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Date: 2023-06-18T00:00:00+00:00

Abstract

The concentration of the natural ultra-trace radionuclides 36Cl and 236U in the uranium depended on the neutron flux. In this article, a method for measuring 36Cl and 236U 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 236U in uranium mining, environmental, and geological research. The two samples were from Guangxi and Shanxi province, China, and their ratios 36Cl/Cl and 236U/238U were measured. More experimental data conduced to understand the natural nuclides in the uranium mineral. We plan to conduct more efforts on the research.

Full Text

Measurement of Natural 36Cl and 236U in Uranium Minerals Using Accelerator Mass Spectrometry

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Abstract

The concentrations of natural ultra-trace radionuclides ^{36}Cl and ^{236}U in uranium minerals depend on neutron flux. This article presents a method developed at the China Institute of Atomic Energy for measuring both ^{36}Cl and ^{236}U in the same uranium mineral sample, providing a protocol with potential applications for ^{236}U in uranium mining, environmental monitoring, and geological research. Two samples from Guangxi and Shanxi provinces in China were analyzed, and their ^{36}Cl/Cl and ^{236}U/^{238}U ratios were measured. Additional experimental data will contribute to understanding natural nuclides in uranium minerals.

Keywords: ^{236}U, Accelerator mass spectrometry, Uranium mineral

Introduction

Both radionuclides ^{36}Cl and ^{236}U possess very long half-lives ($T_1/_2$) of 3.01$×10^{5}$ years and 2.342$×10^{7}$ years, respectively [1]. Due to these long half-lives, these isotopes persist in the environment for periods far exceeding human lifetimes. However, this characteristic can be advantageous, as ^{36}Cl and ^{236}U can serve as isotopic tracers in various fields including environmental science, geology, and nuclear safeguards research [2–7].

In nature, the abundance of natural ^{236}U is extremely low [2], with ^{236}U/^{238}U ratios in different minerals expected to range from 10^{-10} to 10^{-14}. The ^{236}U is primarily produced through the ^{235}U(n,γ)^{236}U reaction, where neutrons are generated by spontaneous fission of ^{238}U or (α,n) reactions on light elements such as Na, Mg, and Al. In 1996, Purser et al. [3] proposed that ^{236}U could be used as a neutron flux integrator, an idea that was further developed by Valenta et al. [8] a few years later. The ^{236}U isotope has potential applications in monitoring the environmental impact of uranium mining by measuring its levels in mine drainage water and in uranium exploration by detecting ^{236}U in groundwater [9]. It is also applicable to environmental and geological research. Similar to ^{236}U, natural ^{36}Cl in deep subsurface environments is produced through the neutron capture reaction ^{35}Cl(n,γ)^{36}Cl.

The production of both ^{236}U and ^{36}Cl depends on neutron fluxes in the thermal and epithermal energy ranges. Combining ^{36}Cl measurements with ^{236}U analysis offers the possibility of determining subsurface neutron fluxes in both thermal and epithermal energy ranges [9]. Because natural ^{236}U and ^{36}Cl exist at ultra-trace levels, their measurement is difficult or even impossible without accelerator mass spectrometry (AMS) [10–14]. Wilcken et al. [9,15] have conducted investigations on the nucleogenic production of ^{36}Cl, ^{236}U, and ^{239}Pu in uranium minerals from several regions to understand the fundamental characteristics of subsurface production of nucleogenic isotopes in uranium-rich rocks. To promote practical applications of ^{236}U in uranium exploration and environmental impact monitoring of uranium mining for geological research, extensive studies of nucleogenic ^{36}Cl and ^{236}U in uranium minerals should be conducted to obtain data from different regions.

This paper describes the measurement of ^{36}Cl and ^{236}U in the same uranium mineral using AMS developed at the China Institute of Atomic Energy (CIAE). Two samples from Guangxi and Shanxi provinces in China were analyzed, and their ^{36}Cl/Cl and ^{236}U/^{238}U ratios were measured. MCNP calculations were performed to understand the neutron production model in uranium minerals.

Sample Preparation

To accurately measure the ^{36}Cl/Cl and ^{236}U/^{238}U ratios in uranium minerals, an extraction and purification method for AMS measurement was developed. To ensure that both isotopes experienced identical neutron flux conditions, ^{36}Cl and ^{236}U were separated from the same uranium mineral sample using the preparation procedure shown in [Figure 2: see original paper]. Due to the difficulty of dissolving large uranium mineral blocks, the samples were ground into 300- m powder.

