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Low temperature hydrothermal oil and associated biological precursors in serpentinites from Mid-Ocean Ridge

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ABSTRACT

The origin of light hydrocarbons discovered at serpentinite-hosted mid-ocean hydrothermal fields is generally attributed to the abiogenic reduction of carbon (di)oxide by molecular hydrogen released during the progressive hydration of mantle-derived peridotites. These serpentinization by-products represent a valuable source of carbon and energy and are known to support deep microbial ecosystems unrelated to photosynthesis. In addition, the pool of subsurface organic compounds could also include materials derived from the thermal degradation of biological material. We re-investigate the recently described relics of deep microbial ecosystems hosted in serpentinites of the Mid-Atlantic Ridge (4–6°N) in order to study the ageing and (hydro)thermal degradation of the preserved biomass. An integrated set of high resolution micro-imaging techniques (Scanning Electron Microscopy, High Resolution Transmission Electron Microscopy, Raman and Fourier Transform Infra-Red microspectroscopy, Confocal Laser Scanning Microscopy, and Scanning Transmission X-ray Microscopy at the carbon K-edge) has been applied to map the distribution of the different organic components at the micrometer scale and to characterize their speciation and structure. We show that biologically-derived material, containing aliphatic groups, along with carbonyl and amide functional groups, has experienced hydrothermal degradation and slight aromatization. In addition, aliphatic compounds up to C_6–C_{10} with associated carboxylic functional groups wet the host bastite and the late serpentine veins crosscutting the rock. These compounds represent a light soluble organic fraction expelled after biomass degradation through oxidation and thermal cracking. The detected complex organic matter distribution recalls a typical petroleum system, where fossil organic matter of biological origin maturates, expelling the soluble fraction which then migrates from the source to the reservoir. Ecosystem-hosting serpentinites can thus be seen as source rocks generating a net transfer of hydrocarbons and/or fatty acids issued from oxidative processes and primary cracking reactions, then migrating upward through the serpentine vein network. This finally suggests that deep thermogenic organic compounds of biological origin can be a significant contributor to the organic carbon balance at and far below peridotite-hosted hydrothermal fields.

1. Introduction

Currently known petroleum deposits largely derive from the thermal maturation of photosynthesis-dependent organic matter through progressive burial within sedimentary basins (i.e. thermogenesis; Tissot and Welte, 1984). Hydrocarbons are also known to result from biosynthetic processes (i.e. bacteriogenesis; Schoell, 1988), while abiotic methane and higher molecular-weight hydrocarbons can also be produced by a variety of water–rock interactions (McCollom, 2013; Sephton and Hazen, 2013 and references therein). Several types of organic compounds have been reported at serpentinite-hosted Mid-Ocean Ridge hydrothermal vents, where large amounts of methane (in the range of 1–2 mmol · kg^{-1}) are expelled along with minor

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Abbreviations: AU, Arbitrary Unit; BPS, Bio Peak Series; FIB, Focused Ion Beam; FTIR, conventional Fourier Transform Infra-Red spectroscopy; DCM, Disordered Carbonaceous Matter; H-Adr, Hydroandradite; HO, Hydrothermal Oil; HRTEM, High Resolution Transmission Electron Microscopy; SEM, Scanning Electron Microscopy; SR-FTIR, Synchrotron Radiation based Fourier Transform Infra-Red spectroscopy; STXM, Scanning Transmission X-ray Microscopy; C-XANES, X-ray Absorption Near Edge Structure at the carbon K-edge; CLSM, Confocal Laser Scanning Microscopy.

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C_{2+}linear hydrocarbons and organic acids (Charlou et al., 2010 and references therein). These organic compounds were first interpreted as the product of abiotic chemical reactions favorable under the strongly reducing conditions (Proskurowski, 2010) produced during the progressive hydrothermal hydration of mantle-derived rocks, a process known as 'serpentinization' (Bach et al., 2006; Mével, 2003). During serpentinization, large amounts of molecular H_2 are produced (up to 10–20 $mmol \cdot kg^{-1}$; Charlou et al., 2010) when water oxidizes ferrous iron-bearing minerals such as olivine and pyroxenes (Mayhew et al., 2013; McCollom and Bach, 2009). Molecular hydrogen drives the reduction of oxidized C-bearing species (CO_2, CO and HCO_3^-) via surface-catalyzed polymerization reactions such as Sabatier reactions or Fischer–Tropsch-Type (FFT) synthesis (e.g., Shock, 1990; Shock and Schulte, 1998). Compound-specific stable isotope measurements of Rainbow and Lost City vent fluids (respectively at 36°14′ and 30°N along the Mid-Atlantic Ridge — MAR) support the abiotic hypothesis for the low molecular-weight saturated hydrocarbons (C_1 to C_4) and formate ($HCOO^-$, e.g. Lang et al., 2010; Proskurowski et al., 2008). An abiotic origin has also been ascribed to hydrocarbons, bitumen and asphaltenes discovered in mantle-derived rocks sampled in ophiolitic complexes and mantle xenoliths (Ciliberto et al., 2009; Florovskaya et al., 1982; Mathez, 1987; Scirè et al., 2011; Sugisaki and Mimura, 1994).

