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Geochemistry of deep sea sediments at cold seep sites in the Nankai Trough: Insights into the effect of anaerobic oxidation of methane

Hisatoshi Sato [a,*], Ken-ichiro Hayashi [b], Yujiro Ogawa [b], Kiichiro Kawamura [c]

[a] Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan
[b] Department of Earth Evolution Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan
[c] Graduate School of Science and Engineering, Yamaguchi University, 1677-1 Yoshida, Yamaguchi City, Yamaguchi 753-8511, Japan

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ABSTRACT

Two types of sediment were recovered from “methane seep” sites in the Nankai Trough: “Cold seep” sediment affected by anaerobic oxidation of methane (AOM), and unaffected “Typical oxic marine sediment,” Concentrations of carbon, sulfur, iron, and trace metals were analyzed in these sediments. The results showed that the sulfur contents of “cold seep” sediments are higher than those of typical oxic marine sediments, although the organic carbon contents of the two types of sediment are identical. The high sulfur contents of seep sediments suggest that AOM was the dominant process at the “cold seep” sites; H_2S produced as a result of AOM was fixed as reduced sulfur such as iron sulfide.

The highest manganese concentrations (approx. 1000 ppm) were found in surface sediments at non-seep sites, whereas a strong enrichment of Mn was not observed in the “cold seep” sediments. Manganese might be released from sediments as soluble Mn^{2+} ion in the reduced environment produced by methane-bearing seepage. The molybdenum content in “cold seep” sediments (up to 28.3 ppm) is about 30 times higher than that in the typical oxic marine sediments. However, a correlation between Mo and organic carbon contents, which is characteristic of anoxic sediment, was not observed in our samples. “Cold seep” sediments are a potential sink in the global geochemical cycle of Mo.

1. Introduction

Geochemical studies on topics such as carbon–sulfur–iron relationships and trace metal concentrations in seafloor sediments have been systematically carried out to reconstruct paleoceanographic conditions. One of the most important pieces of information in regard to marine environments is the redox state of both the seawater and bottom sediments. Several important reactions that occur in bottom sediments are controlled by the oxygen concentration of the seawater, examples of which are the inorganic reduction of ferric iron, and sulfate reduction by bacterial metabolism accompanying consumption of organic matter. Microbial sulfate reduction is accelerated under oxygen-poor conditions and written as

$$SO_4^{\ 2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^{\ -}. \tag{1}$$

As a result of Eq. (1), the hydrogen sulfide produced subsequently reacts with Fe^{2+} to form Fe–S compounds (Berner, 1982; Jørgensen, 1982). Therefore, the systematic relationships between organic carbon, sulfur and iron can be used to elucidate the redox condition of deep-sea sediments (e.g., Calvert and Karlin, 1991; Middelburg, 1991; Lyons and Berner, 1992; Schenau et al., 2002).

In addition to the behavior of iron, the concentrations of metals in sediments, especially redox-sensitive metals (e.g., Mn, V, U, Mo, Cd and Re), indicate the redox conditions (Warning and Brumsack, 2000; Böning et al., 2004). The concentrations of trace metals in sediments are controlled by the redox conditions of the seawater, and the supply rate of trace metals that is peculiar to the depositional setting (Morford and Emerson, 1999; Brumsack, 2006; Tribovillard et al., 2006). Because of their value in clarifying the depositional environment, the concentrations of these elements in sediments have been measured at several locations. However, C–S–Fe relations and the behavior of trace metals have not been studied extensively in “cold seep” systems.

At “cold seep” sites, methane is oxidized anaerobically, which is termed the anaerobic oxidation of methane (AOM), which is a microbial reaction between methanotrophic archaea and “sulfate-reducing” bacteria and is promoted in methane-rich environments (Boetius et al., 2000). Although the metabolic pathways are controversial, the net reaction of AOM is as follows (Hinrichs and Boetius, 2002; Moran et al., 2008):

$$SO_4^{\ 2-} + CH_4 \rightarrow HS^- + HCO_3^{\ -} + H_2O. \tag{2}$$

AOM enables bivalves, gastropods, tubeworms and bacterial mats to prosper in chemosynthetic colonies around seep-vents. These organisms,

* Corresponding author. Tel.: +81 3 5734 2618; fax: +81 3 5734 3538.
E-mail address: sato.h.al@m.titech.ac.jp (H. Sato).

