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Clay mineralogy and B isotope data of mud volcano sediments of the Gulf of Cádiz: evidence of interactions of hydrocarbon- rich fluids with clays at depth

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Clay dehydration at depth generates fluids and overpressures, and the thermal maturation of organic matter during burial produces gas (mainly methane) and oil. Organic matter can release considerable content of B, so, oil fields can contain B-rich fluids. These fluids are ^{10}B-rich and, this light-B can be incorporated to the tetrahedral layers of illite in the process of illitization of smectite at depth. The crystal-chemical and geochemical characterization of illite, smectite or interlayered clay minerals can be an indicator of depth and reactions with the basin fluids. The aim of this study is to determine the detailed clay mineralogy, B content and isotopic composition in illite-smectite rich samples of 20 mud volcanoes of the Gulf of Cádiz from Anastasya01, MVseis08 and Chica0211 cruises, in order to evaluate interactions of hydrocarbon- rich fluids with clays. Although the clay mineralogy described so far consisted mainly of smectite, deconvolution of XRD peaks on $<2\mu$m glycolated fractions with MacDiff 4.2.5. gave a series of R0 inter-layering of illite-smectite and smectite. Transmission Electron Microscopy (TEM) coupled with EDS analysis on fine particles allowed us to determine the detailed clay mineralogy: smectite and illite-smectite mixed- layers and minor mica, chlorite, kaolinite and palygorskite, but also the size, shape and structural formula of detrital smectite and neoformed B-rich illite-smectite. B content and $\delta^{11}B$values, performed with a Cameca 6f SIMS instrument at Arizona State University on mannitol washed and NH_4Cl exchanged samples gave values ranging from (82 - 163) ppm, av value (119) and $\delta^{11}B$ranging from (-12.7 – 12.3) on mannitol washed samples and from (-9.5 to 11.8) on NH_4Cl exchanged samples. The B abundances obtained in this study can be interpreted in sedimentary basins as high, and consistent and possibly related to deep oilfields brines. Low B isotopic values on bulk, cation exchanged and mannitol treated samples, indicate that most of the B is located in the tetrahedral layer (structurally bound), so B has to be equilibrated at depth with hydrocarbon related fluids during their crystallization. In the case of the Gulf of Cádiz, clay mineralogy and B data and the coexistence of low- and high- illite-layer proportion I-S, indicates detrital smectite together with a prograding diagenetic sequence neoformed and interacting with deep fluids below the mud volcanoes close to the temperature conditions of oil generation. These data are consistent with previous results of B data on interstitial fluids suggesting that fluid formation may be caused by clay mineral dehydration at several kilometers depth and temperatures of up to 150 ^{o}C, in agreement with the occurrence of thermogenic methane. Authors are thankful to (RNM-3581 CADHYS Project).