Chapter 8

ACTIVATION MEASUREMENTS FOR THERMAL NEUTRONS

Part F. ^{36}Cl Measurements in Japan

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Introduction

The development of the accelerator mass spectrometry (AMS) system at the Tandem Accelerator Center of the University of Tsukuba was started in 1995, using the university's own molecular pilot beam technique. Presently, it is the only facility in Japan used to measure ^{36}Cl (Nagashima et al. 2000). The sensitivity of the ^{36}Cl AMS system is around 10^{-14} ^{36}Cl/Cl atom ratio, which is enough to measure the natural level of the ^{36}Cl/Cl ratio. The system is characterized by long-term stability, enabling high-quality, continuous measurements over many hours.

Our AMS system was used to measure ^{36}Cl produced in soil by neutrons released into the environment at the time of the JCO criticality accident in Tokai-mura in 1999 (Seki et al. 2003). At the beginning of 2001, our group joined the collaborative efforts to investigate and clarify the discrepancy observed between measurements and calculations of neutron activities induced by the atomic bombings in Hiroshima and Nagasaki. Using our AMS system, ^{36}Cl was measured in granite samples from Hiroshima exposed to atomic-bomb neutrons and in distant, unexposed samples.

Sample Processing

We measured a total of 19 granite samples from Hiroshima, including 16 samples provided for intercomparison (No. 1-No. 16) and two samples provided additionally (No. 17 and No. 18-1 and 18-2). Twelve of them were classified as exposed samples (Table 1), while the other seven samples were taken as distant control samples to investigate the natural level of ^{36}Cl (Table 2).

To minimize variation of measurement data by surface contamination and depth, big samples were cut into strata of about 10 mm thick, starting with the surface layer. We removed the surface part and measured the second or third stratum to standardize the depth from the surface. On the

Table 1. $^{36}Cl/Cl$ ratios of granites exposed to atomic-bomb radiation in Hiroshima

Sample		$^{36}Cl/Cl$	Error	GR (m)	σ GR (m)
No.1	Motoyasu Bridge (20-30 mm)	2.13E-10	1.4E-11	133	17
No.1	Motoyasu Bridge (20-30 mm)	2.09E-10	1.3E-11	133	17
No.1	Motoyasu Bridge (20-30 mm)	1.89E-10	1.3E-11	133	17
No.1	Motoyasu Bridge (20-30 mm)	1.71E-10	1.2E-11	133	17
No.1	Motoyasu Bridge (10-20 mm)	1.54E-10	2.6E-11	133	17
No.2	Shirakami Shrine（20-30 mm）	2.85E-11	2.6E-12	504	18
No.2	Shirakami Shrine（10-20 mm）	2.22E-11	1.8E-12	504	18
No.2	Shirakami Shrine（10-20 mm）	2.17E-11	1.5E-12	504	18
No.2	Shirakami Shrine（10-20 mm）	1.94E-11	1.4E-12	504	18
No.3	Honkeiji Temple (10-20 mm)	1.43E-12	1.0E-13	896	21
No.3	Honkeiji Temple (20-30 mm)	1.27E-12	1.2E-13	896	21
No.4	Myochoji Temple（10-20 mm）	1.07E-11	9.9E-13	639	19
No.5	Old Pref. Bldg. (0-20 mm)	2.57E-12	2.0E-13	877	44
No.5	Old Pref. Bldg. (20-30 mm)	2.45E-12	1.5E-13	877	44
No.5	Old Pref. Bldg. (0-20 mm)	2.40E-12	1.8E-13	877	44
No.5	Old Pref. Bldg. (20-30 mm)	2.32E-12	5.2E-13	877	44
No.6	Enryuji Temple（10-20 mm）	1.78E-12	2.6E-13	925	18
No.7	Shingyoji Temple (10-20 mm)	1.17E-12	1.6E-13	915	21
No.8	City Hall Pavement (10-20 mm)	4.66E-13	5.3E-14	1022	26
No.8	City Hall Pavement (20-30 mm)	4.06E-13	6.1E-14	1022	26
No.8	City Hall Pavement (10-20 mm)	3.98E-13	3.2E-14	1022	26
No.8	City Hall Pavement (10-20 mm)	3.61E-13	5.7E-14	1022	26
No.9	Kouzenji Temple（0-20 mm）	2.13E-13	4.2E-14	1177	20
No.18-1	E-building (No.1)	2.11E-13	2.2E-14	1385	17
No.18-2	E-building (No.2, 3)	1.81E-13	3.3E-14	1385	17
No.17	Kikkawa Ryokan (whole sample)	1.20E-13	1.3E-14	1424	21

Note: GR is the ground range (distance) from the hypocenter.

