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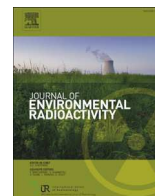


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Study of uranium oxidation states in geological material



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ARTICLE INFO

Article history:

Received 9 May 2012

Received in revised form

6 March 2013

Accepted 17 April 2013

Available online

Keywords:

U oxidation states

Wet chemistry

Extraction

XANES

ABSTRACT

A wet chemical method to determine uranium (U) oxidation states in geological material has been developed and tested. The problem faced in oxidation state determinations with wet chemical methods is that U redox state may change when extracted from the sample material, thereby leading to erroneous results. In order to quantify and monitor U redox behavior during the acidic extraction in the procedure, an analysis of added isotopic redox tracers, ²³⁶U(VI) and ²³²U(IV), and of variations in natural uranium isotope ratio (²³⁴U/²³⁸U) of indigenous U(IV) and U(VI) fractions was performed. Two sample materials with varying redox activity, U bearing rock and U-rich clayey lignite sediment, were used for the tests. The Fe(II)/Fe(III) redox-pair of the mineral phases was postulated as a potentially disturbing redox agent. The impact of Fe(III) on U was studied by reducing Fe(III) with ascorbic acid, which was added to the extraction solution. We observed that ascorbic acid protected most of the U from oxidation. The measured ²³⁴U/²³⁸U ratio in U(IV) and U(VI) fractions in the sediment samples provided a unique tool to quantify U oxidation caused by Fe(III). Annealing (sample heating) to temperatures above 500 °C was supposed to heal ionizing radiation induced defects in the material that can disturb U redox state during extraction. Good agreement between two independent methods was obtained for DL-1a material: an average 38% of U(IV) determined by redox tracer corrected wet chemistry and 45% for XANES.

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1. Introduction

Spent nuclear fuel (SNF) consists primarily of UO₂ and represents a potential of water to breach a repository containing SNF, corrode through the multi-barriers of the repository, and eventually reach the SNF. A key property influencing dissolution of the SNF and the radioecological behavior of released U and other actinides (An), is oxidation state (Silva and Nitsche, 2001). Therefore, U oxidation state determinations are important to studies related to assessing U release from and migration around the U source. For example, removal of a significant amount of U from groundwater via immobilization onto fractured mineral surfaces has been reported (Blomqvist et al., 2000). However, it remains unclear whether immobilization is due to surface sorption, precipitation or a result of reduction of U(VI) to less soluble U(IV). The availability of a simple and reliable method for U oxidation state determination on fractured surface materials would especially facilitate elucidating the role of redox processes in U immobilization.

There are two basic approaches to determine U oxidation states: wet chemical means (ion-exchange and extraction/separation techniques) and spectroscopic, non-destructive methods (e.g., XAS, XPS). The first wet chemistry methods to separate actinide into valence fractions were developed based on cation-exchange (Diamond et al., 1954) and anion-exchange (Kraus et al., 1956) processes. These methods were later modified by Hussonnois et al. (1989) and Fattahi and Guillaumont (1993). The methods yield reliable results, however, only for laboratory systems in which U oxidation state ratios remain stable prior, during and after the analysis, i.e. void of redox active species which can disturb the original redox potential of the system. Natural solid samples can contain a variety of redox active agents, so that reliable U oxidation state information can only be obtained if the original U redox state is not disturbed during U extraction from the sample material. Iron extracted from ferric and ferrous mineral phases in the sample material is the main natural redox active element that can disturb the original redox potential (Ervanne, 2003). Redox tracers with known amount (activity) of an artificial isotope in the appropriate oxidation state can be used to study chemical behavior during the wet chemistry analysis. This was first studied by Foti and Freiling (1964) and Anderson, 1984 et al. used ²³⁶U(VI) and ²³²U(IV) isotopes as redox tracers to determine U oxidation state in natural waters. Following the added redox tracers

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in the wet chemical analysis allows researcher to identify inadvertent redox changes and use these results to make corrections for the original solid sample under investigation.

