Nuclear Science and Techniques **24** (2013) 020202

Measurement of the natural ^{36}Cl and ^{236}U in uranium mineral with accelerator mass spectrometry

WANG Xianggao[1,2,*] JIANG Shan[2] HE Ming[2] DONG Kejun[2] GUAN Yongjing[1]

[1]*College of Physics Science and Technology*, *Guangxi University*, *Nanning 530004*, *China*

[2]*China Institute of Atomic Energy*, *Beijing 102413*, *China*

Abstract The concentration of the natural ultra-trace radionuclides ^{36}Cl and ^{236}U in the uranium depended on the neutron flux. In this article, a method for measuring ^{36}Cl and ^{236}U in the same uranium mineral with accelerator mass spectrometry was developed in China Institute of Atomic Energy, providing a protocol of the potential application of ^{236}U in uranium mining, environmental, and geological research. The two samples were from Guangxi and Shanxi province, China, and their ratios ^{36}Cl/Cl and ^{236}U/^{238}U were measured. More experimental data conduced to understand the natural nuclides in the uranium mineral. We plan to conduct more efforts on the research.

Key words ^{236}U, Accelerator mass spectrometry, Uranium mineral

1 Introduction

Both the radionuclides ^{36}Cl and ^{236}U have a very long half-life ($T_{1/2}$) up to 3.01×10^5 a, and 2.342×10^7 a[1], respectively. Because of the long half-life, these isotopes persist longer periods than human lifetimes in the environment. But this feature can be turned to advantage by using ^{36}Cl and ^{236}U as isotopic tracer in many fields, such as the environmental, geological, and the nuclear safeguard research[2–7].

In nature, the natural ^{236}U is very low[2], and the ratio of ^{236}U/^{238}U in different minerals are expected in the level range of 10^{-10}–10^{-14}. The ^{236}U is mainly produced by the ^{235}U(n,γ)^{236}U reaction, where neutrons could be produced by spontaneous fission of ^{238}U or the (α,n) reaction on light elements such as Na, Mg, and Al. In 1996, Purser *et al.*[3] proposed that the ^{236}U can be used as a neutron flux integrator, which was extended further by Valenta *et al.*[8] a few years later. The ^{236}U is potentially applied to monitor the environmental impact of uranium mining by measuring the levels in drainage water of the mine and uranium exploration by searching the ^{236}U in ground water[9], respectively. Also, it is applicable to environmental and geological research. Like ^{236}U, the natural ^{36}Cl under the deep subsurface is produced by the neutron capture reaction of ^{35}Cl(n,γ)^{36}Cl.

The produced ^{236}U and ^{36}Cl depend on the neutron fluxes in the thermal and epithermal energy ranges. The combination of the ^{36}Cl measurements with ^{236}U offers the possibility of determining subsurface neutron fluxes in the thermal and epithermal energy ranges[9]. Because the natural ^{236}U and ^{36}Cl are ultratrace, their measurement is difficult or even impossible without accelerator mass spectrometry (AMS)[10–14]. Wilcken *et al.*[9,15] have conducted some investigations on the nucleogenic of ^{36}Cl, ^{236}U, and ^{239}Pu in uranium minerals from several region to understand the essential features of the subsurface production of nucleogenic isotopes in uranium rich rocks. In order to promote practical application of ^{236}U in uranium exploration and monitor the environmental impact of uranium mining in geological research, the nucleogenic of ^{36}Cl and ^{236}U in uranium minerals should be conducted extensively to obtain the data from different region.

In this paper, the ^{36}Cl and ^{236}U in the same uranium mineral are measured by AMS, which is developed in China Institute of Atomic Energy (CIAE).

Supported by National Natural Science Foundation of China (No. 41166002), Guangxi Natural Science Foundation (No. 2012GXNSFBA053004), Scientific Research Foundation of Guangxi Higher Education (No. 201102ZD001) and Scientific Research Foundation of Guangxi University (No. XBZ100773)

* Corresponding author. *E-mail address:* wangxg@gxu.edu.cn

Received date: 2012-04-28

Two samples are from Guangxi and Shanxi province, China, respectively. The ratios of ^{36}Cl/Cl and ^{236}U/^{238}U are measured, and calculated by MCNP to understand the neutrons production model in uranium minerals.

