

$^{230}\text{Th}/^{234}\text{U}$ dating of Holocene mollusk shells from Jeju Island, Korea, by multiple collectors inductively coupled plasma mass spectrometry

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ABSTRACT: The $^{230}\text{Th}/^{234}\text{U}$ ages of fossil mollusk shells collected from the Sinyangri and Hamori Formations, the youngest stratigraphic units on Jeju Island, Korea, were estimated using multiple collectors inductively coupled plasma mass spectrometry. Seven aragonite shells yielded $^{230}\text{Th}/^{234}\text{U}$ ages ranging from 3434 ± 40 yr to 4980 ± 33 yr ($2\sigma_m$), in concordance with radiocarbon ages for samples containing little ^{232}Th . Our data suggest that the $^{230}\text{Th}/^{234}\text{U}$ method can be a potentially useful tool for dating Holocene mollusks, provided that there is no evidence for severe recrystallization, cementation, and considerable amount of common thorium. An early uptake of uranium immediately after burial and subsequent maintenance of closed system for uranium and thorium can be assumed for our mollusk samples. This study, together with previous radiocarbon and optical dating results, demonstrates that the Hamori Formation where human footprints were recently discovered deposited during the middle Holocene.

Key words: mollusk shells, $^{230}\text{Th}/^{234}\text{U}$ ages, Jeju Island, MC ICP-MS, Holocene

1. INTRODUCTION

Nuclear and chemical processes including recoil, partial melting, weathering, transportation, and deposition can disturb a state of secular radioactive equilibrium between nuclides in a decay chain of geological materials containing uranium and thorium. Such disequilibrium has been successfully applied to various studies concerning the magma chamber processes and geological dating, as summarized by Ivanovich and Harmon (1992), and Bourdon et al. (2003). After ten half-lives of the daughter nuclides, equilibrium at the 99.9 % level is re-established and thus uranium-series disequilibrium dating efficiently covers the last million years. Uranium-series dating methods can be divided into two groups; the daughter-deficiency methods based on accumulation of decay products of uranium, and the daughter-excess methods based on decay of unsupported intermediate nuclides in the series (Ku, 1976; Ivanovich and Harmon, 1992). The former includes $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ dating of carbonates virtually free of initial thorium and

protactinium. ^{230}Th dating has been successfully applied to corals (Bard et al, 1990a, b), calcite deposits in caves (Li et al., 1989), aragonitic carbonate bank deposits (Slowey et al., 1996), and lacustrine precipitates (Schramm et al., 2000).

^{238}U decays to ^{234}U by alpha emission with a half-life of 4.468×10^9 years (Steiger and Jäger, 1977). The half-lives of following daughter nuclides in ^{238}U chain, ^{234}Th , ^{234}Pa , ^{234}U , and ^{230}Th were reported at 24.1 days, 6.7 hours, $245,250 \pm 490$ years, and $75,690 \pm 230$ years, respectively (Cheng et al., 2000). ^{230}Th ultimately decays to stable ^{206}Pb through a series of intermediate daughters. Practically uranium-series disequilibrium dating covers about five half-lives of the daughter nuclides and thus $^{230}\text{Th}/^{234}\text{U}$ dating is applicable to c. 380,000 years.

The study of U-Th disequilibrium series has been dependent upon alpha-particle counting method (Ivanovich and Harmon, 1992) and thermal ionization mass spectrometry (Chen et al., 1986; Rubin, 2001), but recent developments in multiple collectors inductively coupled plasma mass spectrometry (MC ICP-MS) (Luo et al., 1997; Pietruszka et al., 2002) have made it possible to measure trace amounts of radionuclides with high efficiency and productivity. We applied MC ICP-MS measurements to ^{230}Th dating of fossil mollusk shells collected from the youngest volcanostratigraphic units in Jeju Island, the largest volcanic island in Korea.

