Response of structurally substituted sulfur in foraminifera shells to glacial-interglacial changes: a 1.0-million-year record from the Ontong-Java Plateau

*Toshihiro Yoshimura[1], Yusuke Tamenori[2], Junichiro Kuroda[3], Azumi Kuroyanagi[4], Naohiko Ohkouchi[1]

1. Japan Agency for Marine-Earth Science and Technology, 2. Japan Synchrotron Radiation Research Institute, 3. Atmosphere and Ocean Research Institute, The University of Tokyo, 4. Tohoku University Museum, Tohoku University

During the Quaternary, the Earth’s surface has experienced large changes in the extent of glaciation, sea-level, and temperature. The preservation of biogenic carbonates in deep-sea sediments reflects changes in deep-water circulation and in rates of production of carbonate and organic carbon in the surface ocean. The response of carbonate alkalinity to glacial-interglacial cycles provides important constraints on past oceanic carbon cycles. Because the relative activity of sulfate ions to carbonate ions in the calcifying fluids would influence sulfate incorporation into $CaCO_3$, sulfate contents (or sulfur to calcium ratio) have been proposed as a potential archive of carbonate ion concentrations. However, the preservation of some trace elements in biogenic carbonates is highly susceptible to physicochemical conditions of sedimentation, thus the spatiotemporal variability of sulfur proxy in foraminiferal calcite is still under debate. Here we show a 1.0-million-year record of structurally substituted sulfur in foraminifera shells from the Ontong-Java Plateau. For this study, we used a synchrotron source micro-X-ray fluorescence (μ-XRF) as well as *K*-edge XANES to show the sulfur content and local coordination environment in mixed-species foraminifera. All chambers of foraminiferal shells were physically broken in a glass vial and then ultrasonically cleaned in de-ionized water, methanol, H_2O_2 and $HClO_4$. The μ-XRF measurements were taken at a photon energy of 3000.0 eV with an acquisition time of 5 s. The ratios of sulfur to calcium is calibrated using carbonate reference standards. The XANES spectra suggested that the sulfur in foraminifera shells is predominantly in structurally substituted sulfate, and S/Ca ratios fluctuate between 1.0 and 1.5 mmol/mol. The glacial-interglacial cycles were not clearly defined in sulfur contents between 0.9-0.6 Ma, whereas after 0.6 Ma, the emergence of quasi-100 ka cycles was observed. To place the sulfur record into paleoceanographic context, we compare the data with water mass, carbon cycle, and the preservation of foraminiferal calcite in deep-sea sediments.

Keywords: glacial-interglacial cycle, sulfur, foraminifera

