Uranium-Series Dating of Bone Samples from the Amud Cave Site¹⁾

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アムッド洞窟の獣骨試料のウラン系列核種による年代測定¹⁾

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東京大学西アジア洪積人類遺跡調査団がネアンデルタール人骨を発見したイスラエルのアムッド洞窟から採取された化石骨試料（主としてカモシカ類）の年代測定を、その中にとりこまれた ^{238}U および ^{235}U からそれぞれ成長した ^{230}Th および ^{231}Pa 量を放射化学的方法で正確に定量することによって行った。さきに求められていた ^{14}C 年代では同様の試料について石器等からも推定される考古年代にくらべ、かなり若い年代となっていたが、本法によって得られた絶対年代 (34,000~62,000年) は考古年代とも矛盾しない。 ^{238}U , ^{234}U , ^{230}Th (^{232}Th は検出されず), ^{231}Pa の放射化学的分離と α スペクトロメトリーを組合せた方法による定量のほか、フィッシュントラック法によるウランの分布と定量も行い、試料中のウラン分布は均一であることも確めた。

Introduction

The skeletal remains of Neanderthaloids were found at Amud Cave near the Lake Tiberia in Israel, by the Tokyo University Expedition to Western Asia in 1961 and 1964 (SUZUKI & TAKAI, 1970). Animal bone samples consisting mainly of skeletons of antelope or deer were excavated there at the same time. The ground plane of the excavated site is shown in Fig. 1, and the cross sectional view from one side is shown in Fig. 2 together with the relative positions where the bone samples were collected. The deposits consist mainly of powders derived from weathering of limestone and there were also some layers of black soil containing decomposed plant material and calcareous cement. Some stone implements were found in these diluvial deposits and their archaeological ages were interpreted (SUZUKI & TAKAI, 1970) to represent the period belonging to the transition from Middle to Upper Palaeolithic, that is, the transitional period of Tabun and Shanidar or the same period from Chatel-Perronian to Levallois-Mousterian of Ksar'Atil.

Fig. 1 The ground plane of Amud site. Horizontal distance between 5-5 and 5-7 is 12m. Contour interval in meters.

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Fig. 2 The vertical cross section with sample locations between 5-5 and 5-17. Depth in centimeters.

Therefore, the ages of these anthropologically important bone samples were estimated archaeologically to be 35,000~45,000 years.

The age of these bone samples was determined to be 7,500~18,800 years by the C-14 dating method (SUZUKI & TAKAI, 1970), but any C-14 age (half-life: 5.73×10^3 years) could include a large error for samples older than $1 \sim 2 \times 10^4$ years, because the specific activity of the carbon in the sample is so low that slight contamination with present-day carbon can easily cause much younger apparent ages. Therefore, it becomes desirable to date the same bone samples by other methods.

Besides the relative age determination of fossil bone based on the content of manganese (SHIMODA, 1967), fluorine or uranium (BROTHWELL & HIGGS, 1963), the absolute age determination by the growth of Th-230 (half-life: 7.52×10^4 years) and Pa-231 (half-life: 3.25×10^4 years) from their parent uranium isotopes has been shown applicable to the dating of fossil bones with an assumption of an ideal closed system with respect to uranium isotopes and their daughter nuclides (CHERDYNTSEV, 1955, 1956; ROSHOLT, 1958).

Several investigators (SZABO, 1969, 1971 1973; HANSEN & BEGG, 1970; HOWELL, 1972) have provided the data of Th-230/U-238 and Pa-231/U-235 ratios in fossil bones and discussed the dating by this method. Even though the evidence of uranium migration has been shown in some cases, this method offers an approach to the dating of fairly old fossil bones, if the accumulation of uranium into the bone had been made within a much shorter interval than the total elapsed time. This report gives the results of the dating by such uranium series nuclides for the Amud fossil bone samples. The reference study has been made for the fossil bone from Tal i Mushuki in Iran, whose age is said archaeologically to be 6,000~7,000 years.

Methods and Results

All the bone samples examined showed the X-ray diffraction patterns of apatite crystal in spite of the various degree of petrification. In order to know the content and the distribution of uranium assimilated into these calcium phosphate materials, the fission track method was applied to both powdered and thin section piece samples of the specimens. The

uranium content of the Amud bones was fairly high as shown in Table 1 and its distribution in any one piece was found to be practically homogeneous. The uranium content of the Iran bones was 7~9 ppm and its distribution was homogeneous as in the Amud samples. The details of these studies were reported elsewhere (YOSHIOKA, 1971). Radiochemical analyses of U-238, U-234, Th-230 and Pa-231 were carried out as follows.