Table 2. $^{36}Cl/Cl$ ratios in Hiroshima background samples

Sample		$^{36}Cl/Cl$	Error	Approx. GR (m)
No.10	Sengyoji Temple (10-20 mm)	2.56E-13	3.4E-14	-
No.11	Kannonji Temple (10-20 mm)	1.31E-13	1.9E-14	-
No.11	Kannonji Temple (20-30 mm)	1.11E-13	1.8E-14	-
No.11	Kannonji Temple (10-20 mm)	0.94E-13	3.1E-14	-
No.12	Senzoubou（20-30 mm）Iyo	1.11E-13	5.2E-14	8790
No.13	Senzoubou（20-30 mm）Jiishi	2.08E-13	2.4E-14	8790
No.14	Senzoubou (Half of block)	2.11E-13	3.0E-14	8790
No.14	Senzoubou (Half of block)	2.04E-13	2.6E-14	8790
No.14	Senzoubou (Half of block)	1.82E-13	3.2E-14	8790
No.15	Myokenji Temple (whole sample)	2.12E-13	2.7E-14	7610
No.15	Myokenji Temple (whole sample)	1.45E-13	2.3E-14	7610
No.16	Myokenji Temple（20-30 mm）	1.02E-13	1.3E-14	7610

other hand, samples that were too small to secure adequate volume (about 100 g), if cut, were used as they were, including the surface. Such small samples, which included the surface, were No. 6 (Enryuji), No. 14 (Senzoubou), and No. 15 (Myokenji).

To remove surface contamination, the granite samples cut into strata were washed. After being washed with ultra-pure water (mili-Q, Milipore), they were ultrasonically washed with acetone solution, 0.5 M nitrate solution, and then 0.5 M sodium hydroxide solution (for 5 min. each). They were ultrasonically washed again with ultra-pure water, rinsed with ethanol and dried. After that, they were crushed and chemically processed so that chlorine in the granite was extracted as silver chloride.

Figure 1 shows the procedure used to extract chlorine from crushed granite. To perform accurate and sensitive ^{36}Cl measurements, it is extremely important to remove in the sample preparation stage as much as possible the ^{36}S isobar, which hinders ^{36}Cl measurements. Using silver nitrate solution, we extracted chlorine in the form of silver chloride precipitate and dissolved it in ammonium solution. Then, using saturated barium nitrate, sulfur impurities were separated and fixed in the form of barium sulfate. This process was repeated.

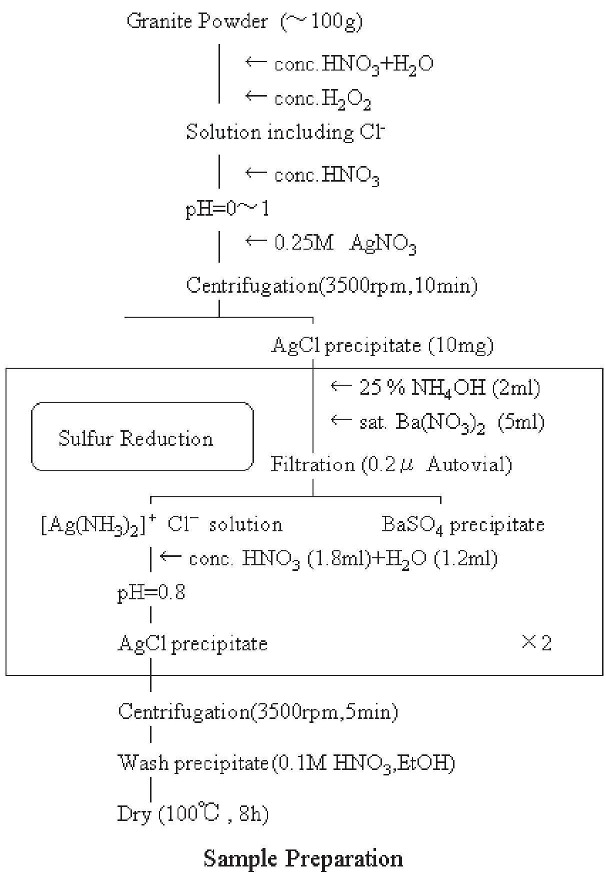

Figure 1. *Sample preparation procedure for ^{36}Cl measurements.*

Measurement Procedure

In the AMS system of the University of Tsukuba, ^{36}Cl is measured as counts per unit electric charge of $^{35}Cl^-$. By standardizing these measurements with standard samples for which $^{36}Cl/Cl$ is known, the $^{36}Cl/Cl$ ratios of the samples are obtained. The quality of the standard samples, therefore, directly affects the accuracy of measurements. Thus, we need high-quality standard samples. In the present measurements, we used standard samples prepared by two methods; samples prepared from a $^{35}Cl(n,\gamma)^{36}Cl$ reaction of nuclear reactor thermal neutron flux, and samples prepared by dilution of ^{36}Cl standard solution purchased from NIST.

