Preliminary B and Li Isotope Data of Illite/Smectite from Mud Volcano Sediments from the Gulf of Cádiz

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INTRODUCTION

Submarine mud volcanoes are one of the seafloor expressions of the expulsion of argillaceous material, mud and clasts, from deeper areas, generated by an extrusion activity involving the transport of sediments, liquids and gas to the seafloor (Kopf, 2002 and references therein). During migration of fluids some of the underlying units are eroded and fluids bring to the surface the solid phase of the mud breccia, therefore the nature of the mud breccia give us important information about the nature and depth of the underlying units.

The origin of the fluids is more complex as different sources of fluids can be present (Hensen et al., 2007). Clay dehydration at depth generates fluids and overpressures and the thermal maturation of organic matter during burial produces wet, dry 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 new crystals concentrate ^{10}B, so the remaining fluids are enriched in ^{11}B (Williams et al., 2001). Illite, smectite and chlorite can also incorporate Li in the octahedral sites and low δ^7Li values can indicate oilfield brines (Williams and Hervig, 2005). Therefore, 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. Mud volcano sediments are made mainly of clay minerals and a systematic increase in smectite has been observed in different areas (Jurado-Rodríguez and Martínez-Ruiz, 1998; Martín Puertas et al., 2007). Although clays are an active part of this fluid system, not much is known on the detailed characteristics of the clay mineralogy of mud volcanoes. The aim of this study is to determine the B and Li content and the isotopic composition in illite-smectite rich samples coming from two different mud volcanoes of the Gulf of Cádiz, in order to evaluate interactions of hydrocarbon-rich fluids with clays.

MATERIALS AND METHODS

Gravity cores were collected during the ANASTASYA/01 and MVSeis 08 cruises on board of Cornide de Saavedra and Hespérides RV, respectively. Samples come from gravity cores taken on the top of two mud volcanoes of the Gulf of Cádiz. A2, Anastasya mud volcano, is located on the Guadalquivir Diapiric Ridge Province at 452 m depth, and TG-08, Almanzor Mud Volcano, is located at the South Arc Front of Western Moroccan field at 1236 m depth (Somoza et al., 2003; León et al., 2012).

Mineralogical analysis of samples has been performed by X-ray diffraction (XRD) on bulk samples and <2μm fractions. In order to determine the type of mixed-layers present, we have used MacDiff software on EG solvated oriented slides especially noting the 15-17° 2θ area. Chemical composition of individual clays has been obtained by Energy Dispersive Spectroscopy (EDS) in a Transmission Electron Microscope (TEM) Philips CM20 working at 200kV of the University of Granada. B and Li analyses have been performed with a Cameca ims 6f SIMS instrument at Arizona State University. Samples were hydrated and centrifugated, then 40 mls of mannitol (1.8% solution) was added, ultrasonified and left to soak 24 hours. The mannitol was washed out of the samples and a 5 μl suspension of mannitol washed sediment was mounted for Secondary ion mass spectrometry (SIMS) analysis. Cation exchange was performed on the remaining mannitol washed sample and a 5 μl suspension of this cation exchanged sediment was mounted for SIMS.

RESULTS

The main minerals of the mud breccia are: quartz, phyllosilicates, carbonates, calcite and dolomite but feldspars and pyrite also occur as minor phases (Martín Puertas et al. 2007). In order to study the I-S mixed-layered phase we selected two samples that according to XRD data showed the highest smectite and mixed-layered I-S contents.

A detailed study of glycolated samples allowed us to differentiate between detrital smectite and mixed-layered I-S phases.

	R0	R0	R0
A2	10	50	75
TG8	25	45	70

Table 1. Types of interlayering: (% illite layers) found in A2 and TG8 sample.

Deconvolution of XRD peaks performed with MacDiff 4.2.5 gave the following results (Moore and Reynolds, 1997). The best results for both samples were

palabras clave: Boro, Illita/esmectita, Hidrocarburos, SIMS | *key words:* Boron, Illite/smectite, Hydrocarbons, SIMS

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obtained (Fig. 1) considering Reichweite 0 (R0) and the types of inter-layering of illite-smectite given in Table 1.

