

U/Ca as a possible proxy of carbonate system in coral reef

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Abstract. Uranium incorporation into coral skeleton of *Goniastrea aspera* was investigated in the laboratory incubation for 8 hours under controlled $p\text{CO}_2$ and temperature. Seawater parameters such as pH and alkalinity as well as calcium and uranium concentrations were measured every 2 hours. pH increased progressively from 8.17 at initial to 8.54 at the end. In contrast, alkalinity significantly decreased from 2292 to 1467 mmol/kg. The apparent distribution coefficients of uranium, λUO_2 , between *Goniastrea aspera* skeleton and seawater were obtained to be 2.7 to 0.7. The data were compiled with those of other studies and the overall data illustrate a negative correlation between λUO_2 and $a\text{CO}_3^{2-}$ with the slope of -0.75 . It is suggested that variation of carbonate ion activity (i.e. carbonate system) controls the distribution coefficient of uranium and hence coral U/Ca. The effect of uranyl carbonate complexes formation on uranium incorporation is discussed.

Key words: Uranium, distribution coefficient, proxy, carbonate system

Introduction

Carbon dioxide is an extremely important greenhouse gas in the atmosphere, playing a significant role in controlling the Earth's surface temperature. The atmospheric carbon dioxide level has already increased from the concentration of 280 ppm in the pre-industrial age to ~ 380 ppm today, and it is predicted to reach ~ 560 ppm before the end of the 21st century (Prentice et al. 2000). Due to the capability of the ocean as a significant reservoir of carbon dioxide from atmosphere, such increases of atmospheric carbon dioxide have some impacts to either physical or chemical properties of oceanic seawater. One of the impacts is the decline of CO_3^{2-} concentration in seawater which is in advance modifying the carbonate system of the surface ocean and eventually affects the metabolism, such as photosynthesis and calcification of marine organisms.

During calcification process of coral, some metal ions are able to be incorporated into carbonate lattice through the ion exchange mechanism between metal and calcium ions. Distribution coefficient of metal (D_{Me}) between coral skeleton and seawater is defined as follows (McIntire 1963; Shen and Boyle 1986; Lea and Spero, 1992):

$$D_{\text{Me}} = \frac{[\text{Me}/\text{Ca}]_{\text{coral}}}{[\text{Me}/\text{Ca}]_{\text{seawater}}} \quad (1)$$

For the case of uranium, Shen and Dunbar (1995) reported that the range in the coral/seawater uranium

distribution coefficient is 0.8–1.0 once uranium concentration is 13.4 nM (Chen et al. 1986). Furthermore, several studies have been measured the uranium distribution coefficient of 0.5–2.0 which is depended on the coral species (Veeh and Turekian 1968; Schroeder et al. 1970; Thompson and Livingston 1970; Flor and Moore 1977; Swart and Hubbard 1982). The measurement of the distribution coefficient of uranium between carbonate and solution is a useful tool for the understanding of the factors controlling the uranium contents of marine calcareous sediments (Kitano and Oomori 1971; Min et al. 1995).

It is well known that uranium in seawater exists not only a uranyl ion (UO_2^{2+}) (Ku et al. 1977) but also anion complexes with carbonate (i.e. UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$) (Grenthe et al. 1992; Shen and Dunbar 1995). It is believed that the formation of such uranyl carbonate complexes is influenced by the carbonate system of seawater. One of parameters to control carbonate system is the carbonate ion activity. Based on this fact, the incorporation mechanism of uranium into coral skeletons is considered as UO_2^{2+} (cation mode) (Kitano and Oomori 1971; Broecker and Peng 1982) or $\text{UO}_2(\text{CO}_3)_2^{2-}$ (anion mode) (Swart and Hubbard 1982; Shen and Dunbar 1995). Such mechanism remains unclear and nowadays still in debate. In this study, the incubation experiment of coral *Goniastrea aspera* was done to test that carbonate ion activity of solution affects the uranium incorporation into coral

skeleton. The incorporation mode (i.e. cation versus anion mode) of uranium is discussed.

