Excess N_2 formation by denitrifcation in the Indian Ocean oxygen deficient zone estimated by simultaneous N_2, Ar, and O_2 measurements

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Accurate measurement of N_2/Ar ratio in seawater at oxygen deficient zones (ODZs) makes it possible to estimate production of excess N_2 by denitrification. We constructed a quadruple mass spectrometer (QMS) system for on-board simultaneous measurement of dissolved gasses (N_2, O_2 and Ar) and applied it for the Indian Ocean oxygen deficient zone during KH-09-5 cruise (*R/V* Hakuho-maru, 27th Nov–16th Dec, 2009).

Approximately 100 ml seawater samples were taken into 300 ml glass bottles which were first poisoned with 250 μl of saturated $HgCl_2$ solution to impede biological activity and then evacuated prior to the sampling [1]. Dissolved gasses were extracted from the seawater in high vacuum line, where H_2O and CO_2 were removed by cold traps. The purified sample gases were injeced into the QMS and ion peaks of N_2, O_2 and Ar were simultaneously measured. Absolute dissolved O_2 concentration was determined by the Winkler titration method independently.

Oxygen minimum zones (OMZs), which was defined as the depth zone O_2 concentration was below 20 μM, were observed in 100–1000 m depth in the staions with their latitudes higher than 14°N. The Δ (N_2/Ar), defined as a deviation of N_2/Ar from the the value at their equilibrium condition with atmosphere, reached a maximum super-saturation value (~+4%) around 200 m depth within the OMZ. Nitrite concentration also increased within the OMZ with a maximum of 4–14 μM around 150 m depth. These results clearly indicated that denitrification was occuring in the OMZ.

We estimated an excess N_2 generated by denitrification process in the OMZ using a proposed equation [2]: $[N_2]_{excess} = [\Delta\ (N_2/Ar)_{sample} - \Delta\ (N_2/Ar)_{background}]*[N_2]_{(T,\ S)}$. Average of the excess N_2 was about 26 μg-at N and maximum was about 30–34 μg-at N around 200 m depth.

[1] Hamme & Emerson (2002) *Geophys. Res. Lett.* **29**(23), doi:10.1029/2002GL015273. [2] Devol *et al.* (2006) *Deep-Sea Res. I* **53**, 1533–1547.

Role of ferric and aluminum ions for silica biodeposition on the surface of microbes

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In order to elucidate the mechanism of silica biodeposition in geothermal field that ferric and aluminum ions participate, adsorption behavior of silicic acid to ferric and aluminum ions combined on Chelex 100 (Fe type Chelex 100 and Al type Chelex 100) was examined. Since the functional group is iminodiacetate, Chelex 100 was selected as a model compound of the surface of microbe. No silicic acid was adsorbed to the original Chelex 100 (Na type Chelex 100), whereas silicic acids were adsorbed to the both Fe and Al type Chelex 100. The ferric and aluminum ions and silicic acid on the Chelex 100 were characterized by ^{57}Fe Mössbauer, XAFS and ^{29}Si MAS NMR and ^{27}Al MAS NMR and SEM-EDX.

From the XANES and ^{27}Al MAS NMR spectra for the Fe and Al type Chelex 100, it was confirmed that ferric and aluminum ions were combined as a tridentate complex with iminodiacetate group. It is suggested for Fe and Al type Chelex 100 before and after reaction with silicic acid that the silicic acids are chemically adsorbed to Chelex 100-Fe, Al-OH sites by the formation of Chelex-100-Fe, Al-O-Si $(OH)_3$ bonds from the ^{57}Fe Mössbauer and ^{27}Al MAS NMR spectra. Judging from the ^{29}Si MAS NMR and SEM-EDX measurements for the surface of Fe and Al type Chelex 100 particles, Chelex 100-Fe, Al-OH sites act as a template for the successive adsorption of silicic acids to form silica. In conclusion, the ferric and aluminum ions combined with the surface of microbes act as adsorption sites of silicic acid and play an important role for the biodeposition of silica from hot spring water.