

^{236}U in well water - a tool for uranium prospection?

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Abstract

The equilibrium ratio of $^{236}\text{U}/\text{U}$ in natural ore is proportional to the thermal neutron flux, which is expected to be proportional to the uranium concentration in first approximation. While uranium in typical crustal rocks is expected to be as low as 10^{-14} , uranium ores show $^{236}\text{U}/\text{U}$ up to 10^{-9} . Since this fingerprint of high grade ore should stay unaltered in withering and dissolution, it should still be detectable in well water which was in subsurface contact with the ore; thus, such wells should be useful as natural probes for uranium prospection. This isotopic signature to be more unambiguous than the uranium concentration in water.

A known highest grade ore deposit was located in Jáchymov, Czech Republic. The ore grade mined at the beginning of the 20th century was typically 60% U_3O_8 [Mayer1950], while today often ores in the permil-range are mined. It is mainly depleted now, but is a perfect test case to investigate whether high grade ore is indicated by high $^{236}\text{U}/\text{U}$ concentration in well water in the vicinity. Thus, the Jáchymov region could be a perfect test case to study ^{236}U in well water as a tool for uranium prospection.

The challenge of this project is the measurement of the very low natural $^{236}\text{U}/\text{U}$ ratio and the possible huge amount of anthropogenic ^{236}U already dispersed to the environment. Accelerator Mass Spectrometry (AMS) is the only detection technique suitable for the low natural isotopic abundance of ^{236}U . Large water

volumes which were not yet contaminated must be processed, without introducing contamination in the laboratory.

Introduction

Uranium, the heaviest naturally occurring element in the earth's crust, is of special importance for the production of nuclear power. Despite it is relatively abundant and ubiquitous in many minerals at low concentrations (typically a few $\mu\text{g/g}$), deposits with economically exploitable concentrations are rare. At the end of 2006, world uranium production (39 603 tU) provided only about 60% of world reactor requirements (66 500 tU), with the remainder supplied from of already mines uranium [RedBook2008]. To meet the still growing demand will depend on also on the identification of new deposits.

^{236}U with a half-life of $2.3 \cdot 10^7$ a is produced via thermal neutron capture on ^{235}U . The cross section $\{\sigma[^{235}\text{U}(n,\gamma)] = 98 \text{ barn}\}$ is about 1/6 of the fission cross section $\{\sigma[^{235}\text{U}(n,f)] = 583 \text{ barn}\}$. Thus, the ratio $^{236}\text{U}/^{235}\text{U}$ is a direct measure for the subsurface neutron flux, integrated over geological time frames [Purser1996].

Natural neutron production results mainly from (α,n) reactions on lighter nuclides [Fabryka-Martin1988]. The α -particles originate from the decay series of uranium and Thorium. Spontaneous fission of ^{238}U , and induced fission of ^{235}U and, in the top few meters of the earth's surface, cosmic rays contribute to neutron

production. The important role of uranium in natural subsurface neutron production suggests that a higher concentration of uranium will be correlated with higher neutron flux, and thus higher $^{236}\text{U}/^{235}\text{U}$ (since the natural ratio of $^{235}\text{U}/^{238}\text{U}$ is constant within the precision relevant for our proposal, we can speak of the $^{236}\text{U}/\text{U}$ ratio in the following instead). $^{236}\text{U}/\text{U}$ isotopic ratios have been measured previously in several uranium ores ([Zhao1994], [Richter1999], [Berkovits2000], [Wilcken2007], [Steier2008], [Wilcken2008]) and the obtained ratios range from $1\cdot 10^{-12}$ to $1\cdot 10^{-9}$. For typical crustal rocks with a uranium and thorium content of only several ppm ratios between $1\cdot 10^{-14}$ and $5\cdot 10^{-14}$ are expected [Steier2008], but no measurements exist so far.