2. GEOLOGICAL BACKGROUND AND SAMPLE COLLECTION

Jeju Island is a major volcanic island of Korea, constructed on the ~100 m-deep continental shelf off the Korean Peninsula during the Quaternary (Fig. 1). The island is composed of basaltic to trachytic, plateau- and shield-forming lavas and dotted with numerous volcanic cones (Sohn and Park, 2004). Sedimentary formations are rare and thin on the surface of the island, found only near a few hydromagmatic volcanoes, including the Sinyangri Formation near the Ilchulbong tuff cone (Kim, 1969; Han et

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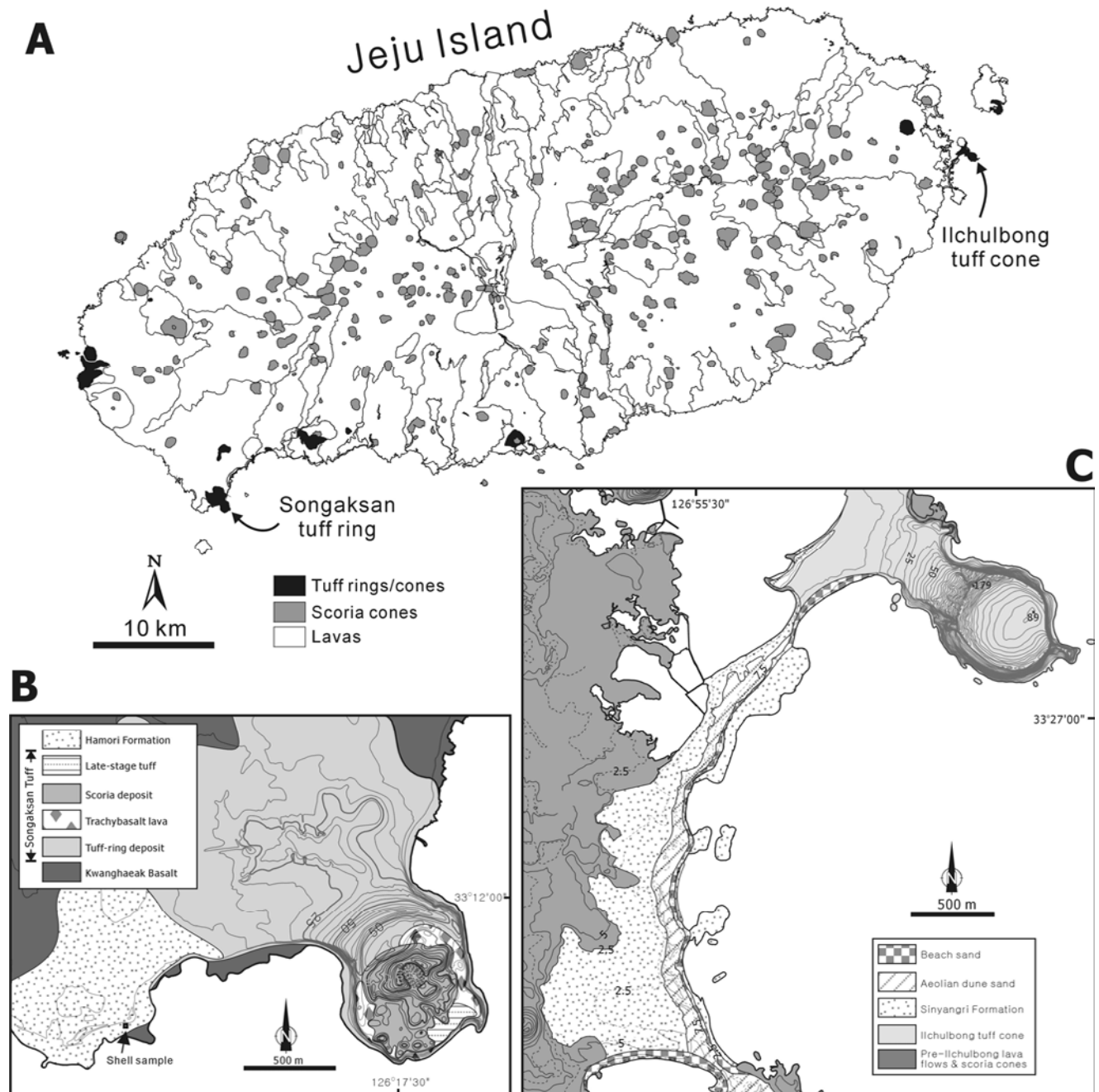


