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U–Th dating of carbonate nodules from methane seeps off Joetsu, Eastern Margin of Japan Sea

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ABSTRACT

We performed U–Th radioactive disequilibrium analyses of carbonate nodules and sediment samples recovered from methane seep sites off Joetsu, of the eastern margin of Japan Sea, to decipher the active period of the methane seep. The carbonates contain ^{230}Th, part of which is located in detritus such as silicate and organics, at the time of precipitation. The initial ^{230}Th renders accurate dating with U–Th radioactive disequilibrium method difficult. We assessed the feasibility of correction using radioactive disequilibrium data of ambient sediment to overcome this difficulty. A (^{230}Th/^{232}Th)–(^{234}U/^{232}Th) isochron drawn by three chips divided from a carbonate nodule (PC05-04-50) passed through data points of local sediments. We conclude that the problem of initial ^{230}Th can be resolved by measurements of local sediments. Results show that carbonate nodules include local sediment as impurities. Furthermore, the results of trace element analyses such as Rb, Zr, Nb, REE, Pb, and Th also support the idea.

In all, 18 carbonate samples were dated with correction of initial ^{230}Th using the mean value of local sediment in this study. The U–Th correction ages show 12–35ka with an isochron age of 26 ± 3ka. Results indicate that during the time interval of U–Th ages, from 12ka to 35ka, environmental conditions must have been favorable for enhanced methane flux through sediment. The extensive methane flow period at 20ka accords with the lowest-stand sea level during the last glacial age. Results of this study also suggest that U–Th ages of carbonate are useful as a reliable chronometer with regard to methane seep activation. In order to acquire U–Th ages of carbonate at methane seep sites, however, it is important to evaluate the amount of initial ^{230}Th accurately using the value of sediment.

1. Introduction

Methane seeps have been observed in many different settings around the world (e.g., Kulmn et al., 1986; Sakai et al., 1992; Aharon et al., 1992). Methane is a strong greenhouse gas, which might strongly affect global climate (e.g., Sloan et al., 1992; Maslin and Thomas, 2003).

For that reason, it is critical to elucidate the activation of methane seeps as follows.

(1) When was methane released from the seafloor?
(2) Is venting from these methane seeps continuous or discontinuous?
(3) What geological factors influence methane seep activity?

Methane seep sites are often associated with authigenic carbonate such as crusts, chimneys and concretion. Carbonate precipitation is triggered by increased alkalinity during anaerobic oxidation of methane via sulfate reduction, as follows (Aharon et al., 1992; Bohrmann et al., 1998).

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

Therefore, authigenic carbonate is a useful chronometer that reflects the time at which methane seep was active. Several attempts have been made at ^{14}C dating of carbonate samples related to methane seeps (e.g., Paull et al., 1989). Carbonate related to methane seep contains dead carbon (Paull et al., 1989; Aharon et al., 1997; Peckmann et al., 2001; Gulin et al., 2003). Therefore, Paull et al. (1989) have reported the obtained ^{14}C ages as maximum ages. Aharon et al. (1997) used ^{14}C in conjunction with δ^{13}C in order to assess the proportion of oxidized thermogenic methane, and only the U/Th age was used for the determination of carbonate formation. Also, Gulin et al. (2003) assessed the amount of dead carbon using stable carbon isotope ratio in order to calculate more appropriate ^{14}C ages.

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Radioactive disequilibrium dating of the ^{238}U decay series has been applied to numerous fields such as paleoclimatology, marine geochemistry, hydrology, archaeology, and volcanology (Bourdon et al., 2003). Under oxidizing conditions, U is soluble in natural water as uranyl ion, whereas Th has extremely low solubility. Carbonate precipitated from water usually contains U and rarely Th (e.g. <1ppb in coral). Hence, the age of carbonate can be determined by measuring the increase of ^{230}Th decaying from ^{234}U, from zero at precipitation to equilibrium, providing that a U–Th system of the carbonate mineral is kept closed after precipitation (Bourdon et al., 2003). However, only a few attempts have been made to determine the ages of carbonates related to methane seeps using U–Th radioactive disequilibrium. The only studies known to us are those of Lalou et al. (1992), Aharon et al. (1997), and Teichert et al. (2003). Why U–Th dating study of carbonate at methane seep areas has not been carried out arises from the fact that those carbonates often contain non-negligible amounts of initial ^{230}Th derived from detritus such as silicate and organic material. The presence of the initial ^{230}Th hampered accurate age determination of carbonate.