^{36}Cl Sample Preparation

Dissolution A 5.0 g uranium mineral sample was placed in a Teflon vessel, and 30 mL of 1 M HNO_3 was added. The Teflon vessel was sealed for approximately 36 hours, shaken by hand every 5 hours, and vibrated using an ultrasonic device for 20 minutes. This process extracted most of the chlorine from the rock into solution. A few residual rock fragments could be dissolved by adding fresh HNO_3 solution. The chlorine concentration in the second dissolution solution was 1% less than in the first. Since AMS only requires measurement of the ^{36}Cl/Cl ratio, it was not necessary to account for this secondary dissolution.

Separation and AMS Sample Preparation The separation procedure involved several steps: (1) The Cl sample solution was mixed with a slight excess of $AgNO_3$ (0.25 M) in a dark room to form AgCl precipitate within 24 hours. (2) After discarding the supernatant, the AgCl was collected by centrifugation for 10 minutes. The residual solution was collected for ^{236}U sample preparation. (3) 10 mL of high-purity water and ammonia were used to dissolve the AgCl at pH > 10. (4) Saturated $Ba(NO_3)_2$ was added to remove sulfur by forming $BaSO_4$ precipitate for approximately 24 hours at 30°C. (5) The chlorine-containing solution was collected and filtered. (6) Excess high-purity HNO_3 was added to reform AgCl, which was collected by centrifugation for 10 minutes. Steps (3)–(6) were repeated three times to ensure complete sulfur removal.

The AgCl was dried at 100°C, placed in a vial, and wrapped in black paper. For AMS measurement, each sample was mixed with high-purity (99.99%) silver powder in a similar volume ratio to improve thermal and electrical conductivity, then pressed into a copper sample holder (40-Sample NEC MC-SNICS ion source). To minimize sulfur contamination, all samples were prepared in an air-purified room without stored HCl or H_2SO_4, and all reagents were 99.99% purity.

^{236}U Sample Preparation

Dissolution The residual rocks from Section 2.1.1 and the solution from step (2) of Section 2.1.2 were used to prepare the ^{236}U sample. A mixture of high-purity HF and HNO_3 was used to dissolve uranium minerals at 80°C for over 24 hours. HNO_3 and HF can dissolve most uranium in uraninite and silicates such as coffinite. After dissolving the silicates and uranium minerals, insoluble fluorides, graphite, sulfides, and highly resistant oxides remained as residues. The samples were filtered, and the resulting filtrate was evaporated to dryness. The uranium-containing dry residue was dissolved in 4 M HNO_3.

Separation and AMS Sample Preparation Dissolved uranium was separated and purified using a CL-TBP column. The column was preconditioned with 2.5 M HNO_3, the sample solution was passed through, and it was washed at a flow rate of 1.5 mL/h to obtain the uranium-containing solution. The uranium-containing solution was dried on a hotplate at approximately 100°C for 1 hour, then placed in an 800°C furnace for at least 2 hours to completely oxidize it to U_3O_8 and reduce $^{238}U^{14}N^-$ formation in the ion source. For AMS measurement, the sample was mixed with 99.99% Nb powder in a similar volume ratio to improve thermal and electrical conductivity, then pressed into an aluminum sample holder (NEC MC-SNICS ion source).

AMS Measurement

Both ^{36}Cl and ^{236}U were measured using the CIAE AMS system based on the HI-13 accelerator. The CIAE AMS system can measure ^{26}Al, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{64}Cu, ^{79}Se, ^{99}Tc, ^{126}Sn, ^{129}I, ^{151}Sm, ^{182}Hf, and ^{236}U for applications in biomedicine, nuclear physics, nuclear astrophysics, geosciences, nuclear environmental engineering, and environmental science [16–22]. In recent years, a new beam line was added to the upgraded CIAE AMS system [25], as shown in [Figure 3: see original paper].

^{236}U Measurement

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 with an accelerating voltage of approximately 7.240 MV, and $^{236}U^{11+}$ ions were selected after acceleration. Since the isobar ^{236}U is not expected to be measured, the key challenge is identifying the ^{236}U ions of interest from isotopes ^{238}U and ^{235}U. The energy differences between the ^{238}U and ^{235}U background ions and the ^{236}U ion of interest are 0.8% and 0.4%, respectively. When passing through the ion optical filters, the time-of-flight (TOF) detector provides sufficient resolution to distinguish ^{236}U from ^{238}U and ^{235}U isotopes. A sensitivity of 10^{-11} for $^{236}U/^{238}U$ is achieved due to the good time resolution of ~500 ps [24], high terminal voltage of the HI-13 accelerator, and relatively small energy straggling of the flying ions.

^{36}Cl Measurement

It is difficult to achieve high sensitivity for medium-heavy mass nuclides due to limitations in beam time and measurement conditions, resulting in insufficient differences in energy losses and unavoidable 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] ([Figure 3: see original paper]). The new beam line includes ion-optical elements, a large Q3D magnetic spectrometer, silicon barrier detectors (SBD), and a multi-anode chamber. The ^{36}Cl was measured using AMS beam line 2.