Uranium can be released during rock weathering and so a total flux of $0.88\cdot 10^{10}$ g U a⁻¹ is transported by rivers and groundwater aquifers to the oceans [Borole1982]. The average natural ratio in river water should lie between $1\cdot 10^{-14}$ and $1\cdot 10^{-13}$ [Steier2008]. Up to now, only one result from a subsurface well (from the "Gasteiner Heilstollen", Bad Gastein, Austria) was published so far with an isotopic ratio of $^{236}\text{U}/\text{U} = 6\cdot 10^{-12}$.

Today a huge amount of anthropogenic ^{236}U exists as it is produced as a by-product in nuclear reactors. A total anthropogenic inventory of 10^6 kg ^{236}U is estimated [Steier2008]. Despite ^{236}U is probably the isotope with the second largest anthropogenic inventory (after ^{239}Pu , [Steier2008]), measurements are hampered by its very low specific activity ($T_{1/2}=23$ Ma), by the fact the energy of its alpha decay is obscured by the abundant ^{235}U , limiting the detection limit to

$^{236}\text{U}/\text{U} = 2 \times 10^{-5}$ [Sanchez1992]. Conventional mass spectrometry is similarly limited by the neighboring abundant isotope ^{235}U . Environmental studies are restricted to the level above 1×10^{-7} , but this was sufficient to detect ^{236}U in shore sediments near the Irish sea (influenced by Sellafield [Marsden et al., 2001]). The AMS technique to detect ^{236}U was developed only recently.

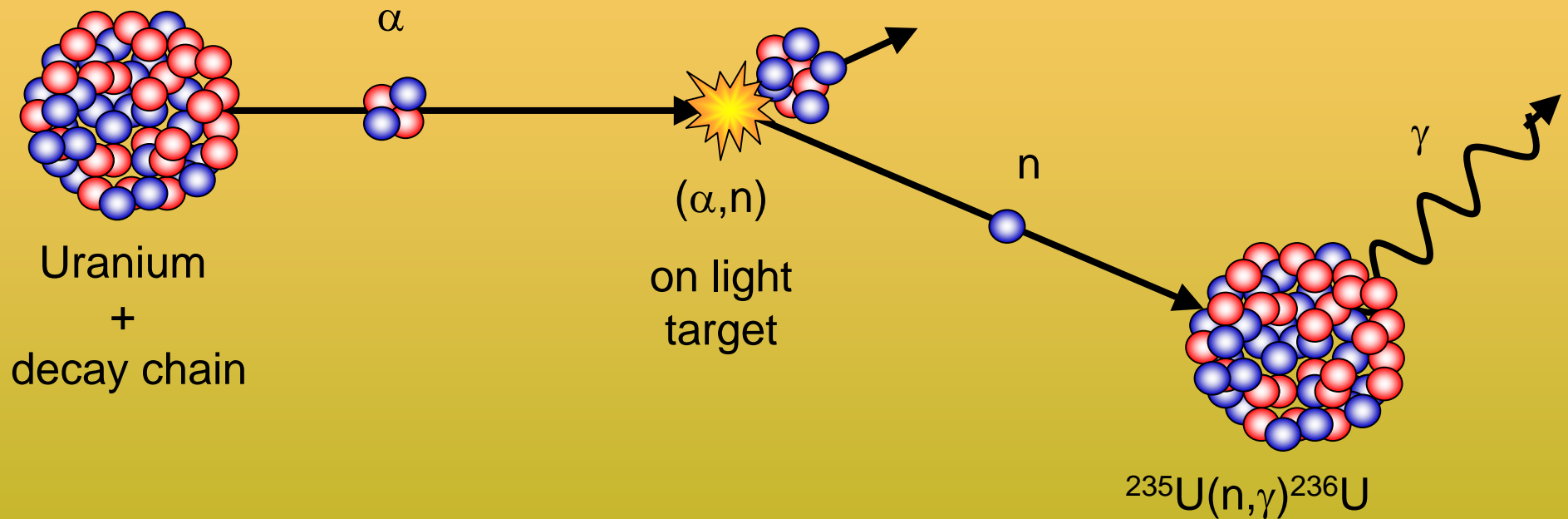
The amount of anthropogenic ^{236}U by far exceeds the natural inventory (some 30 kg, [Steier2008]). Whether and how far this anthropogenic contribution has entered the environment is unclear. $^{236}\text{U}/\text{U}$ ratios from 10^{-7} up to 10^{-3} have been measured in soils from the vicinity of the Chernobyl power plant ([Vance2006], [Mironov2002], [Hotchkis2000]), near two uranium processing factories in the USA [Mironov2002] and in sediments from the Irish Sea affected by the Sellafield (UK) nuclear reprocessing plant [Mironov2002],[Ketterer2003]. Close to a shut-down nuclear power plant, however, [Quinto2009] found levels ($^{236}\text{U}/\text{U}$ up to 10^{-8}) close to their detection background ($^{236}\text{U}/\text{U} \sim 10^{-9}$).

