SCIENTIFIC REPORT OF STSM

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Purpose of the STSM

Mud volcanoes are geological structures that expel large volumes of detrital material (rock and clast fragments), together with hydrocarbon-rich fluids (e.g. methane), representing “natural windows to the deep geosphere”. This eruptive behavior provides key geological and geochemical information on the nature of deep sources feeding the mud volcanoes, and offers insights into the diagenetic processes operating at depth, such as the formation/dissociation of gas hydrates, mineral transformations, the degradation of organic matter and high pressure/temperature-reactions (e.g., Dählmann and de Lange, 2003; Haese et al., 2006; Hensen et al., 2007; Scholz et al., 2009; Magalhães et al., 2012).

In mud volcanoes, the upward migration of hydrocarbon-rich fluids is conditioned by over-pressurized material from deeper sedimentary layers. The venting activity in a seepage field is not always homogeneous and can vary from site to site (Haese et al., 2006). In the same field of mud volcanoes, individual and neighboring structures can have different scales and intensities of fluid discharge, which not only controls the level of seepage activity but also affects the composition of the expelled fluids.

Mud volcanoes in the Alboran Sea occur under a convergent tectonic setting, and hence constitute key settings to explore the interplay between tectonics, detrital sediments, authigenic mineral precipitation, deep fluids and the deep biosphere under active plate boundary. The scope of this FLOWS STSM has been focused in investigate the interaction between active seepages and deep fluids from geochemical proxies and isotopic compositions of mud breccias from the Carmen mud volcano from the Alboran Sea (westernmost Mediterranean). At the time we have also evaluated the main diagenetic processes that may affect the fluid composition through its ascending transport by the application of numerical modeling using integrated data of pore water analyses, in combination with sediment data from the mud breccia

Description of the work performed during the STSM

During the 35 days of my stay at the Department of Earth Sciences at Utrecht University (Utrecht, the Netherlands), I have performed the preparation, analysis and interpretation of the organic carbon and nitrogen content as well as stable carbon isotopes of solid phases of mud breccia samples (matrices) from the Carmen mud volcano (Alboran Sea).

For this aim and prior to the geochemical analysis, all discrete samples of mud breccias were previously dried in an oven at 40 ºC and later ground and homogenized in an agate mortar. 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 at the facilities of the Andalusia Earth Sciences Institute (CSIC-UGR; Granada, Spain).

During my stay in the Earth Science Department at Utrecht University I run the specific preparatory method for total organic carbon (TOC), total nitrogen (TN) contents as well as for carbon isotope compositions of the organic carbon ($\delta^{13}C_{org}$ (‰)). Thus 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 whereas for stable carbon isotopes weights were between 0.5-4 µg. After weighing, TOC and TN were determined on a Fisons Instruments NCS NA 1500 analyzer using dry combustion at 1030ºC. In addition, the carbon isotope compositions of the organic carbon ($\delta^{13}C_{org}$ (‰)) was determined with a VG SIRA 24 mass spectrometer in the shore-based laboratory at the Department of Earth Sciences, Geochemistry (Utrecht University). 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).

Description of the main results obtained

The total organic carbon (TOC) content and the stable carbon isotopes on mud volcano-related sediments from Carmen mud volcano are particularly useful to determine the origin of the organic matter and their influence on fluids generation. During this FLOWS STSM these analyses have been successfully performed. Preliminary results have shown that all mud breccia samples have similar geochemical characteristics. Total organic carbon (TOC) content in the mud breccia samples has demonstrated that the extruded materials in Carmen MV are rather similar among them and consequently show constant distribution in depth. Similarly, nitrogen content also exhibits similar values. 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 obtained pore water data, in order to understand the potential impact of organic matter degradation on sediment-water interactions and constrain the mechanism of fluid migration. In addition, during this FLOWS STSM I also had the opportunity to work in collaboration with the specialist researcher Dr. J. Mogollón, running a numerical-reaction model, in order to estimate variations in methane fluxes as well as the timing of the mud eruptions. With all the new obtained data as well as with the use of previous geochemical data on both solid and fluids phases we will be able to estimate the origin and quantify migration rates of deep fluids. This study will allow understanding how this type of fluids can influence the mud volcano activity, composition and generation of deep fluids as well as their linkage with microbiological and geochemical reactions.

Future collaboration with the host institution

The Department of Earth Sciences is the largest academic Earth Sciences institute in the Netherlands, and among the larger ones in Europe. The 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 collaborate with Dr. José Mogollón and also 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.

Scientific contributions and publications resulting from the STSM

All data that have been obtained during the development of this short-term scientific mission are being processed and corrected. Once results will be interpreted 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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