

In the study area small coral banks and carbonate crusts were found at the Pen Duick escarpment at the southern flank of the Renard Ridge. The Pen Duick escarpment is a fault scarp about 4.5 km long, 100 m high, and the water depth at the top is 525 m. The eastern part of the platform is characterized by a hummocky topography, to the west the pattern changes to parallel elongated ridges. On basis of the TV lines, TV guided grab samples were taken from dead coral banks and from a fault zone with carbonate slabs. The coral bank consisted of a dead coral framework with terrigenous mud matrix and few living corals at the top. It is indicative of a more favourable coral habitat in the past, probably related to strong currents in this area. The carbonate slabs consist of carbonate cement with shells, corals and debris.

## MULTIDISCIPLINARY STUDY ON SEEPAGE FEATURES FROM THE BLACK SEA

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During a recent marine survey (TTR-11 Cruise, 2001) in the Black Sea, three main areas of active fluid venting were explored and differing types of authigenic carbonate rocks were discovered. Using acoustic and sampling techniques, hydrocarbon fluid seep-structures (including eight mud volcanoes) were localised and sampled below the oxic zone.

A multidisciplinary study including petrographic and geochemical analyses was conducted on the large variety of carbonate deposits recovered from the sea floor and the shallow subsurface. Structural and petrographic observations allowed the distinction of five different types of authigenic carbonate; three of these (Type U1, U2, U3) comprise cemented hemipelagic sedimentary units (Unit 1, Unit 2, Unit 3) that broadly characterise the Black Sea; while the last two consist of cemented mud breccia sediment (Type MB) and authigenic micrite slabs (Type MS). Mineralogically, the carbonate cements consist of micrite, Mg calcite and, in one case, dolomite.

Carbon ( $\delta^{13}\text{C}$ ) stable isotope analyses performed on all the carbonate cements, show a defined signature for each sampling location and a common  $^{13}\text{C}$  depletion value, indicating the contribution of light carbon from methane seepage. All the samples analysed can be divided into two main clusters. The first group includes the samples from Area 1, from NIOZ and Odessa mud volcanoes (Area 3), that reveal high depletion in  $^{13}\text{C}$ , on average higher than  $-40\%$ . The second group comprises samples from Area 2 (Vassoevich, Kovalevsky mud volcanoes) and from Kazakov mud volcano (Area 3) that show higher carbon values rarely lower than  $-23\%$ . A similar trend is observed for gas (methane) carbon isotopic analyses. Isotopic results, and the observed thick microbial mats, confirm that authigenic carbonates originate from the microbially mediated oxidation of methane (archaea) coupled with the sulphate reduction (sulphate reducing bacteria), and from oxidation of organic matter or methane mixed with sea water derived carbon.

A proposed formation model for the layered authigenic carbonates (Type U1-U3) suggests that the cement precipitates after methane oxidation that is concentrated preferentially on the interface between the more impermeable clayey layers. Non-layered types presumably form directly on the seafloor (Type MS) or can be buffered by overlaying slabs or sedimentary units (Type MB). The sediment gas saturation in several volcanic structures is confirmed by the presence of clathrates. Sedimentary structures often control the distribution and the shape of the gas hydrates. Their spatial association with authigenic carbonates, as well as the structural similarities (tabular and leaf-shaped in layered hemipelagic sedimentary units, and irregular shapes and pore filling in the mud breccia sediment) suggest an intimate connection between the two. X-ray diffraction on the carbonate cements indicates the predominance of high magnesium calcite and shows that crusts of the same type, regardless of different sampling location, usually

have a similar composition. Geochemical analyses on gas extracted from sediments associated with authigenic carbonates reveal that methane is the main gas component. Compositional gas signature indicates that each structure has differently rooted gas. Methane carbon isotopes helped to distinguish between the thermogenic and biogenic gases. Comparison between methane and authigenic carbonate carbon isotopes shows that they follow a similar  $^{13}\text{C}$  depletion trend for each studied feature. The distinct signature shared by gas and authigenic carbonates further indicates that they are intimately related. Similarly, pore water compositional analyses provided relevant information about the mud volcanoes' activity and their fluid compositions.

## **LITHOLOGY AND ORGANIC MATTER IN ROCK FRAGMENTS FROM MUD BRECCIA OF CAPTAIN ARUTYUNOV MUD VOLCANO**

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The Captain Arutyunov mud volcano is located in the central part of the Gulf of Cadiz at 35°39.5'N - 7°20.0'W. It has a conic form of about 80 m high with a base of 3 km in diameter. This mud volcano was recently active and is characterized by gas venting and presence of gas hydrates. Using a TV-controlled grab a large sample of mud volcanic deposits was collected (TTR-12-AT393GR). The main aim of this investigation was to study lithology of rock clasts from mud volcanic deposits and to determine the content and composition of organic matter in these clasts.

Rock fragments were studied in thin sections under polarizing microscope. Lithological characteristics such as color, structure and composition were defined. Dating of some rocks was based on studying calcareous nannofossil assemblages (performed by A. Sautkin). The age of the others was determined by comparing them with rocks from other mud volcanoes of the Gulf of Cadiz (Ovsyannikov, 2000). Then geochemical investigations were carried out using fluorescent-bituminological analysis (to characterize extractable organic matter (EOM)), determination of total organic carbon (TOC) content and Rock-Eval pyrolysis.

On the base of lithological investigations and micropaleontological studying all clasts, separated from mud breccia from Captain Arutyunov mud volcano, were subdivided into 15 groups. They are mainly represented by limestones, claystones and sandstones. The age of rocks varies from Upper Cretaceous to Pliocene. The Upper Cretaceous rocks are represented by claystones and limestones. Most limestones are of the Miocene-Pliocene. The sandstones were formed during Eocene and Miocene. The values of TOC content in the majority of rocks are relatively low - 0.2 % in average, but several samples are characterized by TOC > 0.5 %.

In the claystones the values of TOC content vary from 0.18 % to 1.69 %, EOM content - from 0.01 % to 0.31%.

The limestones are characterized by TOC = 0.26 - 0.54 %, EOM = 0.005 % - 0.01%.

The sandstones are poor in organic matter: TOC = 0.05 - 0.07 %, EOM - 0.01%.

According to the results of pyrolysis of several samples, the organic matter belongs to kerogen of types II and III (humic/sapropel mixed and humic matter (Tissot, Welte, 1984)). The maturity of these rocks is corresponded to the beginning of oil window ( $T_{\text{max}} = 430 - 436\text{ }^{\circ}\text{C}$ ).

### **References**

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