

Geochemical study of the sediments at Site 1179, ODP Leg 191 - Direct observation of the oxidation states of Mn and Ce -

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[Introduction]: The geochemical signature of abyssal sediment reflects the source material and formation environment of the sediment. Many geochemical indicators using the abundance of some elements, such as the MnO/TiO₂ ratio, REE patterns, the La/Ce (ratio of normalized values) against the Al₂O₃/(Al₂O₃ + Fe₂O₃) ratio, are employed to elucidate depositional environment. However, to use these abundance data as geochemical signatures, it is necessary to study carefully the various factors that can alter the initial signature during diagenesis. It is considered that some elements, such as Mn and Ce are immobile in their oxidized forms (Mn(IV) and Ce(IV)), whereas they may be more mobile in their reduced forms (Mn(II) and Ce(III)). In this study, we compared the depth profiles of abundances and oxidation states of these elements in the sediment column to estimate the influence of diagenesis. The direct observation of the oxidation states of these elements was used to explain the variation of abundances of Mn and Ce in the sediment column.

[Samples and Experiment]: Sediment samples were recovered from Site 1179, ODP Leg 191 (41.4degrees N, 159.6degrees E), ranging from 0.01 mbsf (meters below sea floor) to 36.1 mbsf. The sediment samples are composed of clay and radiolarian bearing diatom ooze. Major element compositions and abundance of rare earth elements (REE) in the sediment samples were determined by XRF and ICP-MS. The samples for the abundances were washed with pure water twice and dried in air. The oxidation state of Mn and Ce were measured by XANES analysis in the fluorescence mode. The samples for XANES were packed in an airtight bag in Ar atmosphere to maintain original redox condition.

[Results and Discussion]: The abundance and oxidation state of Mn: The depth profile of Mn contents in the sample sediment shows high Mn contents for samples from surface region (0-1 mbsf) and low Mn content (0.5 wt.%) for samples in deeper region. The depth profile of dissolved Mn concentration in pore water shows that the Mn content in pore water are low (13.9 mM) for sediment (0.20 mbsf) rich in Mn, and are high (255.6 mM) for sediment (6.45 mbsf) poor in Mn. The maximum of Mn concentration in sediments is found in 0.31 mbsf in this study, which is consistent with the well-known fact that the Mn content is highest near the sea floor. The depth profile of Mn oxidation state shows that Mn in the sediment is tetravalent at 0.60 mbsf and divalent at 6.45 mbsf. This observation suggests that the Mn(II) dissolved in pore water is diffused upward, oxidized to Mn(IV), and fixed in the sediment to form Mn rich layer. The MnO/TiO₂ ratio can be an indication of depositional environment; the ratio is 5.20 for samples from surface region (0.01-0.1 mbsf), while 0.57 for deeper region (1-35 mbsf). If this ratio is used to elucidate depositional environment, the surface sediment (0-1 mbsf) would be classified as pelagic, whereas the sediment below 1 mbsf shows the MnO/TiO₂ ratio which is more peculiar to the hemipelagic region.

REE signature and the oxidation state of Ce: The REE patterns for all the sediments studied here exhibit similar trends showing relative enrichment of LREE (light rare earth elements). This result implies that chemical processes in this sedimentary setting have been rather similar during the past 1 Ma (corresponding to the depth of sediment at 35 mbsf). The La/Ce ratios are 1.05 for samples in surface region (0.01-0.31 mbsf), while 1.17 for samples in deep region (0.41-35 mbsf), showing the difference of 10 % between surface and deeper region. The XANES spectra show that Ce(III) is predominant in the sediment samples. However, some Ce(IV) (less than 10 % of total Ce) is incorporated in the sediment at 0.60 mbsf. This supports the idea that Ce(IV) was adsorbed on Mn at surface region, which produce a variation of the La/Ce ratio between surface and deeper region.