Material and Methods

Coral incubation

We used a coral colony of *Goniastrea aspera* for incubation experiment. Fig. 1 shows a schematic picture of coral incubation. We incubated *G. aspera* (18×26×15 cm³) in the seawater tank (27×38×24 cm³) under direct sunlight for 8 hours, and collected seawater samples in the polyethylene bottles every two hours. Photon flux was measured to be 200–800 μmol/m²/s and temperature of the system was 24.5±1.5°C during incubation.

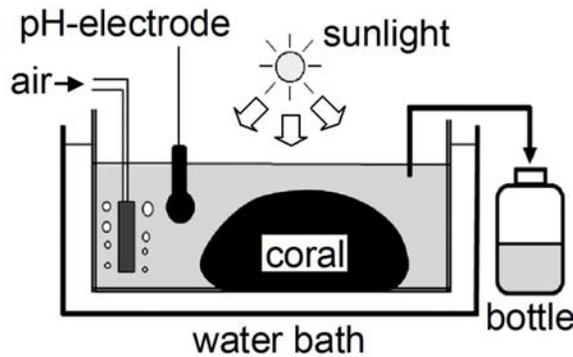


Figure 1: Schematic picture of incubation experiment.

Seawater analysis

The seawater pH was measured immediately after collecting seawater sample. The collected seawater was filtered on a Millipore HA (0.45 μm pore size) filter, and analyzed for alkalinity. The remaining seawater sample was preserved by adding conc. HCl to pH=2, and then was stored for subsequent analysis of total Ca and U.

The pH of seawater was measured by pH meter (Orion 290 A+Thermo, Japan). In each set of measurement, pH meter was calibrated using NBS-scaled buffer solutions (TOA, Golden buffer) at pH=7 (6.863) and pH=4 (4.006) at 25°C. Reproducibility of the measurements ($n=11$) was found to be ±0.003 pH unit (1σ).

Total alkalinity was measured potentiometrically using an auto titration system (TIM 860 Radiometer, TitraLab, France). Reproducibility of the measurements ($n=9$) was found to be ±3 μmol/kg (1σ).

Water salinity was measured by a salinometer (Model 8410A, Canada) using the reference standard seawater of IAPSO ($K_{15}=0.99987$, $S=34.995$). Reproducibility of the measurements ($n=11$) was ±0.001‰ (1σ).

Calcium in seawater samples were determined by EGTA titration method (Kanamori and Ikegami 1980) using an auto titration system (TIM 865 Radiometer, TitraLab, France) equipped with Ca selective electrode. The equivalence point for each titration was obtained by a Gran's plot method. Reproducibility of the measurements ($n=11$) was ±0.01 mmol/l (1σ).

For the determination of uranium in solution, 15 ml of seawater sample in 30 ml of conc. HCl was passed firstly to anion exchange resin (Dowex 1×8, 100–200 mesh) column to separate uranium from matrix elements. After washed with 8N HCl, sample was eluted by 25 ml of 0.1 N HCl. Recovery of the separation was ~98% and reproducibility of the measurement of 3 ppb uranium was ±0.08 ppb ($n=10$; 1σ). The eluted-seawater samples were then introduced to ICP-MS (Hewlett Packard, HP 4500) with Ar-H₂ gas carrier for uranium quantification.

The apparent distribution coefficient of uranium (λ_{UO_2}) associated with CO₃²⁻ ion activity during experiment was calculated with the Doerner-Hoskins' equation (Doerner and Hoskins 1925; Kitano et al. 1968):

$$\lambda_{\text{UO}_2} = \frac{\log(M_{\text{UO}_2, \text{initial}} / M_{\text{UO}_2, \text{final}})}{\log(M_{\text{Ca, initial}} / M_{\text{Ca, final}})} \quad (2)$$

where $M_{i, \text{initial}}$ denotes the molar concentration of i species dissolved in an incubated seawater at $t=0$ and $M_{i, \text{final}}$ denotes i species at a given time of reaction.