Synchrotron radiation-based techniques are useful, non-destructive methods for An speciation in the natural systems (Brown and Sturchio, 2002) and can be used to validate results from wet chemical analysis. X-ray near edge structure (XANES) analysis has been used for *in situ* U speciation in a wide variety of matrices, without prior separation, i. e. in contaminated soils and sediments (Bertsch et al., 1994) in evaporation ponds with greatly varying U concentrations (Duff et al., 1997) and in tertiary sediments from a natural analog site using a micro-focused X-ray beam (Denecke et al., 2005). In Noseck et al. (2008), the micro-XANES results from Denecke et al. are compared to wet chemical analysis. Using a focused beam to study concentrated areas or hot spots in a heterogeneous area helps to alleviate the problem of U concentration in some materials that are too low to be reliably analyzed by conventional methods (Denecke et al., 2009). A limitation of the use of synchrotron-based XANES is their limited availability.

In this work we present a portion of efforts to develop a scientifically sound wet chemical method for U oxidation state determination in a different type of low U concentration solid materials. The concrete work consists of various experiments used to quantify U oxidation state changes caused by the sample's own redox active components during the wet chemical procedures. The effects are assessed through application of artificial U isotope redox tracers added to the extraction solution and determining their recovery in U(IV) and U(VI) fractions. To study the role of ionizing radiation on U redox behavior, rock material was heated at different temperatures 300, 500 and 1000 °C before extraction. Heating was assumed to heal defects caused by ionizing radiation (alpha-emission as internal radiation source) that are able to affect U redox state changes during extraction. Main wet chemistry results are compared with those obtained from U L₃ XANES analyzes.

2. Materials and methods

2.1. Sample material

Two well-characterized sample materials were used in the tests; a rock material and a tertiary sediment. Certified reference U–Th ore (DL-1a) was used as the rock material. DL-1a is a waste rock from U ore excavation and is therefore assumed to have been exposed to intense natural ionization radiation for geological time periods. The material contains 0.0116% U as $UO_2 + x$ ($0 < x < 0.25$) and brannerite $(U,Ca,Ce)(Ti,Fe)_2O_6$ as the main U minerals and redox-active elements Fe (0.93%) and S (0.41%), which may potentially disturb the U redox state during analysis. The main mineral components have been identified as quartz, muscovite (mica), pyrite and iron oxides (Steger and Bowman, 1980). The approximate chemical composition is shown in Table 1. The second sample was tertiary U-containing clayey sediment from the Ruprechtov natural analogue site, Czech Republic (Noseck et al., 2012). Two samples from different drill core depths, designated as OC 2_3 and OC 4_1, having 539 and 172 ppm of U, respectively, were selected for study. Uranium phases identified in the sediment material are UO_2 and trisramite, $(Ca,U,Fe)(PO_4,SO_4) \cdot 2H_2O$.

The potential formation of Fe(III) phases in siderite ($FeCO_3$) and pyrite which were also found in the sediment (Noseck et al., 2008) led to an extra challenge for the analysis.

2.2. Experimental

The following steps and aspects were applied in the experimental design: (1) preparing appropriate and reliable redox

Table 1

Approximate chemical composition of DL-1a (Steger and Bowman, 1980).

Constituent	Weight-%
SiO ₂	85.5
Al	5.3
Fe	0.93
S	0.41
Ca	0.29
K	0.23
Mg	0.19
Na	0.09
Ti	0.09
U	0.0116
H ₂ O (105/°C)	0.2

tracers; (2) quantitative U extraction from original untreated and annealed sample material (extracted insoluble U is considered to be present as U(IV)); (3) analyzing the U(IV)/U_{total} ratio for natural and tracer U fractions; (4) comparison of extraction results with those from XANES studies. The extraction experiment results and their transfer to determine the original U redox state in the solid material using the redox tracer correction.