Cl^{-} ions were selected for injection into the HI-13 Tandem Accelerator, with a typical output beam current of about 3 A at the Lower Energy Faraday Cup (LEFC). The Cl^{-} ions were accelerated by the tandem terminal voltage, which was typically set at 11.0 MV. A carbon foil (3 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 maximum mass-energy product of 200 MeV • amu was used to select ^{36}Cl^{8+} (and ^{36}S^{8+}) at 99.11 MeV.

No process can separate ^{36}Cl from its stable isobar ^{36}S. After the switching magnet, 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- m thickness was mounted at the entrance of the Q3D as an absorber to produce different energy losses for ^{36}Cl and ^{36}S. After passing through the Si_3N_4 membrane, the ^{36}Cl^{8+} and ^{36}S^{8+} ions had energies of 81.48 MeV and 82.64 MeV, respectively, and the 14^{+} charge state was analyzed by the Q3D magnetic spectrometer. The ^{36}Cl and ^{36}S were separated based on 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 ([Figure 4: see original paper]), defined as the ratio of the peak difference to the full width at half maximum (FWHM). To increase detection efficiency and achieve further separation of isobaric interferences, a multiple-anode ionization chamber (MAIC, with four anodes in this work) with an entrance window of 100 mm × 40 mm Mylar foil was accurately mounted at the Q3D focal plane to record the ^{36}Cl ionization signals. The ionization chamber was filled with propane at 4.2 kPa. By selecting the appropriate magnetic field, a suppression factor of about 10^5 for ^{36}S ions was achieved, while most ^{36}Cl ions were recorded by the MAIC.

Results

[Figure 5: see original paper] shows the TOF spectra and two-dimensional TOF versus energy spectra for uranium mineral samples, demonstrating sufficient resolution to distinguish the nuclide of interest, ^{236}U, from ^{238}U and ^{235}U.

[Figure 6: see original paper] shows two-dimensional spectra of Er versus Et for ^{36}Cl standards and a uranium sample (where Er and Et are the energy loss signals from anode 4 and the total energy, respectively), indicating that the Q3D method can clearly identify ^{36}Cl from its isobar ^{36}S. These results suggest that the sample preparation method for ^{36}Cl and ^{236}U in uranium minerals is satisfactory for AMS measurement.

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

Discussion

The ^{36}Cl yield in samples depends on several reactions: ^{35}Cl(n,γ)^{36}Cl, ^{40}Ca(n,2n3p)^{36}Cl, ^{39}K(n,2n2p)^{36}Cl, ^{40}Ca($^{-}$,γ)^{36}Cl, ^{39}K(n,α)^{36}Cl, and ^{39}K($^{-}$,2np)^{36}Cl. Compared to the cross-section for ^{35}Cl(n,γ)^{36}Cl (~43 barns), the cross-sections for ^{40}Ca($^{-}$,α)^{36}Cl (~4.3 mb) and ^{39}K($^{-}$,2np)^{36}Cl (~5 mb) are small, making the contribution from $^{-}$-induced reactions generally negligible. The ^{236}U yield in samples depends on the ^{235}U(n,γ)^{236}U reaction with a large thermal neutron cross-section of ~8.3 barns. Therefore, the natural yields of both isotopes depend on the neutron flux in the uranium mineral and the fractions of elements that absorb neutrons.

Neutrons are produced by (α,n) reactions on light elements such as B, Na, Mg, and Al, with yields depending on the major element abundances in the sample. The elemental compositions of the samples are listed in .

Neutron yield also depends on ^{238}U spontaneous fission as a principal source of α-particles. Two points regarding neutron absorption must be considered: (1) The neutron energy thermalization process in the uranium-bearing rock is essential for producing ^{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 must be accounted for. The ratios of ^{36}Cl/Cl and ^{236}U/^{238}U calculated with MCNP are similar to the works of Fabryka-Martin et al. [25] and Wilcken et al. [8]. The MCNP calculations assume an infinite, homogeneous mineral body with elemental composition equal to each individual mineral. Individual neutrons starting with 1–2 MeV are tracked through the matrix using Monte Carlo methods, with probabilities of scattering or absorption by various elements calculated at each step.

As shown in , the MCNP calculation results are basically consistent with the AMS measurements. More experimental data on ^{36}Cl and ^{236}U will help understand the natural nuclides produced in uranium minerals and establish nucleogenic ^{236}U as reference data for background levels. This is important for the practical application of ^{236}U in environmental and geological research.

Conclusions

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

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Note: Figure translations are in progress. See original paper for figures.