Figure 2 shows results of measurements using these two types of standard samples and standard samples provided by the University of Tokyo. The abscissa represents calculated $^{36}Cl/^{35}Cl$ ratios (expected values) and the ordinate represents actual measurements. Over the range of calculations from 10^{-12} to 10^{-11}, measurements are aligned in a straight line, and the ratio between calculation and measurement shows excellent correspondence for all the samples. Because the measurements of the standard samples prepared independently by different methods are aligned in a straight line, the calculations are assumed to be very close to true values. In view of the departure of the measurements from the approximate line, it can be said that the true values are within about 1% of the calculations.

We measured the standard samples before and after sample measurements, with one set consisting of three measurements: measurement of a standard sample, measurement of a sample, measurement of a standard sample. We conducted three sets of measurements for each sample to obtain average values. Depending on the ^{36}Cl concentration of the samples, one set of

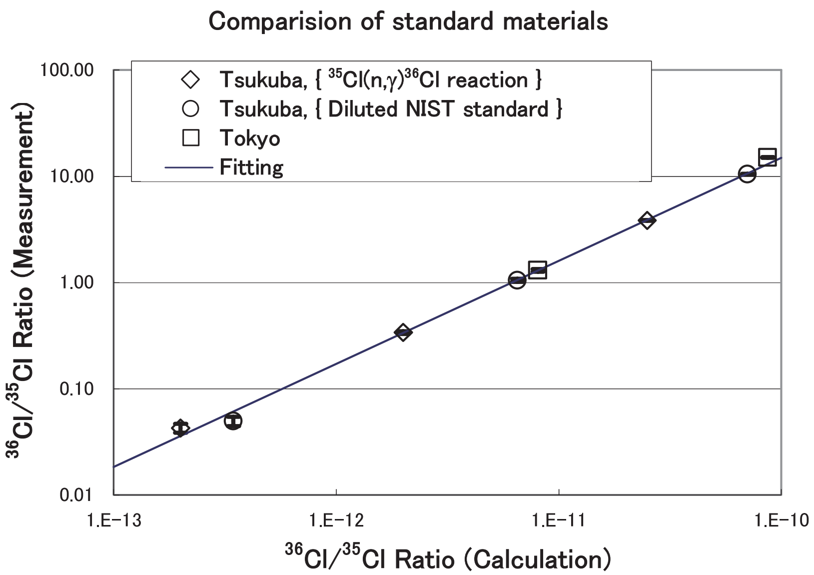

Figure 2. *Calculation vs measurement of $^{36}Cl/^{35}Cl$ ratio of standard materials.*

measurements required 20-30 min., and we completed measurement of one sample in about two hours. The values obtained from the measurements were ^{36}Cl counts and $^{35}Cl^-$ electric charge, which we used to calculate the $^{36}Cl/Cl$ ratio of the samples by the following formula:

$$({}^{36}Cl/Cl)\{\text{sample}\} = \frac{({}^{36}Cl\,/\,{}^{35}Cl^{-})\{\text{sample}\}}{({}^{36}Cl\,/\,{}^{35}Cl^{-})\{\text{standard}\}} \times ({}^{36}Cl/{}^{35}Cl)\{\text{standard}\} \times 0.7577$$

Measurement errors were obtained by combining the following errors:

- Statistical error of ^{36}Cl counts of samples: About 1% for No. 1 (Motoyasu Bridge) and around 15% for No. 8 (City Hall)
- Measurement error of $^{35}Cl^-$ electric charge of samples: Reading error of electric current integrator (1% or less)
- Statistical error of ^{36}Cl counts of standard samples: The same standards are used (about 2%).
- Measurement error of $^{35}Cl^-$ electric charge of standard samples: Reading error of electric current integrator (1% or less)
- Variation of beam transfer rate of the accelerator: At worst, about 4% in 2 hours
- Error of calculations of standard samples: The error was thought to be about 1% or so given in the preceding section, but in view of the discrepancy between measurements and calculations of several points (Figure 2), it was estimated to be 6%.

