

## Chemical forms of arsenic in marine sediments and dissolution mechanisms into porewater of Kumano Basin, Nankai Trough

Haruka Yoshinishi<sup>1</sup>, Shigeshi Fuchida<sup>2</sup>, \*Harue Masuda<sup>1</sup>, Emilie EVEN<sup>1</sup>

1. Graduate School of science, Osaka City University, 2. Center for Global Environmental Research, National Institute for Environmental Studies

The purpose of this study is to clarify the accumulation process of arsenic and the behavior during an early stage of diagenesis in modern marine sediments.

The cored sediments and porewaters at Sites C0002 and C0022, Nankai Trough. At the Site C0002 (0-1050mbsf), sediments at <800mbsf was composed of forearc basin sedimentary rock (terrestrial sediment) and the lower part was of accretionary prism.

In the Site C0002, total arsenic concentrations of sediments increased at 0-330mbsf with depth. The highest concentration was recorded at 330mbsf (13ppm). Then, the concentration decreased, and became constant about 5ppm below 500mbsf. Total arsenic concentration was higher in forearc basin sedimentary rocks than the underlying accretionary prism sediments. It suggests that the primary arsenic was mostly derived from subareal region via detrital fragments.

The result of BCR sequential extraction analysis showed that about 40% of As in the sediment was fixed in insoluble phases, i.e., structure of sulfide and/or silicate minerals. Arsenic in insoluble phase was >80% in the sediment at 1000mbsf, implying that the arsenic was fixed in authigenic pyrite in the deep part of the sediment column.

The ratio of dissolved arsenic arsenic<sub>(porewater)</sub> to Total arsenic of the sediment was especially high at those depth. Thus, the arsenic dissolution was promoted at those depth. Similar high dissolved arsenic ratio was shown at 100-200mbsf, Site C0022, suggesting the same mechanisms to release arsenic in the sediment at these depth.

Speciation of arsenic-bearing phases in the adsorbed fractions onto sediment particles were analyzed by HPLC and analyzed by ICP-MS/MS. Arsenate, arsenite, MAA, and AsB were only detected from the sediments at C0002, C0022. Total concentration of these arsenic compounds was 60% of total arsenic of the sediment, and most of them were arsenate and arsenite. It indicates that over half of total arsenic in the sediment was adsorbed as inorganic arsenic onto the mineral surface. The concentration of arsenite increased below 100mbsf, suggesting that the arsenate was reduced below this depth. The MAA was not large compared to the total arsenic, however, it is important to evaluate the contribution of microbiological activity to the arsenic cycle in the marine sediments. As mentioned above, arsenic fixed in the sediments releases into the porewater at 100-200mbsf. Decomposition of organic matters are extensive in 0-150mbsf evidenced by increasing concentration of NH<sub>4</sub><sup>+</sup> of porewater and Br<sup>-</sup> (accumulate in red algae). Thus, MAA would be a product of decomposition of organic arsenic compounds, such as arsenosugar contained in algae.

Below 200mbsf, increasing pH controlled arsenic dissolution. The average of pH was 7.79 in 0-200mbsf, then gradually increased below this depth. It's peak was about 7.98 at 400mbsf. Surface potential of iron oxyhydroxides/oxides changes at pH=7.9. Negatively charged arsenic (mainly arsenate) was intensely released into the solution at pH>7.9. Observation of this study showed that the small change of pH considerably controls the dissolved arsenic in porewater.

This study demonstrates the importance of input of subareal detrital materials for the arsenic cycle in the crust through hydrosphere and microbiological activity to change the arsenic phases in the marine sediments at the very early stage of diagenesis.

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