Fig. 1. A) Simplified geologic map of Jeju Island, showing outlines of lava flows and distribution of volcanic cones (after Sohn and Park, 2005). B) Geologic and topographic map of the Songaksan tuff ring and the Hamori Formation (after Sohn et al., 2002). C) Geologic and topographic map of the eastern margin of Jeju Island, showing the morphology of the Ilchulbong tuff cone and the distribution of the Sinyangri Formation (after Sohn et al., 2002). Altitudes shown in meters and contours shown in 5-m intervals.

al., 1987) and the Hamori Formation near the Songaksan tuff ring (Sohn et al., 2002) (Fig. 1). These formations are composed of basaltic volcanoclastic materials and show planar stratification, low- to high-angle cross-stratification, and abundant ripple marks. Radiocarbon dating of mollusk shells from these formations (Kim et al., 1999; Sohn et al., 2002), together with sedimentological observations (Sohn et al., 2002), shows that these formations were deposited in

a high-energy nearshore setting during the middle to late Holocene when the sea level nearly reached to the present horizon.

In this study, we chose four samples from the Sinyangri Formation, three samples from the Hamori Formation, and one living shell specimen. Four analyzed specimens from the Sinyangri Formation were obtained from a shell-bearing, gravel-rich layer in the middle part of the formation.

All are bivalve fragments although they could not be identified by species level. Mollusk shells from the Hamori Formation, either fragmented or intact, were obtained from the basal part of the formation directly above the underlying Kwanghaeak Basalt (Fig. 1). Most of shells are thought to have inhabited upon the basalt in a shallow marine environment before burial by the volcanoclastic materials produced by the eruption of the Songaksan tuff ring. All the analyzed specimens are avalone, which are preserved in an archive form. The species of a living shell representative of the present seawater condition is *Maetra chinensis*, which lives in the coastal areas around the Korean Peninsula.

3. EXPERIMENTAL METHODS

3.1. Sample Pretreatments

The existence of any secondary alteration in the mollusk samples was checked after the identification of crystal structure by X-ray diffraction (XRD) analysis at the Seoul center of Korea Basic Science Institute (KBSI) and microscopic examination. The fresh surface of analyzed specimen was brushed, cleaned with 1N HNO_3 and deionized water, and dried in the air. Each specimen was powdered and homogenized within agate mortar. 1~2 g of powder sample was weighed and digested with purified conc. HNO_3 after spiking appropriate amount of ^{236}U (15 pg) and ^{229}Th (4.5 pg).

U and Th were separated from the sample matrix through two steps. The first step is the Fe coprecipitation. About 0.3 mg of Fe was added to digested solutions, and Fe was precipitated by the addition of ammonia up to pH 8.5-9. Discarding a supernatant after centrifugation, precipitates were dissolved with conc. HNO_3 . After $\text{Fe}(\text{OH})_3$ was precipitated again, it was dissolved with 8N HNO_3 . The second step is a standard nitrate column using anion exchange resin (AG1-X8, 100-200 mesh). Following the conditioning of column, the passage of sample solution and the decontamination of Fe with 8 M HNO_3 , Th fraction was eluted with 9N HCl solution and then U fraction was eluted with 1N HCl solution. Total recoveries of Th and U through two separation procedures were about 80% and 70%, respectively. Since U and Th concentrations within shells are a few ng/g level, all the acids used in above procedures were high-purity grade like AA-10 (Tampure Ltd) and all the wares were acid-cleaned thoroughly.

3.2. MC ICP-MS Measurements

The U and Th isotopes were analyzed on the AXIOM MC at KBSI in Daejeon, which has high resolution and multiple collection functions. Detailed instrument configuration for this MC ICP-MS was reported in Aggarwal et al. (2003). The hot plasma mode and desolvated micro-nebu-

lizer (MCN 6000; CETAC Technology) were used. Samples were introduced into the instrument using MCN 6000 at an uptake rate of 100 ml/min by a peristaltic pump. Typical sensitivities (ion efficiency) for U and Th were about 0.1%, respectively.