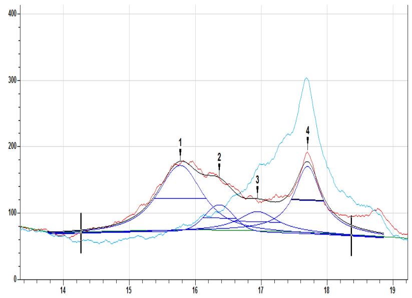

fig. 1. Deconvoluted XRD patterns calculated by MacDiff software for A2 sample. Red line: experimental EGC-XRD; Sky-Blue: air-dried-XRD; Dark blue: Mac Diff deconvoluted peaks; Black: sum of deconvoluted peaks.

TEM-EDS ANALYSES

The average smectite structural formula of A2 and TG8 samples (Table 2) show variations in interlayer cations

A2	$Na_{0.29}K_{0.25}Ca_{0.02}(Si_{7.45}Al_{0.55})(Al_{2.95}Mg_{0.76}Fe^{3+}{}_{0.53})O_{20}(OH)_4$
TG8	$K_{0.25}Ca_{0.04}(Si_{7.73}Al_{0.27})(Al_{2.97}Fe^{3+}{}_{0.61}Mg_{0.60})O_{20}(OH)_4$

Table 2. Structural formula of smectite on the basis of 44 negative charges

B AND LI GEOCHEMISTRY

Table 3 shows B content and $\delta^{11}B$ values for bulk, mannitol and cation exchanged samples. In both samples $\delta^{11}B$ values are light and B content is high.

	B (ppm)	$\delta^{11}B$ ‰
A2	347	-8.35±0.04
A2 + M	211±1	-5.6±0.04
TG8	202	-4.53±1.92
TG8 + M	123±3	-0.1±2
	Li (ppm)	$\delta^{7}Li$
A2 + xc	105±2	-7.9±0.5
TG8 + xc	59±6	-5.9±0.2

***Table 3**. B content (ppm) and $\delta^{11}B$ values of bulk and mannitol washed samples (M) and Li content (ppm) and $\delta^{7}Li$ values of cation exchanged samples (xc)*

The Li and B abundances obtained in this study can be interpreted in sedimentary basins, as high and consistent and possibly related to deep oilfields brines (Collins, 1975; Williams et al., 2001).

DISCUSSION

Low B and Li isotopic values on both samples (bulk, cation exchanged (xc) and mannitol treated (+M) samples), indicate that most of the B and Li is located in the tetrahedral and the octahedral layer respectively (structurally bound), so B and Li equilibrated with deep hydrocarbon related fluids during their crystallization.

In the case of the mud volcanoes of the Gulf of Cádiz, B-Li data and the coexistence on both samples of low- and high- illite-layer proportion I-S indicates detrital smectite together with a prograding diagenetic sequence below the mud volcanoes. These data indicate that, at least, there is a clay source unit that underwent deep diagenesis for the two mud volcanoes.

Mineralogical and isotopic data confirms that the clays that are now at the sea floor surface, being part of the mud breccia, were involved in deep processes and transformations close to the temperature conditions of oil generation and in relation to it. Clay and marly units underneath mud volcanoes in the Gulf of Cádiz, can be Mesozoic and Tertiary in age (mainly Tortonian-Messinian) and have been considered as the oil source rock in the area.

These data are consistent with previous results shown by Hensen et al. (2007) that based on B and Li isotope data on interstitial water, suggested that fluid formation might be caused by clay mineral dehydration at several kilometers depth and temperatures close to 150 ºC, in agreement with the occurrence of thermogenic methane.

Although more data from different areas are necessary to fully understand all these processes, this study prove that clay mineral evolution (I/S crystallization from detrital smectite) is related to the generation of deep fluids that can be one of the driving forces of mud volcanism in the area.

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