Lalou et al. (1992) reported that carbonate cements and chimneys at the Nankai accretionary prism have Th concentration of 0.8–4.5ppm. They reported ^{230}Th–^{234}U ages of the carbonates as from 20 to >350ka, without making corrections of the initial ^{230}Th. Aharon et al. (1997) determined Th concentrations of carbonate cements in the Gulf of Mexico of 0.2 to 1.0ppm, and presented corrected ages using the ($^{230}Th/^{232}Th$) activity ratio of local sediment. Teichert et al. (2003) reported that authigenic carbonates at Hydrate Ridge have Th concentration of less than 50ppb. They calculated corrected ages using the value of the residue that remained after a sample was leached by acetic acid. Subsequent studies have not confirmed whether local sediments shared the same ($^{230}Th/^{232}Th$) with carbonate. Aside from the results of Teichert et al., who used less-contaminated carbonate, it remains uncertain whether the corrected ages are accurate. In this study, we tackled the problem using an isochron of a carbonate nodule at methane seep, aiming at testing the feasibility of judging whether the age of carbonate can be corrected accurately by the value of sediment and deciphering the timing of the methane seep based on U–Th dating of carbonate.

As a case study, we selected carbonate nodules and sediments recovered near active methane seeps off Joetsu, the eastern margin of Japan Sea. In this paper, two methods were examined to estimate the amount of initial ^{230}Th. The first one is the isochron method. Another method is correction of initial ^{230}Th in a carbonate with the mean value of sediments recovered near the carbonate. Comparing the two approaches, the accuracy of U–Th dating and the geological implications will be discussed.

2. Sample descriptions and geological setting

The studied site is located at the 900-m depth: the sedimentary basin off Joetsu, on the Eastern Margin of Japan Sea (Fig. 1A). Offshore of Joetsu is the boundary between the Eurasia Plate and North American Plate. During summer 2004, the R&T/V Umitaka-maru of Tokyo University of Marine Science and Technology investigated a

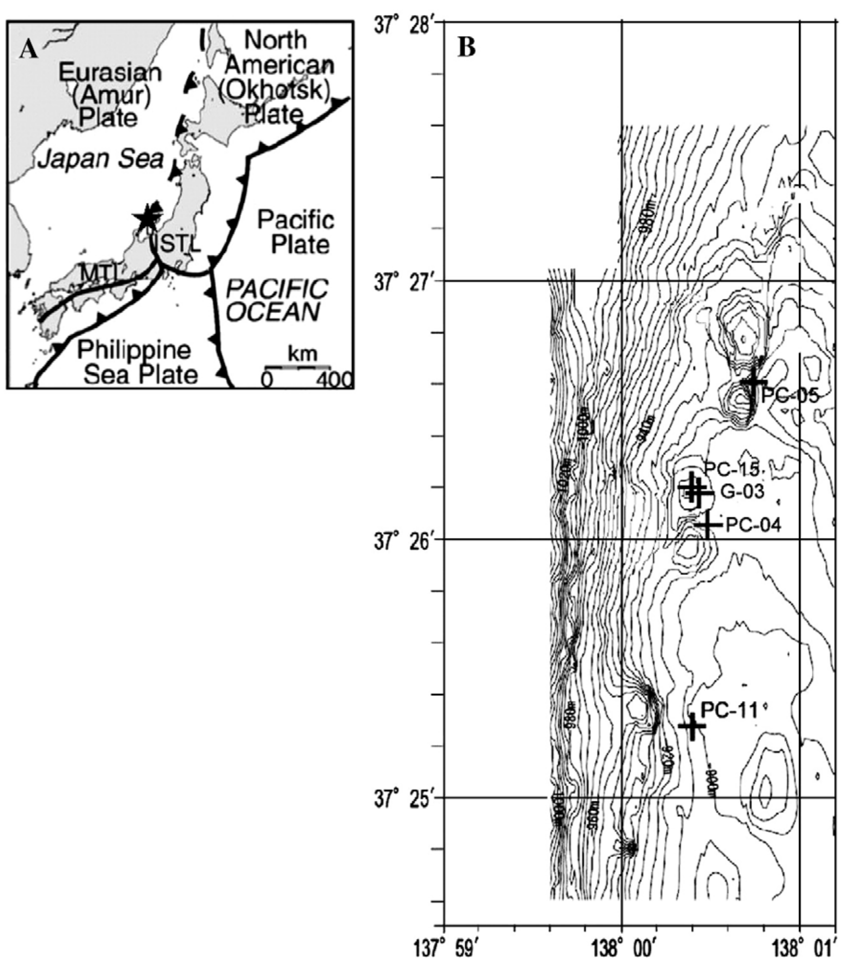

Fig. 1. (A) Geological setting of Japan. The star represents the methane seep area off Joetsu. (B) Detailed map of study area. Black crosses show the positions of piston core and grab samplings in 2004 cruise.