Marine and Petroleum Geology 56 (2014) 51–62

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo

Research paper

Last glacial emplacement of methane-derived authigenic carbonates in the Sea of Japan constrained by diatom assemblage, carbon-14, and carbonate content

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ARTICLE INFO

Article history:
Received 25 October 2013
Received in revised form
7 April 2014
Accepted 11 April 2014
Available online 21 April 2014

Keywords:
Methane-derived authigenic carbonate
Stable carbon isotopic composition
Uranium/Thorium dating
Radio carbon fourteen
Calcium carbonate content
Last glacial maximum
Diatom assemblage
Sea of Japan

ABSTRACT

We studied diatom assemblages and $CaCO_3$ contents of methane-derived authigenic carbonates from the eastern margin of the Sea of Japan and assessed the formation time of these samples. Radioactive ^{14}C date was determined in selected samples to obtain the maximum age of the time. The results of our study suggest mass formation of carbonate nodules in a glacial period within ~40 ky, consistent with a published U/Th dating result of carbonate nodules in the study area. Diatom assemblages and contents in the carbonate nodules (abundance of ~10^6/g, dominance of neritic-littoral species, warm/cold water species ratio lower than ~25) differ from the near-seafloor sediments in the study area, which have characteristics of Holocene sediments in the Sea of Japan, and suggest cementation of glacial sediments. Laminated sediments in some nodule samples are glacial sediments because laminations are records of a low sea level period in the semi-enclosed ocean. Similarity of diatom assemblages and contents in all carbonate samples is another evidence of glacial sediments in nodules. Glacial sediments with oceanic cold water species as low as Holocene sediments restricts the sediment age to before 20 cal. ky BP. Carbonate contents higher than 78 wt% suggest the cementation of poorly compacted sediments near the seafloor, and the date of carbonate cementation is, therefore, close to that of the cemented sediments. Most carbonate nodule samples in this study were formed in a glacial period and detection of ^{14}C restricts this period to within ~40 ky.

1. Introduction

Seafloors with a high methane flux, such as those at methane seep sites, are often characterized by the presence of authigenic carbonates (Aloisi et al., 2000; Bohrmann et al., 1998; Gieskes et al., 2005; Greinert et al., 2001; Naehr et al., 2007; Peckmann and Thiel, 2004; Peckmann et al., 2001; Ritger et al., 1987; Stakes et al., 1999). This authigenesis is in most cases due to an increase in the alkalinity of sediment interstitial water caused by anaerobic oxidation of methane (AOM) (Aloisi et al., 2002; Boetius et al., 2000; Reeburgh, 1976; Ritger et al., 1987). It is thought that the date of formation of these carbonates can reveal the mechanism of methane seep activation. Because the carbon is methane-derived, calibration of radio carbon (^{14}C) date (Gulin et al., 2003), ^{14}C dating of fossil shells in carbonates (Bian et al., 2013), or Uranium/Thorium dating has been applied as an indicator of the time of onset of active carbonate precipitation (Aharon et al., 1997; Bayon et al., 2009, 2013; Berndt et al., 2014; Feng et al., 2010; Libetrau et al., 2010; Teichert et al., 2003; Watanabe et al., 2008; Wirsig et al., 2012). Although U/Th dating with the isochron approach has been most successfully used for subsurface samples, alternative methods are necessary for some samples. Hydrous oxides of manganese and iron absorb Th from seawater and distribute it in sediments near the seafloor through reduction dissolution (e.g., Froelich et al., 1979; Hunter et al., 1988). Therefore, carbonate formations near the seafloor have the potential to incorporate metal oxide-derived Th, which disturbs the isochron approach (e.g., Bayon et al., 2009; Cochran et al., 1986; Henderson et al., 2001; Lin et al., 1996).

In this study, we assessed the formation time of methane-derived carbonate nodules at a gas hydrate area in the Sea of

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http://dx.doi.org/10.1016/j.marpetgeo.2014.04.005
0264-8172/

Japan by an independent method and compared the results with the published U/Th dating result of Watanabe et al. (2008). The aim was to determine the diatom assemblages, $CaCO_3$ content, and ^{14}C content of $CaCO_3$ in nodule samples from approximately 0–5 m below the seafloor. Several subsamples from Watanabe et al. (2008) were included in this study. We also determined the water content of sediments in order to interpret the $CaCO_3$ content of nodules.

Diatom assemblages in the Sea of Japan provide a good indicator of a time transition from glacial to interglacial sedimentation (Burckle and Akiba, 1978; Koizumi et al., 2006; Koizumi and Yamamoto, 2011). In the case of the Sea of Japan, a drop in sea level around the last glacial maximum (LGM) caused surface water freshening due to the fact that the sea is semi-enclosed by four shallow straits (Fig. 1a and Oba et al., 1991). Diatom assemblages record such environmental changes around the LGM.

