Sediment acidification on Majuro Atoll

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Soil acidification often occurs due to various factors such as NO_x and SO_x from anthropogenic combustion substances. In the process of rock weathering or nitrification, protons are also released which causes soil acidification. It is difficult to evaluate each factor independently in industrial countries, since the many factors are affected one another, which makes it difficult to evaluate each factor. On the other hand, it is relatively easy to discuss anthropogenic impacts and natural effects independently in the case of atoll, since atoll sediments are composed of bio-clastic sand such as foraminifera and coral that are made from calcium carbonate ($CaCO_3$), which exhibits simpler composition compared with other areas with more heterogeneous geology. Here, we investigated the degrees of acidity in Majuro Atoll, one of the atolls of Marshall Islands. In Majuro Atoll, human residence has lasted for about 2000 years, which is the longest history among atolls around the world (Yamaguchi et al., 2005, 2009). However, the traditional life style in the atoll has changed and more industrial products such as motor vehicles have been used after 20th century.

In this study, we focused on factors which have a possibility to change surface environment of reef islands in atoll in terms of both artificial and natural factors. We evaluated the correlation between the elements contained in the sediment and sediment pH at different depths. We also examined the mechanism to acidify the pH of the sediment.

Samples were taken at different depth of the sediments in both inland area and ocean side of each reef island which are named as Laura, Calalen, and Jelto. All the surface layers are black-colored and well-vegetated. The grain size is medium to fine sand.

We examined concentrations of major elements such as calcium (Ca) and magnesium (Mg) by XRF. Concentration of inorganic ions (NO_3^-, SO_4^{2-}, and NH_4^+) were measured by ion chromatography and absorption spectrophotometry, respectively. Concentration of organic acid was calculated by pH titration. Mineral composition of foraminifera, which is the main component of the sediment was examined by XRD. Porosity of foraminifera were calculated using X-ray micro-Computed Tomography (μ-CT) and Image J. Stable isotope of nitrogen (^{14}N and ^{15}N) and triple oxygen isotopes (^{16}O, ^{17}O, and ^{18}O) in nitrate contained in the sediment were measured by the denitrifier method (Hattori et al., 2016) to identify the origin of the nitrate. ^{13}C solid state Nuclear Magnetic Resonance (NMR) spectroscopy were used to identify the organic matter which was concentrated in the upper layer.

As a result, sediment pH decreased near the surface layer and the concentration of Mg decreased. Mg-calcite fraction to total $CaCO_3$ (calcite + magnesian calcite (Mg-calcite)) of foraminifera also decreased near the surface. In contrast, the porosity of foraminifera, concentrations of NO_3^-, NH_4^+, TOC, and organic acid increased in the upper layer, whereas concentration of SO_4^{2-} fluctuated and especially became higher in the lower layer which is close to the water-table. Therefore, SO_4^{2-} may be originated from seawater, which did not induce acidification of the sediment. According to NMR analysis, organic matter enriched in the upper layer was identified as fulvic acid. Both the concentrations of nitrate and organic acid as fulvic acid had high correlation with sediment pH in the range from pH 7.5 to 8.0. Therefore, it is considered that both factors contribute to the acidification and dissolution of foraminifera test in the upper layer. From the analysis of the stable isotopes, the average of $\Delta^{17}O$ was close to 0‰ over all the areas, which suggested that nitrate was produced by bacterial activities. Therefore, we can conclude that highly concentrated nitrate produced during the excess nitrification and subsequent

release of proton during the process should be the main factor to acidify the sediments on Majuro Atoll.

Keywords: sediment acidification, reef island, nitrification

