Determination of Plutonium and Uranium Radionuclides in Glacier Ice Samples by MC-ICP-MS

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Abstract: A radiochemical procedure for the determination of plutonium (Pu) and uranium (U) radionuclides in ice samples by multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) is presented. Pu and U radionuclides are preconcentrated by coprecipitation and then separated by extraction chromatography. The purified Pu and U fractions are analyzed by MC-ICP-MS. Detection limits of 2×10^{-3} and 3×10^{-6} mBq kg^{-1} were achieved for ^{239}Pu and ^{236}U, respectively. Surface ice samples collected from the Gauli glacier (Switzerland) were analyzed by this method. The surface of the Gauli Glacier retains historical records of ^{239}Pu, ^{240}Pu and ^{236}U from the nuclear weapon testing (NWT) period. Pu and U radionuclides were found to be consistent in terms of pattern, showing two peaks possibly related to the two main periods of the NWTs (1954–1958 and 1961–1963). ^{3}H measurements, also released by the NWT, further confirmed the Pu and U results. The ^{240}Pu/^{239}Pu ratio ranged from 0.14 to 0.25, and ^{236}U/^{239}Pu ranged from 0.14 to 0.81. The Pu atom ratios ranged within the limits of global fallout in the most intensive period of NWT (1952 to 1962).

Keywords: Gauli glacier · MC-ICP-MS · ^{239}Pu · ^{240}Pu/^{239}Pu · ^{236}U

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1. Introduction

Alpine glaciers are an important source of historical information on past atmospheric pollution and climate change. The age range of the alpine glaciers vary typically between 100 and 1000 years.[1] Obtaining an accurate and reliable ice core chronology, needed to interpret any proxy time series, is often a challenge.[2] Radiometric methods based on the analysis of artificial fallout radionuclides are widely used for this purpose.[2,3]

Aboveground nuclear weapons testing during the 1950s and 1960s is the major source of artificial radionuclides in the global environment.[4] During the testing period, large amounts of these radionuclides were injected into the stratosphere, which then

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slowly returned into the troposphere.[5] A significant injection of artificial radionuclides into the stratosphere started in 1952 and reached a maximum in the Northern Hemisphere in 1962.[4] These well-dated nuclear fallout features are found in ice layers and widely used to develop ice core chronologies.[2,3,6]

Among the artificial radionuclides, plutonium-239 (^{239}Pu, half-life: 24 100 yr), plutonium-240 (^{240}Pu, half-life: 6 561 yr), and tritium (^{3}H, half-life: 12.31 yr) have found important use in dating ice cores with ages up to 70 yr old.[2,3,6b] Other radionuclides such as uranium-236 (^{236}U, half-life: 2.3 10^7 yr) are less reported, mainly due to the high analytical demands to detect them.[7] Pu and U radionuclides are nowadays routinely measured by mass spectrometry techniques.[2,3] Through this analysis, information on the isotope ratios (e.g. ^{240}Pu/^{239}Pu) is obtained.[8] This information is particularly important for assessing different sources of plutonium contamination.[9]

Pu and U radionuclides need to be purified from the matrix and potential interferences by refined radiochemical methods in order to measure them accurately.[6a,7] Activity concentrations of Pu radionuclides in ice samples are very low in the order of few to several hundred μBq per kg ice.[6a,b,10] The corresponding low number of atoms (1 μBq of ^{239}Pu corresponds to 1.097 10^6 atoms of ^{239}Pu, and 0.435 10^{-15} g of ^{239}Pu) necessitates samples of several kg ice.[7] This large sample size hinders routine measurements of ice samples. Here we show that our radiochemical method for analyzing Pu isotopes reduces the required sample of ice to maximum 1 kg (Fig. 1).

We present a radiochemical procedure for the determination of Pu and U radionuclides in ice samples by MC-ICP-MS. The procedure is based on the use of extraction chromatography resins in combination with co-precipitation methods. The amount of ^{242}Pu used as radiochemical yield tracer has been optimized in order to reduce the potential contamination of the analyte of interest by impurities present in the tracer. In a second part of this work, the radiochemical method is applied to determine these artificial radionuclides in surface ice samples collected at the Gauli Glacier (Switzerland, Fig. 1). We analyzed the quantity of Pu and U radionuclides and the atom ratios ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu in glacial ice. We aimed at investigating the absolute age of glacier surface ice.[6c] For cross checking the Pu and U data, measurements of tritium (^{3}H) in aliquots of the same samples were performed.

