Research paper

Manganese cycling and its implication on methane related processes in the Andaman continental slope sediments

P.P. Sujith [a,b], Maria Judith B.D. Gonsalves [a,*], V. Rajkumar [a], V. Miriam Sheba [a]

[a] Aqua-Geomicrobiology Laboratory, National Institute of Oceanography, Council of Scientific and Industrial Research, Dona Paula, 403 004, Goa, India
[b] Microbiology Laboratory, National Institute of Oceanography, Council of Scientific and Industrial Research, Dona Paula, 403 004, Goa, India

ABSTRACT

In the deep subsurface sediments of the Andaman continental slope, in situ methane generation/oxidation could be coupled to the cycling of Mn, as the fluid flow characterized by high methane and Mn could occur in accretionary wedge sediments by diagenetic and tectonic processes. Laboratory studies on Mn cycling by subsurface sediment microbial communities were therefore undertaken 1) to study, further, possible in situ mechanisms of Mn cycling and 2) to examine how Mn redox reactions might be coupled to methane generation/oxidation. Biotic experiments were conducted with uniformly mixed subsamples amended with 100 μM Mn^{2+} in the presence (G^+) and absence (G^-) of added glucose (55.5 μM). The corresponding abiotic controls included set-ups poisoned with 15 mM sodium azide. Further, to relate the results of in vitro experiments on Mn cycling, to the methane related processes occurring in the subsurface sediments, pore water concentration of Mn, total cell numbers and the abundance of methanogens, methanotrophs and fermenters were determined. Results of the experiment on Mn cycling showed the immobilization of Mn occurred under oxic conditions and mobilization under suboxic conditions in the absence of added glucose at $P \leq 0.001$ with abiotic > biotic. Whereas, in the presence of added glucose, immobilization occurred under both oxic and suboxic conditions at $P \leq 0.001$ with biotic > abiotic, oxic > suboxic. The biotic cycling of Mn at 360 mbsf coincided with the total cell numbers (1.53×10^8 cells g^{-1}), increased methane levels (89,100 ppm-v) and the abundance of methanogens (1.0×10^3 MPN g^{-1}). Besides, the distribution of aerobic methanotrophs decreased in abundance with depth. Also, the abundance of fermenters (3.5×10^3 cells g^{-1}) at 626.7 mbsf coincided with the relatively high concentration of Mn (319.1 μM) in sediment pore water. The results indicate that subsurface sediments harbor microorganisms that partake significantly in the cycling of Mn wherein, the availability of organic carbon dictates the direction in which the reactions occur. Besides, aerobic oxidation of methane and Mn has been reported to occur under reducing conditions. Thus, the present findings suggest that Mn redox changes affect the methane oxidation/production rates by serving either as an electron donor and/or an electron acceptor.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Continental margins are important for intense biogeochemical processes as they are regions for high biological production and sedimentation. During the degradation of buried organic matter in sediments, the microorganisms inhabiting the subsurface derive energy by transferring electrons to a wide variety of electron acceptors such as nitrate, nitrite, Mn(IV), Fe(III), sulfate and CO_2 (DeLong, 2004). However, the preference for potential terminal electron acceptors for anaerobic respiration depends mainly on

their availability, energy yield and the accessibility of a suitable carbon substrate. In the continental margins, the availability of carbon required for methanogenesis is met from the high burial of organic matter which in general consists of fine-grained terrigenous matter, biogenic opal and particulate organic matter (Rixen et al., 2005). During the organic carbon degradation great amounts of methane are formed in situ from acetate fermentation and CO_2 reduction. Besides, methane may also form in subsurface sediments from migration from a shorter distance, recycling during hydrate formation and dissociation following sedimentation (Kvenvolden and Lorenson, 2001).

The methane that formed from organic carbon degradation in the subsurface, depending on its concentration, solubility in pore water and relatively high pressure and low temperature may lead

* Corresponding author. Tel.: +91 832 2450624; fax: +91 832 2450606.
E-mail address: mjudith@nio.org (M.J.B.D. Gonsalves).

to its occurrence in a dissolved state, stable form as hydrate, or a free gas (Riedel et al., 2006). Under ideal conditions, the hydrates may form typically at depths >1000 m in the gas hydrate stability zone (GHSZ) (Kvenvolden and Lorenson, 2001). The sediments of the present study constrained to depths >1000 m (134 m and 638 m) within the GHSZ is characterized by nanofossil ooze, presence of ash and methane hydrates (Collett et al., 2008) and, hence is idealistic for the understanding of subsurface microbial processes associated with the hydrates. The global estimates show methane carbon in the hydrates to range from 0.5 to 24 teratonnes with methane representing more than 99% of the gas mixture present in the hydrate (Kvenvolden and Lorenson, 2001). The emission of methane from such sediments has increasing concerns due to its significant effect on the global climate and the carbon cycle (Jiang et al., 2013). On the other hand, the oxidation of methane by aerobic methanotrophs and anaerobic oxidation of methane (AOM) by anaerobic methanotrophic archaea (ANME) (Hanson and Hanson, 1996), controls the escape of methane to the atmosphere. Besides, AOM mediated by ANME counterbalances the net production to the oxidation of methane (Joye, 2012; Haroon et al., 2013) via "the back reaction" catalyzed by the key enzyme of methanogenesis, the methyl coenzyme M reductase (Scheller et al., 2010).

