SCIENTIFIC REPORT OF STSM

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Reference COST Action ES1301
Host Institution: Utrecht University, Department of Earth Sciences
Period: 01/04/2017 to 30/04/2017
Reference Code: **COST-STSM-ES1301-36149**

Purpose of the STSM

In sedimentary basins, overpressure development and pressure release result in submarine fluid and gas discharges into the ocean, which can occur slowly or abruptly and in cases, can reach the atmosphere. Understanding fluid escape processes and submarine mud volcanism in ocean basins is a key research topic for marine exploration and basin analysis. Its scientific interest concerns in particular the linkages between mud diapirism/volcanism and the presence of deep oil and gas reservoirs. The occurrence of mud volcanoes (MVs) indicates hydrocarbon-rich fluid migration and provides a key to unraveling the hydrocarbon potential at depth (*Ivanov, et al., 1998; Kholodov, 2002; Dählmann and de Lange, 2003; Haese et al., 2006; Hensen et al., 2007; Scholz et al., 2009; Magalhães et al., 2012, Hensen et al., 2015)*.

Recent studies have identified active discharge of methane-rich fluids based on geochemical profiles of pore waters (e.g., *Haese et al., 2006; Hensen et al., 2007; Scholz et al., 2009)*. However, these investigations focused on liquid and gas phases without analyzing and integrating data from sediments and rocks that are expelled to the subsurface. Rocks and sediments are intimately linked with gases and fluids, and they are excellent indicators of source strata and oil potential of deep parent bed layers where MVs root. We pursue in assessing the impact of mud volcanism within the West Mediterranean based on cutting-edge multidisciplinary approaches in marine research using sensitive geochemical, mineral and sediment techniques. The scope this FLOWS STSM is to recognize single eruptive events to give more accuracy and quality in the quantification of discharge rates of hydrocarbons (mainly methane)-rich fluids and to understand mechanisms controlling migration and generation of fluids to lately understand the chemical fluxes besides patterns of MV-activity. Data will contribute to a thorough understanding of the behavior of recent eruptions, to obtain specific details about the hydrocarbon potential of deep reservoirs and deep fluid fluxes, which may contribute for further monitoring of submarine geologic hazards linked to mud volcanism and mud diapirism.

Description of the work performed during the STSM

During the 30 days of my stay at the Department of Earth Sciences (DES) at Utrecht University (Utrecht, the Netherlands), I have performed the preparation, analysis and interpretation of a variable set of data, including major and trace elements, total organic carbon, total nitrogen,

bulk and clay mineral assemblages of solid phases of mud breccia matrices from the active Carmen mud volcano (Alboran Sea).

To achieve the main target I sub-sampled the piston core GP09PC from Carmen mud volcano. Prior to perform the geochemical and mineralogical analysis, all discrete samples of mud breccia matrices were previously dried in an oven at 40 ºC and later ground and homogenized in an agate mortar.

For Coupled plasma atomic emission spectroscopy (ICP-OES) was performed for major element determinations (Al, Ca, Mg, K, Fe, Mn, Na, P, S). Analyses were done by spectrometry via a Perkin Elmer Optima 8300 (Dual vision) and autosamples Perkin Elmer S10.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was performed for trace element and rare earth element (REE) determinations and on the same samples as for ICP-OES. Measurements were done by spectrometry via a Perkin Elmer Scienx-Elan 5000 spectrometer.

For total organic carbon (TOC) 1000 mg of each sample was decalcified using 1 M HCl. The decalcified samples were again dried at 40 ºC and finely ground using an agate mortar. Decalcified samples were afterwards put into specific silver cups and carefully weighted in a high precision microbalance. For TOC and TN contents samples were weighted between 5-20 µg. After weighing, TOC and TN were determined on a Fisons Instruments NCS NA 1500 analyzer using dry combustion at 1030ºC. The isotope data were reported in the conventional delta notation with respect to VPDB. Precision (≤0.1‰) and accuracy were established using international (Graphite quartzite standard NAXOS (GQ)), and in-house standards (Ammonium Sulphate (ASS), Acetanilide, and Atropine).

