge axis, then hydrothermal field scale fluxes, in relation to the local magmatic context.

## **Microbial and metazoan metabolisms leave distinct isotopic traces during degradation of marine particles**

**H. G. Close**<sup>1</sup>, P. K. Wojtal<sup>1</sup>, S. C. Doherty<sup>1,2</sup>, L. C. Henderson<sup>1</sup>, K. C. Grabb<sup>3,4</sup>, N. Wallsgrave<sup>5</sup>, C. C. S. Hannides<sup>5</sup>, A. L. Bour<sup>6</sup>, M. D. McCarthy<sup>6</sup>, J. C. Drazen<sup>7</sup>, B. N. Popp<sup>5</sup>

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The intensity of heterotrophy at the ocean's surface and the vertical distribution of heterotrophy beneath the surface modulate the distribution of organic carbon in marine water columns, but the relative importance of microbes and metazoans in this process is difficult to constrain. Recently we have distinguished the effects of microbial and metazoan heterotrophy on small and large particles that contribute to vertical flux and deep-sea food resources using relative differences in the  $\delta^{15}\text{N}$  values of individual amino acids. From these patterns, we have developed a multivariate classification of the trophic history of detrital organic matter. We find differing contributions of unaltered phytodetritus, zooplankton-influenced material, and microbially-altered detritus between particle size classes and across depths spanning from the surface to upper bathypelagic depths in contrasting ocean locations. We suggest that some observed variations across water columns may result from upper ocean ecosystem structure and/or the transport of material by vertical migrators. I will additionally discuss how different microbial metabolisms and mechanisms of degradation may shape our interpretation of the sedimentary stable isotope record.

## **An assessment of the global on-axis hydrothermal element fluxes**

**A. Diehl<sup>1</sup>, W. Bach<sup>1</sup>**

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The global hydrothermal on-axis element flux between oceanic lithosphere and the ocean can be calculated by relating vent fluid compositions and their respective temperatures to the energetic budget of the oceanic lithosphere. Today these element fluxes are still barely constrained although they play an important role in affecting ocean chemistry. Uncertainties in estimating these element fluxes arise by two factors: First, calculations have been carried out with one unique vent fluid composition that is meant to represent the global compositional range of hydrothermal fluids (ignoring the chemical diversity of vent fluids). Secondly, the role of different geological settings (eg. mid-ocean-ridges, back-arc basins, volcanic arcs) and sediment-hosted vs. sediment-free hydrothermal systems has been neglected. The recently established MARHYS vent fluid database helps to improve the estimation of global on-axis element fluxes by enabling an assessment that considers the chemical diversity and nature of hydrothermal fluids in different geologic settings to provides a more robust estimation of these fluxes.

## **ISODRAPES: Spatial Variability in the Provenance, Vintage and Quality of Organic Carbon accumulating on the Ocean Floor**

**Timothy I. Eglinton<sup>1</sup>**, Sarah Paradis<sup>1</sup>, Hannah Gies<sup>1</sup>, Negar Haghypour<sup>1</sup>, Charlotte Schnepfer<sup>1</sup>, Melissa Schwab<sup>1,\*</sup>, Elena Bruni<sup>1</sup>

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The cycling and burial of organic matter (OM) on continental margins is relevant to a broad range of topics including benthic-pelagic coupling, seafloor biodiversity, sedimentological processes, paleoclimate reconstruction, marine bio- (fisheries) and geo- (mining) resources, and carbon stocktaking. Carbon cycling over continental margins is highly dynamic and spatially heterogeneous, resulting in complex patterns in the content and composition of OM as well as the mineralogical and granulometric characteristics of underlying sediments. Improved assessment of the factors leading to the role and sensitivity of organic carbon (OC) burial requires comprehensive understanding of OC sources as well the processes that influence its fate. To address this issue, we are synthesizing available geochemical and sedimentological data, and combining this information with new measurements in a nascent margin-centric surface sediment database, MOSAIC. In particular, we focus on <sup>14</sup>C measurements as a means to constrain OC supply and dispersal over continental margins. We will highlight the strong hydrodynamic and mineralogical controls on the distribution and composition of sedimentary organic matter, and the pervasive influence of lateral transport processes on continental margins. Ultimately, we seek to derive a more spatially-nuanced view of the amount, nature and age of organic matter accumulating in continental margin sediments and its role in the global carbon cycle.

## **Carbon-cycle in sedimentary basins intruded by sills - differing responses and implications from depth to the seafloor**

**C. Galerne**<sup>1</sup>, N. Lenhardt<sup>2</sup>, O. Rabbel<sup>3</sup>, C. Wiggers<sup>1</sup>, J. Hasenclever<sup>4</sup>, O. Galland<sup>5</sup>, A. Götz<sup>6</sup>, W. Bach<sup>1</sup>, W.-A. Kahl<sup>7</sup>, A. Teske<sup>8</sup>, D. Lizarralde<sup>9</sup>, C. Berndt<sup>10</sup>, T.W. Höfig<sup>11,\*</sup>, and Expedition 385 Scientists

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A 20-year-old paradigm postulates that rapid emplacement of large-volume of magmatic sills into basins of organic-rich sediment infill caused some of the greatest mass extinctions in Earth's history. The suggested underlying process is the intrusion of low-permeability sedimentary strata by basaltic magma, which released gases from cracking of organic matter trapped within the host sedimentary rock. The mobilized thermogenic gases were carried upward by epithermal fluids and discharged violently at the basin floor through hydrothermal vents. Here, we report on results of two studies that suggest that sills may act as a trap for some of the thermogenic gas mobilized in the lower part of their contact aureole, a mechanism that may actually lessen the thermogenic gas emission flux. Additionally, new research related to magma-sediment interactions in the seafloor indicate that very little thermogenic gas is mobilized and emitted from young unconsolidated sediments. We present conclusions on the nature of magma-sediment interactions and the role magmatic intrusions in sedimentary basins may play in carbon-cycling within the seafloor and the transfer of gases across the ocean floor.

## Trace Metal Dynamics in Shallow Hydrothermal Plumes at the Kermadec Arc

C. Kleint<sup>1,2</sup>, R. Zitoun<sup>3,4</sup>, M. Walter<sup>2,5</sup>, L. Klose<sup>1,2</sup>, S.M. Chiswell<sup>6</sup>, R. Middag<sup>7</sup>, P. Laan<sup>7</sup>, S. G. Sander<sup>3,4</sup> and A. Koschinsky<sup>1,2</sup>

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Hydrothermal vents are a source of many trace metals to the oceans. Compared to mid-ocean ridges, hydrothermal vent systems at arcs occur in shallower water depth and are much more diverse in fluid composition, resulting in highly variable water column trace metal concentrations. During R/V Sonne cruise SO253 in 2016/2017, hydrothermal plumes from two hydrothermally active submarine volcanoes along the Kermadec arc in the Southwest Pacific Ocean were sampled: (1) Macauley, and (2) Brothers. At both volcanoes, results indicated strong plumes of dissolved trace metals, notably Mn, Fe, Co, Ni, Cu, Zn, Cd, La, and Pb, some of which are essential micronutrients. Dissolved metal concentrations commonly decreased with distance from the vents, as to be expected, however, certain element/Fe ratios increased, suggesting a higher solubility of these elements and/or their stronger stabilization. Our data indicate that at the magmatically influenced Macauley and Brothers cone sites, the transport of trace metals is strongly controlled by sulfide nanoparticles, while at the Brothers NW caldera wall site iron oxyhydroxides seem to dominate the trace metal transport over sulfides. Our study presents the first data on several dissolved trace metals in the Macauley system, and extends the existing plume dataset of Brothers volcano. Our data further indicate that chemical signatures and processes at arc volcanoes are highly diverse, even on small scales.



