Organic matter-clay interaction along a seawater column of the Eastern Pacific upwelling system (Antofagasta bay, Chile): Implications for source rock organic matter preservation

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ABSTRACT

Natural Organic Matter (OM) preservation and sedimentary burial mechanisms are still poorly understood despite their importance in oil source rock characterization and carbon cycle issues. It is now recognized that mineral sorption contributes significantly to OM preservation by conferring steric protection and preventing enzymatic access. Most of the studies dealing with OM preservation have focused on settled OM, omitting aggregation in the water column. For the first time, we have tested the complexation of natural OM on 3 types of clays in seawater in-situ conditions. Samples of Na exchanged montmorillonite (Na MMt), synthetic montmorillonite (S Na MMt) and natural kaolinite (Kaol) were immersed in an upwelling zone (Antofagasta bay, Chile). Three depths were studied: 15 m (photic zone), 40 m (oxygen transition zone) and 80 m (anoxic zone). The clayey samples were kept immersed for different durations and analyzed after removal, via GC/MS, Py-GC/MS, flash elementary pyrolysis, DOC analyzer and XRD. The main results are: (1) for the shortest immersion times, DOC analyzes performed on clays' proximal water indicated excessive DOC concentrations compared to seawater values. This attraction effect was however temporary, as values tended to rebalance with seawater concentrations for the longest immersion times. (2) Molecular analyses performed on seawater organic extracts indicated that fatty acids, alkanes, alkyl benzenes and methoxy-benzenes were the main dissolved lipid groups. (3) These lipids were also the main sorbed compounds identified on immersed clays, with a predominance of fatty acids. This is due to the higher availability and better affinity of fatty acids with the clayey samples. (4) Because of its higher specific area and CEC, Na MMt exhibited the best sorption rates compared to Kaol and SNa MMt. X ray analyses performed on Na MMt indicated d_{001} spacing growths, but these growths are not attributed to OM intercalation. Sorbed OM is probably located on the external surfaces leaf edges of clays.

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1. Introduction

In hydrocarbon resources research, it is widely acknowledged that Organic Matter–Clay Interactions (OMCI) are involved in the successive steps of oil genesis. In fact, the quasi systematic association observed between hydrocarbon resources and fine-grained rocks has triggered numerous studies focusing on the contribution of organo-mineral interactions to sedimentary Organic Matter (OM) preservation (Ransom et al., 1998; Pichevin et al., 2004; Wagai and Mayer, 2007; Kögel-Knabner et al., 2008; Mikutta et al., 2009). A positive correlation between specific surface and organic carbon content has been highlighted for continental shelf sediments (Mayer, 1994a, 1994b). The validity of this interdependence relationship is related to the environmental configuration, especially the position of sediments on continental slopes (Milliman, 1994), since the low oxygen concentrations encountered in the lower slope zones induce an excess of organic carbon/surface area ratios (Mayer, 1994a; Keil and Cowie, 1999). Based on the observation of the relationship between organic content and surface area, physical mechanisms of OM and mineral particle association have been investigated. A preliminary distribution model of OM suggested a monolayer coating of OM on mineral surfaces (Mayer, 1994a). This monolayer model was subsequently revised (Mayer, 1999) and nowadays, natural OM distribution on mineral surfaces is considered as patchy (Arnarson and Keil, 2001).

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From sedimentary genesis to industrial recovery, several studies have highlighted the impact of OMCI in oil-source rock deposition processes. These interactions are observed in sedimentary OM preservation, kerogen thermal cracking, crude oil migration and hydrocarbon composition change in oil reservoirs (Wu et al., 2012). The catalytic characteristics of clays enhance kerogen cracking (Fan et al., 2004), while diagenetic transformations of clays occurring during the burial process favor crude oil migrations. For example, smectite/illite alteration releases interlayer water molecules (Zhang et al., 2010; Cai et al., 2012), inducing an increase in fluid pressure which drives oil migration. In addition to their interferences in oil migration, clay minerals also interact with crude oil during its accumulation in reservoir rocks. Thus, the adsorption of heavy compounds (resins and asphaltenes) by clay-sized components in reservoirs increases the saturated hydrocarbon concentration in free oil, leading to the enhancement of oil rank (Pan et al., 2005). OMCI is also a crucial factor in the crude oil extraction process. The surfactants usually added to chemical slurries in order to reduce capillarity retention by reservoir rocks are frequently lost due to clay adsorption (Liu et al., 2004; Amirianshoja et al., 2013). Surfactant loss minimization methods are currently being developed in the enhanced oil recovery investigation field. Organo-clay processes are involved at each step of the oil genesis and exploitation chain.

The fate of OM in natural aquatic environments has interested the organic geochemistry communities for several decades. Lakes and upwelling marine areas are sedimentary environments with the most favorable physicochemical conditions for high organic productivity. These environments are propitious for the deposition of hydrocarbon-rich organic sediments if the OM produced escapes oxidation and bacterial activity. Thus OM preservation at the water/sediment interface has been studied through several approaches (Largeau et al., 1984; Tissot and Welte, 1984; Tegelaar et al., 1989). Most of these studies focused on bulk sediments, establishing three OM preservation pathways. In fact the model based on microscopic observation indicates that the process may be selective (Largeau et al., 1984; Mayer, 2004). Alternatively, sedimentary OM preservation could arise from successive steps of degradation and condensation (Tissot and Welte, 1984). It could be favored by a natural sulfurization mechanism, via the incorporation of sulfur atoms in anoxic environments (Tegelaar et al., 1989; Sinninghe Damsté and de Leeuw, 1990; Boussafir et al., 1995). Depending on the sedimentary basin configuration and the biotope typology, the effect of these different paths may be combined. Yet, none of these studies considered early intra column organo-mineral flocculation and its possible impacts on the preservation process occurring in underlying sediments.

