



Organic matter sulfurization on protracted diagenetic timescales: The possible role of anaerobic oxidation of methane



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ABSTRACT

Kerogens from the anoxic sediments of the Cariaco Basin spanning the last 130 ky were analyzed in order to determine the organic matter (OM) preservation pathways, and the evolution of these pathways with time. The kerogens were isolated using a protocol avoiding the formation of artificial melanoidins. Bulk elemental content, spectroscopic and pyrolytic features of the kerogens show that sulfurization is an important process in the insolubilisation of the OM, even in the most recent sample studied (~400 a). The degree of OM sulfurization on the studied interval depends on the redox conditions of the sediment during deposition and is largely correlated to the total organic carbon content of the sediment. A trend of downward increasing sulfurization of the organic matter is observed in the sediments of the studied two interglacials. From the available porewater analyses of Cariaco sediments and comparison with Black Sea sediments, the data suggest that downward progressive sulfurization of the OM is mainly due to the production of H₂S by sulfate-dependent anaerobic oxidation of methane occurring at the sulfate/methane transition zone located a few meters below sea floor.

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1. Introduction

Since the definition of type II-S kerogens (Orr, 1986), the modes and processes of natural sulfurization of organic matter (OM) in sediments have been the object of numerous studies (see reviews in Sinninghe Damsté and de Leeuw, 1990; Werne et al., 2004; Amrani, 2014). It is now well characterized that OM sulfurization occurs diagenetically, through reaction of reduced sulfur species, mostly H₂S/HS⁻, present in sediment pore water, with functionalized OM. Such reactions require anoxic conditions, but also low contents of reactive iron oxides as the latter are in competition with OM for reaction with reduced sulfur species (Sinninghe Damsté and de Leeuw, 1990; Canfield, 1989). The detailed mechanisms and factors influencing the degree and timing of OM sulfurization however remain to be ascertained. While some lipids are rapidly sulfurized in surface sediments such as phytol derivatives, branched isoprenoids, carotenoids and steroids (Adam et al., 2000; Fukushima et al., 1992; Hartgers et al., 1997; Kok et al., 2000; Wakeham et al., 1995), others require much longer timescales to get sulfurized, as for instance hopanoids whose sulfurized counterparts are not described in recent sediments but are frequent in Cenozoic and older sediments (Schaeffer et al., 1995, 2006). Another important question is the quantitative significance of natural sulfurization for the burial of organic carbon on geological timescales. Sulfurization is

recognized as a preservation pathway for sedimentary OM (Sinninghe Damsté and de Leeuw, 1990; Tribovillard et al., 2015), and has been shown to allow for the preservation of very labile organic compounds (Riboulleau et al., 2000, 2002; Sinninghe Damsté et al., 1998b; van Kaam-Peters et al., 1998). In addition, black shales containing sulfurized marine OM can reach very high TOC contents (Herbin et al., 1986; Kuypers et al., 2004; Riboulleau et al., 2000; van Kaam-Peters et al., 1998). However, it is commonly considered that the sulfide ions involved in OM sulfurization originate from the degradation of OM by bacterial sulfate reduction (BSR) (Werne et al., 2004). Sulfurization therefore paradoxically implies that OM has to be partly degraded in order to get better preserved.

During the last decades, the sediments of the Cariaco Basin, located on the continental shelf of the northern coast of Venezuela, have been the object of several studies pursuing to document the modes and timing of sulfurization (Aycard et al., 2003; Werne et al., 2000a, 2003, 2008; Raven et al., 2015). The Cariaco Basin is characterized by high surface-water productivity (Goñi et al., 2003; Muller-Karger et al., 2001) and anoxic-sulfidic conditions below ~300 m depth (Richards and Vaccaro, 1956; Scranton et al., 1987; Thunell et al., 2000). The Cariaco Basin is the second largest euxinic basin on Earth after the Black Sea, but is the largest with a truly marine water column. For this reason, biogeochemical processes in the water column and sediments of the Cariaco Basin have been extensively studied, because they can be regarded as modern analogues for understanding oceanic anoxic events (e.g. Benitez-Nelson et al., 2007; Deuser, 1973; Goñi et al.,

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2003; Taylor et al., 2001; Wakeham and Ertel, 1988; Werne et al., 2003, 2008). Because of the high amounts of OM in the sediment and the prevailing sulfidic conditions, the Cariaco Basin also presents ideal conditions for natural sulfurization (Sinninghe Damsté and de Leeuw, 1990). However, the extent of sulfurization in the sediments of the Cariaco Basin is still a matter of debate. Aycard et al. (2003) suggested that despite favorable conditions, natural sulfurization was a minor process in the formation of the kerogens in the Cariaco Basin. Kerogens isolated from recent sediments showed an important contribution of melanoidin-like moieties, indicating that degradation-recondensation was the most important pathway for OM preservation (Aycard et al., 2003). However, the acid treatment used by Aycard et al. (2003) for kerogen isolation was shown to produce artificial melanoidins when used on fresh OM (Allard et al., 1997). For this reason, the abundant melanoidins observed by Aycard et al. (2003) could be artifacts.