## **A global perspective on microbial activity in marine sediments**

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Microorganisms have been found throughout marine sediments. Little is known about what reactions these organisms are catalyzing or at what rate they are active. As a result, the influence that microorganisms have driving global element cycles in a significant fraction of Earth's habitable volume is poorly understood. In this presentation, I will describe recent modeling work that is designed to quantify what microorganisms are doing and how fast they're doing it in energy-limited marine sediments on a global scale.

## **Tectonic controls on melting and oceanic crust composition at mid-ocean ridges.**

**L. Mezri<sup>1</sup>, J. Garcìa-Pintado<sup>1</sup> and M. Pérez-Gussinyé<sup>1</sup>**

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Superfast and ultraslow ridges are end-members of the Earth's ridge system, where oceanic crust forms, and displays a great diversity in composition, hydrothermal systems and biological communities. At both ridge types, the thickness of the seismic crust varies across the axis, with the wavelength of oscillations being longer at slower ridges. The emerging consensus proposes this to reflect the alternation between magmatism and tectonics, which is controlled by an oscillating magma supply. While the role of magmatism on tectonics has been extensively studied, the role of tectonics on magmatism is not yet understood; the two are even thought to be dissociated. We address this by modeling ridge systems starting from continental extension. Our dynamic models simulate melting, serpentinization, hydrothermal cooling, and ocean loading. For ultraslow systems, we find that the importance of tectonics is controlled by ocean loading promoting long offset faults, and the balance between hydrothermal cooling and heat release processes, driven by serpentinization and magma emplacement in the crust. In our model, faulting mode influences crustal composition, mantle flow beneath the ridge and melt productivity, which can have a major impact on hydro- and eco-systems. At superfast ridges, we find that the lower crust is a dynamic environment in which molten lower crustal and mantle rocks mix, at the location where magma chambers are seismically imaged. We hypothesize that this influences the chemical composition of MORB.

# **Impact of geosphere-biosphere interactions at the sediment-basement interface**

**Beth N. Orcutt**

Bigelow Laboratory for Ocean Sciences, East Boothbay, Maine, USA

Ocean floor element fluxes predominantly focus on the water-sediment interface, yet appreciable elemental transfer can also occur at the sediment-basement interface. These transfers can alter the elemental composition of crustal fluids to such a degree that the elemental fluxes can rival riverine inputs to the ocean. Whether or not microbial processes within deep sediments and/or basement appreciably contribute to the elemental transfers is unclear. In this presentation I will review what is known about elemental transfer and microbial processes at the sediment-basement interface, including new results from recent IODP Expeditions.

# Hydrothermal circulation at mid-ocean ridges – insights from the joint interpretation of models and data

Lars Rüpke<sup>1</sup>

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Hydrothermal discharge at so-called black smokers along the global mid-ocean ridge system continues to amaze and fascinate the interdisciplinary marine sciences community. Seawater penetrates into the newly formed seafloor along cracks and fractures to reach and react at high temperatures with partially molten rock to form a metal-rich hydrothermal fluid that rises buoyantly towards a vent site at the seafloor. These systems efficiently mine heat from the young ocean crust, sustain unique ecosystems in the other bleak environment of the deep seafloor, and modulate global biogeochemical cycles. Much has been learned about these systems and their role in the Earth System from marine surveys of mid-ocean ridge segments and direct observations of vent sites at the seafloor. Yet, the deep chemical and physical processes that control hydrothermalism remain inaccessible to direct sampling and observations. Here numerical models can help as they can be used to relate seafloor observations to processes and to elucidate the physical connections between interdisciplinary data sets. In this talk I will review the current state of hydrothermal flow modeling and show examples of how a joint interpretation of models and data can lead to a more fundamental understanding of hydrothermal activity on the ocean floor.

## **Anaerobic sediments host an efficient microbial barrier that consumes deep-subsurface-derived oil and gas**

**Gunter Wegener<sup>1,2</sup>**

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In deep marine sediments, geothermal heat transforms organic matter into crude oil and natural gas, primarily composed of alkanes. The alkanes tend to migrate towards the sediment surface, however an efficient microbial barrier refuses their passage to the water column. My team studies the coupling of alkane oxidation to sulfate reduction and methane formation, the primary sinks of alkanes in the seafloor and reservoirs. From gas and oil-rich sediments, such as the Guaymas Basin, Gulf of California, we culture key taxa and resolve their function. The cultures consist of dual-species consortia of archaea and bacteria. The archaea face the challenge to activate substrates with only very stable C-H bonds. They master it with specific variants of methyl-coenzyme M reductases (MCR), an enzyme class that was before described to release methane in methanogens. All alkane-oxidizing archaea completely oxidize their substrates to CO<sub>2</sub>, but they do not have respiratory pathways. In contrast, they transfer the reducing equivalents to their sulfate-reducing partner bacteria, organized via direct interspecies electron transfer. Our research illuminates the role of archaea in alkane transformations, and emphasizes the syntrophic interrelations microorganisms, which have the key role in the gas and oil transformations in the largest known microbial REACTOR on Earth, also known as the oceanfloor.

## **List of Abstracts: Posters**

### **Algal sulfated fucan: a global carbon sink**

**Aman Akeerath Mundanatt**<sup>1</sup>, Silvia Vidal-Melgosa<sup>1,2</sup>, Jan-Hendrik Hehemann<sup>1,2</sup>

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Sulfated fucans are fucose-containing sulfated polysaccharides, which are produced by brown algae and by diatoms. Sulfated fucans from brown algae typically consist of an  $\alpha$ -1,3- or  $\alpha$ -1,3;1,4-linked-L-fucose backbone, sulfate groups on different positions, and also different side chains with fucose and/or other monosaccharides. A high level of diversity is observed in the structures of sulfated fucans produced by different species of algae. Algae are also known to modify the structures of sulfated fucans depending on the season. The complexity and heterogeneity of their structures make it hard for bacteria to degrade them. In addition, negatively charged sugars like sulfated fucans can assemble into polymeric gels, which can aggregate with other particles and may eventually sink to the deep sea and sediment. Hence, we hypothesized that sulfated fucans can sink to deep depths and the sediment while resisting bacterial degradation, thereby acting as a carbon sink. We tested our hypothesis by investigating the presence of sulfated fucan in sediments of different depths from various regions i.e., the Black Sea, the Mediterranean Sea, the Bransfield Strait, and the South Pacific. We used monoclonal antibody-based methods like enzyme-linked immunosorbent assay and microarray analysis with the monoclonal antibody BAM1, which binds to an un-sulfated epitope of sulfated fucans. By the antibody-based methods, we were able to detect the presence of sulfated fucans in sediment from the different regions. We detected sulfated fucan in sediments as old as 11.5 ka and 125 ka. This indicates sulfated fucans can indeed sequester carbon for several millennia.

## Limited duration of carbonate formation in Louisville Seamount basalts revealed by *in situ* U–Pb dating

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Hydrothermal carbonate formation in basaltic oceanic crust is recognized as a major CO<sub>2</sub> sink that contributes to regulating the Earth's long-term climate. The controls on and duration of carbonate formation remain, however, incompletely understood.

Here, we present *in situ* U–Pb age dating to determine calcite and aragonite precipitation ages within basalts drilled at the Louisville Seamount chain, SW Pacific. We show that the carbonates formed between ~72 and 37 Myr ago—that is, relatively speaking, >90% grew within 20 Myr after seamount formation. Carbonates in vesicles mostly precipitated within 8 Myr (median = 2.9 Myr) after seamount formation whereas carbonate growth in veins took place over longer periods of time (median = 8.1 Myr). Geochemical and isotopic data imply carbonate formation at <25°C under oxidizing to slightly reducing conditions, pointing to variable seawater–rock reaction.