2 Sample preparation

Sample 1 was collected from Guangxi province, China; and Sample 2 from Shanxi province, China (Fig.1). Two samples were under the deep subsurface of more than 1 m, avoiding the ^{36}Cl produced by the cosmic-ray spallation on Ar, K, and Ca.

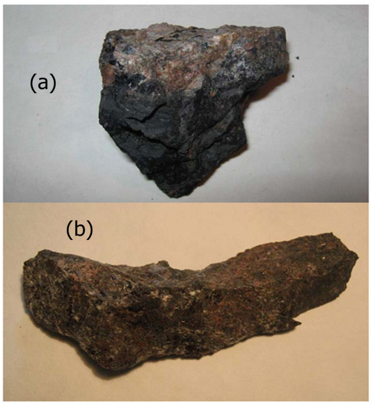

Fig.1 Pictures of uranium samples. (a) Sample 1 from Guangxi province, China; and (b) Sample 2 from Shanxi province, China.

To precisely measure the ratios of ^{36}Cl/Cl and ^{236}U/^{238}U in a uranium mineral, a method of extraction and purification sample for AMS measurement was developed. In order to ensure products of an identical neutron flux, the ^{36}Cl and ^{236}U were separated from the same uranium mineral and sample preparation procedure (Fig.2). Hard to dissolve, the big block uranium mineral was grounded into 300-μm powder.

2.1 ^{36}Cl sample

2.1.1 Dissolution

After the uranium mineral sample (5.0 g) was put into a Teflon vessel, 1 M HNO_3 (30 mL) was added. Teflon vessel was closed tightly for about 36 h, shaken by hand at every 5 h, and vibrated by ultrasonic device for 20 min. Most of Cl in the rock was extracted into the solution. A few residual rocks could be dissolved by adding the new HNO_3 solution. The Cl concentration was 1% less in the second dissolution solution than in the first. Because the AMS only needs to measure the ^{36}Cl/Cl, it is not necessary to take into account the second dissolution. The few residual rocks, which contained some insoluble uranium-bearing minerals, were transferred to another Teflon vessel to prepare the ^{236}U sample.

2.1.2 Separation and AMS sample preparation

(1) the Cl sample solution was added to slight excess $AgNO_3$ (0.25 M) in the dark room to form AgCl within 24 h. (2) After discarding the supernatant, the AgCl was collected by centrifugal machine for 10 min. Besides, the residual solution was collected to prepare the ^{236}U sample. (3) 10 mL high-purity water and ammonia was used to dissolve the AgCl at pH of more than 10. (4) Saturation $Ba(NO_3)_2$ was added to remove the sulfur for about 24 h at 30ºC to enough form $BaSO_4$ precipitate. (5) The Cl-containing solution was collected and filtered. (6) The excess high-purity HNO_3 was added to form AgCl, and collected with centrifugal machine for 10 min. In order to remove the sulfur, the steps of (3)–(6) were three times repeated.

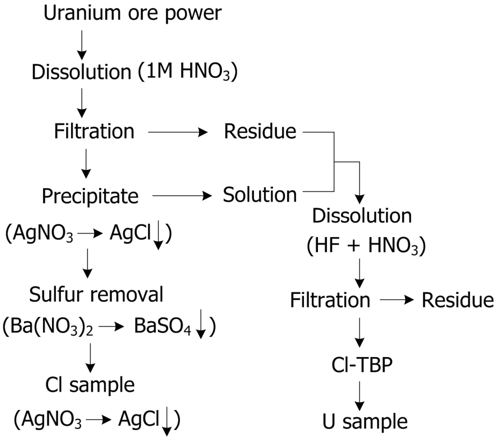

Fig.2 The sample preparation procedure.

The AgCl was dried at 100ºC, put into a vial, and wrapped by black paper. In the AMS measurement, each sample was mixed with high purity (99.99%) silver powder according to their similar volume to improve thermal and electric conductivity, and pressed into a Cu sample holder (40-Sample NEC MC-SNICS ion source).

To minimize any additional contamination by sulfur, all the samples were prepared in an air-purified room without the reserved HCl and H_2SO_4. All reagents were 99.99% purity.