$^{234}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{236}\text{U}$ ratios were measured simultaneously. Three static sequences with masses 234, 235 and 236 measured on the multiplier were run with the measurement of masses 235 and 238 on the faradays. For sequences with masses 234 and 236 on the multiplier, mass bias for isotopic ratio with mass 238 was corrected by exponential law relative to natural $^{235}\text{U}/^{238}\text{U}$ ratio (1/137.88). The correction factor for the collector efficiency between multiplier and faraday for the measurement of $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios was obtained by comparing $^{235}\text{U}/^{238}\text{U}$ ratio on two faradays in the first sequence with that measured on multiplier and faraday in the second sequence. After the mass bias and the collector efficiency were corrected, actual $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios were calculated. In addition, we can obtain corrected $^{234}\text{U}/^{236}\text{U}$ ratio by dividing $^{234}\text{U}/^{238}\text{U}$ with $^{236}\text{U}/^{238}\text{U}$ ratio for the isotopic dilution. Certified reference material for U isotopes (U015, New Brunswick Laboratory) of U 20 ng/ml concentration was run at every three samples for the confirmation of correction factors. With ten runs of U015 during the sample analysis (total 6 hrs), mean $^{234}\text{U}/^{238}\text{U}$ ratio was 0.00008638 ± 13 and coincident to the certified value (0.0000863 ± 9).

$^{230}\text{Th}/^{232}\text{Th}$ and $^{230}\text{Th}/^{229}\text{Th}$ ratios were measured simultaneously. Two sequential measurements of masses 229, 230 and 232 were performed with multiplier for masses 229 and 230, and faraday for mass 232. Background of each mass was measured at half mass such as 229.5 and 230.5 for mass 230. Mass bias of Th isotopic ratio measurement has been corrected by the addition of natural U solution to the Th fraction using natural $^{235}\text{U}/^{238}\text{U}$ ratio (1/137.88) (Luo et al., 1997; Pietruszka et al., 2002). Those previous studies measured isotope ratios for concentration and isotopic ratio in the separate split of Th fraction. In addition, Pietruszka et al. (2002) used large amounts of ^{229}Th spike for the direct quantification of ^{232}Th . However, in order to measure the concentration and isotope ratio simultaneously, the use of large amount of ^{229}Th was not favorable because of the ^{230}Th impurity in spike solution. Therefore, we adopted the bracketing multiplier-faraday measurement using an appropriate standard reference material.

Since the abundance sensitivity of AXIOM MC is as much as about 10 ppm at 1 amu apart, the precise and accurate measurement of $^{230}\text{Th}/^{232}\text{Th}$ ratio is very difficult for low ^{230}Th and high ^{232}Th level. Tailing from ^{232}Th peak affects mass 230 but conventional half-mass zero estimation of the baseline makes the signal overcorrected. As the tail profile observed on the AXIOM is exponential, log-mean calculation is the most appropriate method (Shen et al., 2002; Deschamps et al., 2003). Figure 2 shows the different results of

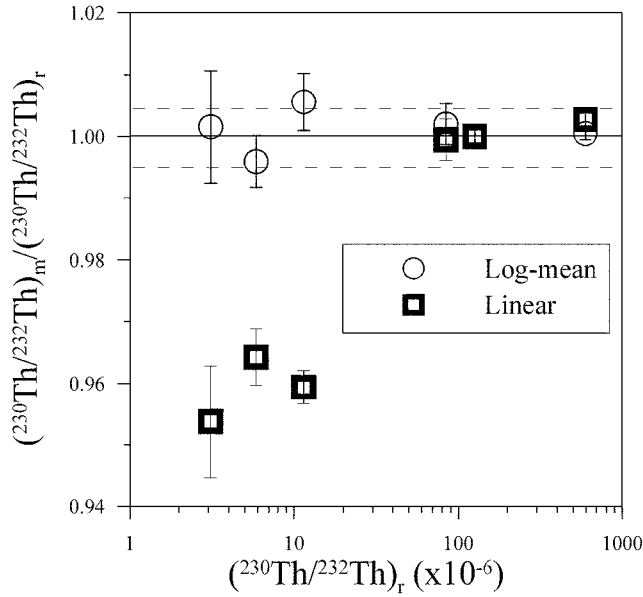


Fig. 2. Comparison of tailing correction methods between long-mean (open circle) and linear (square) calculation of half-mass background measurements. Measured $^{230}\text{Th}/^{232}\text{Th}$ ratios over the reference value are plotted according to the ratio level.