Bulk and clay mineral composition was determined by X-ray diffraction (XRD). Separation of the <2 µm fraction and preparation of samples for XRD analyses were performed by sequential decalcification and centrifugation. X-ray diffractograms were obtained using a PANalytical X´Pert PRO diffractometer equipped with an X'Celerator solid-state linear detector, using a step increment of 0.01° 2θ and a counting time of 1 s/step, with Cu-Kα radiation (45 kV, 40 mA) and an automatic slit. Scans were run from 3-50º for untreated clay preparation as well as for glycolated samples.

Description of the main results obtained

Inorganic and organic geochemical determinations on expelled mud volcano materials from Carmen mud volcano serve as proxies elucidating past activity so as to reconstruct ancient pulses of methane seepage and paleo-sulfate-methane transition zones and at the time provide relevant information about the nature of source units feeding MVs, whereas bulk and clay mineral data provide information about mineral transformation, diagenesis and fluid sources.

During this FLOWS STSM sample preparation and a wide range of analyses have been successfully performed. Preliminary results have shown that mud breccia samples from piston core GP09PC have similar geochemical characteristics compared to mud breccia samples from core GP05PC, which was investigated during the previous STSM. In the case of GP09PC, depth trends have revealed enriched fronts in redox-sensitive elements (e.g., Mo, V, Ni). Also

the carbonate ($CaCO_3$) content of mud breccia matrix from GP09PC show similar values compared with other mud volcanoes. Sr/Ca vs Mg/Ca signatures reveal most likely Mg-calcite (after *Bayon et al., 2007*), being thus in line with other mud breccia matrices investigated in neighbors gravity and piston cores at Carmen MV. Total organic carbon (TOC) content in the investigated mud breccia matrix samples has reported some interesting peaks in depth. Similarly, nitrogen and sulfur content also exhibit comparable trends. All these findings provide key information about the geochemical signatures of the solid phases of the extruded materials from Carmen MV. Preliminary results obtained during this FLOWS STSM are also being compared with previous sediment data from piston GP05PC, also obtained during a FLOWS STSM in 2016, as well as with complementary data of porewaters (*López-Rodríguez et al., 2017*), in order to find paleo-SMTZ within the mud breccias and make an assessment of rates of fluxes methane in the past.

New datasets together with previous geochemical data from mud breccias from piston GP05PC, and the combination of porewaters data, we will be able to estimate the activity and dynamics of the Carmen mud volcano. This study will permit to date methane-rich mud discharge events, to evaluate their impact in the seafloor and will help to predict potential mud eruptions in the future.

Ongoing work and collaboration with the host institution

The Department of Earth Sciences is one of the most important research unit in Europe dedicated to the study of earth sciences and geochemistry and an excellent institution to carry on multidisciplinary research. The Department combines field data with experimental, modeling and theoretical approaches to elucidate biogeochemical cycles and mineral transformations along the aquatic realms and the associated shore-based Geo-Lab is the main laboratory facility of the Faculty of Geosciences which has a wide range of lab facilities available for measuring bulk rock geochemistry, bulk rock stable isotopes (H, C, N, S), in situ stable and radiogenic isotopes (U,Pb-dating), in situ major and trace elements and crystallography. The development of this research project has been an excellent opportunity to be trained in preparatory methods for specific geochemical analyses as well as to be formed in discusses and interprets geochemical data. It has permitted to continue the closely work under the supervision of Prof. Gert De Lange, ensuring the well development and completion of this research. This short-term scientific mission has enormously contributed in the ongoing collaboration between the host institution and our scientific group in Spain, favoring new discussions and geochemical issues which will be the target of further short-term scientific missions and potential Postdoc projects.

Scientific contributions and publications resulting from the STSM

All data that have been obtained during this short-term scientific mission are being processed and corrected. We have planned to increase to improve the geochemical record with additional samples from the investigated piston core GP09PC and thus work on a high-resolution dataset. We expect to find other interesting fluctuations along the mud breccias which will help to locate ancient SMTZ, leading to provide relevant information about the Carmen mud volcano dynamics and eruption timing. Once results will be interpreted and discussed they will be integrated as

part of a scientific manuscript which will be submitted in highly internationally-reputed journal in Earth Science (e.g., Geochimica e Cosmochimica Acta, Chemical Geology or Earth and Planetary Science Letters) and presented in international geological congresses (e.g., European Geosciences Union General Assembly, Goldschmidt Conference).

