NOTE

U-Th radioactive disequilibrium analyses for JCp-1, coral reference distributed by the Geological Survey of Japan

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The U-Th radioactive disequilibrium measurements with Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) were applied to a coral reference; JCp-1 distributed by the Geological Survey of Japan to evaluate homogeneity of the standard material. The two times of standard deviations (2SDs) of \([^{235}U]/[^{238}U]\) isotope ratio, \([^{234}U]/[^{238}U]\) isotope ratio, U abundance, \([^{230}Th]/[^{232}Th]\) isotope ratio, and Th abundance results for four repetitive measurements were 0.1%, 1%, 1%, 39%, 15%, respectively. Those of \([^{234}U]/[^{238}U]\) isotope ratio and U abundance analyses are slightly larger than the analytical reproducibility. Those of Th isotope and abundance analyses are, however, much larger than the analytical reproducibility, suggesting that U is relatively homogeneous in JCp-1, whereas Th is not.

Although JCp-1 was prepared from a living coral, the apparent U-Th disequilibrium ages range from 0.82 to 1.14 ka. Th abundances varied from 46 ppb to 56 ppb, which is significantly higher than ordinary coral. It is possible that the observed high Th abundance may have resulted from contamination during preparation steps for the rock powder. Or it may have caused by inclusion of sandy material during the growth of the coral. The presence of residue after nitric acid dissolution indicates the presence of non-carbonate component. The correction of the contribution of \(^{230}Th\) from the contaminant, however, still gives ages older than zero. In addition, \([^{234}U]/[^{238}U]\) isotope ratio of JCp-1 is higher than the value of present seawater, suggesting the coral may have experienced some diagenesis.

Keywords: U-Th radioactive disequilibrium, JCp-1, coral, ICP-MS, reference material

INTRODUCTION

Coral has records the composition of surface seawater as chemical composition in the skeleton during the growth. Therefore, several chemical components in coral play powerful role as indicators to decipher the sea surface environmental conditions. The Geological Survey of Japan has issued JCp-1 (Coral *Porites* sp.) as coral reference and reported major, minor and trace data (Okai et al., 2002, 2004).

\(^{230}Th\) ages of coral are important for characterizing sea level in the Late Quaternary, for calibrating the \(^{14}C\) time scale, and for elucidating the age of tectonic event (Bourdon et al., 2003). U is soluble in natural water as uranyl ion and in various uranyl carbonate forms under oxidizing conditions, whereas Th has extremely low solubility. Carbonate precipitated from water usually contains U and rarely Th; for example, coral contains around a few thousands ppb (ng g\(^{-1}\), hereafter shown as ppb) of U and less than 1 ppb of Th. Hence, we can determine a sample’s age by measuring the increase of \(^{230}Th\) decaying from \(^{234}U\), from zero at the precipitation to equilibrium. The \(^{230}Th\) age for a carbonate is calculated as:

\[
\left(\frac{^{230}Th}{^{234}U}\right) = \left(\frac{^{238}U}{^{235}U}\right) \left(1 - e^{-\lambda_{30}t}\right) + \frac{\lambda_{30}}{\lambda_{30} - \lambda_{34}} \left(1 - e^{-\left(\lambda_{30} - \lambda_{34}\right)t}\right)
\]

where \(t\) is the age in years and \(\lambda\) represents the decay constant for each nuclide; a rounded ratio in a parenthesis indicates an activity ratio. Although the U-Th radioactive disequilibrium dating has been widely applied to carbonates, there is no available standard material. We examined homogeneities of U-Th radioactive disequilibrium age in...
to two aliquots for abundance measurements. The U and Th spikes, which were prepared with 2 g of JLs-1 was divided into five aliquots. Each aliquot was subdivided for isotope and abundance measurements (Watanabe and Nakai, 2006). The solution was digested completely. We carried out repetitive measurements of a stock solution of JLs-1 limestone standard rock, issued by Geological Survey of Japan, in the large tail of the 232Th, for 230Th acquisition. The abundance sensitivity, high enough to cut increases the abundance sensitivity, high enough to cut increments of Yokoyama et al (1999). These separations were carried out for both spiked and unspiked aliquots of sample solutions. The Th and U recoveries were greater than 80%. Total blanks through the chemical procedure were 14 pg for U and 11 pg for Th, respectively.

The recovered spiked and unspiked fractions were dissolved in 2% HNO3. These isotopic compositions were measured using a MC-ICP-MS (IsoProbe, GV instruments). A retardation filter fitted in the mass-spectrometer in the mass-spectrometer defined as (count rate on m/z 236)/ (count rate on m/z 238) was measured as \( 3 \times 10^{-3} \), using a uranium solution which is low enough compared with typical carbonate samples (230Th/232Th > 1 \times 10^{-3}). We carried out repetitive measurements of a stock solution of JLS-1 limestone standard rock, issued by Geological Survey of Japan, to evaluate reproducibility of our measurements (Watanabe and Nakai, 2006). The solution prepared with 2 g of JLS-1 was divided into five aliquots. Each aliquot was subdivided for isotope and abundance measurements. The respective precisions of U abundance and [235U/238U]isotope ratio, [234U/238U]isotope ratio were 0.1%, 0.1% and 0.1%. The precision of Th isotope ratio and abundance using 0.9 ng of Th were around 1 and 0.4%.