Our timescales of carbonate growth in these seamounts are very similar to those observed in mid-ocean ridge basalts, even though seawater circulation through the seamounts is not inhibited by low-permeability sediments and likely continues long after carbonate precipitation has ceased. Our results hence suggest that such open circulation of seawater is not the primary control on the formation of carbonates. Further, despite the vast number of seamounts worldwide that react with the ocean over tens of Myr, the limited duration of carbonate growth may confine their potential to take up CO<sub>2</sub>.

## The Sr-isotope signature of pre-Messinian fluid sources in pore fluids of eastern Mediterranean mud volcanoes

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New Sr-isotope data of pore waters from three mud volcanoes (MVs) and two brine pools with high chlorine concentrations ( $\text{Cl}^- > 5128 \text{ mM}$ ) located in the Mediterranean Ridge Accretionary Complex show low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios typical of late Miocene to Oligocene seawater. During the Messinian Salinity Crisis, the Mediterranean Sea was cut off from the global oceans, resulting in a gradual decrease of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of Messinian seawater. Messinian evaporites thus captured the Sr isotopic signatures of the Messinian seawater. The Napoli MV was the first structure discovered during ODP Leg 160 at the MedRidge to show highly saline pore waters influenced by the dissolution of underlying Upper Messinian evaporites. Pore waters from additional samples of Heraklion MV, Gelendzhik MV and two brine pools, collected during RV SONNE cruise SO278 in 2020, show a similar  $^{87}\text{Sr}/^{86}\text{Sr}$  signature as the Napoli MV. The Gelendzhik MV though, which is located on a major strike-slip fault, contains pore waters with low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and exceptionally high Sr concentrations (2.22 mM), which plotted over Sr/B indicates the involvement of a second, major fluid source. These fluids are possibly derived from carbonates, stratigraphically deeper than the Messinian Evaporites. Comparison of the pore water  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios with the global Sr-isotope curve point to an Oligocene or older carbonate source for the pore waters.



## Well-Hidden Methanogenesis in Deep, Organic-Rich Sediments

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Despite the ubiquity of methanogens in anaerobic marine sediments and their crucial role in carbon cycling, the controls on their biogeography and contribution to methane production in the deep subsurface remain unclear. In this study, we focus on deep, organic-rich sediment samples from three sites at Guaymas Basin, Gulf of California with different levels of sill induced thermal sediment alteration (none, ancient, current). Using a multidisciplinary approach of thermodynamic calculations, metagenomic analysis, microbial enrichments, and methane isotope analyses (traditional and multiply substituted), we address the distribution of methanogens and methanogenic pathways and the microbial contribution to methane production in deep Guaymas sediments. We also aim to clarify if and how thermal alteration by magmatic sills impacts these distributions. Our results reveal methylotrophic methanogenesis pathways yield more Gibbs energy than the canonical hydrogenotrophic and acetoclastic methanogenesis throughout the sediment column of all sites. Phylogenetic clustering of key genes (*mcrA*, *mtaB*, and *mttB*) with known methylotrophic methanogens further supports the potential to utilize this pathway.

Overall, however, we find little genetic evidence of methanogens, suggesting they are a small proportion of the microbial community. Yet, at all sites, traditional ( $^{13}\text{C}/^{12}\text{C}$  and D/H) and multiply substituted ( $^{13}\text{CH}_3\text{D}$  and  $^{12}\text{CH}_2\text{D}_2$ ) isotope measurements indicate methane is predominantly of microbial origin near the SMTZ. This microbial signal is overprinted by non-microbial (thermogenic or abiotic) sources with depth, but the rate of overprinting varies significantly between sites, depending on the presence/absence and age/depth of a sill. We argue a multidisciplinary approach, such as the one used here, is necessary to capture the complexities of systems like Guaymas Basin.

## Similar but different: Comparative analyses of symbiotic and free-living methane-oxidizing bacteria (*Methyloprofundus*) from hydrothermal vents and cold seeps

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At deep-sea hydrothermal vents and hydrocarbon seeps, primary production is fuelled by free-living chemosynthetic bacteria as well as symbiotic chemosynthetic bacteria from invertebrate hosts. To reveal the ecological and evolutionary relationships between chemosynthetic free-living and symbiotic bacteria that use methane for gaining energy and carbon, we analysed the genomes of 50 methane oxidizers from the *Methyloprofundus* clade. Unexpectedly, we found evidence for repeated evolutionary transitions between free-living and symbiotic lifestyles, based on analyses showing that both lifestyles were interspersed throughout the phylogenomic tree. Ancestral state reconstruction revealed that some genes were conserved across both life styles, particularly those for core metabolic pathways gaining energy and carbon from methane, while others differed, such as genes for the degradation of polysaccharides, which were enriched in free-living species.

To investigate physiological differences between methanotrophic lifestyles, we compared the transcriptomes of two cultured *Methyloprofundus* species, one planktonic and one that forms biofilms, with those of three symbiotic species from deep-sea *Bathymodiolus* mussels. Contrary to our expectations, the transcriptomes of the symbiotic species were more similar to the free-living, biofilm-forming species, than the two free-living species were to each other. For example, genes for denitrification and quorum sensing were upregulated in both the mussel and biofilm methanotrophs, compared to the planktonic species. This suggests that for methanotrophs, life within a host cell more closely resembles that in a biofilm, than a planktonic lifestyle.

## **Natural asphalt seeps are potential sources for recalcitrant oceanic dissolved organic sulfur and dissolved black carbon**

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Natural oil seepages contribute about one-half of the annual petroleum input to marine systems. Yet, environmental implications and the persistence of water-soluble hydrocarbons from these seeps are vastly unknown. We investigated the release of oil-derived dissolved organic matter (DOM) from natural deep sea asphalt seeps using laboratory incubation experiments. Fresh asphalt samples collected at the Chapopote asphalt volcano in the Southern Gulf of Mexico were incubated aerobically in artificial seawater over 4 weeks. The compositional changes in the water-soluble fraction of asphalt-derived DOM were determined with ultra-high-resolution mass spectrometry (Fourier-transform ion cyclotron resonance mass spectrometry, FT-ICR-MS) and by excitation–emission matrix spectroscopy to characterize fluorescent DOM (FDOM) applying parallel factor (PARAFAC) analysis. Highly reduced aliphatic asphalt-derived DOM was readily biodegraded, while aromatic and sulfur-enriched DOM appeared to be less bioavailable and accumulated in the aqueous phase. A quantitative molecular tracer approach revealed the abundance of highly condensed aromatic molecules of thermogenic origin. Our results indicate that natural asphalt and potentially other petroleum seepages can be sources of recalcitrant dissolved organic sulfur and dissolved black carbon to the ocean.

## Brown algae inject fucoïdan carbon into the ocean

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Brown algae annually convert gigatons of carbon dioxide into carbohydrates, including the complex extracellular matrix polysaccharide fucoïdan. Fucoïdan sequesters brown algal carbon due to its persistence in the marine environment. The lack of techniques to identify and quantify complex polysaccharides in seawater has impeded accounting for fucoïdan carbon in the ocean. We adapted the techniques of anion exchange chromatography, enzyme-linked immunosorbent assay and biocatalytic enzyme-based assay for detection and quantification of fucoïdan in seawater. They revealed that fucoïdan constitutes up to half of brown algal exudates, a considerable fraction of primary production. *Fucus vesiculosus* in the Baltic Sea secreted 0.3% of their biomass as fucoïdan per day. Dissolved fucoïdan concentrations in seawater adjacent to algae reached up to 0.48 mg L<sup>-1</sup>. *F. vesiculosus* secreted fucoïdan at a rate of 28-40 mg C kg<sup>-1</sup> h<sup>-1</sup>, accounting for 44-50% of all exuded dissolved organic carbon. Our most recent results demonstrate that both Laminariales and Fucales enrich the surrounding seawater with fucoïdan, which shows little no degradation over weeks. Composed only of carbon, oxygen, hydrogen and sulfur, fucoïdan secretion does not consume nutrients enabling carbon sequestration independent of algal growth. Extrapolated over a year, the algae sequester more carbon into secreted fucoïdan than their biomass. The global utility of fucoïdan secretion is an alternative pathway for carbon dioxide removal by brown algae without the need to harvest or bury algal biomass.