2.2 ^{236}U sample

2.2.1 Dissolution

The residual rocks in the section 2.1.1, and the solution in the (2) step of the section 2.1.2 were used to prepare the ^{236}U sample.

A mixture of the high-purity HF and HNO_3 was used to dissolving uranium minerals at 80°C for over 24 h. The HNO_3 and the HF can dissolve the most of the uranium in uraninite and silicates such as coffinite. After dissolving the silicates and uranium minerals, the insoluble fluorides, graphite, sulfides, and high resistant oxides remained as residues. The samples were filtered and the resulting filtrate was dried by evaporation. The U-containing dryness residue was dissolved in 4 M HNO_3.

2.2.2 Separation and AMS sample preparation

The dissolved uranium is separated and purified by the CL-TBP. The CL-TBP column was preconditioned with 2.5 M HNO_3, passed through by sample solutions, and washed at the flow of 1.5 mL/h, to obtain the U-containing solution.

The U-containing solution was dried on a hotplate at about 100°C for 1 h, and placed in 800°C furnace at least 2 h to completely oxidize it into U_3O_8 and decrease the $^{238}U^{14}N^-$ in the ion source. In the AMS measurement, sample was mixed with 99.99% Nb powder according to similar volume to improve thermal and electric conductivity, and pressed into an Al sample holder (NEC MC-SNICS ion source).

3 AMS measurement

The ^{36}Cl and ^{236}U were measured by using CIAE AMS based on HI-13 accelerator. The CIAE AMS can be used to measure ^{26}Al, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{64}Gu, ^{79}Se, ^{99}Tc, ^{126}Sn, ^{129}I, ^{151}Sm, ^{182}Hf and ^{236}U in the fields of biomedicine, nuclear physics, nuclear astrophysics, geosciences, nuclear environment engineering, and environmental science[16–22]. In the recent years, a new beam line was granted to the upgraded CIAE AMS system[25], as shown in Fig.3. The ^{36}Cl and ^{236}U was measured as following.

The ^{236}U was measured on AMS beam line 1, as described by Wang and Jiang *et al.*[22]. Negative UO^- ions were extracted from the ion source by accelerating voltage of about 7.240 MV, and $^{236}U^{11+}$ ions were selected after acceleration. Because the isobar ^{236}U is not expected to measure, it is the key how to identify the interest of ^{236}U ions from isotope ^{238}U and ^{235}U. The energy difference between the ^{238}U and ^{235}U background ions and the ^{236}U interested ion is 0.8% and 0.4%, respectively. On happening to pass the ion optical filters, the time of flight (TOF) detector has sufficient resolution to distinguish ^{236}U from the isotopes ^{238}U and ^{235}U. A sensitivity is 10^{-11} lower for $^{236}U/^{238}U$ than for ^{236}U due to the good time resolution of ~500 ps[24], high terminal voltage of HI-13 accelerator and the relatively small energy straggling of the flying ions.

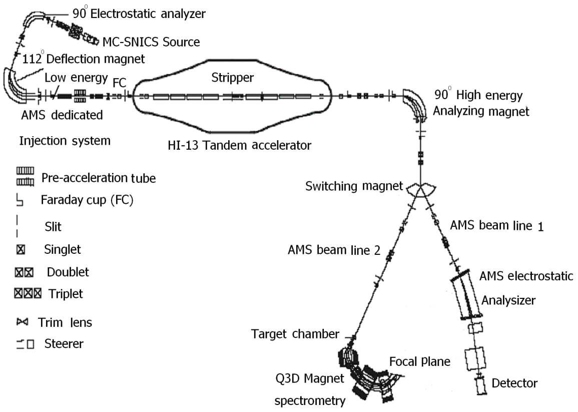

Fig.3 Schematic representation of the accelerator mass spectrometer based on the HI-13 accelerator at the CIAE.

3.1 ^{36}Cl

It is difficult to heighten sensitivity of the medium-heavy mass nuclides because of the limitation of beam time and measurement conditions, thus resulting in insufficient difference of energy losses and ineluctable energy straggling of medium-heavy radioisotopes. A new beam line equipped with a ΔE-Q3D detection system has been installed on the HI-13 tandem (AMS beam line 2)[23] (Fig.3). The new beam line is equipped with some ion-optical elements, a large Q3D magnetic spectrometer, SBD and multi-anode ionization chamber. The ^{36}Cl is measured by AMS beam line 2.