The sample (about 5 grams) cleaned from soil was pulverized and dissolved in 8M HCl; any residues were decomposed completely with conc. HNO₃. Definite amounts of tracer nuclides, U-232, Pa-233 and Th-234, were added and carbon dioxide gas was expelled by boiling. After standing over one day for isotopic exchange, partial precipitation was made by passing ammonia gas to the sample solution diluted with water. The precipitation should be partial not to precipitate the large amount of phosphate ion in this process, because the phosphate ion prevents the subsequent solvent extraction of uranium and protactinium with tri-norlaioctyl-amine from 8M HCl solution. The radiochemical purification of thorium was made by the calcium oxalate coprecipitation, followed by the cation exchange separation. Protactinium and uranium, stripped sequentially with 8M HCl-0.5 M HF and 3M HClO₄-6M HCl from the organic phase, were purified respectively by the solvent extraction with diisobutyl ketone and the anion exchange separation (KOMURA, 1967; SAKANOUE, 1968). From each purified fraction, the counting so-

urces were prepared by electrodeposition and subjected to both alpha spectrometry and beta counting.

The analytical results of fossil bones are presented in Table 2 together with the representative uranium data from Table 1 obtained by the fission track method. Though the uranium contents agree fairly well with the values of the samples from the same horizon, no correlation between the uranium content and the depth of sampling was found. The ratios of several nuclides in equivalent uranium unit are presented in Fig. 3, together with the ages calculated from Th-230/U-238 and Pa-231/U-235, respectively. The isotopic weight ratio of U-235/U-238 was assumed to be constant (0.0072). Since no

Table 1. Uranium contents of fossil bones from Amud by means of powder fission track technique. Sample location in cubic coordinate system

		U (ppm)
(6-10-I)	B-1 upper	7.37
		5.90
		5.50
(6-13, B' 10~20)	B-1	3.91
		3.45
		2.95
(6-13, B' 70~80)	B-2 middle upper	7.75
		6.96
		5.37
(6-17, 85~GP)	B-2 middle	4.87
		4.81
		4.09
(6-16, M-N)	B-2 lower	2.64
		2.22
		1.95
(6-17, T~Base)	B-4 lower	4.66
		4.24
		2.62

Table 2. Analytical results concerning with uranium, thorium and protactinium isotopic composition of Amud and Iran fossil bones.

	U ppm (Fiss. Tr.)	²³⁸ U (dpm/g)	²³⁴ U (dpm/g)	²³⁰ Th (dpm/g)	²³¹ Pa (dpm/g)
Iran	7.17	5.64±0.38	8.03±0.52	0.182±0.011	0.0387±0.0148
B-1 upper	7.37	4.80±0.44	5.28±0.48	1.44 ±0.20	0.1117±0.0271
B-1	2.95	1.82±0.34	2.14±0.36	0.767±0.044	0.0539±0.0220
B-2 middle upper	6.96	4.13±1.11	4.91±1.27	1.47 ±0.07	
B-2 middle (a)	4.87	3.10±0.97	3.49±1.14	0.711±0.083	
B-2 middle (b)	4.33	1.50±0.54	1.81±0.56	0.780±0.079	0.0529±0.0268
B-2 lower	2.22	1.25±0.15	1.37±0.17	0.607±0.045	
B-4 lower	4.24	2.63±0.32	2.86±0.35	2.45 ±0.13

Fig. 3 The activity ratios of several nuclides and estimated ages for fossil bone samples.

alpha energy peak of Th-232 was found in any alpha spectra from the thorium fraction, all Th-230 found may be derived by the radioactive decay of uranium in the samples. Due to very low contents of Pa-231, the estimated ages by Pa-231/U-235 have large statistical errors.

Discussion and Conclusion

The ages obtained by Th-230 growth method (about 34,500~62,000 years) seem to be acceptable from the archaeological point of view except one sample from 6-17, T~Base (B4-lower). The Pa-231 growth method has given the ages of about 30,200~69,200 years which are nearly concordant with Th-230 ages. Though there is no exact way to prove no leaching of uranium from fossil bones, the cross checking of ages by both the Th-230 and Pa-231 methods may be useful for this purpose. The age of the Iran sample was calculated to be 2,520 years which is less than the archaeological age for this sample. As the sample indicates an anomalously high U-234/U-238 radioactivity ratio, this apparent younger age may be due to the recent addition of uranium with high U-234/U-238 ratio.

The U-234/U-238 ratios for the Amud samples were found to be close to unity (radioactive equilibrium value), and tend to show that the lower the depth of layer, the smaller this ratio. Therefore, it is interpreted that the old uranium fraction assimilated into the sample during the initial period comprises the greater part of the uranium content and recent addition scarcely contributed to the whole uranium content.

In conclusion, it may be said that the Amud samples have been kept in an environment of a fairly good closed system with respect to uranium, thorium and protactinium, and the Th-230 and Pa-231 growth method could give more reasonable ages than the C-14 decay method.

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