In the solvent-soluble fraction of the upper 4 m of sediment, Werne et al. (2000a) observed the progressive disappearance with depth of the triunsaturated tricyclic triterpenoid, (17E)-13 β (H)-malabarica-14(27),17,21-triene, and conversion to its sulfurized counterpart. This precursor-product relationship allowed to constrain the timing of sulfurization of malabaricatriene to approximately 10 ky (Werne et al., 2000a). On the basis of kerogen analysis, Aycard et al. (2003) also observed a general increase of OM sulfurization with time and suggested that carbohydrates were sulfurized prior to the sulfurization of lipids. Their oldest studied sample was ~6 ky old and this kerogen was only moderately sulfurized (Aycard et al., 2003). These results are consistent with previous observations that sulfurization of OM has different kinetics according to the type of involved molecules (Wakeham et al., 1995), and suggest that sulfurization of OM continues further in older sediments. The Cariaco Basin has been continuously euxinic for the last 14.7 ky and has regularly known periods of anoxia for the last 580 ky (Peterson et al., 2000b), allowing to study the progression of OM sulfurization on longer timescales than the ~13 ky of the previous studies (Aycard et al., 2003; Werne et al., 2000a, 2003, 2008).

With this in mind, the aims of our study were: i) to reconsider the presence of melanoidins in the kerogens of the Cariaco Basin: to this end, kerogens were prepared using an artifact-free method (e.g. Quijada et al., 2015) and ii) to follow the processes involved in kerogen formation, and in particular the role of natural sulfurization, on a longer timescale than previously studied. To this end we studied the kerogens

from sediments spanning the last 130 ky and deposited during periods of continuous water column anoxia in the Cariaco Basin. This approach allows to examine the role of time and geochemical environment in OM sulfurization and consider the factors influencing the degree of OM sulfurization in sediments.

2. Geological setting

The Cariaco Basin is a pull-apart basin located in a system of active right-lateral strike-slip faults in the northwestern Venezuelan shelf (Fig. 1; Audemard, 2007). This basin is isolated from the Caribbean Sea by a shallow sill which precludes the renewal of bottom waters below ~200 m. Trade wind-induced seasonal upwelling of intermediate waters advected from the Caribbean Sea allows the important development of planktonic activity in the water column from December to May (Muller-Karger et al., 2001). Degradation of the organic matter and water column stratification induce a depletion of oxygen and the development of anoxic-sulfidic conditions below a water depth of ~300 m (Muller-Karger et al., 2001; Scranton et al., 1987). The Cariaco Basin has experienced anoxic conditions for the last 14.7 ky, and climate-induced fluctuations from oxic to anoxic conditions are known for the last 580 ky (Peterson et al., 2000b; Yarincik et al., 2000). This millennial scale variability is recorded in the sediments of Cariaco Basin through organic rich dark-colored laminated sediments deposited during warm periods (interglacials and interstadials) alternating with light-colored bioturbated sediments deposited during cold periods (last glacial maximum, interstadials; Peterson et al., 2000a).

3. Methods

3.1. Sampling

The sediment samples studied were collected from dark and laminated intervals from three cores. The uppermost 5 samples were collected from the piston core MD03-2625 (10° 40' 39" N and 64° 58' 14.5194" W; water depth 850 m) collected during the PICASSO (IMAGES XI) campaign of the RV *Marion Dufresne* in May 2003 (Laj and Shipboard Scientific Party, 2004), covering the Holocene. The other eight samples were collected from the cores 1002D and 1002E recovered on the central saddle of the Cariaco Basin during the ODP Leg 165 at site

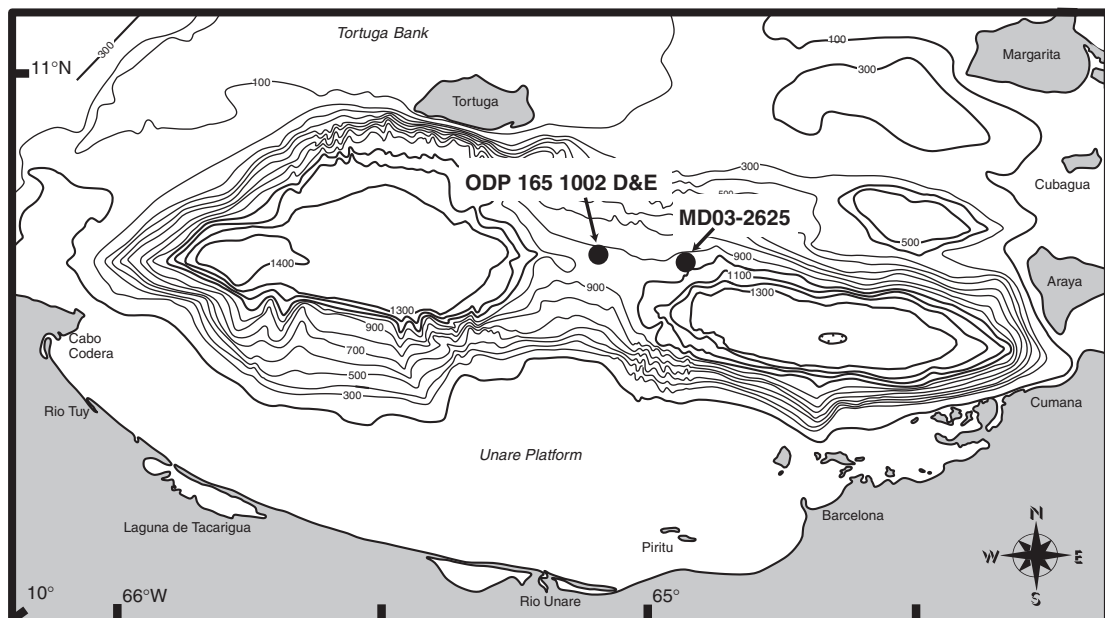


Fig. 1. Location map of the Cariaco Basin and of the studied sediment cores.

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