As several trace metals are important in enzymatic pathways of methanogenesis (Zerkle et al., 2005), the production of methane in the subsurface could be affected by the presence/absence of metals. Of the different elements, iron, nickel, cobalt, zinc, copper, molybdenum and tungsten are considered to be crucial in methanogenesis (Unal et al., 2012). Nonetheless, small amounts of Mn are also important in methanogens for the stability of the enzyme methyltransferase (Scherer et al., 1983; Takashima et al., 1990; Glass and Orphan, 2012). Besides, Mn is a part of four metalloenzymes, manganese superoxide dismutase, mangani-catalase, arginase and O-phosphatases (Christianson, 1997; Shi, 2004). Other than functioning as a stabilizing agent and cofactor of enzymes, Mn is also required for a large number of cellular functions that includes protection from toxic metals, predation or viruses, breakdown of natural organic matter into metabolizable substrates, maintenance of an electron-acceptor reservoir for use in anaerobic respiration, oxygen production and protection against oxidative stress (Christianson, 1997; Crowley et al., 2000; Spiro et al., 2010). It also contributes to the stabilization of bacterial cell walls (Doyle, 1989) and plays an important role in bacterial signal transduction (Jakubovics and Jenkinson, 2001).

The oxides of Mn act as storage of an electron acceptor in sediment systems until carbon and energy become available. Through scavenging reactions, it controls the distribution and fate of trace elements that are important in different biogeochemical reactions (Tebo et al., 2005). The impact of Mn on redox and cation-exchange reactions affects the chemistries of sediments and associated fluids. Also, its complexation with iron in sediments controls the availability of nutrients (Kirchner and Grabowski, 1972) and at times provides a means to derive energy from refractory organic matter through oxidative degradation of humic substances (Tebo et al., 2005; Sujith and Loka Bharathi, 2011). The close coupling of AOM with Fe oxide, Mn oxide, sulfate, nitrate and nitrite reduction counterbalances the net production to the oxidation of methane (Beal et al., 2009; Joye, 2012). Thus the cycling of Mn has considerable impact on the biogeochemical cycling of carbon in the subsurface sediments. However, we are unaware of the importance of Mn in the cycling of methane associated with the subsurface gas hydrates. In the Andaman continental slope sediments, in situ methane generation/oxidation could be coupled to the cycling of Mn as the fluid flow characterized by high methane and Mn could occur in accretionary wedge sediments, by diagenetic and tectonic

processes. This Mn might be distributed in different patterns among the various phases of the metal such as water soluble, exchangeable, reducible and residual/crystalline depending on the pH and Eh (Reddy and DeLaune, 2008). Therefore, to cover the various phases of Mn formed through different mechanisms of activity, the two broader terms namely immobilization and mobilization has been used. Immobilization represents the conversion of ions present in the soluble to the insoluble or bound state by mechanisms such as biosorption, bioaccumulation, redox reaction and complex formation. Whereas, mobilization represents the conversion of ions present in the insoluble state to the soluble state by redox, acidic and complexation reactions (Brandl and Faramarzi, 2006).

In the subsurface sediments of the Andaman continental slope in situ methane generation/oxidation could be coupled to the cycling of Mn. To further understand the implications of Mn cycling on methane related processes, laboratory studies were conducted with the following objectives 1) to study, further, possible in situ mechanisms of Mn cycling and 2) to examine how Mn redox reactions might be coupled to methane generation/oxidation.

2. Methods

2.1. Study area and sample collection

The Andaman Basin has an area of 800,000 km^2 separated from the Bay of Bengal by the Andaman-Nicobar Ridge (Rodolfo, 1969). The water depth of the site is ~1344 m and the sediments have <1% by weight total organic carbon (Ramaswamy et al., 2008; Johnson et al., 2009). The study site NGHP-01-17A is located at 10°45.1912′N (lat), 93° 6.7365′E (long) in the eastern coast of the Andaman Islands. Pressure cores were collected from this location during the Leg 4 cruise of Expedition 01 (2006). The sediments of the core are characterized by nanofossil ooze, presence of ash and methane hydrates (Collett et al., 2008). The cores identified for microbiological sampling were cored with drilling fluid spiked with contamination tracers according to ODP/IODP standard core handling procedures (Smith et al., 2000; Riedel et al., 2006). On board, the appropriate sections were taken on the catwalk and then transferred immediately to the microbiology laboratory on the forecastle deck. The core was sub-sectioned onboard for 25 depths between 134 and 637.5 mbsf (meters below seafloor) and was transported to the laboratory at 4 °C. The samples were then used for the microbiological and geochemical studies of subsurface gas hydrate sediments. It was also used as the natural medium for conducting laboratory studies on Mn cycling.

The site NGHP-01-17A was chosen for this study mainly because 1) it is located at the accretionary wedge of the Sunda subduction zone on the Andaman continental slope where fluid flow characterized by high methane and Mn could occur by diagenetic and tectonic processes and 2) to explore the biogeochemical reactions of Mn associated with subsurface gas hydrates. Besides, the deeper depths were chosen as they fall in the GHSZ and these samples were available for the study.

2.2. Extraction of pore water by centrifugation and analysis of geochemical parameters

The analysis of geochemical parameters like methane and Mn in pore water was studied as it throws light on the subsurface processes with reference to organic carbon mineralization. For the extraction of pore water, all containers and tubes were cleaned carefully with acid, rinsed at least three times with double distilled water and dried before use. Sediments in its native form were purged with nitrogen while introducing into the centrifuge tubes which were capped