The standard material.

In this study, we repeatedly analyzed U-Th isotope ratios and the abundances in JCp-1 coral reference to evaluate homogeneity of JCp-1 and its suitability as a standard for U-Th disequilibrium analyses. Our analytical procedure was the combination of MC-ICP-MS and isotope dilution technique that utilized commercially available U and Th reagents as spikes. This paper is the first report of U and Th disequilibrium analyses in the standard material.

**EXPERIMENTAL**

All experiments were carried out in a clean room under class 1000 conditions. Evaporation of sample solutions was performed under airflow that was cleaned using a HEPA filter. Our detailed analytical procedures, which are described in Watanabe and Nakai (2006), are as follows.

First, JCp-1 was weighted about 1 g. Coral samples were digested using 7 M HNO3. White residue, observed after the acid digestion, was digested sequentially using HF/HClO4 and HCl/H3BO3. Through these acid digestions, JCp-1 was dissolved completely.

Next, digested sample was dissolved in 7 M HNO3. It was subsequently divided into three aliquots for isotope dilution analyses and isotope measurements in these proportions: two-fifths was used for Th isotope dilution analysis; one-twentieth was used for U isotope dilution analysis; and the remainder was used for isotope ratio measurements. The U and Th spikes, which were prepared by 234Th, 235U depleted reagents, were added respectively to two aliquots for abundance measurements.

Then, 8 mg of Fe dissolved in 1 M HNO3 was added to sample solutions. The U and Th in solutions were co-precipitated with Fe by the addition of ammonium hydroxide. The mixture was centrifuged and the supernatant was discarded. The precipitate was dissolved in 7 M HNO3 with Fe by the addition of ammonium hydroxide. The mixture was centrifuged and the supernatant was discarded. The precipitate was dissolved in 7 M HNO3. The Th and U recoveries were greater than 80%. Total blanks through the chemical procedure were 14 pg for U and 11 pg for Th, respectively.

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respectively.

A coral sample received from the USGS (J. B. Paces, U.S. Geological Survey, written commun., 2005) was analyzed for $^{230}$Th dating to confirm the accuracy of our analytical scheme (Watanabe and Nakai, 2006). The ages obtained with our method, $115.9 \pm 8.3$ and $111 \pm 17$ ka, agree well with the average age of the same sample measured using TIMS. The U-Th radioactive disequilibrium ages measured by TIMS range from 109.3 to 124.0 ka, with the average of $119.6 \pm 1.9$ ka ($n = 17$). In addition, our $\delta^{234}$U results are consistent with the reference value. The consistency of our age and $\delta^{234}$U results demonstrates the accuracy of our analytical procedure.

**RESULTS AND DISCUSSION**

**U-Th radioactive disequilibrium analyses**

The results of the analyses in JCp-1 are shown in Table 1 and Fig. 1. Ages and initial $^{234}$U/$^{238}$U ratios were calculated using IsoPlot (Ludwig and Titterington, 1994). The radioactive disequilibrium ages were calculated from isotopic abundances with the following decay constants, $\lambda_{230\text{Th}} = 9.158 \times 10^{-6}$ yr$^{-1}$, $\lambda_{234\text{U}} = 2.826 \times 10^{-6}$ yr$^{-1}$, $\lambda_{232\text{Th}} = 4.933 \times 10^{-11}$ yr$^{-1}$, $\lambda_{238\text{U}} = 1.551 \times 10^{-10}$ yr$^{-1}$ (Cheng et al., 2000, Firestone and Baglin, 1999). In Table 1, $\delta^{234}$U means $[(^{234}\text{U}/^{238}\text{U})_{\text{time of precipitation}}/(^{234}\text{U}/^{238}\text{U})_{\text{equilibrium}} - 1] \times 10^3$.

Our results of U abundance measurements almost agree with the reported value of Okai et al. (2004), 2900 ppb. Homogeneity of abundances and isotope ratios of U and Th can be evaluated by Fig. 1. The 2SD of $[^{235}\text{U}/^{238}\text{U}]_{\text{isotope ratio}}$ was 0.1%, whereas the 2SDs of $[^{234}\text{U}/^{238}\text{U}]_{\text{isotope ratio}}$ and U abundance were 1%. Furthermore, the 2SDs of $[^{230}\text{Th}/^{232}\text{Th}]_{\text{isotope ratio}}$ and Th abundance were 39% and 15% respectively. The results indicate that U abundance and isotope ratios are relatively homogeneous in JCp-1, whereas Th abundance and isotope ratio are heterogeneous even in sample scale of one gram. The observed extent of heterogeneity of Th distribution is common for coral samples.