The Cl^- ions were selected to inject into the HI-13 Tandem Accelerator. Its typical output beam current at the Lower Energy Faraday Cup (LEFC) was about 3 μA. The Cl^- ions were accelerated by the tandem terminal voltage which was typically set at 11.0 MV. The carbon foil (3 $\mu g/cm^2$) was employed to break up the Cl^- ions and produce atomic ions with high charge states. The resulting Cl^+ ions were further accelerated by the same terminal voltage. A 90° double focusing High Energy Analyzing Magnet (HEAM) with a maximal mass energy product of 200 MeV·amu was used to select $^{36}Cl^{8+}$ (and $^{36}S^{8+}$) with 99.11 MeV.

None of processes can separate ^{36}Cl from its stable isobar ^{36}S. After switching magnet, the particles were transported to the ΔE-Q3D system to separate ^{36}Cl from ^{36}S and detect ^{36}Cl. A homogeneous Si_3N_4 membrane of 3.0-μm thickness was mounted at the entrance of Q3D as an absorber to produce different energy losses of ^{36}Cl with ^{36}S. After passing through the Si_3N_4 membrane, these $^{36}Cl^{8+}$ and $^{36}S^{8+}$ ions have 81.48 MeV and 82.64 MeV, and the charge state of 14^+ were analyzed by the Q3D magnetic spectrometer. The ^{36}Cl and ^{36}S were separated by their residual energies. The peak distance between ^{36}Cl and ^{36}S on the focal plane was about 81 mm with a separation factor of 2.4 (Fig.4), which is defined as the ratio of the peak difference to the full width of half maximum (FWHM). In order to increase the detection efficiency and further separation of isobaric interferences, a multiple-anode ionization chamber (MAIC, four anodes in this work) with an entrance window of 100 mm×40 mm Mylar foil was accurately mounted at the Q3D focal plane, thus recording the interested nuclide ^{36}Cl. The ionization chamber was filled with propane of 4.2 kPa. By choosing the suitable magnetic field, a suppression factor of ^{36}S ions about 10^5 was achieved, while most of the ^{36}Cl ions are recorded by the MAIC.

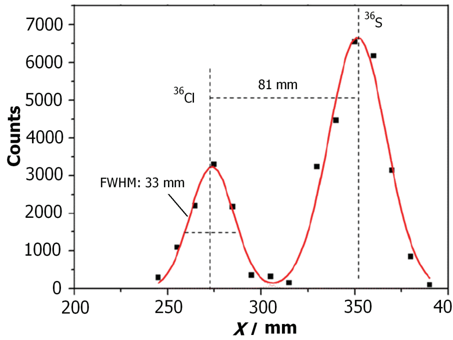

Fig.4 Position spectra of ^{36}Cl and ^{36}S on the Q3D focal plane.

4 Results

Figure 5 shows the TOF spectra and their two-dimensional spectra vs. energy for uranium mineral samples, distinguishing the interested nuclide ^{236}U from the ^{238}U and ^{235}U has sufficient resolution.

