



# Increase in methane flux and dissociation of iron and manganese oxides recorded in a methane-derived carbonate nodule in the eastern margin of the Sea of Japan



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## ABSTRACT

High resolution analyses of an aggregate of aragonite crystals in a methane-derived carbonate nodule revealed evolution of interstitial water geochemistry associated with increases in methane flux at the Umitaka Spur gas seep site in the Sea of Japan. Geochemical data were obtained from the aggregate using Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), millimeter-scale powdering, and electron probe micro analysis. Most elements measured by LA-ICP-MS, and carbon and oxygen isotopic compositions ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively) of aragonite, have symmetrical patterns in the aggregate. Concentrations of Ba,  $\delta^{13}\text{C}_{\text{CaCO}_3}$ , and  $\delta^{18}\text{O}_{\text{CaCO}_3}$  increase monotonically towards the center of the aggregate ( $\delta^{13}\text{C}_{\text{CaCO}_3}$ ; from  $-12\text{‰}$  to  $-4\text{‰}$ VPDB), while rare earth elements (REEs) and Mn oscillate. Iron peaks are located closest to those of light REEs, and the shale-normalized pattern of a REE peak event is enriched in middle REEs, suggesting dissociation of Fe-oxides as the source of the REEs. The monotonically changing geochemical data and fan-shaped, acicular aragonites growing inwardly from the aggregate rim, suggest aggregate formation from rim to center. Therefore, the peak position of Mn to the interior of that of Fe, suggests an increase in dissolved Mn after the dissociation of Fe-oxides. The isotopic trends continue into the surrounding matrix, where  $\delta^{13}\text{C}_{\text{CaCO}_3}$  reaches  $\sim -20\text{‰}$ VPDB, close to the  $\delta^{13}\text{C}$  of dissolved inorganic carbon currently found in the sulfate-methane transition (SMT). The trends of  $\delta^{13}\text{C}_{\text{CaCO}_3}$  and Ba, and the evidence of dissociation of Fe-oxides suggest upward migration of the SMT during carbonate cementation, which is initiated in the SMT.

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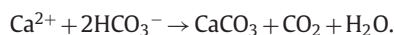
## 1. Introduction

The seafloor in areas with high methane flux are often characterized by concretions of calcium carbonate, called methane-derived authigenic carbonates [2,12,32,33,64,70,71,77,86,88]. This is caused by the production of bicarbonate ( $\text{HCO}_3^-$ ) through microbial activity known as the anaerobic oxidation of methane (AOM) interacting with sulfate ( $\text{SO}_4^{2-}$ ) [11,74], according to:



The increased alkalinity from the production of  $\text{HCO}_3^-$  in the presence of dissolved Ca causes the precipitation of carbonate

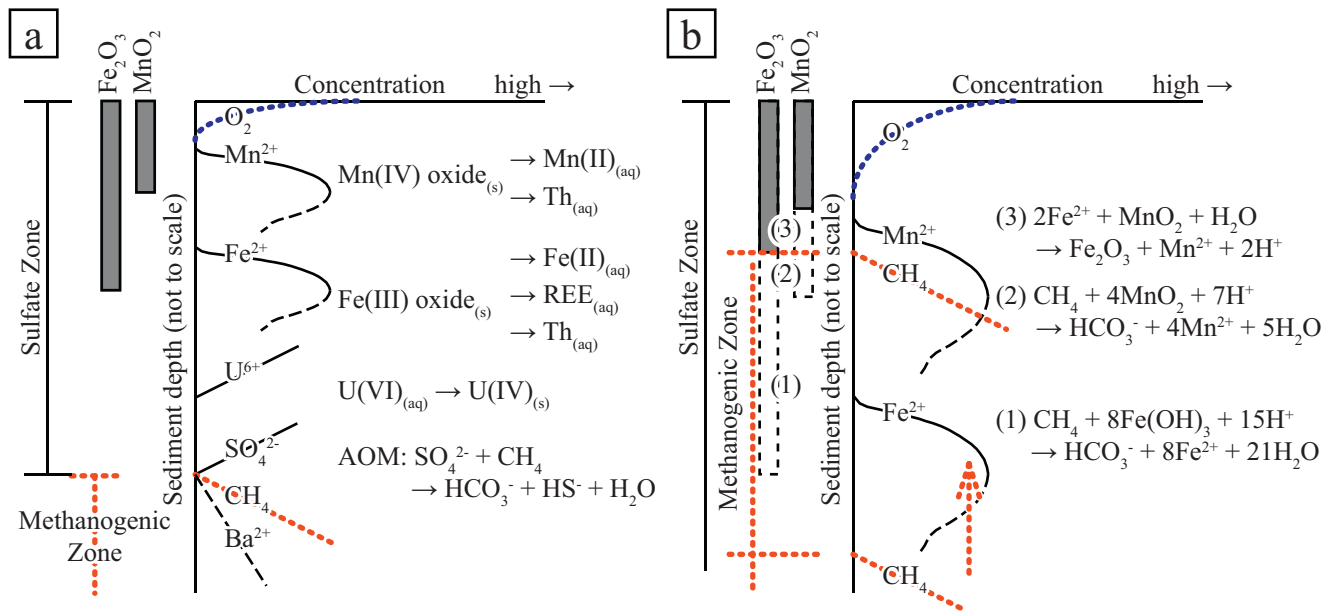
[2,56,77], according to:



Beneath the oxic seawater in marine sediments, bacterial and thermodynamic chemical reactions follow a decreasing energy order and generate chemical zonation with sediment depth (Fig. 1a). Methane originates from organic matter in sediment and migrates from deep, whereupon  $\text{SO}_4^{2-}$  is the first oxidizer encountered. The upper part of the methanogenic zone, which is characterized by methane dissolved in the interstitial pore water, overlaps with the sulfate zone containing  $\text{SO}_4^{2-}$ . The overlap of both zones is referred to as the sulfate-methane transition (SMT) or sulfate-methane interface, when the thickness of the overlap is negligible [13,15,47,57,58]. Rapid  $\text{SO}_4^{2-}$  consumption by active AOM shifts the SMT upwards. Owing to the conversion of  $^{13}\text{C}$ -depleted carbon from methane into  $\text{HCO}_3^-$ , the carbon isotopic composition of  $\text{HCO}_3^-$  ( $\delta^{13}\text{C}_{\text{DIC}}$ ) has the lowest value within the SMT [14,19,96].