Another important contribution to anthropogenic ^{236}U was created in above-ground nuclear explosions and globally distributed. [Ketterer2007] and [Sakaguchi2009] have determined the ratio $^{236}\text{U}/^{239}\text{Pu}$ to be approx. 0.2 in global fallout (^{239}Pu can be measured well by several methods and the global distribution of plutonium isotopes is fairly well known). Only a few measurements of the environmental distribution of anthropogenic ^{236}U exist so far. [Srnecik2010] have determined the abundance of ^{236}U in Austrian surface waters, far from known local anthropogenic sources, and observe $^{236}\text{U}/\text{U}$ of several times 10^{-7} ,

for some samples even significantly higher; on the other hand, several samples are still in agreement with their (relatively high) measurement background of 10^8 atoms ^{236}U . This and the low ratio found for the water from the "Gasteiner Heilstollen" suggest that one can still expect to find water not yet influenced by anthropogenic ^{236}U .

Among others, the measurement of decay chain and fission products is an established method to locate new deposits. The concentration of uranium in wells is used in uranium prospecting, and was recently investigated e.g. in [Mehra2007]. This concentration can depend on details of rock weathering and the chemical conditions of the water, while the isotopic composition of uranium (and thus the $^{236}\text{U}/\text{U}$ fingerprint) will not be altered by these processes.

Production of natural ^{236}U ($t_{1/2} = 23 \text{ Myr}$) in uranium ores



- Uranium ore deposits show enhanced natural neutron flux, mainly from α -decay and (α, n) reactions on light target nuclei.
- This leads to enhanced ^{236}U production by $^{235}\text{U}(n, \gamma)$

However, comprehensive geological expertise is needed for proper selection of the water samples and for interpretation of the measured isotopic ratios. Water samples should be protected from contamination by surface water, and, in the case of a positive ^{236}U detection, hydrology must provide the link to the location of the ore deposit. This is not only the case for future true applications in uranium prospecting, but also for the feasibility study to be performed for Jachymov. Proper subsurface wells have to be identified, which carry water which was in contact with the ore body. The "Radon Spa" in Jachymov might fulfill these requirements.

Additionally, samples from several wells in various geological settings unaffected by the deposit are needed to serve as a "blank" control set. One suitable water from the "Heilstollen" in Bad Gastein, Austria, was already measured, with no known uranium ore in the vicinity. It yielded low $^{236}\text{U}/\text{U} = 5 \times 10^{-12}$, despite it carries the highest known uranium concentration in an Austrian well (70 ug/L).