More complex organic compounds, such as long-chain linear and aromatic hydrocarbons including isoprenoids and carboxylic acids, have also been reported in these environments. For such compounds a predominant biological origin has been proposed. The biological material may be either externally derived, such as the input of Dissolved Organic Carbon from seawater (Delacour et al., 2008) or internally derived, such as the thermal degradation of endemic vent-hosted communities (Bassez et al., 2009; Kelley et al., 2005; Konn et al., 2009, 2011; Simoneit et al., 2004). Altogether these studies suggest that the thermal degradation of the microbiological communities hosted in ocean-floor hydrothermal environments constitutes a robust alternative source for hydrocarbons in the oceanic lithosphere.

In the present study, our goal is to document the fate of reduced organic compounds generated by the deep biosphere and trapped in serpentinized rocks below the seafloor. For this purpose, we implemented a set of in situ high resolution microspectroscopy techniques to characterize the organic matter, and to unravel the associated paragenesis, ageing and (hydro)thermal degradation processes.

2. Background

2.1. Geological setting

The studied samples come from the 4–6°N region of the equatorial MAR, southeast of the Sierra Leone Fracture Zone, and were dredged during the joint Russian–Italian cruise S22 of the R/V *Akademik NikolajStrakhov* (Peyve et al., 2003). This is a magma starved region representative of large sectors of the oceanic ridge system where the Atlantic, Indian and circum-Antarctic ridges are characterized by low to ultraslow spreading rates (<60 mm/y). In such a context, mantle rocks are continuously rafted to the seafloor by ridge faced normal faults opening tectonic windows to the interior of the oceanic crust. Consequently, hydrothermal circuits are rooted in a mantle-dominated section resulting in pervasive serpentinization of the upper few kilometers of the oceanic crust (Mével, 2003). In the dredged region, the rift zone is morphologically characterized by isolated basins, tectonically separated by transverse uplifts (3000–2100 m below seafloor) made up by gabbroic and peridotitic rocks. Studied samples have been collected on the flank of one of these unsedimented uplifts in crust aged <1 My in the dredge haul S2232 (6°08.9′ N; 33° 25.4′ W), where 200 kg of variably-serpentinized peridotites has been recovered (Peyve et al., 2003). The peculiar geological setting results in large exposures of serpentinized rocks that have never been buried by sediments. Hence, this site presents favorable conditions for the study of organic compounds synthesized at depth in the rock basement while avoiding potential contamination by thermogenically-derived hydrocarbons from an overlying sediment cap (Proskurowski, 2010).

2.2. Sample petrography

Our study is based on a completely serpentinized mantle-derived peridotite (sample S2232-17). We refer to Ménez et al. (2012) for a detailed description of the reaction sequence and timing summarized hereafter. The hydrated paragenesis is that usually found in serpentinized mantle rocks along the Mid-Ocean ridges: olivine (Ol) has been replaced by a lizardite + magnetite assemblage forming the characteristic hour-glass texture; orthopyroxene (Opx) is pseudomorphically replaced by fine grained lizardite, commonly defined as bastite; late mm-thick serpentine veins crosscut the whole rock. Bastitized Opx are intersected by secondary mineralization represented by chains or globular clusters of subhedral hydroandraditic garnets growing along microfractures (H-Adr: $Ca_3Fe_2^{3+}(SiO_4)_{3-x}(OH)_{4x}$). The H-Adr commonly found in serpentinites usually grows over bastite under high pH and Ca^{2+} activity at low O_2 fugacity and temperature below 200 °C (Frost and Beard, 2007 and references therein). Low CO_2 and SiO_2 activities prevent the precipitation of calcite and other silicates (Beard and Hopkinson, 2000). In sample S2232-17, H-Adr grains have undergone a dissolution process that selectively affected the grain cores. This process leads to the formation of large inner cavities interpreted by Ménez et al. (2012) as the result of a cryptoendolithic microbial activity. A secondary mineral paragenesis comprising polyhedral serpentine spherules, polygonal serpentine and iron oxides crystallizes inside the cavities.

2.3. Organic matter description

Two types of organic matter are intimately associated with the H-Adr. Here we adopt the definitions of Ménez et al. (2012) that described the two organic matter occurrences as BPS and DCM, based on Raman spectroscopy. BPS, standing for Bio Peak Series, is characterized by the presence of complex organic molecules comprising aliphatic compounds along with carbonyl and amide functional groups and minor aromatic moieties. On this basis BPS has been interpreted as a remnant of microbial colonization. The second type referred as Disordered Carbonaceous Matter (DCM) occurs as dense carbon aggregates filling the H-Adr porosity and fractures and less frequently in the nearby bastite. Raman spectroscopy provides primary evidence for a very weak structural organization and low degree of carbonification. The presence of such evolved matter has been related to the progressive hydrothermally-driven degradation of the former complex organic material identified in BPS. The reader is referred to Ménez et al. (2012) for a detailed analysis of the Raman spectra and their interpretation and implication.

3. Methods

3.1. Sample preparation

In order to minimize laboratory contamination, the inner centimetric core of the samples was extracted by sawing. Special attention was paid to preserving a clean organic-free environment by treating the saw with 5% sodium hypochlorite and cutting the rock surfaces with sterilized demineralized water. Double-polished resin-free chips (few tens of μm thick) were manually prepared using silicon carbide polishing disks for Scanning Electron Microscopy (SEM), Raman microspectroscopy, Confocal Laser Scanning Microscopy (CLSM), conventional Fourier Transform Infra-Red spectroscopy (FTIR), and Synchrotron Radiation based FTIR (SR-FTIR) microscopy. High Resolution Transmission Electron Microscopy (HRTEM) and synchrotron based Scanning Transmission X-ray Microscopy (STXM) require the sample to be electron and X-ray transparent, respectively. Therefore, Focused Ion Beam (FIB)