# Beyond Spreading Rate: Controls on the Thermal Regime of Mid-Ocean Ridges

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The thermal regime of mid-ocean ridges (MORs) reflects a balance between heat supplied by magma cooling and crystallization, and heat lost through hydrothermal circulation. Given a global average crustal thickness ( $H_c$ ) of 6 km, standard thermal models predict that thermal regimes of the MOR drastically cool as the full spreading rate ( $U$ ) decreases below 60 km/Ma (Phipps Morgan and Chen, 1993). This prediction is widely accepted as it fits well with depths of seismically-imaged crustal mush zones (low velocity anomalies and/or axial melt lenses (AMLs) reflectors) at fast and most intermediate spreading ridges. However, at slow and ultraslow ridges ( $U < 40$  km/Ma), the standard model fails to predict crustal mush zones, although they were discovered at the center of magmatically robust segments such as Lucky Strike on the Mid-Atlantic Ridge and 50.5°E on the Southwest Indian Ridge. Here we present 2-D thermal modelling results that couple repeated melt injections and convective hydrothermal cooling. We benchmark AML depths predicted by our model against the standard model, assuming  $H_c = 6$  km and  $U > 60$  km/Ma. Our calibrated model indicates that melt flux ( $U \times H_c$ ), not spreading rate, is the primary control on AML depth. At  $U < 40$  km/Ma, other factors such as the rate of dike intrusion relative to the plate separation, the depth extent and permeability of the hydrothermal domain, and cyclic changes in melt supply also play important roles.

## Untargeted mapping of polar organic compounds in suspended particulate organic matter off Cape Blanc, NW Africa

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Well-known biomarkers provide important chemotaxonomic information on biological communities and carbon fluxes in different environmental settings. However, the focus on the known can be laborious, time-consuming and informative, yet unknown, compounds may be overlooked. To overcome these limitations, we applied an untargeted approach to examine organic molecules detected by HPLC-MS in suspended particulate matter (SPM) collected in the Eastern Boundary Upwelling system off Cape Blanc. The Canary Current upwelling system off Cape Blanc offers an ideal natural laboratory to study the microbial production of biomarkers under different environmental conditions and their decomposition during lateral and vertical transport in the water column. Here, samples from six stations along a transect from organic-rich shelf waters to the oligotrophic North Atlantic were analyzed.

The untargeted approach detected 93,134 compounds. The majority cannot be identified and may have been neglected by traditional HPLC-MS data processing routines. Principal component analysis (PCA) revealed three distinct molecular assemblages across the investigated transect: a) shallow near-shore; b) intermediate; and 3) deep-offshore. Paired with environmental data and isotopic variations ( $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$ ) of the bulk C species (DOC, POC, DIC), untargeted lipid characterization will significantly improve our understanding of the fate of OM on its journey through the water column, from primary production to burial in sediments.

## Impact of phytoplankton composition on aggregate formation and carbon export in the southern Weddell Sea

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Climatic changes in the Southern Ocean have strong implications for the global marine carbon cycle, for example through changes in phytoplankton community composition. These changes can affect the strength and efficiency of the biological carbon pump, which exports carbon to the deep sea via the aggregation and sinking of phytoplankton and other organic matter. For the Southern Ocean, specifically the Weddell Sea, we only have limited data on carbon export due to the difficulties of accessing these remote and often ice-covered regions. Based on phytoplankton bottle incubations simulating future climatic changes, a possible shift in phytoplankton composition from large diatoms to small flagellates such as *Phaeocystis* sp. is indicated, with unknown consequences for nutrient cycling and carbon export. To address these unknowns, we conducted *in situ* measurements and roller tank experiments with contrasting diatom-to-*Phaeocystis* ratios during a cruise to the Southern Weddell Sea to characterize the formation, degradation and sinking of marine snow. To our surprise, preliminary results reveal that once out of the euphotic zone, *Phaeocystis*-rich aggregates are very good at exporting carbon to depth despite the purported lack of ballasting minerals. The complex interplay between ballasting effects and transparent exopolymeric particle content effects that *Phaeocystis*-dominated communities do not seem to impede carbon export in the Weddell Sea, but may actually enhance it.

# Organic matter degradation in Arctic shelf sediments: controls and feedbacks on organic carbon burial, nutrient fluxes, and benthic carbonate chemistry

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The Arctic Ocean is disproportionately influenced by climate change driven changes in sea-ice cover and circulation, ocean acidification and seawater warming with poorly known consequences for ocean primary productivity and carbon cycling. Even more uncertain is the response of the benthic ecosystems and seafloor processing of carbon to such conditions. To address this knowledge gap, we carried out a model-data study with focus on the Barents Sea shelf.

We targeted a sea-ice and water mass gradient to quantify benthic organic matter degradation and its impacts on benthic processes. Our results reveal that the reactivity of organic matter exerts the main control on degradation processes, which are decoupled from the environmental gradient imposed by sea-ice cover. We also find that nutrient efflux is largely driven by reactivity patterns, with contributions from internal redox controls. Degradation rates also control downcore changes in pH and saturation state, which are further modulated by bottom water chemistry. Despite that, alkalinity and DIC benthic fluxes show a clear zonal trend along the transect, which is amplified by CaCO<sub>3</sub> contents of sediments. Finally, we performed a series of sensitivity tests to estimate how plausible climate change scenarios may impact benthic organic matter dynamics. We find that fluctuation of organic matter fluxes to the seafloor have a drastic impact on both (in)organic carbon burial and benthic fluxes of nutrients, alkalinity and DIC.



# One million years of interplay between tectonics and hydrothermal activity in a rifting ocean basin

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Hydrothermal flow at the seafloor is the near-surface expression of heat transfer from the core of the Earth, and influences ocean and subsea chemistry, providing a basis for chemosynthetic ecosystems and development of mineral deposits. The characteristics of hydrothermal fields reflect a dynamic interplay between three major factors: heat sources and heat flow across the seafloor; permeability of faults, fracture networks and geological formations; and fluid flow patterns, such as large-scale groundwater convection, recharge and fluid chemistry. Computer simulations help to understand these dynamics. Yet, the wildly different spatiotemporal scales of extensional tectonics and the fast-moving fluid flow, leads to strong computational limitations when trying to couple both. This has narrowed the scope of numerical simulations of hydrothermal flow in active rifting and ocean spreading to static geological situations, perhaps including the effect of heat release by magmatic bodies. Here we describe the dynamics of the interplay between the extensional geological system and basin-scale hydrothermal circulation with a coupled Thermo-Hydro-Mechanical (THM) model for one million years. The reorganization of fluid patterns can clearly be seen responding to the development of faults and fractures, which themselves see their life expectancy modulated by the cooling or heating of the advecting flow.

# High-resolution insight into microbial community zonation in hydrothermal sediments via mass spectrometry imaging of intact polar lipids

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Intact polar lipids (IPLs) are a powerful tool to describe microbial communities based on their biogeochemical imprint in sediment. However, the spatial resolution is limited by the sample sizes required in traditional biomarker analysis. Here we conduct high-resolution mass spectrometry imaging (MSI) on hydrothermal sediment from the Guaymas Basin to obtain unprecedented insight into the spatial distribution of IPLs, representative of distinct microbial communities responding to steep thermal and geochemical gradients. The highly resolved distribution of IPLs not only shows great consistency with corresponding concentration profiles obtained by extraction-based approaches but sheds light on fine-scale shifts not captured by conventional analysis. The sediment is characterized by a thermally induced habitat compression to a narrow zone in the surface layers, dominated by signals of anaerobic methane-oxidizing archaea (ANME). Small-scale shifts in geochemical conditions are well reflected in MSI, as ANME-derived biomarkers abruptly decline at 2.5 cmbsf, coinciding with sulfate depletion. Likewise, a millimeter-scaled intrusion of oxygenated porewater at the sediment surface is marked by an appearance of intact archaeols below 0.5 cmbsf. Our study provides a basis for exploring fine-scale microbial community zonation in response to subtle shifts in the geochemical environment, ultimately enhancing our understanding of the complex biogeochemistry in hydrothermal sediment.