2. Experimental

2.1 *Reagents and Equipment*

All reagents were of analytical grade. Deionized water from an arium® pro UF Ultrapure Water system (Sartorius), 65% nitric acid p.a. (prepared on a quartz sub-boiling apparatus), 40% hydrofluoric acid suprapur, 37% hydrochloric acid suprapur and ammonium iron (II) sulphate hexahydrate pro analysis (all from Merck) were used for the analyses. Uranium isotope standard IRMM-187 and IRMM-184 (all from Joint Research Centre, Belgium) were used for isotope ratio calibration and validation. A standard solution of ^{242}Pu (Joint Research Centre, Belgium) was used as radiochemical yield tracer. Standard solutions of uranium, thorium (Th) and indium (In) were purchased from Alfa Aesar (Germany). The extraction chromatography resins TEVA and UTEVA were purchased from Triskem International (Bruz, France). The certified reference material IAEA-381 (Irish Sea Water) was obtained from the International Atomic Energy Agency (Vienna, Austria). All U and Pu radionuclide measurements were performed on a MC-ICP-MS Neptune (Thermo-Fisher). The U content in the melted ice samples was analyzed in a sector field sf-ICP-MS Element 2 (Finnigan MAT, Germany). The ^{3}H measurements were performed in an ultra-low level liquid scintillation counter (LSC) Quantulus 1220 (PerkinElmer).

Fig. 1. Sampling ice at the Gauli Glacier (Photo courtesy of L. Gnägi).

2.2 *Glacial Ice Sampling and Sample Preparation*

More than two hundred glacier surface ice samples were collected in summer 2019 from the Gauli Glacier. Detailed information on the sampling work is published elsewhere.[6c] Briefly, the ice samples were collected by the 2nd company of the Swiss Armed Forces' NBC Defence Laboratory 1 during the Refresher Course (Wiederholungskurse, WK), with the support of the Swiss Armed Forces Alpine Command and the Swiss Air Force (Fig. 1). The surface ice was sampled at intervals of 25 to 50 m in lines roughly following the glacier flowlines, and from a region identified by flow models to most likely contain ice from the period 1950s to 1970s.[6c] The amount of water recovered from each ice sample was about 1.2 kg. During three weeks, the radiochemistry group of the 2nd company of the Swiss Armed Forces' NBC Defence Laboratory 1 processed over 200 samples for Pu and U analysis as described below. Here we report results of only one of the sampled lines.

All ice melt samples were acidified with conc. HNO$_3$ (about 6 mL per kg water). An aliquot of 50 mL of each sample was used for tritium analyses. All aliquots for tritium were distilled as explained elsewhere,[11] and the distillate counted by LSC. A detection limit for ^{3}H of 9.8 TU (1 TU equal to 0.118 Bq kg^{-1}) was achieved for a counting time of 1440 min. About 20 mL of each sample was taken to analyze the U content in a sf-ICP-MS Element 2. This information is used to calculate the U separation yield and to quantify ^{236}U in the final U fractions. The remainder of the water sample was spiked with about 0.3 pg of ^{242}Pu as radiochemical yield tracer. The certified reference material IAEA-381 and blank samples (deionized water) were also analyzed in the same way.

The Pu and U radionuclides were separated and purified using extraction chromatography materials (TEVA and UTEVA resins), following methods described elsewhere.[8,12] Briefly, Pu and U radionuclides were concentrated by co-precipitation with $Fe(OH)_3$ at pH 6. The precipitate was dissolved in a few mL of HNO_3 4.5 M, and a few mg of ammonium iron (II) sulphate hexahydrate were added to the solution to adjust the oxidation state of Pu to (4+).[12] Pu was then separated from U and Th (thorium) using a 2 mL TEVA column. This resin is selective to elements with (4+) valence state. After conditioning the TEVA resin, the sample was loaded and the breakthrough containing the U (6+) radioisotopes was collected for further purification. The TEVA column was rinsed with 25 mL of HCl 6 M (to remove Th radioisotopes) and then with 50 mL of a 3 M HNO_3 solution. Pu radionuclides were eluted in 20 mL as described elsewhere.[13] A known amount of an In standard solution was added to the Pu fraction for the MC-ICP-MS measurement.