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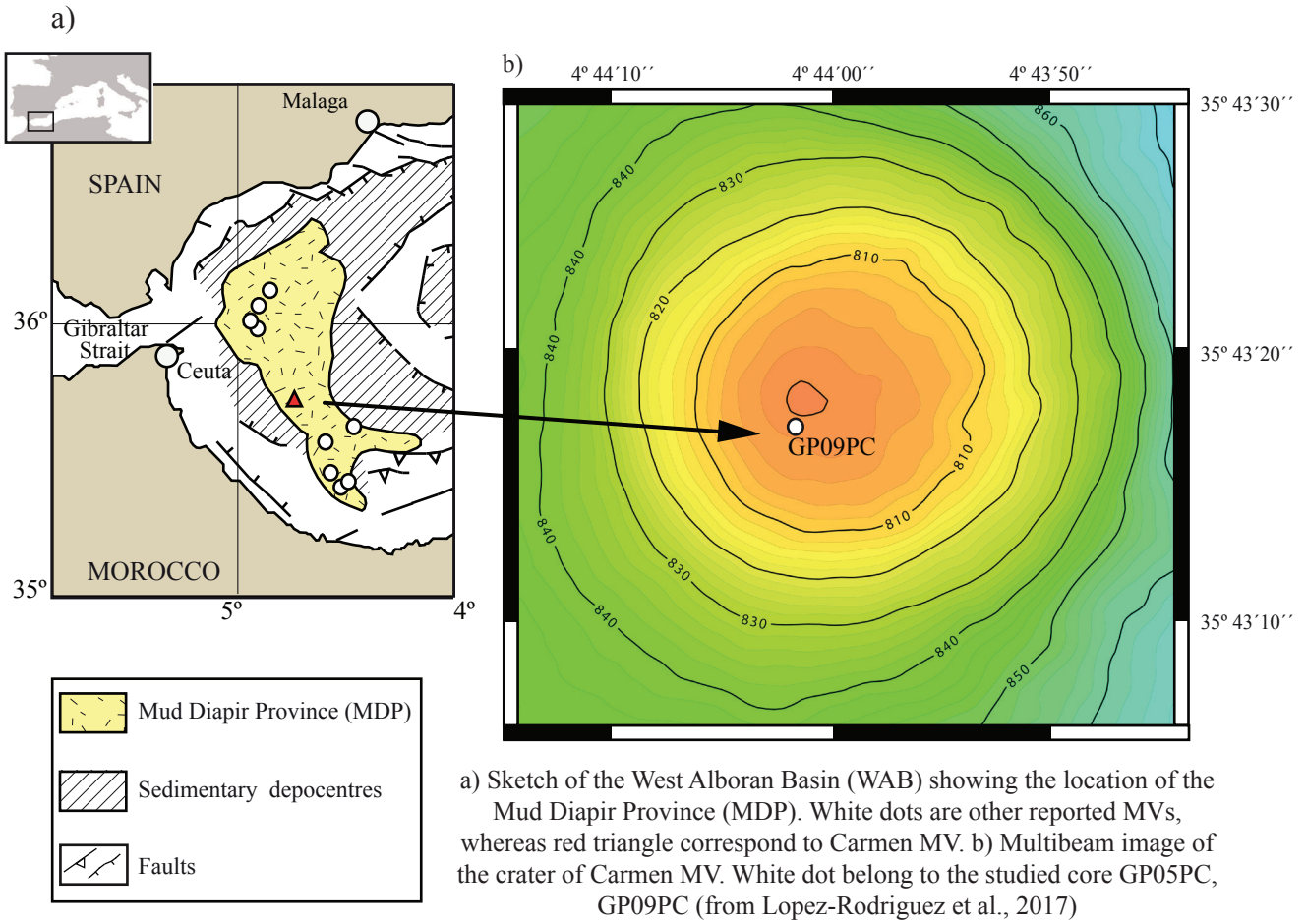
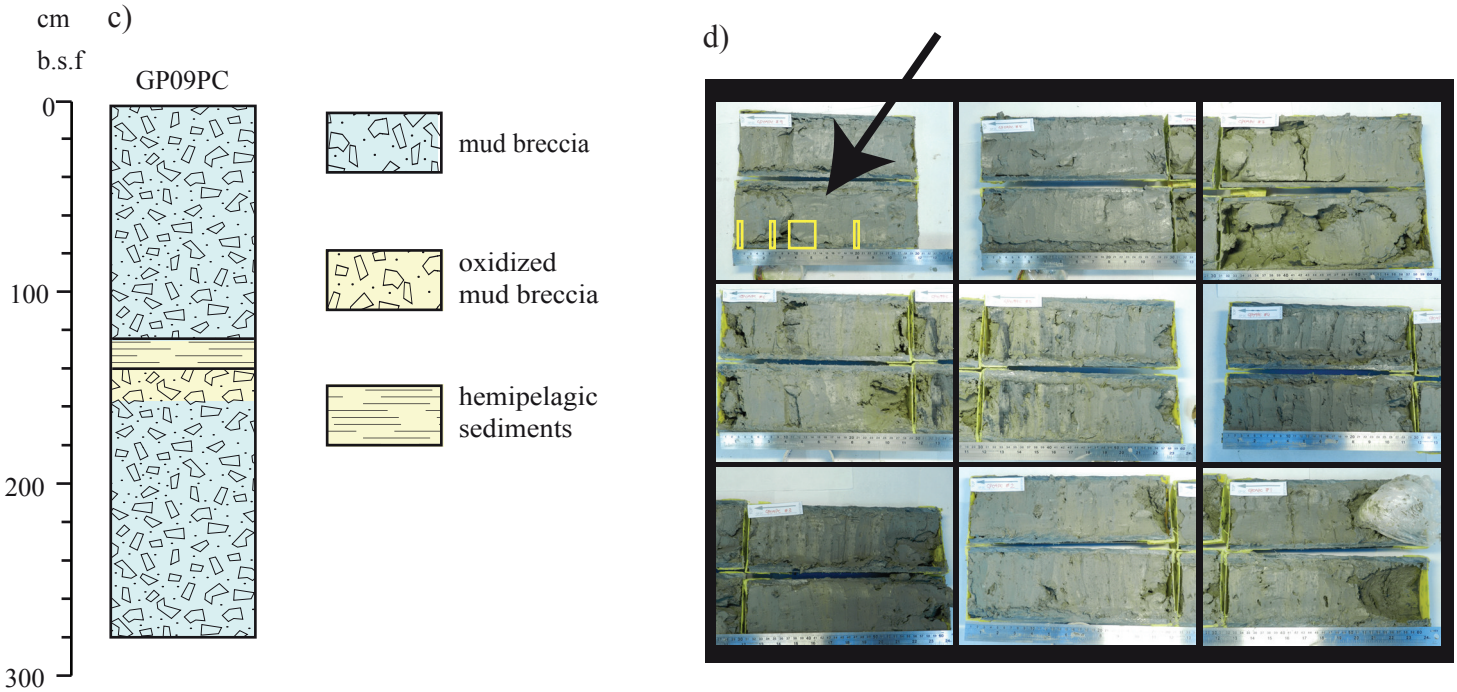


a) Sketch of the West Alboran Basin (WAB) showing the location of the Mud Diapir Province (MDP). White dots are other reported MVs, whereas red triangle correspond to Carmen MV. b) Multibeam image of the crater of Carmen MV. White dot belong to the studied core GP05PC, GP09PC (from Lopez-Rodriguez et al., 2017)



c) schematic core log showing the main sediment facies from the studied core GP09PC. d) Sediment sections from core GP09PC. Arrow and yellow rectangles show preliminar sub-sampled areas.