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Halogen concentrations in pore waters and sediments of the Nankai Trough, Japan: Implications for the origin of gas hydrates

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Abstract

Presented here are halogen concentrations (Cl, Br and I) in pore waters and sediments from three deep cores in gas hydrate fields of the Nankai Trough area. The three cores were drilled between 1999 and 2004 in different geologic regions of the northeastern Nankai Trough hydrate zone. Iodine concentrations in all three cores increase rapidly with depth from seawater concentrations (0.00043 mmol/L) to values of up to 0.45 mmol/L. The chemical form of I was identified as I^-, in accordance with the anaerobic conditions in marine sediments below the SO_4 reduction depth. The increase in I is accompanied by a parallel, although lesser increase in Br concentrations, while Cl concentrations are close to seawater values throughout most of the profiles. Large concentration fluctuations of the three halogens in pore waters were found close to the lower boundary of the hydrate stability zone, related to processes of formation and dissociation of hydrates in this zone. Generally low concentrations of I and Br in sediments and the lack of correlation between sediment and pore water profiles speak against derivation of I and Br from local sediments and suggest transport of halogen rich fluids into the gas hydrate fields. Differences in the concentration profiles between the three cores indicate that modes of transportation shifted from an essentially vertical pattern in a sedimentary basin location to more horizontal patterns in accretionary ridge settings. Because of the close association between organic material and I and the similarity of transport behavior for I^- and CH_4, the results suggest that the CH_4 in the gas hydrates also was transported by aqueous fluids from older sediments into the present layers.

1. Introduction

Forearc areas have been recognized as the location of major processes leading to the dewatering of the subducting slab and the overriding wedge, accompanied by the storage or release of major quantities of CH_4. Expression of these processes is the ubiquitous presence of gas hydrates associated with active margins as well as the frequent occurrence of mud volcanoes in forearc locations. Gas hydrates are crystalline structures of water ice which have trapped gas molecules, mostly CH_4 with minor

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additions of higher hydrocarbons (Sloan, 1998). They are common along all continental margins in water depths typically greater than 800 m within 50–400 m below the seafloor. The lower boundary of the stability field for gas hydrates depends on the thermal gradient in a given location and is indicated by a strong seismic reflector, called the bottom simulating reflector (BSR). Below the BSR, gas hydrates are not stable, but the area typically contains considerable amounts of free gas. The frequent recognition of BSRs in seismic surveys has led to estimates that the amount of C present in gas hydrates is of similar magnitude as all of the traditional fossil fuel reservoirs combined (e.g. Kvenvolden, 1999), although the precise quantity is still debated (e.g. Milkov et al., 2003). Because gas hydrates have been recognized as an important C reservoir, they have been mentioned prominently as a potentially large source of energy and of greenhouse gases (Kvenvolden, 1999), but are increasingly also invoked in discussions concerning the global C cycle and rapid changes in ocean circulation and climate (e.g. Dickens et al., 1997; Dickens, 2001; Kastner, 2001; Kennett et al., 2003). Although the occurrence of gas hydrates is not restricted to active continental margins, the presence and formation of gas hydrates in active margins has attracted increased attention, specifically during recent ODP Legs (201 and 204), IODP expedition 311 and in several large projects on gas hydrates in the Nankai area, carried out by Japanese organizations. The origin of the fluids and, more specifically, of the CH_4 in the fluids in these settings is still a major topic of debate. The three halogen elements used for the investigation presented here can give important clues on the origin and formation of gas hydrate occurrences, mainly related to the different degrees of association with organic material shown by these elements: they range from the strongly biophilic characteristic of I to the essentially conservative behavior of Cl in waters associated with gas hydrates, with Br taking a position in between the other two elements. It is possible that Br is also derived from silicate weathering (Martin, 1999). While Cl concentrations are determined routinely in cores from the ODP program or similar activities, I and Br concentrations are less commonly measured. The strong enrichment of I in pore waters associated with gas hydrate fluids was shown first at the Peru Margin (Martin et al., 1993), and has been found in the meantime in all marine gas hydrate locations where I has been determined (e.g. Egeberg and Dickens, 1999; Fehn et al., 2003; Fehn et al., 2006). Because of the close association of I with organic matter and the similarity in diffusion coefficients between I^- and CH_4, it is likely that these two compounds are transported together in aqueous fluids and that I can be used as a proxy for the origin of CH_4 in gas hydrate fields.

Results are reported here from three deep cores taken from gas hydrate fields in the Nankai Trough area. The cores were taken within a program organized by the Japanese Ministry of Economy, Trade and Industry (METI) between 1999 and 2004. The three cores reached depths between 243 and 342 mbsf, and went in all cases below the BSR, i.e. covering the entire thickness of the gas hydrate occurrence and parts of the underlying sections containing free gas. Results are reported here of determinations of Cl, Br and I concentrations in pore waters and associated sediment samples taken from these cores. Overall, the three halogens were determined in 281 pore water samples; I and Br were measured in 111 sediment samples.

2. Geologic setting

The Nankai Trough formed by the subduction of the Philippine Sea Plate under the Eurasian Plate and is associated with an accretionary margin running roughly parallel to the eastern coast of southern Honshu, Shikoku and Kyushu (Fig. 1a). It has been the focus of several drilling expeditions: ODP drilling was focused on the accretionary wedge in the mid section of the trough area (e.g. ODP Legs 808; 1178), and recent investigations organized by Japanese research groups took place in the northeastern section of the Nankai Trough area. Samples recovered from drill sites in the gas hydrate area are the focus of this investigation (Fig. 1b).

A schematic cross section through the Nankai margin is shown in Fig. 2, which also indicates the different tectonic settings of the gas hydrate fields in this area (Baba and Yamada, 2004). The subducted crust in the Nankai Trough is about 20 Ma (Jarrard, 1986) with a relatively thin package of subducting marine sediments (<2 km; Hyndman et al., 1992). The accretionary prism is bounded by a ridge, separating it from the sedimentary basin formed between the currently active accretionary wedge and the remnants of an earlier subduction configuration. This prism was generated when the Pacific Plate was subducted under the Eurasian Plate in this region and the proto-Izu Bonin Arc