## **Dissecting the intricate Mg systematics during hydrothermal basalt glass alteration – insight from experiments at 70, 150 and 250°C (40 MPa)**

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Magnesium is crucially affected by interactions between seawater and the oceanic crust and thus has great potential as a sensitive indicator for the associated mass transfer. But the use of Mg isotopes as tracer has been limited, as isotope fractionation is masked by a quantitative Mg loss that occurs during high T hydrothermal alteration of fresh basaltic crust. In 3 batch experiments we reacted fresh basalt glass with seawater over a range of temperatures (70, 150 and 250°C) at which Mg removal can remain incomplete and associated isotope fractionation becomes significant. All experiments were characterized by a loss of Mg from the fluid. At 250°C, the removal was complete after 6 days, while at 150°C, 30% of the Mg were left after the 57 days. At 70°C, even 84% of Mg were left after 328 days. At 150 and 250°C (16.3 and 27.8 wt.-% reaction turnover (RT)), the retrieved glass was densely overgrown by smectite as the only secondary Mg phase, while anhydrite had precipitated in the interstitial space between grains. At the higher T, Mg loss from the fluid came with a preferential incorporation of the heavier Mg isotopes into smectite. A preferential loss of the lighter isotopes was observed in the 70°C run when the mass-balanced RT was only 1.8 wt.-%. Careful mass balancing of the evolving fluid composition reveals how Mg isotope ratios are variably dominated by basalt glass dissolution and by precipitation from the oversaturated solution throughout the alteration process.

## Iron and DOM transformations in coastal sands

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Sandy permeable sediments allow for advective porewater transport and thus rapid solute entrainment, which strongly shapes the conditions under which organic matter degradation occurs. Depending on hydrodynamics, fluctuating oxygen inflow leads to a high temporal variability of redox conditions in the sediment. Further, a strong divergence in mass transport occurs for substances that are subject to changes between solid and dissolved phases, such as iron and adsorbed/co-precipitated compounds. Here we present highlights of several studies investigating the change of DOM composition and iron phases under advective porewater flow and changing redox conditions. Experiments showed that Fe(III) oxyhydroxides were the major electron acceptors during anoxic incubations, and most of the reduced Fe (96%) remained in the solid phase throughout. The washout of dissolved Fe<sup>2+</sup> was minor and the reduced Fe was available for re-oxidation with the next oxygen inflow. Further experiments revealed that DOM composition is significantly altered during the passage through the sand, showing an increase of chemo-diversity and decrease in bulk <sup>14</sup>C radiocarbon age, suggesting the preferential uptake of 'young' (labile) DOM. In field samples we found that DOM was loosely adsorbed to solids and a distinct fraction was preserved by labile iron minerals. In summary, these findings suggest a dominant Fe redox cycling in sands with a strong control on the preservation/mobilization/consumption of distinct DOM fractions.

# Dissolved As, Sb, Tl, Pb, Ag, Cd and Co in hydrothermal vent fluids from the Atlantic, Indian and Pacific Ocean

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Most submarine hydrothermal activity occurs along mid-ocean ridges, intra-oceanic island arcs, and in back-arc basins. According to the location, a wide range of pressure, temperature, pH and redox conditions, variable host rocks as well as magmatic degassing can affect the composition of hydrothermal vent fluids and their associated precipitates. The variable impact of these processes on the composition of major (e.g., Cl, SO<sub>4</sub>, Na, Mg) and minor and trace elements (e.g., Ca, Sr, Li, Si, Fe, Mn, Cu, Zn, REE) elements in vent fluids has previously been studied. However, data for dissolved concentrations of more “*exotic*” trace-metals such as As, Sb, Tl, Pb, Ag, Cd, Co are significantly less common.

Here we report on the distribution of these “*exotic*” elements in hydrothermal vent fluids from the Atlantic, Indian and Pacific Ocean with different tectonic settings and variable host rock compositions spanning ultra-mafic rocks to rhyolites. The analyzed vent fluids are affected by water-rock interaction, sub- and super-critical phase separation, (subsurface) conductive cooling and/or cooling by mixing with ambient seawater, mineral precipitation induced by mixing or phase separation, and input of magmatic volatiles in some cases. This data set allows for assessing the relative importance of these processes and their effect on preventing or facilitating the release of these trace-metals into the ocean.

## **The effect of permeability on the pressure regime in 2D outcrop-to-outcrop submarine hydrothermal flow models**

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The significant discrepancy between the observed conductive heat flow and predictions by thermal models for oceanic lithosphere younger than 50 Ma is interpreted to result from hydrothermal circulation between basement outcrops. Numerical fluid flow simulations between such outcrops performed in previous studies revealed that establishing horizontal pressure gradients to drive a siphon flow requires high aquifer permeabilities and a contrast in the outcrops' transmittance. However, most studies focused on the parameters that sustain a hydrothermal siphon, while the physical processes that create it in the first place remain poorly constrained. To shed more light on the physics behind the flow, a synthetic 2D model was set up. Fluid flow modelling was done by using hydrothermalFoam, a hydrothermal transport model based on the computational fluid dynamics toolbox OpenFOAM. Our initial results reveal two key points that are essential to generate a flow: First, the outcrops permeability has an effect on its average pressure. High permeabilities lead to a rather "cold" hydrostatic pressure regime with lower temperatures and hence higher average pressure. Lower outcrop permeabilities are accompanied with a rather "warm" hydrostatic pressure regime. Secondly, fluid convection in the aquifer is necessary to establish a siphon flow. The aquifer permeability must be sufficiently high to overcome Darcy resistance and yet low enough to prevent the flow from being solely diffusive.

## Sulfur formation in the Kemp Caldera hydrothermal system

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The Kemp Caldera is a submarine arc caldera volcano, which belongs to the southernmost part of the South Sandwich island arc, located in the Scotia Sea. The caldera was discovered by the R/V *James Clark Ross* research cruise JR224 in 2009. Hydrothermal activities were observed within the caldera, especially around the resurgent cone in the center of the caldera, where extinct chimneys and white smoker vent fields are found. A phenomenon of the Kemp Caldera hydrothermal system is the occurrence of elemental sulfur at uncommonly high pH values. Samples of elemental sulfur from the white smoker vent fields Great Wall and Toxic Castle, located at the eastern flank of the resurgent cone, were recovered with a remotely operated vehicle during the R/V *Polarstern* PS119 expedition in 2019. The sulfur at Great Wall is crystalline, while at Toxic Castle the sulfur is liquid and forms pearl-like structures. The fluids of both sites have temperatures in the range from 63 to > 200 °C with pH<sub>25 °C</sub> values > 5. The most interesting thing, however, is the isotopic composition of the elemental sulfur, ranging from  $\delta^{34}\text{S}$  values of +5.2 to +5.8 ‰. Commonly, disproportionation of magmatic SO<sub>2</sub> explains the formation of sulfur in arc/back-arc systems. Elemental sulfur precipitates from highly acidic hydrothermal fluids with pH-values  $\leq 1$  and shows negative  $\delta^{34}\text{S}$  values due to isotope fractionation. However, disproportionation cannot explain the moderate fluid pH and the positive  $\delta^{34}\text{S}$  values for sulfur that would indicate SO<sub>2</sub> disproportionation. It is suggested that the sulfur formation in the Kemp Caldera hydrothermal system is a result of SO<sub>2</sub> and H<sub>2</sub>S synproportionation. From a thermodynamic point of view, this formation mechanism is feasible and it has been experimentally demonstrated that it can take place in natural hydrothermal systems. Our study focuses on the formation of elemental sulfur in the Kemp Caldera hydrothermal system and shows that the diversity of hydrothermal arc/back-arc systems may be greater than previously assumed.