The UTEVA resin was used to separate and purify the U radioisotopes.[13] After conditioning the TEVA resin, the sample (breakthrough from the TEVA resin) was loaded onto the UTEVA resin. The column was rinsed with 10 mL HCl 6 M and then with 10 mL HNO_3 3 M. U radioisotopes were eluted with 20 mL of a 0.2% HNO_3/0.002% HF solution. A known amount of an In standard solution was added to the U fraction for the MC-ICP-MS measurement.

2.3 Radionuclide Measurement

The mass spectrometry (MS) analysis of Pu and U radionuclides was carried out using a MC-ICP-MS Neptune equipped with nine Faraday collectors and five ion counters (SEM). Aqueous solutions were introduced in the MC-ICP-MS using a CETAC Arridus II desolvator (Elemental Scientific Inc.) to enhance the signal and to achieve low hydride and oxide formation. All Pu isotopes were measured with the SEM detectors. In this configuration, the sensitivity for actinide isotopes in the eluate was about 150 counts per second (cps) per one fg mL^{-1} which led to a signal for the ^{242}Pu tracer in the Pu-eluates (15 fg mL^{-1} ^{242}Pu) of 2000 cps. Pu isotope concentrations were calculated from the signal of the ^{242}Pu tracer. The contributions of the Pu isotopes from the tracer and tailing from U and Th were corrected mathematically based on the isotope ratios from the certificate and abundance sensitivity measurements of U and Th standards. The total acquisition time per sample was 3 min. The ^{239}Pu signal was 3000 cps for the samples with the highest Pu concentrations. The detection limit was around 1000 times lower, which corresponds to concentrations of 900 ag (attogram) ^{239}Pu in one kg of ice (1 ag = 10^{-18} g).

^{235}U and ^{238}U were measured by Faraday detectors and the minor uranium isotopes by SEM detectors. The uranium tailing for the minor isotopes was corrected with a baseline subtraction. For the measurement of ^{236}U, a RPQ filter was used to lower the abundance sensitivity. Tailing contribution in the order of 10^{-8} was corrected. The total acquisition time per sample was 18 min. Standard sample bracketing using the IRMM-187 uranium isotope standard was applied for all measurements. IRMM-184 uranium isotope standard solutions with approximately the same uranium concentrations as in the uranium eluates were used for quality assurance.

3. Results

The results of the analysis of the certified reference material IAEA-381 are given in Table 1. The Pu radiochemical yield in both measurements was nearly 100%. Measured ^{239}Pu activity and ^{240}Pu/^{239}Pu atom ratio in the certified reference material were in good agreement with the target values. In all cases, the measured values are within the 95% confidence interval reported for this reference material. These results highlight the good precision and accuracy of the radiochemical method.

The analysis of ^{239}Pu in the blank samples was in all cases below the detection limit of 2 µBq kg^{-1} [871 ag kg^{-1}]. This detection limit is in the order of the ^{239}Pu concentrations (75 to 2823 ag kg^{-1}) reported in freshly fallen snow in the Alps.[7] A few data exist for Pu in surface waters in Switzerland. For example, in surface water collected at Val Piora (Tessin), $^{239+240}$Pu activity concentrations of 7 to 8 µBq kg^{-1} were reported.[14] In spring water from the Chaudron Spring at the Venoge River, $^{239+240}$Pu activity concentrations between 4 and 22 µBq kg^{-1} were found.[15] Taking into account that Pu in these waters originated solely from NWTs, characterized by a ^{240}Pu/^{239}Pu activity ratio of 0.67, activity concentrations of ^{239}Pu in surface water of 2.4 to 13.2 µBq kg^{-1} can be calculated. Hence, our detection limit is below the ^{239}Pu activities reported in surface fresh water in Switzerland (2.4 to 13.2 µBq kg^{-1}). In all the above studies, sample volumes corresponding to 60 to 200 kg water were analyzed. Our method reduces the required water volume to about 1 kg, while still achieving sufficiently low detection limits allowing to determine ^{239}Pu in most environmental waters and ice contaminated by the global fallout from the NWTs.

The ^{236}U concentration in global fallout from the NWTs follows the ^{239}Pu concentration and is assumed to be 1/3 of the massic concentration of ^{239}Pu. The detection limit for ^{236}U by ICP-MS depends on the natural U concentration because of the tailing from the isotopes ^{235}U and ^{238}U. The U concentration in glacier ice was in the range of 10^{-11}–10^{-10} g per g of ice. Because of the very low U concentrations, ^{236}U/^{238}U atom ratios of down to 10^{-5} were measured for glacier ice from the global fallout maximum. However, the natural U concentration in river waters is 10–100 times higher and the ^{239}Pu 1000 times lower than in ice samples. Therefore, ^{236}U/^{238}U atomic ratios are expected to be below 10^{-9}. Such low atomic ratios can only be measured with thermal ionization mass spectrometry (TIMS) or accelerated mass spectrometry (AMS).[6] The ^{236}U detection limit for ice samples was estimated to 0.003 µBq kg^{-1}.