2.2.1. Preparation of redox tracers

Two isotopic redox tracers $^{232}U(IV)$ and $^{236}U(VI)$ were prepared. $^{232}U(IV)$ was prepared by reducing $^{232}U(VI)$ by adding a few drops of 15% $TiCl_3$ (3 M HCl) into the tracer solution. Reduced U was expected to be oxidized back to U(VI) after the reduction capacity of $TiCl_3$ had been used, the time depending mainly on concentrations of U, Fe and O (Hussonnois et al., 1989). The oxidation half-life time for U in the mixture of 4.5 M HCl + 0.03 M HF solution at a U concentration of 10^{-5} M has been determined to be 292 h, equivalent to oxidation of <1% during the analysis time (Ervanne and Suksi, 1996). Oxidation kinetics were monitored by taking samples from the $^{232}U(IV)$ solution as a function of time and analyzing U(IV) and U(VI) fractions using ion-exchange chromatography. After ion-exchange separations 2–3% of total ^{232}U was repeatedly found in the U(VI) fraction. $^{236}U(VI)$ solution was prepared by evaporating ^{236}U tracer solution to dryness and dissolving the evaporate into 4.5 M HCl. The amounts of $^{232}U(IV)$ and $^{236}U(VI)$ tracers used in the experiments were 660 mBq and 100–400 mBq. Corresponding U masses were 0.8 pg and 0.04–0.16 µg, thus having from 2 to 7 orders of magnitude lower masses than the natural U extracted (5–50 µg or 62–620 mBq).

2.2.2. Extraction of U and U(IV)/U(VI) separation

The solution used for U extraction was prepared by mixing 4.5 M HCl with 0.03 M HF using commercial acids, and then bubbling with Ar gas for several minutes to remove dissolved oxygen. Three DL-1a rock samples were annealed at different temperatures (300, 500 and 1000 °C) prior to extraction. This was done by placing a few grams of material into a quartz vessel and heating under Ar gas flow to the desired temperature during 1.5 h. After annealing, a portion of the sample was ground and used for U extraction.

Original (untreated) and annealed DL-1a samples were extracted in 4.5 M HCl + 0.03 HF. Sediment samples were extracted in 4.5 M HCl + 0.03 HF with addition of ascorbic acid to prevent U(IV) oxidation by Fe(III) formed as a result of Fe(II) oxidation during the storage of samples. After U extraction, the supernatant was immediately filtered over a 0.2 µm Millipore membrane to separate the solid residue. The average extraction time was 10 min. Redox tracers were added into the extraction solution just before the extraction. U(IV) and U(VI) fractions in the resulting filtered extraction solution were separated in an anion exchange column

(Dowex 1 × 4, 50–100 mesh) regenerated with 4.5 M HCl. U(IV) was collected in the first 20 ml of 4.5 M HCl. U(VI) is initially retained on the column and then eluted with 20 ml of 0.1 M HCl (Ervanne and Suksi, 1996). Both fractions were analysed for U. U activity concentration was determined using α -spectrometry. Alpha activities were measured by PIPS-detectors of 450 mm² area with a nominal resolution of 20 keV.

2.2.3. XANES

U L₃ XANES measurements were performed at the 2.5 GeV synchrotron light source ANKA, at the INE-Beamline for actinide research (Rothe et al., 2012). All U L₃-XANES spectra were recorded in fluorescence detection mode by registering the U L_{2,1} fluorescence intensity at ~13.6 keV as a function of the incident photon energy by means of a five-element high purity Ge solid state detector (Canberra). Up to seven scans were collected at room temperature and averaged for each sample. XANES spectra were isolated from raw averaged data scans following subtraction of a linear pre-edge background function and normalization of the edge jump to unity. IFEFFIT-ATHENA software (Ravel and Newville, 2005) was used for spectra treatment and calculation of U oxidation state ratios. Original (untreated) OC 2_3 and OC 4_1 Ruprechtov samples, DL-1a residue left after acidic extraction and DL-1a that had been annealed at 300, 500 and 1000 °C were studied with U L₃ XANES. For the measurements 30–40 mg of each sample material was mixed with cellulose powder and pressed into the pellets 9 mm in diameter and about 1 mm thickness. UO₂ and schoepite (pure U(VI)-containing mineral) were used as U oxidation state references.