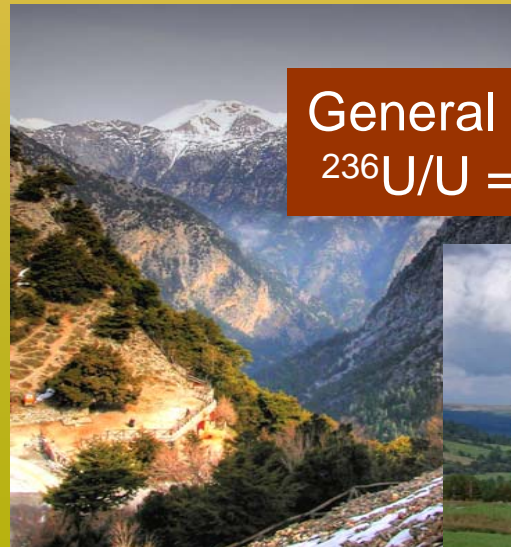
Enhanced natural $^{236}\text{U}/\text{U}$ in uranium ores



AMS measurement in
uranium ores:
 $^{236}\text{U}/\text{U} = 7 \times 10^{-11}$ (typ.)



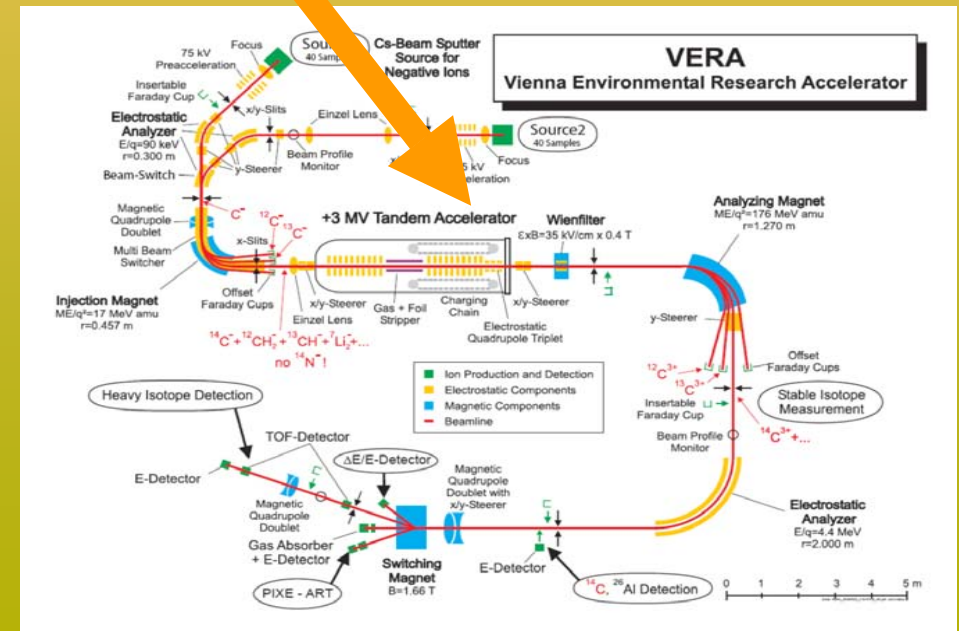
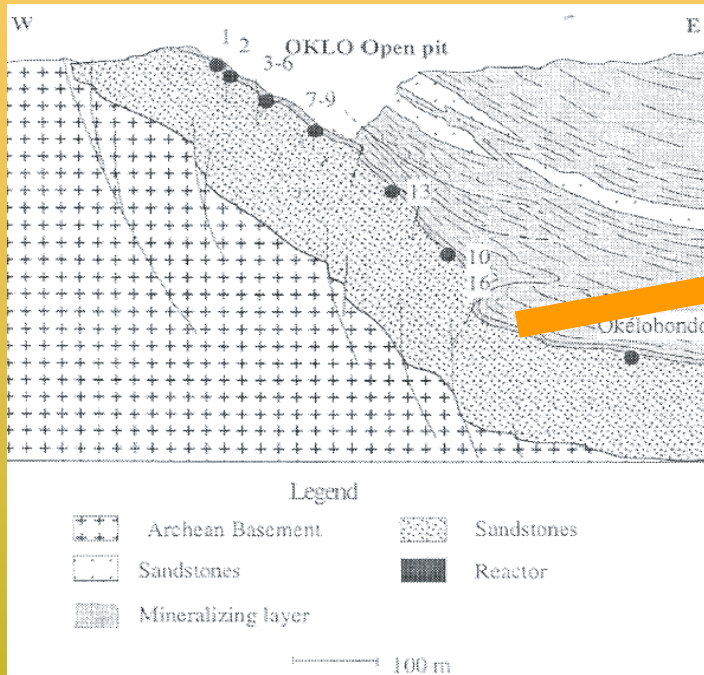
The isotopic ratio $^{236}\text{U}/\text{U}$ in ores
is significantly higher than in
"ambient" crustal uranium.