Radiochemical yields for Pu and U were above 90% in the majority of the ice samples, with typical values close to 100%. Results of the ^{239}Pu, ^{236}U and ^{3}H activity concentrations and the ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu atom ratios in ice samples from one of the sampled flow lines of the Gauli Glacier are presented in Table 2. The profiles for ^{3}H, ^{239}Pu and ^{236}U activities are depicted in Fig. 2. All these radionuclides were found to be consistent in terms of pattern. The shapes of the ^{3}H, ^{239}Pu and ^{236}U profiles showed a clear maximum for the sample 246. The ^{239}Pu and ^{236}U profiles depicted a second peak for the sample 248. The two peaks observed in the Pu and U profiles may be related to the two main periods of the atmospheric NWTs (1954–1958, 1961–1963).[4] In the case of ^{3}H, the second peak was not observed. Possibly, because of the

Sample	Measured values		Certified values	
	^{239}Pu	^{240}Pu/^{239}Pu	^{239}Pu	^{240}Pu/^{239}Pu
	mBq kg^{-1}	atom ratio	mBq kg^{-1}	atom ratio
IAEA-381	0.0088 ± 0.0003	0.23 ± 0.01	0.0081 ± 0.0010	0.22 ± 0.03
IAEA-381	0.0085 ± 0.0003	0.23 ± 0.01	0.0081 ± 0.0010	0.22 ± 0.03

Table 1. Results of ^{239}Pu activity and ^{240}Pu/^{239}Pu atom ratio in the certified reference material IAEA-381. The expanded uncertainty (k = 2) is reported.
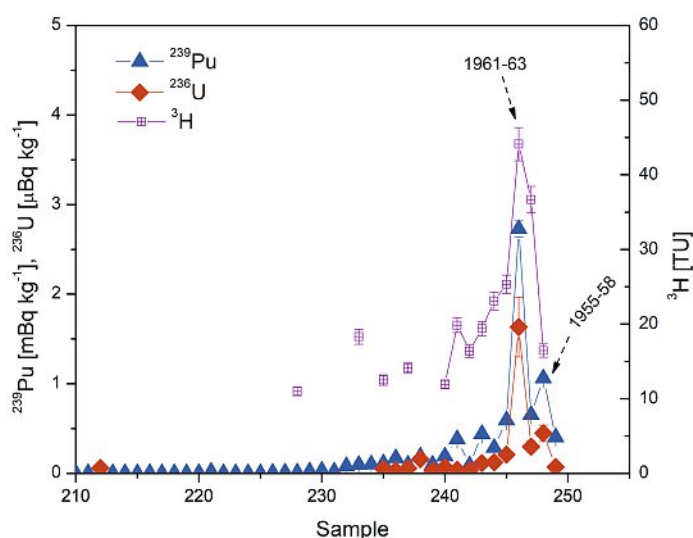
Fig. 2. Activities of ^{239}Pu, ^{236}U and ^{3}H along one sampled line from the Gauli Glacier (Switzerland).

short half-life of this radionuclide, the originally deposited activity has nowadays decayed to levels below the detection limit of the method.

The highest activity of ^{239}Pu in surface ice from the Gauli Glacier was 2.7 mBq kg^{-1} (Table 2). This activity is about 2 to 3 times lower than the highest activities found in ice cores from Colle Gnifetti, in Switzerland (7 mBq kg^{-1})[10] and the eastern Tien Shan, in Central Asia (5.5 mBq/kg).[6a] However, it is slightly above the highest activity (2.17 mBq/kg) measured in an ice core extracted from the Dome du Gouter, Mont Blanc, France.[16] The maximum activity of ^{236}U of 1.6 µBq kg^{-1} (Table 2) is comparable to the maximum found in the ice core from the eastern Tien Shan glacier (1.5 µBq/kg).[6a] The ^{3}H profile showed a maximum activity of about 44 TU. Assuming that this ice corresponds to the year 1963 (maximum fallout from the NWTs), the ^{3}H activity at the snow deposition time would be 1020 TU. This calculated activity for 1963 is about 3 to 5 times lower than the ^{3}H activities reported in precipitation at mid-latitudes for this time period,[17] which suggest that this ice does not correspond to the year 1963. The ^{3}H and ^{239}Pu data indicate that the 1963 radioactive fallout maximum was most likely not found in the collected ice samples from the Gauli Glacier. Possibly, this peak was missed due to the 25 to 50 m sampling intervals (Fig. 3).[6c]