The 90s saw the rise of a new hypothesis, namely trapping by mineral materials, specifically clays, which is thought to be a full preservation process. OMCI can be divided into three morphological concepts: (i) sorption of small molecules on surfaces via 'classic' mechanisms. These mechanisms are now well characterized: cation bridges, van der Waals effects, ligand exchanges and hydrophobic effects (Arnarson and Keil, 2000; Drouin, 2007; Keil and Mayer, 2014); (ii) sorption of high molecular weight polymers (e.g., proteins); (iii) global flocculation and aggregation phenomena inducing the main physical and steric protection. The importance of organic–mineral interactions in the fossilization of organic matter is well established. Several studies have already suggested that the weight increase resulting from organo-mineral complexation is indirectly involved in OM preservation, by helping to reduce the transfer time in water columns (Wakeham et al., 1984; Jackson, 1990). Beyond this subsidiary role, evidence highlighting the correlation between organic and mineral sizes in sediments suggests that OMCI interactions could provide effective protection against degradation agents of labile OM (Mayer, 1994a; Keil et al., 1994). Some studies subsequently attempted to further characterize the clay/OM relations in natural sediments, or to model their interaction process in laboratory studies in order to understand their principles and to apprehend their role in the organic carbon cycle.

However, these previous investigations have often based their conclusions on the study of sediments only. Interaction processes that occur in areas of OM production, where OM is likely to be trapped, are poorly investigated. Therefore, the involvement of mineral phases in protecting OM remains today relatively poorly understood. Nowadays it is assumed that sorption of organic molecules reduces their availability to bacterial degradation (Sugai and Henrichs, 1992; Mayer, 1994b; Hedges and Keil, 1995). Rare experimental studies show that in-situ sorption by clays can be considered as a stable mechanism of preservation of hydrocarbon-rich OM (Satterberg et al., 2003; Drouin et al., 2010).

Our work focuses on the initial steps of early diagenesis. The objective is to understand the agglomeration of organo-clays in the water column, in order to better characterize the contribution of OMCIs to the preservation process of kerogen precursor OM. We have chosen to test the role of clays in the adsorption and fossilization mechanism of dissolved OM. For this purpose, the OM sorption of three types of clays was tested in a marine productive upwelling system in three specific physicochemical zones of the water-column. Lipid composition and in situ OM/clay aggregated complexes were investigated via GC/MS and py-GC/MS in order to identify the main molecular groups favored by the sorption process. Sorbed masses were quantified in order to distinguish the most propitious physicochemical zone along the water column and also to identify the most favorable clay type in such a productive upwelling sedimentary environment. The mechanical behavior of expandable clays during the sorption process was also tested along the seawater column.

2. Materials and methods

2.1. Studied site

Adsorption experiments were performed in Antofagasta bay off the Mejillones peninsula, Chile (Fig. 1). An arid climate prevails in Antofagasta's hinterland, with rainfalls barely superior to 0.5 mm/year (Clarke, 2006). The bay undergoes the Humboldt current (Iriarte et al., 2000), which thrusts cold water along the South American coast, from high southern latitudes to north Chilean latitudes. The Humboldt circulation system is locally associated with upwelling currents inducing more than 200 g C/m^2/year of biomass (Levin and Rathburn, 2003). A multi parameter probe (YSI®) was used to determine seawater column characteristics (temperature, dissolved oxygen, fluorescence, salinity).

2.2. Clays and immersion traps

Three clay samples were selected for this study: two smectites (natural and synthetic, respectively) and one natural kaolinite. The natural smectite is the SWy-2 Wyoming montmorillonite supplied by the Source Clay Minerals Repository of the Clay Minerals Society. This SWy-2 montmorillonite was sodium-saturated by exchange in 1 M NaCl, as described in Le Forestier et al. (2010). After dialysis and decantation, the <2 μm fraction of Na-SWy2 samples was recovered, dried and finely hand ground in an agate mortar. This sample is hereafter named Na MMt. The synthetic smectite, S Na MMt, was synthesized at hydrothermal conditions (350 °C, 120 MPa) during 28 days in an autoclave system (Tuttle-type, externally heated, cold-seal pressure vessels) from a gel of anhydrous composition (0.33Na$_2$O–1.67Al$_2$O$_3$–0.66MgO-8SiO$_2$), using the procedure of Le Forestier et al. (2010). The natural Na MMt smectite still contained impurities (quartz, pyroxene) after purification, whereas the synthetic S Na MMT was characterized by a higher purity with one crystalline phase. Kaolinites were sampled at Ploemeur kaolin stone-pit (Morbihan, France) which is a deposit deriving from hydrothermal and climatic alteration of Hercynian leucogranites.

In terms of specific surface and cationic exchange capacity, natural kaolinite presents significant differences with the smectites (Table 1).