General crust:
 $^{236}\text{U}/\text{U} = 2 \times 10^{-14}$ (est.)



Isotopic signal $^{236}\text{U}/\text{U}$ in well water as probe for ore deposits



The $^{236}\text{U}/\text{U}$ fingerprint of ores should be preserved in water from wells "probing" the (yet unknown) deposit and could be detected with the newly established measurement method by AMS.

Jáchymov is a good case for a feasibility study

- Jáchymov produced highest grade ore
- The mine with the best studied $^{236}\text{U}/\text{U}$

Difficulties:

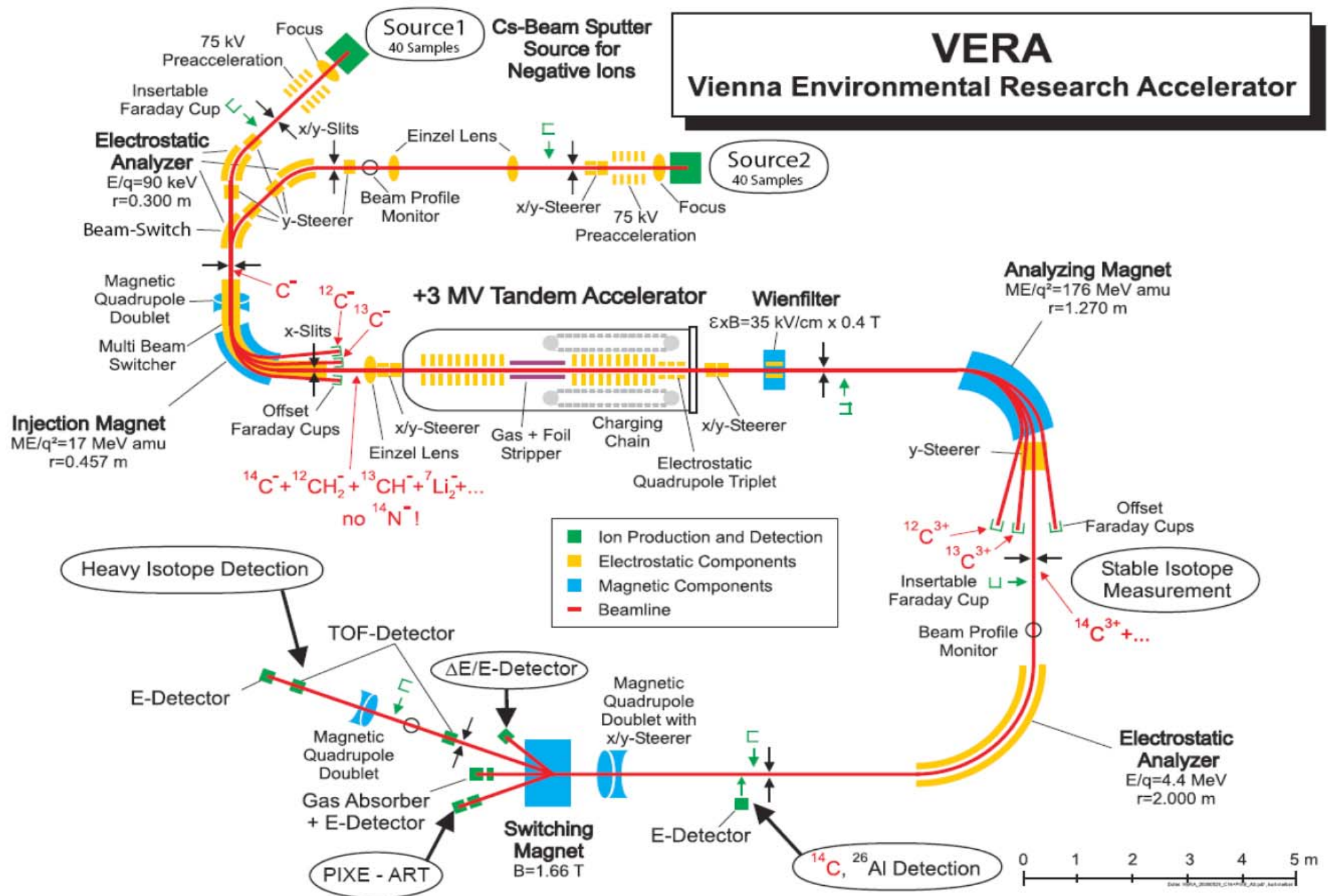
- Only recently, natural ^{236}U can be measured with Accelerator Mass Spectrometry (AMS).
- Anthropogenic contamination from global weapons-test fallout
- Most commercial reagents seem to be contaminated with ^{236}U
- Measurement of expected natural background ($^{236}\text{U}/\text{U} = 2 \times 10^{-14}$)