Carbonate nodules can potentially record some information regarding the burial conditions of unconsolidated sediments before $CaCO_3$ cementation (Ritger et al., 1987). High $CaCO_3$ content is generally indicative of less compacted sediments near the seafloor (Ritger et al., 1987). Below the seafloor, void space among sediment grains is filled with water and sediment burial compaction reduces the void space. Instead of porosity, we use water content as a proxy of compaction and calculate $CaCO_3$ content after pore space filling by $CaCO_3$. Sediment burial depth before $CaCO_3$ cementation was estimated from comparison of $CaCO_3$ content in nodule samples with the calculated content.

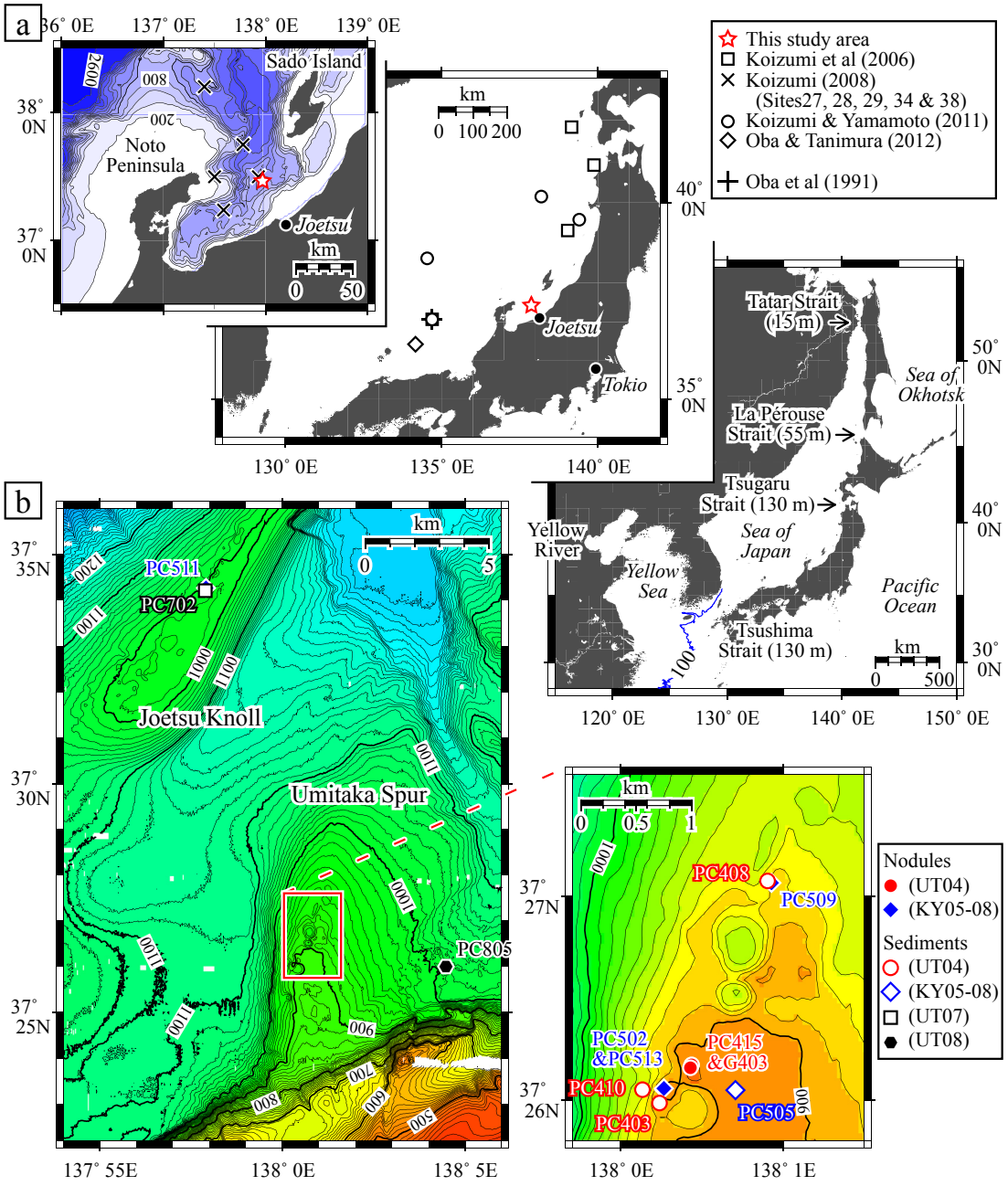

Figure 1. Piston coring and grab sampling sites: (a) The Sea of Japan with four straits and a close-up of the eastern margin. The Tsushima Warm Current enters the sea through the Tsushima Strait. The 100 m contour line in the Yellow Sea indicates the approach between the river mouth and the strait during low sea level. (b) Areas where carbonate nodules were obtained from the two gas seep sites at Umitaka Spur and the central gas seep site at Joetsu Knoll.