Reconstruction of interstitial water geochemistory at an ancient cold-seep site.

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A cold-seep fossil assemblage occur in the Lower Pleistocene Koshiba and Ofuna Formations, northern part of Miura Peninsula, Pacific side of central Japan. Seven cores had been recovered from the outcrop where the assemblage occur. Examination of the cores revealed that aggregated horizons of chemoautotrophic bivalves, *Lucinoma*, *Conchocle*, and *Archarax*, are stacked normal to bedding plane in coexisting with precipitated massive authigenic carbonates. Among the seven cores (cores A-E, J, K), we study authigenic carbonates of the core E that had been recovered normal to bedding, 107m in core length and 6cm in core diameter, and located in peripheral part of the inferred center of the seep where chemoautotrophic bivalves occur aggregately and authigenic carbonates are massively developed.

The core E is described as follows:

1) Six seep stages are recognized based on the distributions of chemoautotrophic bivalves: Stage 1 in 107m; Stage2 in 59m; Stage 3 in 34-21m; Stage 4 in 21-16m; Stage 5 in12-6m; and Stage 6 in 4-0m.

2) Each six seep stage is associated with authigenic carbonates, (aragonite, high Mg calcite, and/or dolomite) which precipitated at or below the bivalve horizon. Each carbonate species occur exclusively in many horizons.

3) These authigenic carbonates are greatly depleted in ^{13}C (d13C = -56.8 to -30.2 permil vs PDB). This clearly indicates clearly indicating that they had been precipitated under the influence of anaerobic methane oxidation (AOM).

We calculated d13C of DIC from d13C of authigenic carbonates assuming an isotopic equilibrium fractionation. The depth profiles of d13C of DIC caliculated from d13C of authigenic carbonates of Stages 2 (core deoth 60-63m) and 5 (core depth 6-15m) are quite similar to the vertical d13C profiles of interstitial water DIC of modern seep sites. In Stages 2 and 5, we can speculate the horizons of sea-floor bed and SMI (sulfate methane interface) when authigenic carbonates had been precipitated: the sea bed in 6m and the SMI in 7-9m at Stage 5, and 59m and 61-63m at Stage 2, respectively. The sea beds are inferred from the upper-limited occurrence of articulate chemoautotrophic bivalves and the SMI by the horizons depleted mostly in ^{13}C of the authigenic carbonates. Furthermore, heavy dolomites (not depleted in ^{13}C) are observed in the core depths 33m and 79m and are interpreted to have been precipitated below AOM when authigenic carbonates of Stages 5 and 2 had been precipitated, respectively.

If the d13C depth profiles of authigenic carbonates of stages 5 and 2 reflect ancient DIC d13C snapshots of sea bottom subsurface, we can draw vertical pH profile of the interstitial water based on d18O of the authigenic cabonates. Oxygen isotopic ratio of marine authigenic carbonates are controlled by the d18O, temperature, salinity, and pH of the sea water. If d18O value of interstitial water, temperature, and salinity of the interstitial water from which authigenic carbonates are precipitated are stable, pH can be calculated from d18O of the authigenic carbonates. The pH profiles calculated in stages 5 and 2 are very similar to subsurface pH profile of modern seep sites where pH is the highest at SMI.