## Characterizing chemosynthetic microbial communities in abyssal serpentinites: a lipid biomarker approach

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Molecular (H<sub>2</sub>) hydrogen produced during serpentinization is considered to strongly promote the sub-seafloor chemosynthetic microbial communities. Nevertheless, unlike in ultramafic hosted hydrothermal systems, evidence of exhumed abyssal serpentinites to harbor microbial life remains inconclusive.

We investigated serpentinites from the Romanche Fracture Zone at the Mid-Atlantic Ridge in order to examine their potential in hosting chemosynthetic endolithic microbial life.

Petrological and geochemical analyses revealed distinct alteration stages at/close to the seafloor where H<sub>2</sub> was likely produced by Fe<sup>2+</sup> oxidation associated with the dissolution of olivine and/or brucite.

Biomarker analyses revealed presence of archaeal and bacterial diether and tetraether lipids as well as a dominance of bacterial glycolipids over phospholipids, which we interpret as a membrane adaptation of endolithic communities to the energy and nutrient-deprived environment. Similar to the unique biomarkers found at the famous serpentinization Lost City hydrothermal vent site, this study also reports the presence of bacterial dietherglycerols (DEGs) with one sugar (1G) head groups in serpentinized abyssal peridotites. Biomarker results together with stable carbon isotope data of the total organic carbon (−27.9‰ to −22.6‰) suggest an in-situ chemoautotrophic source of the detected biomass, and hence provides strong evidence for endolithic microbial communities to have been present in Romanche serpentinites.



## Clumped methane isotopologue-based temperature estimates for sources of methane in submarine gas hydrates

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Gas hydrates stored in the world's continental margins represent the largest global reservoirs of methane. Stable isotope ratios ( $^{13}\text{C}/^{12}\text{C}$ , D/H) of methane and the molecular ratio of hydrocarbons ( $\text{C}_1/(\text{C}_2+\text{C}_3)$ ) have traditionally been applied to infer methane sources. However, the interpretation of compositional information can be complicated by postgenetic mixing and alteration.

We measured the abundance of clumped methane isotopologue ( $^{13}\text{CH}_3\text{D}$ ) alongside  $\delta^{13}\text{C}\text{-CH}_4$ ,  $\delta\text{D}\text{-CH}_4$ , and  $\text{C}_1/(\text{C}_2+\text{C}_3)$  for submarine gas hydrate specimens from 11 regions of the world's oceans associated with different seafloor seepage features. With this data, we assigned isotope-based ranges of apparent temperatures to the different geological processes. The average apparent equilibration temperatures of methane from the  $\Delta^{13}\text{CH}_3\text{D}$  geothermometer increase from cold seeps (15–65 °C) and pockmarks (36–54 °C), to oil-associated gas hydrates (48–120 °C), which matched putative formation processes. These temperatures are largely consistent with a dominance of microbial methane production. Methane from mud volcanoes yielded a wide range of temperatures (15 to 313 °C). These formed two distinct geochemical groups for mud volcanoes located at active convergent plate margins and for those in tectonically less active or passive settings. This study is the first to document the link between isotopologue-based temperature estimates and key seafloor seepage features, and validate previous models about geologic driving forces.

# **Towards an investigation of the transport of particles along and across the Irish continental shelf – hydroacoustic measurements during MSM107**

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We aim at a better understanding and prediction of the transport of sediment and biogenic particles by oceanographic processes along and across continental margins, their deposition on the shelves and slopes, and the interaction between biogeochemical cycles and sediment properties. To do this, we require the hydrodynamics forcings (e.g. strength and direction of tidal and residual currents), the surface and subseafloor sedimentological properties and seabed morphology in key areas, such as the Irish continental shelf.

As part of MARUM's Cluster of Excellence, "The Ocean Floor – Earth's Uncharted Interface", a cruise was organized from 17 May to 4 June 2022 on the research vessel Maria S. Merian to investigate the formation, transport and transformation of organic material on and off the western Irish shelf. During the cruise, hydroacoustic and oceanographic measurements were conducted in order to characterize hydrodynamics, sedimentology and seafloor geomorphology. Specifically, current measurements were taken with ship-based and lowered Acoustic Doppler Current Profilers (ADCP), bathymetry was recorded using a multibeam echosounder, subsurface sedimentary layers and water column were imaged with a PARASOUND sub-bottom profiler, and sediment samples were acquired using a multicorer and a Van Veen grab. Here we present some preliminary results of these hydroacoustic and oceanographic measurements collected during the cruise.

## **Particle-associated bacteria produce a versatile collection of extracellular enzymes throughout the Western North Atlantic**

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The fate of organic matter in the deep ocean is dependent in part on the activities of heterotrophic microbes. These bacteria initiate remineralization of organic matter by producing a diverse array of extracellular enzymes to hydrolyze complex substrates to smaller sizes that can be taken into the cell. The enzymatic repertoire of specific members of a microbial community—and the community as a whole—determine the extent to which complex organic matter can be recycled in different zones of the ocean. We compared the composition and functional capabilities of particle-associated and whole seawater communities at three depths and eleven stations in the western North Atlantic. At most depths and locations, particle-associated bacteria hydrolyzed a considerably broader spectrum of peptide, glucose, and polysaccharide substrates than whole water communities. These differences in enzymatic capability between whole water and particle-associated communities were typically greater at offshore locations, and with increasing depths. Higher cell densities and concentrations of organic matter on particles provide a suitable environment for a wider array of enzymatic tools, accounting for the rapid transformation of particulate organic matter sinking in the ocean. Thus, the efficiency of the biological pump—and ultimately the nature and quantity of carbon reaching the ocean floor—depends in part on the activities and enzymatic capabilities of these particle-associated communities.

# Signatures and Proportions of Lithogenic, Hydrothermal and Authigenic Mineral Fractions in Ridge Flank Sediments of the East Pacific Rise

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Ridge flank sediments of the East Pacific Clarion Clipperton Zone are intriguing research targets due to their complex mineralogy and dynamic geochemical zonation. Our study reconstructs the sediment sources and formation of abyssal sediment core SO240-69SL (12° 39.855' N, 119° 13.374' W, 4275 mbsf) back to 3.59 Ma by combining rock-magnetic and element composition data with endmember-modelling. The sediment appears to consist of four major components: (1) a bottom-current transported lithogenic source, derived from weathering of crustal rocks, (2) a low-temperature hydrothermal component of iron-rich clay minerals, (3) a calcareous fraction limited to the lower part, and (4) authigenic iron-manganese minerals that precipitated at present and past redox boundaries.

Low-temperature hydrothermal precipitation alongside with biogenic carbonate preservation dominated the high sediment input from 3.59 to 2.82 Ma. From this time onward, endmember-modelling shows an upward decrease in hydrothermal precipitation, possibly related to increasing distance from the hydrothermal source. A pronounced change in sediment colour as well as magnetic and geochemical properties marks a pause in deposition from 2.41 to 1.14 Ma, indicating a major shift in the sedimentary environment towards lithogenic-dominated sediments accompanied by a decrease in sedimentation rates from 1.02 to 0.25 cm ka<sup>-1</sup>. Thus, the core provides a unique record of hydrothermal, lithogenic and authigenic sediments in the Clarion Clipperton Zone.