tailing correction methods between linear and log-mean calculation for solutions with variable ratios of $^{230}\text{Th}/^{232}\text{Th}$. These solutions were made by mixing appropriate amounts of IRMM 061 (certified reference ^{230}Th solution; JRC, Belgium) with IRMM 035 (certified reference Th solution for $^{230}\text{Th}/^{232}\text{Th}$ ratio; 0.0000115) gravimetrically. UCSC-Th-A (0.00000586; Rubin, 2001) and IRMM 036 (0.00000313) were also measured for $^{230}\text{Th}/^{232}\text{Th}$ ratio. Mass bias and collector efficiency of multiplier and faraday were corrected by the bracketing method using a solution with $^{230}\text{Th}/^{232}\text{Th}$ ratio of 0.0001264 (± 5) which was also used as bracketing standard solution for samples. With log-mean calculation of

half-mass background measurement, accurate isotope ratio could be obtained even for samples with very low isotope ratio (1/300,000) and linearity of correction using a standard might be achieved up to at least two orders (Fig. 2). However, even though log-mean correction scheme may be applied, the proportion of tailing of ^{232}Th on mass 230 will be significant and the measurement error of $^{230}\text{Th}/^{232}\text{Th}$ ratio increases. For example, if the activity ratio of $^{230}\text{Th}/^{232}\text{Th}$ in a sample is 1 (atomic ratio of 1/185,097), tailing of ^{232}Th signal at mass 230 occupies about 35.5% of mass 230 signal because the tailing at 2 amu apart contributes as much as 3 ppm. As a result, the measurement error may increase as much as 1.7 times than counting statistics. For the contribution of tailing to be less than 5 % of total ^{230}Th signal, the activity ratio of $^{230}\text{Th}/^{232}\text{Th}$ should be higher than 10.

In order to confirm the accuracy of above analytical method for ^{238}U concentration and $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios, we also analyzed the same coral sample (AC-U11-top) previously reported in Esat et al. (1999). The result is summarized in Table 1. Two of three sub-samples showed the same isotope ratios and ages as the reported values within the confidence limits but one sub-sample showed slightly older age.

4. RESULT AND DISCUSSION

^{234}U and ^{230}Th concentrations and isotopic compositions of analyzed mollusk samples are presented in Table 2, together with radiocarbon ages of four selected samples. Radiocarbon ages were measured for comparison, using an accelerator mass spectrometry at Geochron Laboratories in Cambridge, USA. Our result confirms previous radiocarbon ages of shells in the Sinyangri and Hamori Formations, respectively reported at 4,400 to 1,570 yr BP (Kim et al., 1999) and around 4 ka (Sohn et al., 2002) (Table 2). The two formations gave consistent $^{230}\text{Th}/^{234}\text{U}$ and radiocarbon

Table 1. U-Th isotope ratios and ^{230}Th -ages of a coral sample (AC-U11-top)

	^{238}U	$\delta^{234}\text{U}(0)^1$, ‰		$(^{230}\text{Th}/^{238}\text{U})_{\text{act}}^2$		Age (kyr) ³		Note
	($\mu\text{g/g}$)	Mean	error ⁴	Mean	error	Mean	error ⁵	
Measured 1	2.82	109	0.4	0.7714	0.0026	125.5	1.0	this study
Measured 2	2.90	100	0.4	0.7616	0.0033	124.7	1.0	
Measured 3	2.84	102	0.3	0.7772	0.0023	129.0	1.0	
Reported 1	2.85	108	1.0	0.7706	0.0009	125.5	0.9	Esat et al., 1999
Reported 2	2.85	100	3.0	0.7646	0.0026	125.7	0.9	

