

The depth profiles of As abundance and As(III)/As(V) ratio in sediments at Site 1179, ODP Leg 191

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[Introduction]

Records of redox-sensitive elements in sedimentary rocks are of importance as a tool to elucidate the paleo-redox environment. In this study, we focus on the factors controlling the abundance of As, one of the redox-sensitive elements, in sediment column. Many reports have suggested the reductive dissolution of Fe(III)-oxides controls the arsenic behavior in environment. However, there are few researches which refer to the redox reaction of As during diagenesis based on the direct analysis of the oxidation state. The aim of this study is to examine a possibility that the mobility of As in the sediment column is not only influenced by Fe(III)-oxides, but is controlled by the As(III)/As(V) ratio, since As(III) is more soluble to water than As(V). In this study, we compared the depth profiles of abundances and oxidation states of Fe and As in a sediment column at the Site 1179 in ODP Leg 191 to estimate the As abundance change with depth during diagenesis. In addition, the results were compared with the data of sequential extraction analysis to clarify the factors controlling the behavior of As in the sediment column.

[Samples and Experiments]

Sediment samples were recovered from Site 1179, ODP Leg 191 (41.4°N, 159.6°E, water depth: 5565 m), 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 (SiO₂: 56-66 wt. %, Al₂O₃: 11-17 wt. %). Major element compositions and trace elements in the sediment samples were determined by XRF and ICP-MS. The oxidation state of Fe and As were measured by XANES analysis in the fluorescence mode. The samples for XANES were packed in an airtight bag in Ar or N₂ atmosphere to maintain original redox condition.

[Results and Discussion]

The abundances and oxidation states of Fe

While the Fe content in sediment is not so high (5-7 wt. %) from sea floor to 6.37 mbsf, the content is highest (10.2 wt. %) in 7.1 mbsf, and decreases toward 9.81 mbsf. The depth profile of average valence of Fe shows that the sediment from sea floor to 6.37 mbsf is close to 2.5. However, the oxidation state of Fe is high in 7.1 mbsf, and is reduced to low oxidation state at 9.81 mbsf. The decrease of Fe content and the reduction of the oxidation state from 7.1 mbsf to 9.81 mbsf imply that Fe redox zone exists in this depth (7-10 mbsf), where Fe-oxides are consumed to decompose organic matter.

The abundances and oxidation state of As

Although the As abundance in sediment from sea floor to 35 mbsf is generally less than 20 ppm, As-enriched layers exist at depths of 5.1 mbsf (30 ppm), 8.66 mbsf (55 ppm), and 13.99 mbsf (60 ppm). The As XANES spectra shows that the proportion of As(V) in these layers are close to 80 % which implies that As(V) contributes to the formation of As(V)-enriched layers.

Above the Fe redox zone (7-10 mbsf), As concentration profile is coincident with the profile of the As(V)/As(III) ratio. Although it is known that Fe-oxides primarily controls arsenic behavior as a carrier of As, the As abundance in the As-enriched layer is mainly controlled by the oxidation state of As itself, since As concentration profile does not correlate with Fe concentration profile. On the other hand, in deeper depth below Fe redox zone, As content displayed a positive correlation with Fe-oxide content, while not with the oxidation state of As. This result implies that As content is associated with Fe-oxides, which acts as a carrier of As.