3. Results and discussion

3.1. DL-1a rock material

First preliminary experiments showed that more than 50% of a sample's U could be extracted with 4.5 M HCl within 0.5 min extraction time. More continuous extraction is necessary to extract U(IV) which is much less soluble than U(VI). Finally the extraction time was brought to 10 min. It was assumed that during this time at least all U(VI) and the majority of U(IV) could be extracted from the sample material. The distribution of U oxidation states in the extraction solution was studied as a function of sample mass to see possible U redox perturbations taking place during extraction. U(IV) and U(VI) fractions with ²³⁶U(VI) redox tracer were separated and the U(IV)/U_{total} ratio was determined (Table 2). The average value for ten U(IV)/U_{total} measurements was 0.7, the small (~50 mg) samples having clearly lower values (0.53) than larger samples (~500 mg), for which the ratio increased to 0.85 suggesting mass controlled reduction of U during extraction.

Table 2

Results of U(IV)/U_{total} measured as a function of DL-1a sample mass and corrected with the help of ²³⁶U(VI) tracer reduced during extraction.

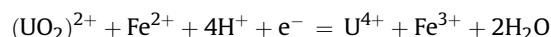
DL-1a	Mass (mg)	U extracted (%)	U(IV)/U _{total} (%)	²³⁶ U(VI) reduced (%)	U(IV)/U _{total} corrected (%)
1	51	95	53	18	41
2	65	84	69	30	41
3	102	92	52	33	38
4	150	92	61	42	35
5	198	81	69	41	40
6	205	85	65	42	41
7	306	86	81	60	41
8	368	75	82	85	33
9	400	84	85	72	36
10	501	76	83	81	36

Table 3a

Amount of ²³²U(IV) tracer oxidized during U extraction.

Sample description		Mass (mg)	²³² U(IV) oxidized (%)
1	DL-1a	49	1.4
2		175	0.8
3		293	0.5
4	Lignite 2_3	51	97
5		205	98
6	Lignite 4_1	104	99
7		302	98

Concurrent reduction of ²³⁶U(VI) was seen as well. A large variation in U(IV)/U_{total} was observed with small sample masses, whereas with large masses a steady state appears (Table 2). The amount of U left in the residue after extraction was 5–25%: all of the residue was considered to be U(IV) which was corroborated by XANES (Table 4). Results obtained for different sample masses indicate disturbance of redox balance which is probably explained by increasing Fe(II) concentration and thus higher Fe(II)/Fe(III) ratio. The larger Fe(II) concentration in the extraction solution increases reducing power promoting faster U(VI) reduction kinetics, according to the equation:



The results show that no significant oxidation of ²³²U(IV) tracer occurred with the DL-1a material; less than 2% of added ²³²U was found in the U(VI) fraction irrespective of the sample mass (Table 3a). On the other hand, the reduction of ²³⁶U(VI) to ²³⁶U(IV) was quite dramatic, at least with the largest sample mass. More than 80% of added ²³⁶U(VI) was reduced when using ~500 mg samples (Tables 2 and 3b). Fig. 1 shows the case for the 500 mg sample: there is a ²³⁶U peak in the α -spectrum of U(IV) fraction indicating partial reduction of the ²³⁶U(VI) tracer. The main complexity of using redox tracers is that they are initially in the solution whereas indigenous U needs to dissolve first to be able to equilibrate with the tracers which may expose to redox perturbation before U dissolution. In order to estimate U redox shifts and calculate original distribution of U oxidation states in the material, reduction of ²³⁶U(VI) was assumed to be proportional to the indigenous U(VI) reduced at the same time. By measuring the exact amounts of ²³⁶U in both valence fractions one can make simple corrections and calculate the original distribution of U oxidation states (Table 2, Fig. 2). It has to be taken into account that U(IV) and U(VI) fractions are slightly overlapping in the anion exchange step (Hussonnois et al., 1989), which would explain the 1–3% leak of the “wrong” fraction.

Table 3b

Amount of ²³⁶U(VI) tracer reduced during U extraction.

