Methane-derived carbonates of the Nankai Trough in southeast Japan: Are they related methane hydrates?

MOHAMMAD HOSEIN MAHMUDY GHARAIE, YIFENG CHEN AND RYO MATSUMOTO

Dept.of Earth and Planetary Science, University of Tokyo, Hongo 7-3-1, Tokyo 113-0033, Japan (hosein@eps.s.u-tokyo.ac.jp)

Fore-arc basin sediments of the Nankai trough is characterized by methane seeps and seep-related phenomenon such as mud volcano and precipitation of authigenic carbonates. Considering the distribution of methane hydrate in the Nankai trough, methane seeps are suspected to be related with methane hydrates. A number of carbonate samples were collected by grabs or piston corers during the GH cruises in 2002, 2003, and 2004. Authigenic carbonates occur either as "chimney"-like cylindrical shape, 25 cm across and 42 cm high, and thick massive bed with occasional shell fragements, ~60 cm thick.

XRD measurement of carbonates has revelaed that almost all carbonates are predominated by high-magnesian calcite with some pyrite and very few dolomite. Mg content of calcite exceeds 10 mol.% (Chen, 2005). The $\delta^{13}C$ values range between -31.2 and -37.3 permil PDB, which indicates that the precipitation of calcite is related with the methane oxidation. Sulfate concentration of the pore waters is observed to decrease with burial, indicating the depth of SMT (Sulfate-methane transitoin) at around 10 to 15 m below seafloor (Matsumoto, et al., 2005). Sulfate-reduction by methane increased [HCO_3^-], alkalinity and the activity of free Mg^{2+} within sulfate reduction zone. These process caused the precipitation of high Mg-calcite.

Methane is generated either through microbial or abiotic thermogenic processes; the former is characterized by relatively light carbon (< -60 permil PDB) whereas the later, by heavier carbon (> -50 permil PDB). Assuming that the carbon in authigenic carboantes is mostly from methane, the Nankai trough carbonates are thought to have been derived from thermogenic methane. However, methane of gas hydrate in the Nankai trough is microbial methane (Waseda et al., 2004). This seems to suggest that methane-bearing cold seep in the Nankai trough is not directly related with subsurface methane hydrate.

References

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Ce anomaly of carbonate rock as a geochemical tracer for redox conditions of paleo-atmosphere

YUZHUO QIU[1,2], WENLING FAN[2] AND LIANG QI[2]

[1]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China (qiuyuzhuo@hotmail.com)
[2]Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

The atmospheric evolution is one of important parts in the Earth System Model. The timing of oxygenation of global atmosphere has been a most controversial issue: the gradual increasing C-W-K-H model vs the constant oxic D-K-O model as summarized by Ohomoto (1997).

Fryer (1977) first suggested 0.8-1.9Ga as the increasing period of atmospheric oxygen based on Eu and Ce anomalies signatures in Precambrian BIFs. The complication of BIF forming condition resulted in severe criticism and argument.

Carbonate sediments are commonly considered to be formed in a shallow seawater which was in equilibrium with contemporary atmosphere in oxygenation condition. The pure carbonate rocks recorded the REE patterns of seawater in which they formed. And the REE are immobile during diagenesis and metamorphism we assumed.

Over 70 rather pure carbonate rocks of Precambrian from China, South Africa and Australia have been analyzed by means of the INAA in Washington University and the ICPMS in both Chinese Geochemistry Institutes. Most of young carbonates show similar REE patterns of present river and sea waters with negative Ce anomalies, while most of old ones with no Ce anomaly. It indicates that the oxygenation conditions of paleo-atmosphere has been changed from redoxyatmoversion to oxyatmoversion. The changing period might be around 1.9 Ga. This result is in good agreement with the gradual increasing C-W-K-H model of atmospheric oxygen evolution, and also with conclusion from other evidence of geological clues, such as the developments of the BIF, red beds, Au-U conglomerates and carbon isotope excursion event.

There were some exceptional samples for this regularity caused by local precipitation environment. More global sampling , especially for those around the changing period, is essential to refine the scale of atmospheric oxygen evolution.

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