The ^{240}Pu/^{239}Pu atom ratios were found to range from 0.14 (± 0.01) to 0.259 (± 0.005), with an average value of 0.178 (±0.03). This average is similar to the ratio of 0.176 (± 0.014) reported in global fallout from the NWTs.[18] This result confirms that Pu contamination in the Gauli Glacier ice mainly originated from

Table 2. Results for the determination of ^{239}Pu, ^{236}U and ^{3}H activities, and ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu atom ratios, in ice samples collected from one line of the Gauli glacier (Switzerland). The expanded uncertainty (k = 2) is reported. The reference date for decay correction is 27.08.2019.

| Sample	^{239}Pu [µBq kg–1]	^{240}Pu/^{239}Pu atom ratio	^{236}U [µBq kg–1]	^{236}U/^{239}Pu atom ratio	^{3}H [TU]
230	31 ± 1	0.14 ± 0.01	0.010 ± 0.003	0.30 ± 0.09	< 9.8
231	21 ± 1	0.19 ± 0.03	0.016 ± 0.005	0.70 ± 0.22	< 9.8
232	81 ± 3	0.21 ± 0.01	0.013 ± 0.004	0.15 ± 0.05	< 9.8
233	97 ± 3	0.184 ± 0.009	0.04 ± 0.01	0.38 ± 0.11	18.3 ± 1.0
234	101 ± 4	0.175 ± 0.007	0.017 ± 0.005	0.16 ± 0.05	< 9.8
235	113 ± 4	0.169 ± 0.009	0.06 ± 0.02	0.51 ± 0.15	12.5 ± 0.7
236	170 ± 6	0.259 ± 0.005	0.03 ± 0.01	0.19 ± 0.06	< 9.8
237	98 ± 4	0.18 ± 0.01	0.07 ± 0.02	0.67 ± 0.20	14.1 ± 0.7
238	187 ± 7	-	0.16 ± 0.05	0.81 ± 0.25	< 9.8
239	99 ± 4	0.178 ± 0.006	0.04 ± 0.01	0.38 ± 0.11	< 9.8
240	190 ± 6	0.209 ± 0.007	0.07 ± 0.02	0.36 ± 0.11	11.9 ± 0.6
241	382 ± 14	0.152 ± 0.006	0.05 ± 0.02	0.14 ± 0.04	19.8 ± 1.0
242	90 ± 4	0.177 ± 0.005	0.04 ± 0.01	0. 44 ± 0.13	16.4 ± 0.9
243	440 ± 15	0.169 ± 0.005	0.15 ± 0.05	0.32 ± 0.10	19.4 ± 1.0
244	285 ± 10	-	0.13 ± 0.04	0.43 ± 0.13	23.1 ± 1.2
245	592 ± 21	0.180 ± 0.003	0.26 ± 0.08	0.43 ± 0.13	25.3 ± 1.2
246	2730 ± 90	0.179 ± 0.003	1.7 ± 0.5	0.59 ± 0.18	44.1 ± 2.2
247	653 ± 24	0.184 ± 0.004	0.4 ± 0.1	0.55 ± 0.17	36.7 ± 1.8
248	1060 ± 36	0.156 ± 0.002	0.5 ± 0.1	0.44 ± 0.13	16.5 ± 0.9
249	404 ± 14	0.168 ± 0.004	0.10 ± 0.03	0.23 ± 0.07	< 9.8
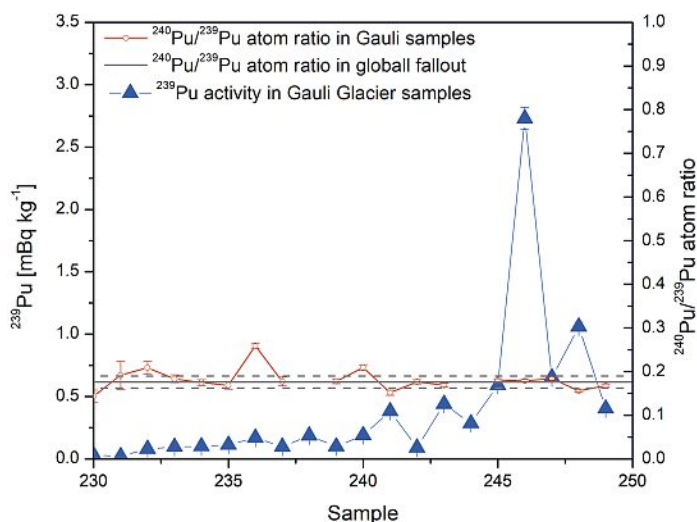
Fig. 3. Results for the determination of ^{239}Pu activities and ^{240}Pu/^{239}Pu atom ratios along one sampled line from the Gauli Glacier (Switzerland). The ^{240}Pu/^{239}Pu atom ratio typically found in global fallout is also represented (0.176 ± 0.014).

