

## Sulfur geochemistry of marine sediments at the Conrad Rise of the Southern Ocean since the last glacial

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The Southern Ocean has played an important role in the global carbon cycle and thus the climate system. The Southern Ocean has been proposed as a candidate for the site of carbon reservoir to account for the 80 ppm decrease in  $p\text{CO}_2$  between the glacial and interglacial periods. In order to examine the potential of the Southern Ocean as a carbon reservoir in the last glacial period, we investigated extent of changes in the redox conditions recorded in the sediment core COR-1bPC recovered at the Conrad Rise (KH10-7 cruise).

The lower part of the core is dark-colored and rich in organic matter (OM) that was likely produced by photosynthesis ( $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2$ ) in the surface ocean and preserved in an anoxic sediment, where bacterial sulfate reduction (BSR) occurs. Relative abundance of S-bearing species in the sediment and their stable isotope compositions hold keys to understand redox environments. We determined abundance of five S-bearing species; pyrite ( $\text{S}_{\text{py}}$ ), sulfate ( $\text{S}_{\text{SO}_4}$ ), acid-volatile sulfide ( $\text{S}_{\text{AVS}}$ ), elemental sulfur ( $\text{S}^0$ ), and organic sulfur ( $\text{S}_{\text{org}}$ ). Isotope compositions of  $\text{S}_{\text{py}}$  and  $\text{S}_{\text{SO}_4}$  were determined by EA-IRMS.

The lower part of the core covering the last glacial (uppermost Pleistocene) has higher  $\text{S}_{\text{py}}$  contents than in the upper part (Holocene), and has average  $\delta^{34}\text{S}_{\text{py}}$  value to be  $-52.9 \pm 2.5\text{‰}$  ( $1\sigma$ ) and  $\delta^{34}\text{S}_{\text{SO}_4}$  value  $+14.6\text{‰} \pm 8.3\text{‰}$ , which is significantly lower than the  $\delta^{34}\text{S}_{\text{SO}_4}$  value of seawater ( $+21\text{‰}$ ). We suggest that such  $\delta^{34}\text{S}_{\text{SO}_4}$  value was due to addition of low- $\delta^{34}\text{S}$  sulfate created by partial oxidation of bacteriogenic sulfides. In the Holocene unit, however, the average  $\delta^{34}\text{S}_{\text{SO}_4}$  value is  $+23.6\text{‰}$  (higher than  $\delta^{34}\text{S}_{\text{SW}}$ ). We suggest that such  $\delta^{34}\text{S}_{\text{SO}_4}$  value was due to active BSR followed by escape of low- $\delta^{34}\text{S}$  bacteriogenic HS<sup>-</sup> from sediment (not fixed as  $\text{FeS}_2$ ).

In the last glacial period in the Southern Ocean, pyrite formation was likely facilitated by elevated eolian Fe flux due to latitudinal high pressure gradient, which triggered enhanced primary production and creation of anoxic condition in sediment (by  $\text{O}_2$  consumption for decomposition of OM). In the Holocene, suppressed Fe flux ultimately inhibited pyrite formation. The  $\sim 80\text{ppm}$   $p\text{CO}_2$  decrease in glacial-interglacial transition is due to changes in the Fe flux.