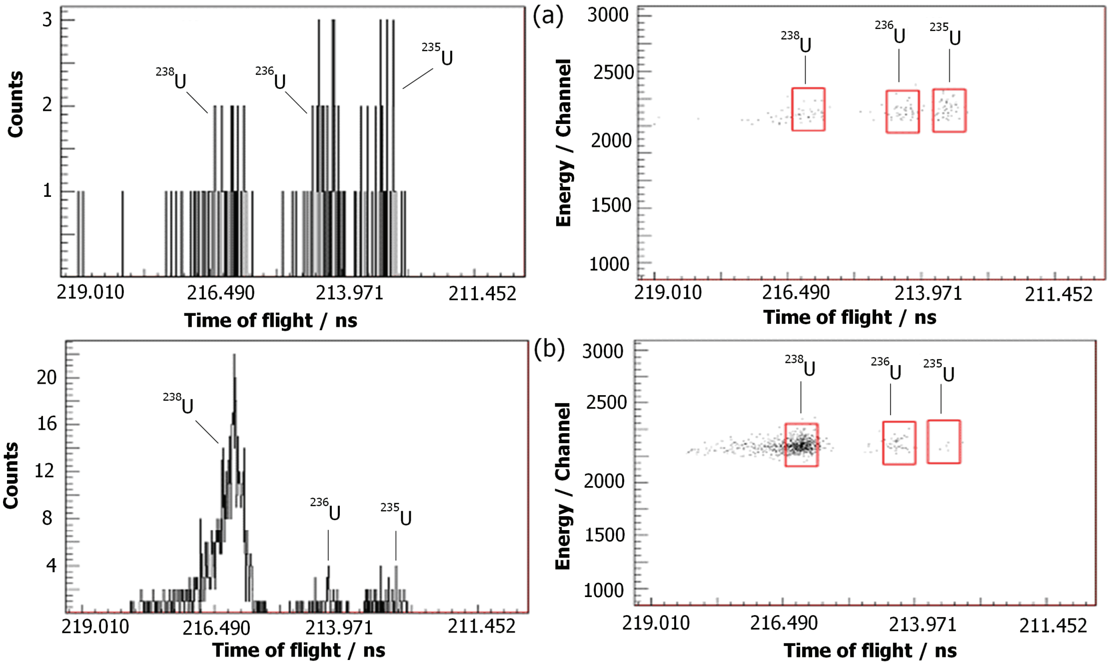

Fig.5 TOF spectra and TOF vs. the energy two-dimensional spectra for ^{236}U. (1) For a standard sample with $^{236}U/^{238}U = 5.00\times10^{-9}$ in 100 s counting time, (b) for sample with $^{36}Cl/Cl = 2.03\times10^{-10}$ in 300 s counting time.

Figure 6 shows two-dimensional spectra of E_r vs. E_t for ^{36}Cl standard and one uranium sample (E_r and E_t are the energy loss signals from anodes 4 and the total energy, respectively), indicating that the Q3D method can identify ^{36}Cl from its isobar ^{36}S clearly. These results suggest that the sample preparation method for the ^{36}Cl and ^{236}U in the uranium minerals were satisfied for the AMS measurement.

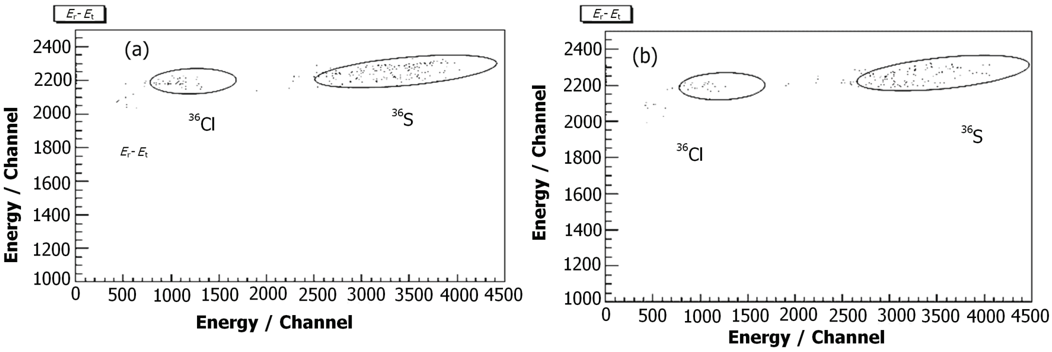

Fig.6 Two-dimensional spectra of E_r vs. E_t for ^{36}Cl standard and one sample (E_r and E_t are the energy loss signals from anodes 4 and the total energy, respectively). (a) For a standard sample with ^{36}Cl/Cl=1.60×10^{-11} in 300 s counting time, (b) for sample with ^{36}Cl/Cl=6.8×10^{-11} in 300 s counting time.

The measurements of natural ^{36}Cl and ^{236}U from the same uranium mineral sample as Fig.6 are listed in Table 1. The uncertainties for isotope ratios include (1σ) counting statistics, reproducibility of the measurement, and a systematic contribution from the measurement relative to reference materials.