Th abundance is higher than values reported for ordinary corals, less than 1 ppb. It might result from the contamination of silicate impurities during crushing JCp-1. Okai et al. (2002) reported high concentrations of Si and Al in JCp-1 and ascribed it to contamination during a grinding step with a ball mill. In Figs. 2a and 2b, four
analyzed points don’t form mixing lines between carbonate component and contaminant. It is possible that the contaminant is heterogeneous regarding U and Th. As Okai et al. (2002) pointed out, it may be that the contaminant is resistant to acid attack resulting in imperfect dissolution, although we observed no residue by microscope after acid digestion. It is also possible that the U-Th system of the starting material of the JCp-1 is inhomogeneous due to diagenesis (see the detail at next section), in addition to the influence of the contamination.

234U/238U activity ratio

In Table 1 and Fig. 3, drawn by IsoPlot, (234U/238U) of our four results are slightly higher than the value of present seawater, 1.150 ± 0.002 (Delanghe et al., 2002), and 1.147 ± 0.001 (Robinson et al., 2004). Since JCp-1 is made from a living coral, the values should be consistent with that of present seawater. Gallup et al. (1994) and Thompson et al. (2003) pointed out a possibility that coral uptake dissolved 230Th and 234Th from ground water during diagenetic events. Short-lived 234Th will decay to 234U after the uptake. Accordingly, the uptake results in correlated increase between (234U/238U) and (230Th/238U), as shown in Fig. 3. A dashed line in Fig. 3 is an expected diagenetic trend departing from a contemporary coral that had experienced no diagenesis. Our data are on the diagenetic trend, suggesting JCp-1 may have uptaken 230Th and 234Th from ground water during some diagenetic process. Gallup et al. (1994) reported that such uptakes give older ages than true precipitation ages.

Evaluation of 230Th age

The apparent ages were from 0.8 to 1.2 ka, as shown as maximum age in Table 1. The analyzed points in Fig. 3 shows the maximum ages, since JCp-1 has so high Th content that contribution of initial 230Th from a contaminant can not be negligible. We subtracted 230Th from the contaminant, assuming initial [230Th/232Th]isotope ratio value of the contaminant as 4.4 × 10⁻⁶, the ratio in equilibrium with a bulk earth 232Th/238U value (3.8 by atomic ratio). The correction still leaves significant amount of initial 230Th and the corrected ages would be around five hundred years, as shown in Table 1. To obtain zero age, [230Th/232Th]isotope ratio of the contaminant needs to be higher. Guo et al. (1995) reported [230Th/232Th]isotope ratio of particulate in seawater from shelf and slope areas of the Gulf of Mexico and off Cape Hatteras in the Middle Atlantic Bight. They revealed that the isotope ratios vary depending on the depth. The Th isotope ratios of particles in surface water were less than 5 × 10⁻⁶, which is similar to the value of the bulk earth value we assumed for the corrections. Thus correction using the particulate value seems to be difficult to obtain zero age. It is not certain if a contaminant introduced during a sample preparation step can have high Th isotope ratio. Although we
cannot conclude exactly the main source for older age, it is likely that the influences of both contamination and diagenetic events give older ages.

CONCLUSIONS

We have analyzed U-Th radioactive disequilibrium in JCp-1 using MC-ICP-MS and isotope dilution technique, to provide the reference data.

The two times of standard deviations of U isotope and abundance analyses are slightly larger than the analytical reproducibility. Those of Th isotope and abundance analyses, however, are much larger than the analytical reproducibility, suggesting that U is relatively homogeneous in JCp-1, whereas Th is not.

Th abundance varied from 46 ppb to 56 ppb, which is higher than ordinary coral. The apparent disequilibrium ages were from 0.8 to 1.2 ka. The observed high abundance of Th and apparent old ages are partly resulted from contamination or inclusion of sandy material. The presence of Th and apparent old ages are partly resulted from contamination or inclusion of sandy material. The presence of residue after nitric acid dissolution of the JCp-1 contamination or inclusion of sandy material. The presence of residue after nitric acid dissolution of the JCp-1 contamination or inclusion of sandy material. The presence of residue after nitric acid dissolution of the JCp-1 contamination or inclusion of sandy material. The presence of residue after nitric acid dissolution of the JCp-1 contamination or inclusion of sandy material. The presence of residue after nitric acid dissolution of the JCp-1 contamination or inclusion of sandy material.

From the results this standard material seems to be heterogeneous with regards to U-Th radioactive disequilibrium system.

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REFERENCES