AMS is the only method able to reach the detection level required for expected natural concentrations of $^{236}\text{U}/\text{U}$. The Vienna Environmental research Accelerator is especially suited for this purpose and easily reachable from Prague. This opens the opportunity to be early in the field to investigate the geological applications of an ubiquitous, but up to now unexplored isotope.

^{236}U , both natural and anthropogenic, will have many (also yet un-foreseeable) applications. We will study the feasibility to use $^{236}\text{U}/\text{U}$ in well waters as a tool for uranium prospection. Our fundamental research will lay the foundation for these far-reaching applications.

VERA

Vienna Environmental Research Accelerator



Methods

The determination of the isotope ratio of $^{236}\text{U}/^{238}\text{U}$ by AMS can be carried out at with at the AMS facility VERA at the Faculty of Physics, University of Vienna.

Water will be sampled in polyethylene bottles and canisters (1.5 L, 5 L and up to 25 L) from subsurface wells. The samples will be stabilized in the field with an appropriate amount of (pre-purified) conc. nitric acid. For the purification of the nitric acid (and also of hydrochloric acid used in later steps of the separation), we plan to use sub-boiling distillation, to remove any traces of uranium. ^{233}U can be used to determine the uranium concentration in the samples directly in the AMS measurement.

Why AMS? - strengths and shortcomings of various detection techniques

Alpha-spectrometry will be used for the chemical yield determination of our sample procedure, as well as for the measurement of the ^{238}U and ^{234}U activity concentrations. The low ^{236}U activities expected in the environment cannot be measured by this method; also the possibility to measure higher ^{236}U activities is limited since its α -energy is close to that of ^{235}U (obscured by the low-energy tail of ^{235}U [Sanchez1992]).

In ICP-MS (Inductively Coupled Plasma Mass Spectrometry), the samples are introduced as aerosol into an Ar plasma. The plasma can be operated at

atmospheric pressure, and the source is coupled by means of differential pumping to the high vacuum of the mass spectrometer. A so-called nebulizer allows to introduce samples directly from solution, significantly simplifying sample preparation. Additionally, the complete ionization of the sample aerosols results in high ionization yields and low fractionation. The high temperature in the plasma leads to a relatively wide energy distribution and a large beam emittance, limiting ^{236}U abundance sensitivity by tailing from ^{235}U . This can be partly compensated by restricting the beam emittance with the object slits of the spectrometer, at the cost of transmission losses. The presence of hydrogen in the solution fosters also the formation of hydride ions, which can be however antagonized by drying the aerosol stream [Boulyga2006]. The abundance sensitivity achievable with ICP-MS is presently around 10^{-7} .