1: $\delta^{234}\text{U} = \{[(^{234}\text{U}/^{238}\text{U}) / (^{234}\text{U}/^{238}\text{U})_{\text{eq}}] - 1\} \times 10^3$ ($^{234}\text{U}/^{238}\text{U})_{\text{eq}}$ is the atomic ratio at secular equilibrium and is equal to $\lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$ where λ_{238} ($1.551 \times 10^{-10} \text{y}^{-1}$) and λ_{234} ($2.835 \times 10^{-6} \text{y}^{-1}$) are the decay constants for ^{238}U and ^{234}U , respectively.

2: Activity ratio

3: Ages are calculated iteratively using $1 - [^{230}\text{Th}/^{238}\text{U}]_{\text{act}} = e^{-\lambda_{230}T} - (\delta^{234}\text{U}(0)/1000)(\lambda_{230}/\lambda_{234})(1 - e^{(\lambda_{234} - \lambda_{230})T})$ where T is the age in years and λ_{230} is the decay constant for ^{230}Th (Esat et al., 1999)

4: Error is 2 sigma

5: Error is determined by propagating from $\delta^{234}\text{U}(0)$ and $(^{230}\text{Th}/^{238}\text{U})_{\text{act}}$ as well as the systematic contributions from the decay constants λ_{230} and λ_{234} through the age equation (Esat et al., 1999).

Table 2. Radiochemical and age data on fossil mollusk shells from Jeju Island, Korea.

type ¹	²³⁴ U (pg/g)	2σ %SE	²³⁰ Th (pg/g)	2σ %SE	²³⁸ U (ng/g)	²³² Th (ng/g)	(²³⁴ U/ ²³⁸ U) _A ³	δ ²³⁴ U (‰)	2σ %SE	(²³⁰ Th/ ²³⁴ U) _A ³	2σ %SE	(²³⁰ Th/ ²³² Th) _A ³	2σ %SE	(²³⁴ U/ ²³² Th) _A ³	(²³⁸ U/ ²³² Th) _A ³	age (yr)	²³⁰ Th/ ²³⁴ U age (yr)	C-14 age ⁴ (yr BP)	δ ¹³ C (‰)
Sinyangri Formation																			
APR-1	A	36.2	0.40	2.74	588	0.89	1.121	121.4	0.40	0.0370	2.77	83.8	2.48			4098±120			
JUN-9	A	26.4	0.38	1.08	417	3.2	1.154	153.9	0.36	0.0311	1.14	14.4	0.74			3434±40		3620±40	1.5
FEB-1		24.9	0.25	0.263	392	0.36	1.157	157.4	0.55	0.0343	0.84	134.8	1.33			3793±32		3890±30	0.5
FEB-3		36.4	0.25	0.504	576	0.46	1.152	151.7	0.43	0.0448	0.65	200.5	0.99			4980±33		4890±40	1.4
Hamori Formation																			
APR-2	A	69.6	0.26	0.697	1161	0.11	1.092	92.1	0.26	0.0332	1.70	1199	0.83			3670±63			
JUN 7-1	A+C	47.6	0.42	0.545	750	4.4	1.156	156.0	0.35	0.0380	1.06	23.1	0.73	608	526	4210±45		3840±40	1.7
JUN 7-2	A+C	50.0	0.71	0.571	787	9.8	1.159	158.6	0.57	0.0379	0.97	10.8	0.53	286	247	4198±41			
JUN 7-3	A+C	44.3	0.47	0.523	697	13.5	1.156	156.3	0.57	0.0392	0.86	7.15	0.47	183	158	4345±38			
JUN-7 ²							1.155	155.0	1.98	0.0376	20.7					4165±880			
JUN-10	A	52.3	0.39	0.559	827	3.3	1.152	152.4	0.34	0.0355	0.71	31.2	0.41			3928±28			
Living Shell																			
JUN-6	A	5.65	0.91	0.00044	89	0.05	1.152	152.4	0.57	0.0003	295	1.56	1.70			33±96			

1. A; aragonite, C; calcite

2. Isochron derived authigenic ratios

3. Activity ratios calculated from atomic ratios at half lives of 4.468×10⁹ y for ²³⁸U, 245,250 y for ²³⁴U, 75,690 y for ²³⁰Th, and 1.401×10¹⁰ y for ²³²Th (Steiger and Jäger, 1977; Cheng et al., 2000).