Results

The temperature ranged from 23–26°C during incubation was a suitable circumstance for metabolism of coral (Coles and Jokiel 1977). Parameters such as pH and alkalinity with respect to coral metabolism changed during experiment. Fig. 2 shows the measurements of pH, alkalinity and salinity of seawater every 2 hours of incubation. pH value ranged from 8.17 at initial to 8.54 at the end with average value of 8.43 (Fig. 2a). The calcification process in which the calcium carbonate skeleton was formed diminished carbonate ions from incubated seawater. Such process decreased the alkalinity from 2292 to 1467 μmol/kg (Fig. 2b). However, for the case of salinity, it slightly increased from 34.6 to 35‰ (Fig. 2c), indicating to a slight evaporation during experiment. Shen and Dunbar (1995) suggests that U/Ca ratio in corals is affected by salinity changes in areas subject to significant rainfall or runoff, however, the salinity changes in this study are on a small scale to have impact to the coral U/Ca.

It is considered that the difference in calcium concentration in solution between initial ($t=0$) and every two hours of incubation time refers to the

amount of cumulative precipitated CaCO_3 during the time (Fig. 3). Therefore, due to calcification process, the cumulative amount of CaCO_3 increased from 0 at initial to 0.41 mmol/l at the end of experiment. Moreover, during calcification process uranium was incorporated into coral skeleton as indicated by the enhancement of precipitated uranium from 0 to 0.4 nmol/l (Fig. 3b).

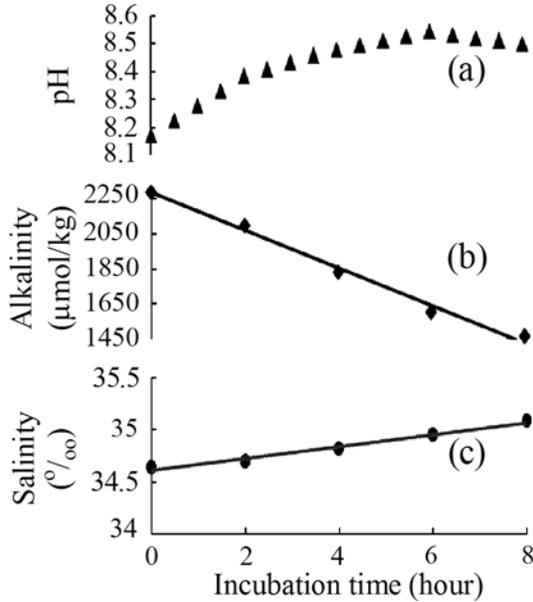


Figure 2: pH, alkalinity and salinity of seawater during experiment.

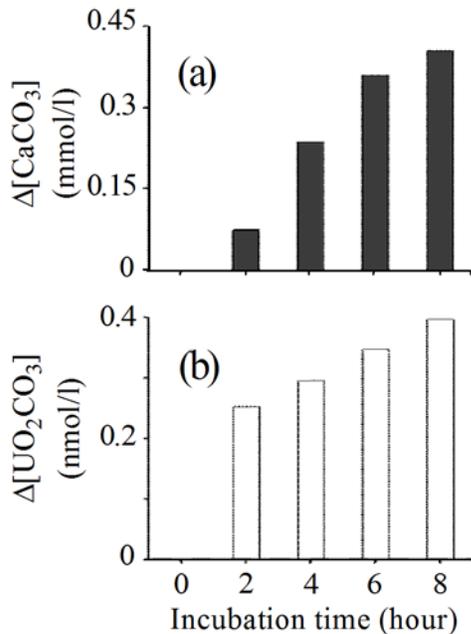


Figure 3: Amount of cumulative precipitation of CaCO_3 and UO_2CO_3 every two hours of incubation time.

Fig. 4 shows the relationship between apparent distribution coefficient of uranium and the carbonate ion activity during experiment. In the present study, distribution coefficient decreased from 2.7 to 0.7 as the carbonate ion activity declined from 5 to 4.4 $\mu\text{mol/l}$. The distribution coefficient data obtained from different coral species as well as inorganic precipitation experiment are also plotted in Fig. 4. The compiled-data reveal a trend of negative correlation between distribution coefficients of uranium and carbonate ion activities with the slope of -0.75 .

