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PE-14 U/Ca ratio in coral skeleton as a proxy of carbonate system in coral reef

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Carbon dioxide (CO<sub>2</sub>) is one of the most important green house gases in the atmosphere. It is recognized that CO<sub>2</sub> concentration has already increased since before industrial revolution to present, owing to increase in the anthropogenic activity. In addition to the green house effect, increasing CO<sub>2</sub> in the atmosphere enhances the CO<sub>2</sub> invasion from atmosphere to ocean. Increasing the amount of CO<sub>2</sub> dissolved in the ocean lowers the pH, and decreases the carbonate (CO<sub>3</sub><sup>2-</sup>) ions and hence the saturation state of the major skeletal carbonate minerals. It is also possible that modifying the carbonate system of the surface ocean affects the metabolism of marine organisms (such as photosynthesis and calcification). During calcification process of marine carbonates (such as coral), some trace elements (e.g. Sr, Mg) can be incorporated into carbonate skeleton and used as a proxy of the environmental change.

The concentration of total uranium in seawater is found to be ~3 ppb and distributed uniformly along the ocean as a conservative ion. Under oxic conditions, uranium mainly occurs as the hexavalent uranyl ion, UO<sub>2</sub><sup>2+</sup>. In seawater, it forms complexes with carbonate ions such as UO<sub>2</sub>CO<sub>3</sub><sup>0</sup>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>. Because of the formation of uranyl carbonate complexes is controlled by pH or CO<sub>3</sub><sup>2-</sup> activity, uranium content of marine carbonates is possibly used to reconstruct the carbonate ion activity change in the past.

Incorporation of uranium into coral skeleton has been investigated through incubation experiment under controlled pCO<sub>2</sub> at 27°C. Distribution coefficient of uranium ( $\lambda_{\text{UO}_2}$ ) between coral skeleton and seawater varied from 0.7 to 2.7 with the change in CO<sub>3</sub><sup>2-</sup> ion activity. The data are in agreement with those of inorganic CaCO<sub>3</sub> precipitation experiment ( $\lambda_{\text{UO}_2} = 0.8$  to 3.7)

The mode of uranium incorporation into calcium carbonate has been considered as ionic exchange of cation; CaCO<sub>3</sub> + UO<sub>2</sub><sup>2+</sup> ⇌ UO<sub>2</sub>CO<sub>3</sub> + Ca<sup>2+</sup> (Kitano and Oomori, 1971; Broecker and Peng, 1982) or anion; CaCO<sub>3</sub> + UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> ⇌ CaUO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> + CO<sub>3</sub><sup>2-</sup> (Shen and Dunbar, 1995).

Such mode of uranium incorporation and its possibility to apply to the proxy of carbonate system in coral reef is discussed.