4. Conventional (not calibrated) age

ages (Table 2); 3,434 yr ~ 4,980 yr for the Sinyangri Formation, and 3,670 yr ~ 4,345 yr for the Hamori Formation.

The XRD analysis showed that all the analyzed samples from the Sinyangri and Hamori Formations are pure aragonite, except for sample JUN 7 which is partly calcitic. Any secondary alteration or cementation was not identified.

The uranium content of a living shell (sample JUN-6, ^{238}U 89 ng/g) is significantly lower than the other samples, suggesting an addition of external uranium to the fossil shells. The living shell has negligible amount of ^{230}Th (0.00044 pg) and thus yields the $^{230}\text{Th}/^{234}\text{U}$ age of present day (33±96 yr BP). The uranium content and $^{234}\text{U}/^{238}\text{U}$ ratio of the fossil mollusks tend to increase with time, violating the closed system assumption (Kaufman et al., 1971). The $^{234}\text{U}/^{238}\text{U}$ ratio of seawater is out of secular equilibrium (Thurber, 1962). Cheng et al. (2000) measured $\delta^{234}\text{U}$ ($=\frac{(^{234}\text{U}/^{238}\text{U})-1}{^{238}\text{U}} \times 1000$) of modern seawater as 145.8±1.7‰, and it is believed that the marine $\delta^{234}\text{U}$ has remained within 10~20‰ of its modern value during the last several hundred thousand years (Hamelin et al., 1991). Two of our samples (APR-1, -2) have distinctly lower $\delta^{234}\text{U}$ than the marine value, indicating the introduction of nonmarine materials after burial. The other six samples including the living shell show marine $\delta^{234}\text{U}$ values. In the range of less than 30 ka, however, the $^{230}\text{Th}/^{234}\text{U}$ age is virtually independent upon initial $\delta^{234}\text{U}$ in the sample. Furthermore, the addition of external uranium cannot be a problem if a mollusk uptakes uranium immediately after burial and has consistently maintained the closed system for uranium and thorium with no or negligible common thorium. This case can be tested by using other independent age constraints and ^{232}Th measurements as described in the following.

The $^{230}\text{Th}/^{234}\text{U}$ ages of samples FEB-1 and FEB-3 are concordant with radiocarbon ages within 2.5% difference. For the last 12 ka, the conventional radiocarbon ages are too low, up to 2 ka because of long-term variation of the initial $^{14}\text{C}/\text{C}$ ratio (Wagner, 1998). This effect should be considered for samples FEB-3 and JUN-7 whose conventional radiocarbon ages are younger than the $^{230}\text{Th}/^{234}\text{U}$ ages. It is also interesting that samples containing relatively high ^{232}Th content (JUN-9; 3.2 ng/g, JUN-7; 4.4~13.5 ng/g) show relatively large difference in ages between the two dating methods. The concentration of ^{232}Th in surface seawater is negligible and thus its detection in marine mollusks would indicate the addition of common ^{230}Th , not originating by decay from its parent, ^{234}U . The contamination by common thorium is clear for our samples because the living shell contains much smaller amount of ^{232}Th (0.05 ng/g) than the other fossil samples (0.11~13.5 ng/g). The $^{230}\text{Th}/^{232}\text{Th}$ ratio of common external component is difficult to define, but average U/Th ratio of upper crust (0.238; Taylor and McLennan, 1981) and assumed secular equilibrium may give an approximate value of c. 1/254,000. In this case, 3.2 ng/g of ^{232}Th in sample JUN-9 contributes 0.0126 pg/g of exter-

nal ^{230}Th , which comprises around 5% of total ^{230}Th . This simple calculation demonstrates a dramatic influence of external materials on ^{230}Th dating of mollusk shells. The influence of common external materials in $^{230}\text{Th}/^{234}\text{U}$ dating has been corrected by several isochron methods as summarized in Ku (2000).