Sample description		Mass (mg)	²³⁶ U(VI) reduced (%)
1	DL-1a	51	18
2		65	30
3		102	33
4		150	42
5		198	41
6		205	42
7		306	60
8		368	80
9		400	72
10		498	81
11	Lignite 2_3	45	0.7
5		203	1.4
6	Lignite 4_1	101	1.2
7		497	0.8

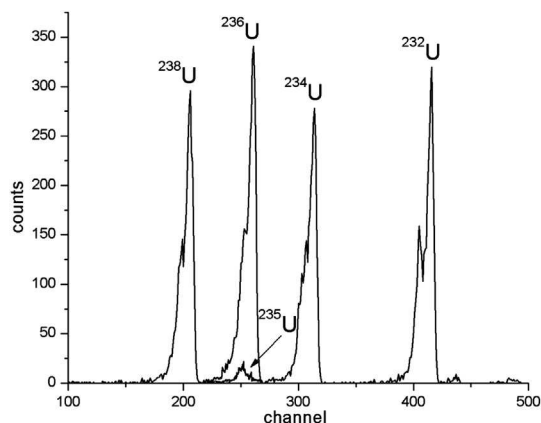


Fig. 1. U isotopes α -spectrum of U(IV) fraction extracted from 500 mg of DL-1a. Both redox tracers ^{236}U and ^{232}U can be seen in the spectrum.

3.2. Annealing experiments

Natural radiation induced processes followed by the decays of U and Th decay series nuclides ionize electrons from atoms of crystalline material like quartz, which are then trapped by negative-ion vacancies in the crystalline lattice defects (Aitken, 1999). Depending on the depth of the traps the storage time of trapped electrons will vary, some traps are sufficiently deep to store charge for geological time periods. When irradiated crystalline material is again heated or exposed to heat or strong light, the trapped electrons are released and can potentially act as a reducing agent. To see if electrons are released from silicate phases during extraction and accepted by U(VI) causing its reduction to U(IV), an annealing experiment was conducted. In the experiment DL-1a material was heated at different temperatures. To detect U redox shifts extraction solution was spiked with $^{236}\text{U(VI)}$. Results showed that after extraction of original DL-1a material (150 mg) 42% of $^{236}\text{U(VI)}$ was reduced to $^{236}\text{U(IV)}$. Reduction of $^{236}\text{U(VI)}$ decreased as a function of annealing temperature, so that at 500 °C or higher temperatures no significant $^{236}\text{U(VI)}$ reduction was observed (Table 5) suggesting the occurrence of the above mentioned process. Another possible explanation for the redox effects observed is the changes heating induced in the mineralogy. The only two prominent phases determined by XRD were muscovite and quartz. The minor phase of

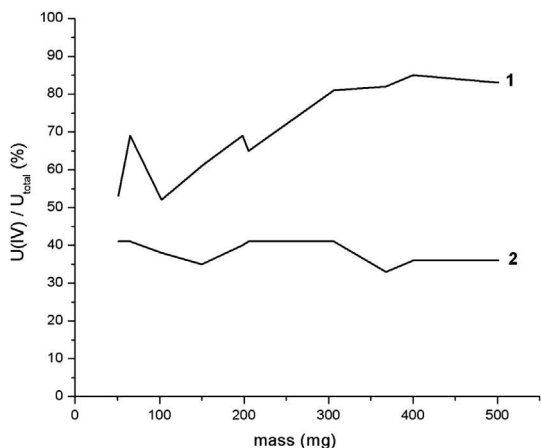


Fig. 2. $\text{U(IV)}/\text{U}_{\text{total}}$ determined for the DL-1a material as a function of sample mass. Curve 1 refers to the results from the direct determination and curve 2 refers to the results corrected with the $^{236}\text{U(VI)}$ tracer.

Table 4

U(IV) distribution in studied material measured by wet chemistry and XANES.