# Geospatial characterization of organic carbon in continental margin sediments worldwide

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Continental margins play an important role in regulating the global carbon cycle since they receive large amounts of terrigenous and marine organic carbon (OC). The contrasting OC sources and diverse environmental conditions along continental margins influence their capacity to effectively sequester OC, leading to highly heterogeneous margins. Using >13500 datapoints of OC and >2500 datapoints of radiocarbon (expressed as fraction modern; Fm) in surficial sediments stored in an updated version of the Modern Ocean Sediment Archive and Inventory of Carbon (MOSAIC) database, we aim to locate sites where new (high Fm) or old (low Fm) OC is deposited and constrain the factors that drive these processes. Large quantities of new OC occur in areas with high primary productivity that supply fresh OC and in oxygen minimum zones that prevent its degradation, acting as sinks of marine OC. In contrast, high concentrations of aged OC are deposited offshore rivers and in high latitudinal settings that receive large amounts of pre-aged terrestrial OC, acting as sinks of terrestrial OC. Broad shelves are characterized by low concentrations of aged OC where continuous cycles of sediment resuspension and redeposition promote its ageing and degradation. This spatial analysis identifies the environmental conditions that promote the preservation of terrestrial or marine OC or its degradation in continental margins, which helps to characterize their role in the global carbon cycle.

# **Particulate organic matter export flux and ecosystem change in the Cape Blanc upwelling region during the last 18 years reflected by dinoflagellate cysts: a sediment trap study**

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For understanding of the natural and human-induced changes in ocean carbon flux it is essential to obtain insight into the variability in particulate organic matter (POM) export flux to the deep ocean during the last decades. Here we present the export flux of dinoflagellate cysts on a sub-monthly resolution over the last 18 years collected by a sediment trap located in the Cape Blanc upwelling system. The location is characterized by year-round upwelling with maximal intensity in winter/spring and frequent input of Sahara dust, both fertilizing the surface ocean. Dinoflagellate cysts are produced by phototrophic and heterotrophic dinoflagellates living in the upper waters and form one of the key-group organisms in marine ecosystems. They can be used as representative for both the phyto- and zooplankton POM export signal as well as indicators for ecosystem change. We show that export flux composition in both trophic levels is highly variable with different association composition in each year at maximum upwelling intensity. Nevertheless, we observed a clear change in association composition at the year 2008 related to the enhanced input of dust in the region. The cyst association suggests that after this time a gradual increase in trophic state of the surface waters occurred. The strong intra- and inter-annual variabilities subscribe the importance of a long-term monitoring in order to determine natural and human induced ecosystem change.

## Quantifying fossil carbon utilization and release from eroding permafrost coastlines – results from an incubation experiment

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The carbon-rich permafrost bounded coastlines of the Arctic represent around a third of the total global coastline. Rising sea-level and temperatures are increasing erosion of these coastlines by tens of meters annually. Coastal erosion results in the mobilization of large quantities of previously freeze-locked fossil organic carbon, which then may become degraded, potentially causing a positive feedback loop. Despite the tremendous impact the mobilized permafrost organic carbon may have on atmospheric greenhouse gas levels, the extent to which eroded fossil permafrost organic matter can be utilized by microbes in the Arctic Ocean is poorly constrained. Hence, previous studies, models, and eventually decisions of policy makers have relied largely on assumptions on the strength of this permafrost carbon feedback. To tackle this issue, we incubated permafrost soil from the Lena delta in natural coastal sea water collected in the Arctic Ocean in the eastern Kara Sea. Using a multi-disciplinary approach combining biogeochemical analyses (C, N, & P), DNA sequencing of bacterial communities and radiocarbon dating, we are now for the first time able to prove and quantify fossil carbon utilization and establish tentative links to microbial communities. Our data clearly indicate that fossil permafrost organic carbon is highly bio-available to water column microorganisms, indicating that coastal permafrost erosion is a source of fossil carbon emissions, thus constituting a self-enhancing positive feedback loop of Arctic climate change.

## **Role of temperature on the seafloor methane emission estimates in the Western Black Sea basin**

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Methane gas emissions reported in the Western Black Sea sub-basin dominantly originate from biogenic sources, i.e., shallow in-situ organic matter degradation. However, basin-scale estimates on the amount of generated and released methane were not yet performed. We use the 3D numerical reconstruction of the Western Black Sea basin to calculate the rates and the total amount of hydrocarbon seepage at the seafloor throughout the basin history (98Ma-present). The model accounts for both biogenic and thermogenic methane formation in the source rocks, gas expulsion and migration towards the upper sedimentary layers and further to the seafloor. In this contribution, we discuss the magnitude and geological situation that controls the methane generation, migration and expulsion from additional sources like previously formed gas hydrate deposits. In this study, we focus on simulating basin-scale biogenic methane emissions in time and space and identify potential controlling factors such as temperature limits of microbial methanogenesis. We apply the temperature limits of 60°C, 80°C and 100°C to study in detail the influence of controlled methanogenesis on biogenic methane generation and migration in the system.



## **Dissolved organic matter cycling in the coastal upwelling zone off Cap Blanc, Mauritania**

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Dissolved organic matter (DOM) in the ocean contains 662 Pg C with a residence time of several thousand years. However, our knowledge of its long-term fate is still hampered by our limited understanding of DOM interactions with particulate organic matter (POM), which may be both, DOM sources and sinks. The Canary Upwelling Ecosystem (CUE) is one of the most productive areas of the North Atlantic Ocean. It is ideal to study POM-DOM interactions because it comprises particles from surface primary production, as well as extensive intermediate and bottom nepheloid layers. In our study we hypothesize that DOM age and molecular composition can be explained by interactions with different POM pools. We quantify dissolved organic N, S, and P in solid-phase extractable (SPE) DOM in combination with the molecular composition analysis via ultrahigh-resolution mass spectrometry. The DOM composition mainly varied with depth from the surface to the deep ocean. At greater depths, more unsaturated, aromatic compounds indicated relatively more recalcitrant DOM. We relate these trends to primary production and photodegradation in the surface ocean as well as rapid microbial degradation of labile compounds and mixing with deep water containing a more recalcitrant DOM pool. However, we found considerable deviations from these depth-related trends on the shelf and below the oxygen minimum zone which appeared to be independent among the different elements and DOM fractions. These differences may be explained by release of DOM from sinking or suspended particles from atmospheric sources or shelf erosion. Using radiocarbon analyses we are currently aiming to constrain the role of particle interactions as DOM sources or sinks in the deep ocean.

# Fluxes and properties of in the proximal hydrothermal plume at the Aurora vent field, Gakkel Ridge, Arctic Ocean

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The Aurora vent field (82°53.83 N 6°15.32 W) is located on a volcanic mount at the western edge of the ultraslow-spreading Gakkel Ridge in the Arctic Ocean, the slowest spreading mid-ocean ridge on Earth. Here, we present data on the water column plume and its fallout particles in the water column and the surrounding sediments, collected in 2014 during RV Polarstern cruise PS86. Dissolved Fe (dFe), dissolved Mn (dMn),  $\delta^3\text{He}$ , and  $\text{CH}_4$  show distinct enrichments in the plume samples relative to a background site. Using the observed maximum rise height of the water column plume of 800 m, the stratification and an estimated vent temperature of 370°C, we calculate the thermal output of the site as 20 MW. In plume particle samples, the Fe/Al ratios are, in contrast to the Mn/Al ratios, elevated compared to samples from background stations. This may indicate that Fe, but not Mn, forms particles in the plume. A positive correlation between Fe/Al, and element/Al ratios like As, P, Mo, V, Cr, Co, and Ni as well as elevated concentrations of these elements in surface sediment samples in close proximity to the active vent may be a sign of scavenging of these elements by the positively charged surfaces of Fe-hydroxide particles. Cu concentrations in surface sediments were found to be up to 8225 mg kg<sup>-1</sup>, while samples from sediment core tops a few kilometers off the site are much lower (around 50 mg kg<sup>-1</sup>), highlighting significant metal flux into sediments in the active vent proximity.