In TIMS (Thermal Ionisation Mass Spectrometry), the samples are evaporated and thermally ionized from a glowing filament. Mass analysis is, similar to TIMS, done with a conventional mass spectrometer. The lower temperature compared to ICP-MS leads to a smaller energy distribution of the ions, and the absence of a carrier gas in this type of ion source allows a better vacuum in the spectrometer, resulting in less tailing from scattering on residual gas. TIMS has allowed to measure natural $^{236}\text{U}/\text{U}$ in samples from Gabon [Richter1999]. However, the relatively high ratios found there ($^{236}\text{U}/\text{U} > 10^{-9}$) are possibly already close to the detection limit.

AMS

uses by far the most complex instrumentation. A particle accelerator is used to accelerate the sample ions from the usual keV energies to several MeV. The so-called tandem accelerator used in almost all existing AMS facilities requires an ion source which produces negative ions. AMS facilities are optimized for abundance sensitivity in the range down to 10^{-18} , so a relatively large number of atoms of the abundant species must be put through the system (μg to mg) before sufficient counts of the rare species are collected. Both requirements can be fulfilled with the so called high-output caesium sputter source [Middleton1989], which is thus almost exclusively used in the field, despite known drawbacks like low ionization yield for many ion species and relatively large probability for formation of molecular ions. In the case of actinides, one disadvantage can partly compensate the other, since molecular UO^- ions are used instead of U^- , which is not sufficiently formed. Still, the ionization yield for the actinides is below 1%, which is much lower than for the techniques described above. An advantage of the caesium sputter source is the narrow energy distribution, and the small beam emittance. The ion source is followed by a first sector-field mass spectrometer which (in the best case) eliminates all but the molecular isobars. The following acceleration helps to achieve the ultimate abundance sensitivity in the following ways:

- (1) By passing the ions through a region of dilute gas, electrons are stripped off and thus molecules broken up. This process requires at least several 100 keV

for actinides [Wacker2005]. By these means, AMS gets rid of molecular isobars completely.

(2) The acceleration reduces the emittance of the beam. This allows for a higher resolution of the subsequent mass spectrometer(s).

(3) Most processes that produce background counts in the detector are based on interaction of the ions with residual gas (mainly electron-exchange processes). The corresponding cross-sections typically scale with negative exponents of the energy [Steier2005]. By these means, the background count rate can be essentially reduced to 0.

(4) The high energy allows to use the full range of detector systems developed for nuclear physics instead of only MCP (multi channel plate) detectors. This includes energy-resolving ionization chambers as well as time-of-flight (TOF). The energy measurement allows to distinguish between ions with the same mass-over-charge ratio (e.g. $^{235}\text{U}^{5+}$ from $^{94}\text{Mo}^{2+}$) which is not possible with electric and magnetic separators alone. Additionally, the large signals induced by the high energy in the detectors allow to use high thresholds for noise rejection, which leads to virtually dark-count free operation.

The VERA setup as used for actinide measurements is described in [Vockenhuber2003]. A caesium sputter source is used to extract negative ions. The yield of UO^- ions (on the order of $6 \cdot 10^{-4}$ ^[2]) is the largest factor in the efficiency calculation. The low-energy mass spectrometer is tuned using $^{238}\text{U}^{16}\text{O}^-$

as a pilot beam. To measure ^{236}U , the mass spectrometers are scaled to $^{236}\text{U}^{16}\text{O}^-$. Negative molecular isobars (namely $^{235}\text{UH}^-$ and $^{238}\text{U}^{14}\text{N}^-$) are destroyed in a tandem accelerator with 3 MV terminal voltage and gas stripping. From the resultant positive ions one charge state is selected by the high-energy mass spectrometer. The stripping yield (and energies) achieved for the 5+ charge state investigated is 5 % for 5+ (18 MeV). A TOF detector with a flight path of 2.8 m, a time resolution of 0.7 ns (FWHM) for ^{238}U at 18 MeV and a transmission of 30% is used. Finally, the energy is measured with an ionization chamber.

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