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**Fig. 1.** Schematic profiles of interstitial water in marine sediments. (a) Steady-state conditions. Although the profiles of dissolved Fe(II) and Mn(II) below the peaks (dashed lines) depend on the amount of relict solid phases in the sediments, these concentrations generally decrease below the peaks. Dissociation of Fe- and Mn-oxides also supplies Th. (b) Upward migration of the methanogenic zone and the probable following reactions: (1) the methanogenic zone will make contact with the Fe(III) oxide zone, and then AOM with Fe oxide will produce dissolved Fe(II) and REEs; (2) AOM with Mn(IV) oxide and production of dissolved Mn(II); and (3) Abiotic oxidation of Fe(II) by Mn(IV) oxide and production of dissolved Mn(II).

Above the SMT, oxides of Mn and Fe are reduced and concentrations of dissolved Mn, Fe and REEs from La to Lu (i.e., N=57–71) in the interstitial water increase [16,23,29,39,54,83,84]. At comparable depths to the Fe reduction, dissolved U in the hexavalent state ( $\text{U}^{(\text{VI})}$ ) is reduced to the less soluble  $\text{U}^{(\text{IV})}$  and precipitated [4,18,51,55,79,82,92]. Dissolved Ba increases below the exhaustion of  $\text{SO}_4^{2-}$ , because  $\text{SO}_4^{2-}$  precipitates Ba as barite [9,22,35,93–95].

The chemistry of these methane-derived carbonates is a geological archive for reconstructing the compositions of paleo-interstitial waters from which the carbonates precipitated [10,25–27,31,41,45,78]. Although measurable samples are limited, it is possible to reveal gradual change in interstitial water chemistry by high resolution analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [41]. We expect high resolution analyses of the many elements that are involved in chemical reactions around the SMT to reveal the influence of changes in methane flux in more detail (Fig. 1b). Because the interference of argon in the ICP-MS carrier gas (i.e., mass of  $^{18}\text{Ar}^{18}\text{O}$  equals  $^{26}\text{Fe}$ ) prevents determination of Fe concentrations through this method, electron probe micro analysis (EPMA) was used to measure the Fe. Although thorium (Th) and strontium (Sr) are not major elements in these reactions, their concentrations were determined for future work and method comparison, respectively. A methane-derived carbonate nodule was selected from a gas hydrate area in the eastern margin of the Sea of Japan, where the methane flux increase and mass carbonate precipitations were expected around the last glacial maximum, given the results of U/Th dating of the carbonate nodules by Watanabe et al. [99].

## 2. Geological setting

The Umitaka Spur, in the eastern margin of the Sea of Japan, is located ~40 km off the Kubiki oil and gas field in Joetsu City (Fig. 2). The anticlinal structure at ~900 m below sea level has two gas seep sites located in the central and northern parts of the crest [3]. The central seep site consists of two mounds, which are both ~150 m in diameter and ~10 m in height. Seafloor observations with a remotely operated vehicle (ROV) revealed outcrops of

massive gas hydrate, gas bubble seepage, and widely distributed concretions at these gas seep sites. The temperature of the bottom seawater was ~0.2 °C, which is consistent with Japan Sea Proper Water (cf. [30,61,87]). Common chemosynthetic, biological communities, such as tube worms and clam beds, were not observed.

Interstitial chloride ion concentrations increase with sediment depth, and associated depletion of deuterium and  $^{18}\text{O}$  in  $\text{H}_2\text{O}$  suggest recent gas hydrate formation under the seafloor at the central gas seep site [42]. The carbon isotopic composition of methane dissolved in interstitial water and captured in gas hydrate is ~–40 ‰ VPDB at the central seep site [44]. Due to the anaerobic oxidation of thermogenic methane, the  $\delta^{13}\text{C}_{\text{DIC}}$  around the near-seafloor SMT is ~–30 ‰ VPDB. The U/Th date of methane-derived carbonate nodules at the Spur ranged between 35 and 12 ka, with an isochron age of  $26 \pm 3$  ka [99]. Shoaling of the base of the gas hydrate stability zone due to sea level drop depressurization and increasing methane flux, which accelerates carbonate precipitation, was expected [99].

## 3. Materials and methods

### 3.1. Sample recovery and preparation

During the KY05-08 cruise (August 2005) by R/V Kaiyo of the Japan Agency for Marine–Earth Science and Technology (JAMSTEC), three piston cores recovered from the central seep site (PC502, PC508 and PC513) contained gas hydrate- and carbonate nodule-bearing sediments [42]. During the cruise, carbonate nodules that were handpicked from the split PVC liner and kept in a refrigerator, were washed with tap water in the vessel and dried in a 60 °C oven [43]. After the cruise, the carbonate nodules were cut into two pieces, and the cut surfaces were polished and air-dried. A piece of one carbonate nodule with an ellipsoidal, massive aggregate of aragonite crystals (PC502-sec.H-(70) at 197 cm below seafloor) was selected for this study (Fig. 3a). Powder and chip samples from another piece suggested aragonite cementation of glacial sediments prior to significant burial compaction [43].

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