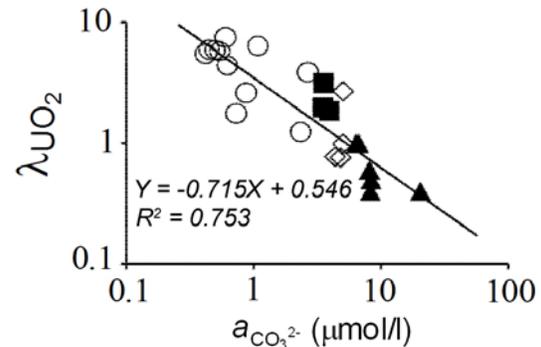
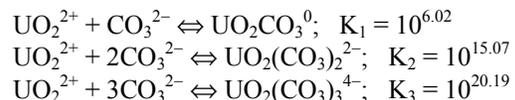


Figure 4: Distribution coefficient of uranium (λUO_2) plotted against the carbonate ion activity ($a_{\text{CO}_3^{2-}}$). \circ = Takaesu, 2008 (Porites sp); \blacksquare = Yoshida, 2000 (Fungia sp); \diamond = this study (*Goniastrea aspera*); \blacktriangle = Kitano and Oomori, 1971 (Inorganic precipitation). The slope of regression line = -0.715 .

Discussion

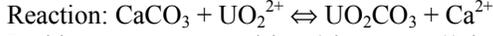
Incorporation of uranium into coral (*Goniastrea aspera*) skeleton under carbonate system change has been a focal point of this study. Fig. 4 shows that the value of the apparent distribution coefficient of uranium (λUO_2) decreased as the carbonate ion activity increased. This phenomenon is considered to be associated with the evidence that uranyl ions form complexes with carbonate ions in solution (Grenthe et al. 1992; Turner et al. 1981). Degree of complex formation of uranyl carbonate increases with increasing carbonate ion activity. Therefore, with increasing of carbonate ion activity, the activity of free uranyl ion dissolved in solution decreases and the distribution coefficient value should decrease (Kitano and Oomori 1971). Speciation of uranyl carbonate complexes in solution is important to discuss the incorporation mechanism of uranium into coral skeleton.

Turner et al. (1981) measured the stability constant (K) for the formation of carbonate species at $T=25^\circ\text{C}$, $P=1\text{ atm}$, $I=0.7$, as follows:



As far as the incorporation of uranium into coral skeleton is concerned, the species being incorporated can be either UO_2^{2+} (cation) or $\text{UO}_2(\text{CO}_3)_2^{2-}$ (anion) if the incorporation follows the ion exchange process stoichiometrically.

Cation hypothesis



In this system, a uranyl ion (charge = +2) in solution replaces a similar charge of calcium in solid (CaCO_3) phase. The distribution coefficient of uranium (K_{UO_2}) is given as follows:

$$K_{\text{UO}_2} = \frac{[\text{UO}_2\text{CO}_3]}{[\text{CaCO}_3]} \cdot \frac{[\text{Ca}^{2+}]}{[\text{UO}_2^{2+}]} \quad (3)$$

Theoretically, the apparent distribution coefficient of uranium is written (Kitano and Oomori 1971):

$$K_{\text{UO}_2} = \frac{1}{1+\alpha} \cdot K_{\text{UO}_2}^T \cdot \frac{\lambda_{\text{CaCO}_3}^S}{\lambda_{\text{UO}_2\text{CO}_3}^S} \cdot \frac{\gamma_{\text{UO}_2^{2+}}^L}{\gamma_{\text{Ca}^{2+}}^L}, \quad (4)$$