Method and sample description	U(IV)/U _{total} (%)	
	Wet chemistry	XANES
DL-1a original (untreated)	38 ± 2	45 ± 4
DL-1a residue from 4.5 M HCl extraction	100	85 ± 5
- annealed at 300 °C, extracted in 4.5 M HCl	39 ± 2	35 ± 8
- annealed at 500 °C, extracted in 4.5 M HCl	65 ± 3	80 ± 5
- annealed at 1000 °C, extracted in 4.5 M HCl	99 ± 7	95 ± 5
Lignite 4_1 extracted in 4.5 M HCl with ascorbic acid	71 ± 2	93 ± 3
Lignite 3_2 extracted in 4.5 M HCl with ascorbic acid	72 ± 2	94 ± 4

pyrite identified in the material must be the main source of Fe(II) which can reduce U(VI) during extraction. Although heating was performed in the inert atmosphere, a part of Fe(II) in the sulfides might be oxidized by occluded air oxygen and absorbed water in the material (Nordstrom, 1982). Heating at temperatures higher than 500 °C recrystallizes muscovite (Guggenheim et al., 1987). It was reported that full recrystallization of metamict brannerite to its original crystalline state occurs between 970 and 1020 °C stabilizing U in hardly extractable U(IV) state (Balek et al., 2002). XANES showed that all U in a 1000 °C heated sample is U(IV) (Fig. 4). It is likely that both processes, i.e. release of electrons and heating induced changes in mineralogy, can result in the observed perturbations in U oxidation states.

3.3. Sediment samples

For the case of sediment samples all $^{232}\text{U(IV)}$ tracer was seen to oxidize during extraction (Table 3a), suggesting oxidation of indigenous U(IV) too. Because oxidation due to ambient oxygen was prevented a possible oxidizing agent is Fe(III) dissolved from the sample material. However, using the redox tracer alone it was complicated to estimate what part of the indigenous U(IV) had been oxidized during extraction. To facilitate estimation oxidation

Table 5

U redox effects after DL-1a annealing (all samples were about 150 ± 2 mg).

Sample description	U extracted (%)	U(IV)/U _{total} (%)	$^{236}\text{U(VI)}$ in U(IV) fraction (%)
DL-1a original (untreated)	92	38 ± 2	42
- annealed at 300 °C, extracted in 4.5 M HCl	94	39 ± 2	23
- annealed at 500 °C, extracted in 4.5 M HCl	75	65 ± 3	2
- annealed at 1000 °C, extracted in 4.5 M HCl	<1	99 ± 7	1

Table 6

U valent forms distribution with corresponding U isotopic activities ratios for studied sediment samples.

Sample description	Mass (mg)	Ascorbic acid (mg)	AR in U(IV)	U (ppm)	AR in U(VI)	U (ppm)	U(IV)/U _{total} (%)
Lignite 4_1	105	No	0.27 ± 0.01	56	1.12 ± 0.02	87	0.51
	245	No	0.28 ± 0.01	37	0.97 ± 0.03	107	0.6
	104	110	0.31 ± 0.01	86	1.55 ± 0.03	55	0.68
	101	318	0.32 ± 0.01	83	1.58 ± 0.05	50	0.71
Lignite 2_3	58	No	0.51 ± 0.01	263	1.65 ± 0.05	152	0.28
	198	No	0.51 ± 0.02	191	1.15 ± 0.03	320	0.59
	48	49	0.51 ± 0.01	365	1.84 ± 0.03	163	0.7
	42	124	0.52 ± 0.01	408	1.77 ± 0.05	154	0.72