# Different micro-FTIR derived molecular characteristics of particular organic matter represented by dinoflagellate cysts with diverse sensibility to preservation

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The molecular composition of particulate organic matter (POM) and the depositional redox environment form key elements influencing marine carbon sequestration. Information about molecular change of POM during early diagenesis is still limited. We enhance this information by investigating the Attenuation Total Reflection micro-Fourier Transform Infrared spectroscopy derived molecular characteristics of POM in different redox settings. We studied recalcitrant POM with a characteristic morphology and close biological affinity represented by the dinoflagellate cysts *Impagidinium aculeatum* and *Impagidinium patulum* which walls consisting of carbohydrate-based polymers.

Spectral inter-specific differences were not observed in oxic and anoxic environments, different areas or different geological times. However, consistent compositional differences showed that *I. aculeatum* contains more C-O compared to *I. patulum*, suggesting the presence of secondary alcohols making it slightly less recalcitrant as *I. patulum*. Literature based comparisons document that vulnerable species show C=N, N-H, N-O, C-N bending/stretching and the presence of C=O and C-O bounds. This suggests the presence of nitrogen and olefins in the macromolecule that makes the molecules more reactive. We suggest that this would also make them more prone to microbial decay when the microbial community shows preference for “food” containing nitrogen, an essential nutrient, often being limited available in the open ocean.

## The Mg conundrum of the Kermadec Arc – new insights from Mg isotopes

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Magnesium is absent in high-temperature hydrothermal fluids, because the formation of Mg-rich minerals in the ocean crust during high-temperature water-rock interaction results in a quantitative loss of Mg from entrained seawater. In contrast, acid-sulphate fluids, another submarine vent fluid type, have Mg concentrations similar to or slightly below seawater, reflecting an absence of high-temperature water-rock interaction and thus no significant loss of Mg from the fluids. The acid-sulphate fluids collected from Brothers and Macauley volcano (Kermadec Arc, Western Pacific) differ from all previously known hydrothermal fluids as they have Mg concentrations above seawater Mg. Since previous studies could not sufficiently clarify and/or prove the origin of the high Mg concentrations, we use B, Li and Mg isotopes as a new approach to further understand the origin of Mg in these fluids. B and Li isotopes in all fluids reflect water-rock interaction with fresh and altered ocean crust. Magnesium isotopes in fluids from Macauley correspond to seawater, implying venting of a brine phase and Mg enrichment through phase separation in the fluids. In contrast, Mg-enriched acid-sulphate fluids from Brothers volcano have higher  $\delta^{26}\text{Mg}$  values than seawater. Our results suggest Mg leaching from unaltered basement and dissolution of caminite that may have formed during an earlier stage of high-temperature interaction with the ocean crust.

# Tackling geomorphological heterogeneity: a comparison of predictors and modelling approaches to assess the distribution of sedimentary organic carbon in submarine canyons

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Continental margins are the primary location of organic carbon (OC) burial in the ocean, and extensive efforts have been made to quantify the distribution of OC in continental margins worldwide. However, these global estimates do not account for the high geomorphological heterogeneity in continental margins, such as the influence of submarine canyons as sites of preferential OC deposition. This is partly due to the complex nature of these geomorphologies, since interpolation methods may not produce accurate predictions of OC deposition. We compare the accuracy of geostatistical external drift kriging with different machine learning approaches to predict surficial OC content in the extensively studied Nazaré Canyon (Central Portuguese margin) and its adjacent continental margin. We found that random forests using explicitly spatial covariates performed slightly better (RMSE=0.527 wt. %) than classical random forests (RMSE=0.534 wt. %) and predict the spatial distribution of OC substantially better than external drift Kriging (RMSE=0.705 wt. %). Distance to the canyon axis and surface rugosity are amongst the most important predictors of OC contents. The Nazaré Canyon contains almost 70% more OC per unit area (151 g m<sup>-2</sup>) in comparison to its adjacent continental margin (89 g m<sup>-2</sup>), proving that canyons are important sites of OC deposition due to their capacity of funnelling large quantities of sediment and OC towards the deep sea. Considering that submarine canyons incise all continental margins and that our findings suggest substantially higher carbon contents within those features, they should be accounted for in global estimates of OC deposition in continental margins worldwide.

## **High carbon mineralization rates in subseafloor hadal sediments - Result of frequent mass wasting**

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In the past 20 years, the exploration of deep ocean trenches has led to spectacular new insights. Even in the deepest canyons, an unusual variety of life and unexpectedly high benthic oxygen consumption rates have been detected while microbial processes below the surface of the hadal seafloor remains largely unknown. The information that exist comes from geophysical measurements, especially related to seismic research, and specific component analyses to estimate the carbon export. In contrast, no information is available on metabolic activities in deeper buried sediments of hadal environment. Here we present the first pore water profiles from 15 up to 11 m long sediment cores recovered during three expeditions to two hadal zones, the Japan Trench and the Atacama Trench. Despite low levels of organic debris, our data reveal that rates of microbial carbon turnover along the trench axes can be similar to those encountered in much shallower and more productive oceanic regions. The extreme sedimentation dynamics, characterized by frequent mass wasting of slope sediments into the trenches, result in effective burial of reactive, microbially available, organic material. Our results document the fueling of the deep hadal biosphere with bioavailable material and thus provide important understanding on the function of deep-sea trenches and the hadal carbon cycle.

## Secondary production and priming effect reshape the organic matter composition in marine sediments

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Organic matter (OM) in marine sediments is a crucial component of the global carbon cycle. OM degradation has been intensively studied but secondary production (production of microbial biomass via heterotrophic OM degradation) and priming effect (stimulation of degradation of recalcitrant OM through addition of labile OM) are often ignored even though they might affect the OM composition and the interpretation of organic and elemental proxies. To quantify the degradation, secondary production, and priming effect, we incubated anoxic sediments from Helgoland with either <sup>13</sup>C-labeled algal lipids or protein for 400 days. The results showed that 2/3 of lipids but only 1/4 of protein were mineralized into CO<sub>2</sub>, indicating that lipids are more easily degraded than proteins. Quantification based on amino acids suggested that ~6% of algal lipids were transformed into new biomass, which was quickly subject to further transformation. RNA-SIP indicated that the added substrates were mainly utilized by minor heterotrophic community members. Detailed reconstructions of the carbon budgets showed algal lipids stimulated substantial priming, which accelerated the degradation of sedimentary OM by a factor of 2.5 to 6. In contrast, protein addition did not induce a priming effect. RNA-SIP showed that sulfate- and iron-reducing bacteria were involved in the priming process. In summary, secondary production and priming effect play a crucial role in reshaping the OM in marine sediments, especially in scenarios with increased OM deposition due to expansion of oxygen minimum zones or glacier retreat.

## **Dinoflagellate cysts production, excystment and transport in the upwelling off Cape Blanc (NW Africa).**

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Gaining insight into particulate organic matter (POM) export production and lateral/vertical transport during settling is essential to understand the marine carbon flux. Here the export flux and settling of particles with a known biological origin (dinoflagellate cysts) was investigated during active upwelling off Cape Blanc (NW Africa) in August 2020.

Dinoflagellate cysts are produced in the upper water column by photo- and heterotrophic plankton. Comparison of their export flux and association composition in subsurface waters with that of deeper waters, notably from intermediate - and bottom nepheloid layers, provides information about lateral and vertical transport of POM particles in the silt-size fraction. Particles were collected in an active upwelling cell, an upwelling filament and along two onshore-offshore transects during two drifting trap surveys and by in-situ pump systems. In the central upwelling cell export production was lower than at its rim probably due to light limitation caused by the up- and downward movement of waters transporting plankton in and out of the photic zone.

Cysts were transported offshore in the surface water upwelling filament as well as in the intermediate- and bottom nepheloid layers with a maximal extension of about 130 km off the shelf break. At the most offshore stations both vertical and lateral cyst transport was observed. Therefore, sediments in the region will receive a mixture of regionally and locally produced POM.