Table 1 Uranium and chlorine concentrations of the sample materials, and their natural ^{36}Cl/Cl and ^{236}U/^{238}U ratios

Sample	U (%)	Cl (ppm)	^{236}U/^{238}U^{a}($\times10^{-11}$)	^{236}U/^{238}U^{b}($\times10^{-11}$)	^{36}Cl/Cl^{a}($\times10^{-11}$)	^{36}Cl/Cl^{b}($\times10^{-11}$)
Sample 1	15.53±0.47	16.2±0.5	20.3±2.1	22.5	10.1±1.0	9.4
Sample 2	1.10±0.02	190.0±2.5	9.1±1.4	8.9	6.8±0.5	6.2

5 Discussion

The ^{36}Cl yield in samples depends on these reactions including ^{35}Cl(n,γ)^{36}Cl, ^{40}Ca(n,2n3p)^{36}Cl, ^{39}K(n,2n 2p)^{36}Cl, ^{40}Ca(μ^{-}, γ)^{36}Cl, ^{39}K(n,α)^{36}Cl and ^{39}K(μ^{-},2np) ^{36}Cl. Relative to the σ(^{35}Cl(n,γ)^{36}Cl) ~ 43b, the cross section for ^{40}Ca(μ^{-}, α) ^{36}Cl(σ ~4.3 mb) and ^{39}K(μ^{-}, 2np) ^{36}Cl (σ ~5 mb) is small, thus the contribution from the μ^{-} induced reaction is generally negligible. The ^{236}U yield in samples depends on the ^{235}U(n,γ)^{236}U reaction with the large thermal neutron of σ~8.3b. Therefore, the natural yield of two isotopes depends on the neutron yield in the uranium mineral and the fractions of the absorbed reaction elements.

The neutron was produced by (α,n) reactions on light elements such as B, Na, Mg and Al, and its yield depends on the major element abundances in the sample. The elemental compositions of the samples are listed in Table 2.

Table 2 Concentrations of the major elements in the samples measured with X-ray fluorescence spectrometry in weight%

Sample / %	B	F	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2
Sample 1	0.098	14.94	N.A.	0.18	2.13	28.49	0.032	N.A.	N.A.	33.06	0.032
Sample 2	0.064	N.A.	0.83	2.69	16.73	50.54	0.024	0.047	6.01	5.28	0.11
Sample / %	Cr_2O_3	MnO	Fe_2O_3	SeO2	Rb	SrO	BaO	Gd	Sm	PbO	Bi_2O_3
Sample 1	N.A.	0.066	1.38	0.022	N.A.	N.A.	N.A.	0.078	0.121	2.39	0.20
Sample 2	0.020	0.35	8.14	N.A.	0.026	0.011	0.049	0.135	0.042	0.032	N.A.

N.A. is abbreviation of no analysis; and bdl, below detection limit.

Also, the neutron yield depends on the ^{238}U spontaneous fission besides the uranium is the principal source of α-particles. Two points for the neutron absorption should be taken into account. (1) The neutron energy thermalization process in the rock is essential to produce the ^{36}Cl and ^{236}U because their reaction cross section excitation functions vary with energy. (2) The concentrations of trace neutron absorbers such as B, Gd and Sm. Also, the ratios of ^{36}Cl/Cl and ^{236}U/^{238}U calculated with the MCNP is similar to the works of Fabrka-Martin *et al.*[25] and Wilcken *et al.*[8]. The MCNP calculations assume an infinite, homogeneous mineral body with an elemental composition is equal to each individual mineral. Individual neutron with starting 1–2 MeV are tracked by the matrix using Monte-Carlo methods; and the probability of scattering or absorption by various elements at each step.

In Table 1, the MCNP calculation results were basically consistent with that of AMS measurement. More ^{36}Cl and ^{236}U experimental data conduce to understand the natural nuclides produced in the uranium mineral and the nucleogenic ^{236}U as a reference data for the background. This is important for the practical application of ^{236}U in environmental and geological research.

6 Conclusions

In this paper, the ^{36}Cl and ^{236}U in the same uranium mineral are measured by AMS at CIAE. The ratios ^{36}Cl/Cl and ^{236}U/^{238}U were studied. The measurement method of ^{36}Cl and ^{236}U in the same uranium provides for extending the potential application of ^{236}U in uranium mining, environmental and geological research.

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