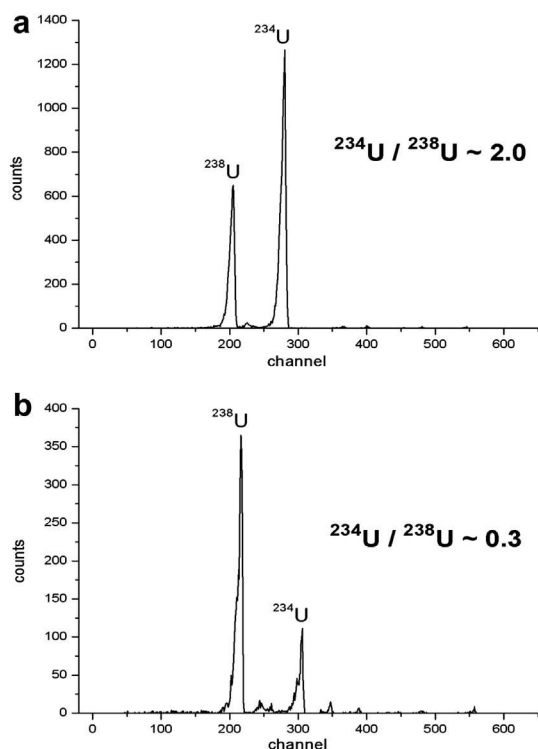


Fig. 3. α -spectra of a) U(IV) and b) U(VI) fractions separated from sediment samples.

by Fe(III) was prevented adding ascorbic acid in the solution before extraction. Ascorbic acid has been reported as a selective reducing agent for Fe(III), while U(VI) stays in its original state (Gavini et al., 1981). The different $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) in samples' own U(IV) and U(VI) fractions, clearly below one in U(IV) and above one in U(VI), that was observed in earlier studies (Noseck et al., 2008) provided an additional tool to assess the redox balance of U. When U was extracted the AR of the U(IV) fraction did not change whereas the AR in the U(VI) fraction decreased as U(IV) oxidized. When ascorbic acid was added to extraction solution the AR in the U(VI) fraction increased notably (Table 6), showing that oxidation of U(IV) and consequent addition of low AR U into extraction solution have been prevented (see an example of respective α -spectra in Fig. 3). However, even excess addition of ascorbic acid could not

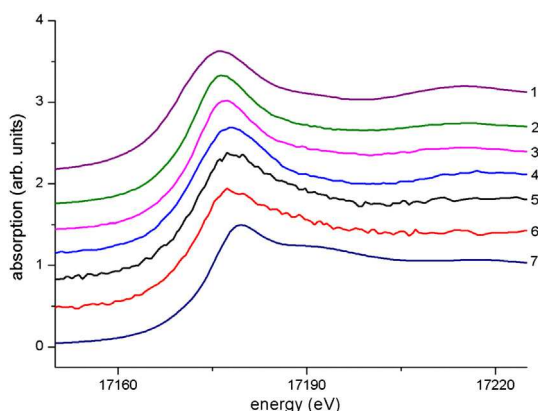


Fig. 4. U L₃ XANES spectra measured at ANKA Synchrotron Center, Karlsruhe Institute of Technology, Germany. (1) U(IV) reference; (2) Lignite 2_3; (3) Lignite 4_1; (4) DL-1a annealed at 1000 °C; (5) Residue left after DL-1a extraction; (6) Original (untreated) DL-1a; (7) U(VI) reference (schoepite).

immediately reduce all Fe(III) and protect part of U(IV) from oxidizing. If taking XANES results (Table 4) as a true value for the U(IV) content, then 20–25% of the U(IV) fraction is still oxidized during the extraction.

4. Summary and conclusions

Wet chemical methods provide a tool to study and determine U oxidation states in geological materials provided that redox perturbations in the analytical procedure can be prevented. Redox effects can be qualitatively and quantitatively determined for a short time extraction experiment using ion-exchange chromatography and alpha-spectrometry techniques. The application of U redox tracers allowed making correction of U redox shifts and transferring wet chemistry results to the original (untreated) solid material state. Some limitations of the method may arise due to the high amount of redox active iron, which may totally oxidize/reduce redox tracers within the duration of the experiment. For more conclusive results experiments with different sample materials and varying experimental conditions (time, sample mass, addition of redox masking agents) are necessary. Good agreement between two independent methods was obtained: an average 38% of U(IV) in DL-1a material for wet chemistry and 45% for XANES. Large error bars from XANES analysis must be taken into account while estimating oxidation state ratio in low U material. For more accurate results synchrotrons with much higher photon flux intensities must be applied.

Acknowledgments

The research leading to these results has received funding from European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007–2011 under grant agreement n° 212287 (RECOSY project) and from the Laboratory of Radiochemistry at the University of Helsinki. We thank the ANKA facility for beamtime and the INE-Beamline staff for their support during XANES experiments.

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