Where γ^L and λ^S denote the activity coefficients of ion species in solution and MeCO_3 in carbonate phase respectively, $K_{\text{UO}_2}^T$ is thermodynamic distribution coefficient of uranium. When $\lambda_{\text{CaCO}_3}^S$, $\lambda_{\text{UO}_2\text{CO}_3}^S$ and $\gamma_{\text{UO}_2^{2+}}^L / \gamma_{\text{Ca}^{2+}}^L$ are taken as unity, K_{UO_2} is depended on α . Since total uranium dissolved in solution ($M_{\text{UO}_2,T}^L$) is:

$$\begin{aligned} M_{\text{UO}_2,T}^T &= M_{\text{UO}_2^{2+}}^L + M_{\text{UO}_2\text{CO}_3^0}^L + M_{\text{UO}_2(\text{CO}_3)_2^{2-}}^L + M_{\text{UO}_2(\text{CO}_3)_3^{4-}}^L \\ &= (1+\alpha)M_{\text{UO}_2^{2+}}^L, \end{aligned} \quad (5)$$

where, the value of α is given:

$$\alpha = K_1 \cdot a_{\text{CO}_3^{2-}}^L + K_2 \cdot (a_{\text{CO}_3^{2-}}^L)^2 + K_3 \cdot (a_{\text{CO}_3^{2-}}^L)^3 \quad (6)$$

Then, equation (4) can be re-written:

$$K_{\text{UO}_2} \equiv \frac{1}{1 + \{K_1 \cdot a_{\text{CO}_3^{2-}}^L + K_2 \cdot (a_{\text{CO}_3^{2-}}^L)^2 + K_3 \cdot (a_{\text{CO}_3^{2-}}^L)^3\}} \cdot K_{\text{UO}_2}^T \quad (7)$$

It is seen that the distribution coefficient of uranium, therefore, is a function of carbonate ion activity.

Based on the equation (7), the relation between K_{UO_2} and $a_{\text{CO}_3^{2-}}^L$ shows a negative correlation with the slope = -1 when the value of $\alpha = K_1 \cdot a_{\text{CO}_3^{2-}}^L$ or UO_2CO_3^0 is a dominant species in solution. Moreover, the slope = -2 or -3 is produced in case of $\text{UO}_2(\text{CO}_3)_2^{2-}$ or $\text{UO}_2(\text{CO}_3)_3^{4-}$ is dominant, respectively, in solution.

We superimpose the modeled slopes of -1 and -2 from equation (7) over the reported distribution

coefficient values (Fig. 4) and is shown in Fig. 5. The compiled-data of distribution coefficients seem in agreement with the slope = -1. It is suggested that UO_2CO_3^0 maybe a main species in incubated-seawater when we consider that uranium incorporation follows a cation mode. However, the data from individual experiments are somewhat scattered. The trend is still un-clarified yet, hence advanced investigation is necessary for clarifying the trend.

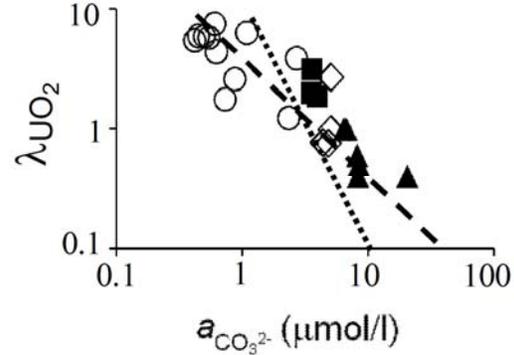
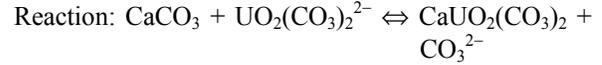


Figure 5: Distribution coefficient of uranium (λ_{UO_2}) plotted against the carbonate ion activity ($a_{\text{CO}_3^{2-}}$). The slopes of = -2, and - - = -1 (see text).