this anthropogenic source. The ^{236}U/^{239}Pu atom ratios obtained in this work fall within a broad range from 0.14 to 0.81, with an average value of 0.40 (± 0.19). This range is similar to the ones reported in ice cores from the Austfonna Glacier in Svalbard (0.18 to 1.4),[19] and from the eastern Tien Shan, in Central Asia (0.27 ± 0.09),[6a] whereas for river water ^{236}U/^{239}Pu atom ratios up to 12 were found.[15]

Fig. 4 shows the determination of ^{238}U concentrations and ^{235}U/^{238}U atom ratios along one sampled line from the Gauli Glacier (Switzerland). The dashed line represents the range of the ^{235}U/^{238}U isotope ratio for natural uranium.[20] Slightly enriched uranium was measured in the region of maximal global fallout similar to the ratios found for ice from the Dome du Gouter.[16]
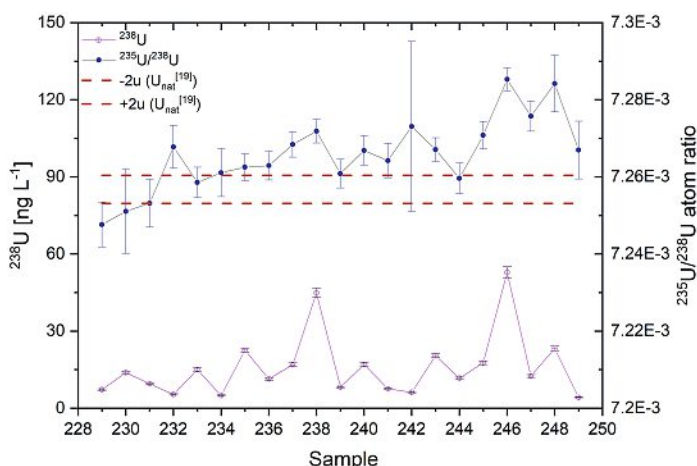
Fig. 4. Results for the determination of ^{238}U concentrations and ^{235}U/^{238}U atom ratios along one sampled line from the Gauli Glacier (Switzerland). The dashed line represents the range of the ^{235}U/^{238}U isotope ratio for natural uranium.[20] Slightly enriched uranium was measured in the region of maximal global fallout (Samples 245 to 249).

4. Conclusions

The surface of the Gauli Glacier maintains historical records of ^{3}H, ^{239}Pu, ^{240}Pu and ^{236}U from the nuclear weapon testing (NWT) period. Pu and U radionuclides were found to be consistent in terms of pattern, showing two peaks possibly related to the two main periods of the NWTs (1954–1958 and 1961–1963). Measurements

of ^{3}H, also released by the NWTs, further confirmed the Pu and U results. The ^{240}Pu/^{239}Pu atom ratios confirmed that Pu contamination originated from the NWTs. Alpine glaciers maintain historical records of artificial fallout radionuclides from the atmospheric NWT period. This data is useful for knowing the absolute age of glacier surface ice. Data from mid-latitudinal alpine glaciers may be of special interest for better understanding interhemispheric transport of radionuclides released during the NWT events.

The optimization of the sample volume to about 1 kg ice facilitated the collection and transport of a large number of samples (more than 200 in this study) to the laboratory. This is usually not the case in other laboratories, where large sample volumes of more than 20 kg are required for the analysis. Moreover, the invaluable support of the Swiss Army in the radiochemistry laboratory allowed us to process and analyze all the samples in a short period of 3 weeks. A similar collaboration between Spiez Laboratory and the Swiss Army would take place in the event of any radiological or nuclear emergency in Switzerland.

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