We selected sample JUN-7 to test the validity of total sample dissolution isochron dating (Luo and Ku, 1991), considering that it contains the largest amount of ^{232}Th and is partly calcitic. This method aims to determine the authigenic $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios respectively from isochrons on $^{230}\text{Th}/^{232}\text{Th}$ vs. $^{234}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ vs. $^{238}\text{U}/^{232}\text{Th}$ diagrams, with the assumption that the sample is a mixture of external and authigenic components. Three fractions of JUN-7 were analyzed and the $^{230}\text{Th}/^{234}\text{U}$ ratio estimated from isochron fitting (not shown here) has a large error (20.7%, $2\sigma_m$). One fraction of the sample (JUN 7-3) even contains around 10 % of external ^{230}Th . Certainly this kind of sample needs the correction for the external component.

On the other hand, samples containing less than 1 ng/g ^{232}Th are only affected by less than 1 % in total ^{230}Th . This kind of external contribution and the inherent error in radiocarbon ages resulted in the apparent discrepancy between the two dating methods in Table 2. However, broad agreement of the $^{230}\text{Th}/^{234}\text{U}$ ages with radiocarbon ages, at least for samples containing relatively small amount of ^{232}Th , strongly suggests that general assumptions of the $^{230}\text{Th}/^{234}\text{U}$ dating are sufficiently satisfactory: 1) The shells took in uranium during diagenesis but immediately after the burial; 2) The shells have maintained the closed system for uranium and thorium for most of their burial history; 3) There is negligible influence of initial common thorium. Although our data highlight the potential usefulness of $^{230}\text{Th}/^{234}\text{U}$ dating for fossil mollusk shells, it is highly desirable to characterize the sample carefully with XRD and microscope, and to measure their thorium content before the isotopic work. Strictly constrained $^{230}\text{Th}/^{234}\text{U}$ dating of mollusk shells can be used as a calibration tool for conventional radiocarbon ages, together with other dating schemes such as $^{230}\text{Th}/^{234}\text{U}$ dating of corals and dendrochronology (Wagner, 1998).

Recently human footprints as well as a number of animal tracks were found in the Hamori Formation. They were announced to belong to the Paleolithic (pre-Holocene) Age by the Cultural Heritage Administration of Korea, although the age of the formation has already been reported at around 4 ka by radiocarbon dating of the shells (Sohn et al., 2002). In spite of recent efforts to constrain the ages of the formation and the footprints (KIGAM, 2005), there still remain some arguments on the age of the footprints. Cheong et al. (2005) reported an OSL (Optically Stimulated Luminescence) age of 5.1±0.3 ka for the Hamori Formation, and 7.0±0.3 ka for the eruption of the parent materials of the formation, the Songaksan Tuff. Cho et al. (2005) reported

the OSL ages of the Hamori Formation at 6.8 ± 0.3 ka and 7.6 ± 0.5 ka. This study, together with recently reported OSL data, leads us to conclude that the footprints are younger than 7 ka.

5. SUMMARY AND CONCLUSION

We carried out the $^{230}\text{Th}/^{234}\text{U}$ dating of fossil mollusk shells from the youngest volcanostratigraphic units in Jeju Island, the Sinyangri and Hamori Formations. The two formations give similar $^{230}\text{Th}/^{234}\text{U}$ ages ranging from 3,434 yr to 4,980 yr. The $^{230}\text{Th}/^{234}\text{U}$ ages of samples containing little ^{232}Th are consistent with radiocarbon data. The slight discrepancy between the two dating methods might be attributed to external contribution to ^{230}Th and inherent error of young radiocarbon ages. Generally, uranium-series dating of mollusks has not provided encouraging results mainly because the closed system is not maintained. Our data, however, highlight the potential usefulness of $^{230}\text{Th}/^{234}\text{U}$ dating for Holocene mollusk shells free of recrystallization and common thorium. This study, together with previous radiocarbon and optical dating works, clearly demonstrates that the Hamori Formation where human footprints were recently discovered was deposited in the middle Holocene.

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