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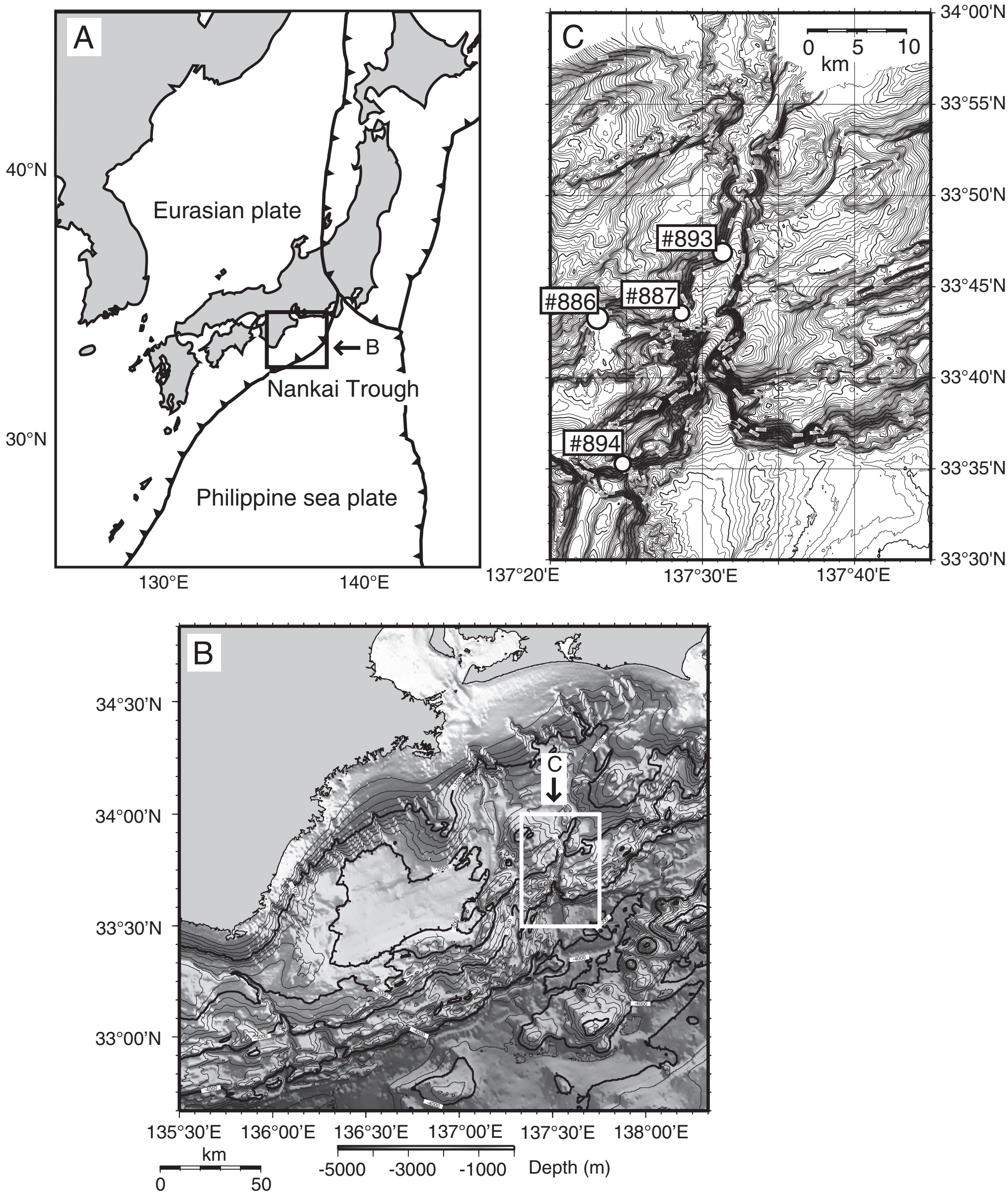

Fig. 1. (A) Map of the study area. The box represents the field surveyed during the YK05-08 cruise. (B) A bathymetry map of the Nankai Trough. The box indicates the survey area of the submersible "Shinkai 6500." (C) A topographic map of Tenryu Canyon. The circles denote the location of core samples.

rather than microbial mat, live off the chemosynthetic bacteria, which utilize hydrogen sulfide derived from AOM as an essential material (Sibuet and Olu, 1998). They inhabit the transition between the underlying oxygen-deficient sediments and the overlying oxygen-rich bottom water. Moreover, AOM accompanies increased alkalinity, which causes the formation of chimneys or crusts through the precipitation of carbonates, which inherit the light carbon isotope ratio of the methane (e.g., Ritger et al., 1987; Bohrmann et al., 1998; Stakes et al., 1999). Recently, AOM has been recognized as the regulator of methane efflux (Dale et al., 2008). In order to evaluate the rate law of AOM and the mechanisms of mineral precipitation, most previous studies have paid attention to the pore-water chemistry of seafloor sediments.

In this study, we describe the behavior of the C–S–Fe group and trace metals in "cold seep" sediments, rather than pore-water, in the Nankai Trough. Our samples were collected *in situ* during dives by submersible from both "cold seep" sites and seafloor sites without seepage; the geochemical characteristics of these samples are compared in order to evaluate the effect of AOM on marine sediments.

2. Geological background

The Nankai Trough is an active plate margin where the Philippine Sea plate subducts under the Eurasian plate, forming an accretionary prism (Fig. 1A). Methane-rich fluids are expelled as cold seeps by tectonic compaction in the accretionary prism (Moore et al., 2005). "Cold seep" sites are distinguishable by the presence of chemosynthetic communities including *Calyptogena* that are distributed around them. In the Nankai Trough, such a community was first found at the Tenryu Canyon (Fig. 1B) where many examples were later studied (Kobayashi, 2002).

Because benthic faunas respire themselves and the metabolization of symbionts entails oxidation of sulfides (Fiala-Médioni et al., 1993), the presence of *Calyptogena* means that the bottom water in the survey area was oxic.

The sediment of this area largely consists of fine detrital siliciclastics that were mostly derived from a terrestrial provenance. They were transported as debris and mudflows to their present position (Kobayashi, 2002).