Anion hypothesis



A uranyl carbonate ion (charge = -2) from solution substitutes for a same charge of carbonate ion from CaCO_3 phase. In this system, contribution from UO_2^{2+} is neglected and $M_{\text{UO}_2,T}^L$ is written:

$$\begin{aligned} M_{\text{UO}_2,T}^T &= M_{\text{UO}_2\text{CO}_3^0}^L + M_{\text{UO}_2(\text{CO}_3)_2^{2-}}^L + M_{\text{UO}_2(\text{CO}_3)_3^{4-}}^L \\ &= M_{\text{UO}_2(\text{CO}_3)_2^{2-}}^L \cdot \left\{ \frac{1}{\beta_2 \cdot a_{\text{CO}_3^{2-}}^L} + 1 + \beta_3 \cdot a_{\text{CO}_3^{2-}}^L \right\} \end{aligned} \quad (8)$$

where β_2 denotes a stability constant of $\text{UO}_2(\text{CO}_3)_2^{2-}$ formation from UO_2CO_3^0 and β_3 represents a stability constant of $\text{UO}_2(\text{CO}_3)_3^{4-}$ formation from $\text{UO}_2(\text{CO}_3)_2^{2-}$. From equation (8), the abundance of $M_{\text{UO}_2(\text{CO}_3)_2^{2-}}^L$ relatives to the total dissolved uranium is:

$$\frac{M_{\text{UO}_2(\text{CO}_3)_2^{2-}}^L}{M_{\text{UO}_2,T}^L} = \frac{1}{\left\{ \frac{1}{\beta_2 \cdot a_{\text{CO}_3^{2-}}^L} + 1 + \beta_3 \cdot a_{\text{CO}_3^{2-}}^L \right\}} \quad (9)$$

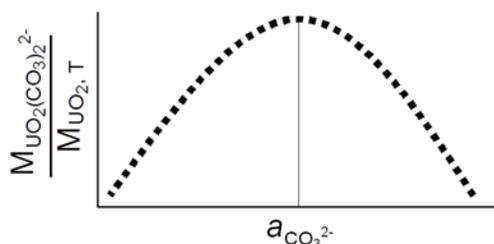


Figure 6: The relative abundance of $\text{UO}_2(\text{CO}_3)_2^{2-}$ plotted theoretically against the carbonate ion activity ($a_{\text{CO}_3^{2-}}$).

Fig. 6 illustrates a conceptual plot of the relation between relative abundance of $\text{UO}_2(\text{CO}_3)_2^{2-}$ and carbonate ion activity in the solution. Vertical line in the middle denotes the critical value of carbonate ion activity. Around this vertical line, $\text{UO}_2(\text{CO}_3)_2^{2-}$ is considered to be a dominant species in solution. Relative abundance of $\text{UO}_2(\text{CO}_3)_2^{2-}$ is controlled by the equilibrium relation with UO_2CO_3^0 at below (i.e. slope = 1) or $\text{UO}_2(\text{CO}_3)_3^{4-}$ at above the critical value (i.e. slope = -1).

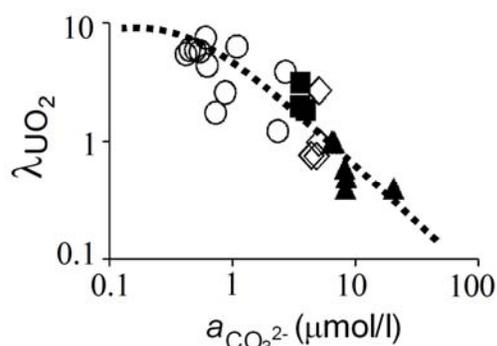


Figure 7: Distribution coefficient of uranium (λ_{UO_2}) plotted against the carbonate ion activity ($a_{\text{CO}_3^{2-}}$). The slope of = -1 (see text).

We superimpose the area of slope = -1 of Fig. 6 on the distribution coefficient values (Fig. 4) and is shown in Fig. 7. The entire data of the distribution coefficient of uranium lie within the slope = -1. It may be possible that $\text{UO}_2(\text{CO}_3)_3^{4-}$ is a dominant species in incubated-seawater when we consider that uranium incorporation as an anion mode.

At present, mode of uranium incorporation into coral skeletons remains unclear. Both candidates (i.e. cation and anion modes) seem valid, yet debatable. More detail studies on the distribution coefficient of uranium are significantly required to provide precise data for clarifying the mode of incorporation.

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