In conclusion, the total error of our measurements was estimated to be about 7%-20%.

Results

Figure 3 shows the results of our measurements, with comparison to the DS02 calculation. The measured values are not corrected for transmission factors, as described in Chapter 8, Part J.

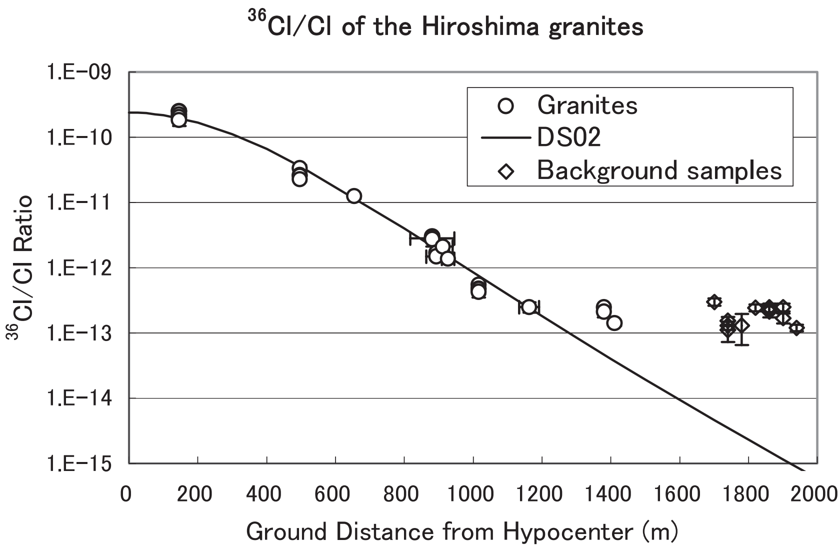

Figure 3. *Results of ^{36}Cl measurements of atomic-bomb exposed and unexposed granites.*

The following items outline the results:

- Values for No. 1 (Motoyasu Bridge) are slightly higher than previous measurements and correspond well with DS02 estimates.
- Values for No. 2 (Shirakami Shrine) and No. 8 (City Hall) are about 20% smaller than DS02 calculations.
- The average value of the seven distant background samples is 1.6×10^{-13}.
- The contribution of the atomic-bomb neutrons is difficult to evaluate for No. 17 (Kikkawa Ryokan) and No. 18 (E-building) because their measured values approach the distant background.

The results in Figure 1 show that the measurements correspond well with DS02 calculation between close-in distance and 1,100 m ground distance (Nagashima et al. 2004).

Conclusions

Using the AMS system at the Tandem Accelerator Center of the University of Tsukuba, we successfully measured ^{36}Cl of the granite samples provided for the intercomparison program to clarify the neutron discrepancy related to the radiation dosimetry of the Hiroshima-Nagasaki atomic bombings.

Measurement of ^{36}Cl/Cl ratio of distant unexposed granite samples (provided for background measurement) was 1.6×10^{-13} on average. Considering that the measurement of No. 9 (Kouzenji Temple) at the ground distance of 1,163 m was 2.5×10^{-13}, the bomb contribution to ^{36}Cl production became difficult to estimate for ranges beyond about 1,100 m.

Our measurements of ^{36}Cl correspond well with the DS02 calculation up to ground distances of 1,100 m, beyond which the natural level of ^{36}Cl seems to become significant.

The results of the intercomparison among three AMS laboratories as well as comparison between ^{36}Cl and ^{152}Eu measurements are found to be quite satisfactory and encouraging for future AMS work.

References

Nagashima, Y.; Seki, R.; Takahashi, T.; Arai, D. “Status of the ^{36}Cl AMS system at the University of Tsukuba.” *Nuc. Instr. Meth.* B. 172: 129-133; 2000.

Nagashima, Y.; Seki, R.; Matsuhiro, T.; Takahashi, T.; Sasa, K.; Sueki, K.; Hoshi, M.; Fujita, S.; Shizuma, K.; Hasai, H. “Chlorine-36 in granite samples from the Hiroshima A-bomb site.” *Nuc. Instr. Meth.* B. 223-224: 782-787; 2004.

Seki, R.; Arai, D.; Nagashima, Y.; Imanaka, T.; Takahashi, T.; Matsuhiro, T. “Determination of ^{36}Cl in environmental samples collected in the JCO by AMS.” *J. Radioanal. Nucl. Chem.* 255: 245-247; 2003.