Geochemistry of terrestrial ferromanganese nodules in soils as a potential paleoclimate indicator

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Ferromanganese (Fe–Mn) nodules grow in not only deep-sea environments but also shallow sea (< 200 m), lakes and terrestrial soils. Fe–Mn nodules, excepting deep-sea Fe–Mn nodules, have been considered to form layered structure due to change of ambient redox potential. Redox potential within soil environments is generally controlled by soil moisture associated with climate; the redox potential decreases under wet conditions and increases under dry conditions[1]. Therefore, the layered structure of terrestrial Fe–Mn nodules can be a potential paleoclimate indicator. However, association between the layered structure and paleoclimate has not been clarified yet.

We performed bulk chemical analysis, computed tomography (CT) analysis, and elemental mapping for the Fe–Mn nodules of up to 2 cm in diameter from Shimajiri-Mahji (dark-red soil) in Okinawa Island. Although the origin of the Fe–Mn nodules in Shimajiri-Mahji has been proposed as both marine and terrestrial, geochemical features of the samples (positive Ce anomaly and low Ni and Cu content) clearly indicate its terrestrial origin. CT images of the samples show that the layered structure comprised three denser layers and two sparser layers at maximum. In elemental maps, the samples show the layered structure showing rhythmical changes of Mn/Fe ratio of 0.34–0.37 mm/cycle from the center toward the rim.

Based on U-Th dating, growth rate of Fe–Mn nodules in Shimajiri-Mahji has been reported to be 61 mm/Myr on average[2]. Therefore, assuming average growth rate of 61 mm/Myr, high or low Mn/Fe layers formed repeatedly at 5.5–6.1 kyr/cycle. This frequency is mostly consistent with the changes in temporal intensity of the East Asian monsoon (6.1, 4.7 and 4.2 kyr/cycle) during the last interglacial–glacial cycle[3]. Therefore, the layered structure of Mn/Fe ratios probably reflects changes in the soil moisture in Shimajiri–Mahji associated with changes in the temporal intensity of the East Asian monsoon.

The dense and sparse layers of terrestrial Fe–Mn nodules shown in CT images have been suggested to result from slower growth in gradual increase of redox potential and faster growth in rapid increase of redox potential, respectively[1]. Therefore, the samples would have experienced up to three periods with gradual increase of redox potential (i.e., gradual drying) and two periods with rapid increase of redox potential (i.e., rapid drying). Assuming average growth rate of 61 mm/Myr, the dense layers would from in relatively humid ambient conditions in warmer periods (<10, 40–50 and ~80 ka). These relatively warm periods and the changing intensity of the East Asian monsoon at the millennial timescale may have resulted in gradual increase of the redox potential (i.e., gradual drying) in Shimajiri–Mahji owing to the high background level of water vapor content in the air, which would have formed dense layers.

This study indicates that the layered structure of terrestrial Fe–Mn nodules is a paleoclimatic indicator. Therefore, it will be possible to discuss paleoclimate from terrestrial Fe–Mn nodules in paleo soils and sediments (sedimentary rocks). However, previous discrimination diagram[4] based on Fe–Mn nodules' chemical composition cannot identify Fe–Mn nodules from shallow sea, lakes and soils. Accordingly, we proposed new geochemical discrimination diagram based on Co/Rb and Al/Na ratios which makes able to identify formation environments of Fe–Mn nodules. Our discrimination scheme will contribute to studies on paleoclimates and the formation process of soils and sediments containing Fe–Mn nodules.

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