



HAL
open science

Tc interaction with crystalline rock from Äspö (Sweden): Effect of in-situ rock redox capacity

Florian Mathias Huber, Yury Totskiy, Remi Marsac, Dieter Schild, Ivan Pidchenko, Tonya Vitova, Stepan Kalmykov, Horst Geckeis, Thorsten Schäfer

► **To cite this version:**

Florian Mathias Huber, Yury Totskiy, Remi Marsac, Dieter Schild, Ivan Pidchenko, et al.. Tc interaction with crystalline rock from Äspö (Sweden): Effect of in-situ rock redox capacity. *Applied Geochemistry*, 2017, 80, pp.90-101. 10.1016/j.apgeochem.2017.01.026 . insu-01715154

HAL Id: insu-01715154

<https://insu.hal.science/insu-01715154>

Submitted on 22 Feb 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

Tc interaction with crystalline rock from Äspö (Sweden): Effect of in-situ rock redox capacity

Florian Mathias Huber, Yury Totskiy, Rémi Marsac, Dieter Schild, Ivan Pidchenko, Tonya Vitova, Stepan Kalmykov, Horst Geckeis, Thorsten Schäfer



PII: S0883-2927(16)30425-5

DOI: [10.1016/j.apgeochem.2017.01.026](https://doi.org/10.1016/j.apgeochem.2017.01.026)

Reference: AG 3837

To appear in: *Applied Geochemistry*

Received Date: 22 October 2016

Revised Date: 19 January 2017

Accepted Date: 22 January 2017

Please cite this article as: Huber, F.M., Totskiy, Y., Marsac, R., Schild, D., Pidchenko, I., Vitova, T., Kalmykov, S., Geckeis, H., Schäfer, T., Tc interaction with crystalline rock from Äspö (Sweden): Effect of in-situ rock redox capacity, *Applied Geochemistry* (2017), doi: 10.1016/j.apgeochem.2017.01.026.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1 Tc interaction with crystalline rock from Äspö (Sweden):
2 Effect of in-situ rock redox capacity

3
4 Huber, Florian Mathias^{1*}, Totskiy, Yury¹, Marsac, Rémi¹, Schild, Dieter¹, Pidchenko, Ivan¹,
5 Vitova, Tonya¹, Kalmykov, Stepan², Geckeis, Horst¹, Schäfer, Thorsten¹

6
7 ¹ Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, D-76021
8 Karlsruhe, Germany.

9 ² Lomonosov Moscow State University (MSU), Department of Chemistry, Leninskie Gory 1-3, 119991, Moscow,
10 Russia

11
12
13 *corresponding author: florian.huber@kit.edu

14
15
16
17 Karlsruhe Institute of Technology (KIT)
18 Institute for Nuclear Waste Disposal (INE)
19 Hermann-von-Helmholtz-Platz 1
20 76344 Eggenstein-Leopoldshafen
21 Germany
22 Phone: +49 721 60 82 2384
23 Fax: +49 721 60 82 3927

24
25
26

27

28 **Abstract**

29

30 The interaction of Tc(VII) with crushed crystalline rock (Äspö diorite; 1-2 mm size fraction)
31 from the Äspö Hard Rock Laboratory (HRL) (Sweden) was studied by laboratory batch
32 sorption and desorption experiments under Ar atmosphere using both natural and synthetic
33 groundwater. The Äspö diorite used in the experiments was drilled, transported and handled
34 as far as possible under anoxic conditions to preserve the in-situ rock redox capacity. For
35 comparison, identical experiments using artificially oxidized Äspö diorite have been carried
36 out to examine the effect of in-situ redox capacity on Tc uptake. According to the batch
37 studies, Tc(VII) uptake on the Äspö diorite is strongly dependent on redox capacity. Uptake
38 on un-oxidized rock is approximately 2 times higher compared to oxidized rock samples,
39 most likely due to higher Fe(II) contents of the un-oxidized rock. Tc redox states and
40 speciation both on the mineral surface and in the bulk were studied using X-ray
41 photoelectron spectroscopy (XPS) and Tc K-edge X-ray absorption near edge structure
42 (XANES) spectroscopy. The spectroscopic results verify a Tc(VII) reduction to Tc(IV) at the
43 rock surface. Distribution coefficients (K_d) and surface normalized distribution coefficients
44 (K_a) were determined and compared to available literature data. The formation of a Tc
45 colloidal phase was not observed under the geochemical conditions prevailing in the
46 experimental studies. Desorption of Tc is very low under anoxic conditions, but after artificial
47 oxidation Tc mobility is strongly increased. The results of this work clearly highlight the effect
48 of in-situ rock redox capacity on Tc retention.

49

50 1. Introduction

51

52 The generally accepted concept of spent nuclear fuel (SNF) and high-level nuclear waste
53 (HLW) long-term storage is by disposal in deep geological formations at depths of around
54 250 – 1000 meters (IAEA, 2001). The repository host rock as part of a multi-barrier system
55 plays an important role as retention barrier for radionuclide migration. Thus, the selection of
56 the host rock formation with appropriate geochemical and hydrogeological properties is a
57 key challenge during nuclear waste repository siting and it requires comprehensive scientific
58 research. Crystalline rocks (e.g. granites and gneisses) are considered as potential host rock
59 formations for the deep geological disposal in several countries (e.g. Sweden, Finland,
60 Russia, Korea). The work described herein focuses on crystalline rock samples from the Äspö
61 Hard Rock Laboratory (HRL) (Sweden) which is a generic underground research laboratory
62 (URL) located on the Äspö island near Oskarshamn in southern Sweden dedicated to in-situ
63 studies of processes in crystalline formations concerning deep geological disposal of spent
64 nuclear fuel (SKB, 2011). Radionuclide transport depends strongly on the bedrock
65 hydrogeological and geochemical conditions (pH, Eh, and ionic strength) and is governed by
66 different immobilization-remobilization processes (Grambow, 2008). The most important
67 retention processes to be considered in fractured crystalline rocks are sorption to rock
68 surfaces, redox reactions and matrix diffusion (Bodin et al., 2003; Neretnieks, 1980; Xu and
69 Wörman, 1999).

70 ⁹⁹Tc is one of the main long-lived U and Pu fission products in SNF and is also generated by
71 medical laboratories and research institutions. Because of its relatively high fission yield (*ca.*
72 6%) and long half-life (2.1×10^5 years) ⁹⁹Tc is considered as a radioactive component of HLW
73 with significant toxic relevance (Kratz and Lieser, 2013). Technetium mobility in natural
74 systems strongly depends on the redox state. The most stable Tc form under aerobic
75 atmosphere is the pertechnetate ion TcO_4^- , which is very soluble and behaves like a
76 conservative tracer under oxidizing conditions (Rard et al., 1999). In an early work by
77 Bondietti and Francis (1979) using a variety of natural rock materials considerable Tc
78 retention due to reduction of pertechnetate was observed in accordance with Eh/pH

79 conditions. The potential of the TcO_4^-/TcO_2 couple was described with the equation (1)
80 (Meyer and Arnold, 1991):

$$81 \quad E_0(TcO_4^-/TcO_2) = 0.738 - 0.0788 \times pH + 0.0197 \times \log[TcO_4^-] \quad (1)$$

82 Under aerobic conditions, reported K_d values of Tc on crystalline rocks are negligible,
83 < 1 mL/g in Allard et al. (1979) (contact time 1 day) and $< 0.1 - 8.6$ mL/g in Videnska and
84 Havlova (2012) (contact time with granitic rocks up to 94 days), whereas under reducing
85 conditions the values are much higher (50 mL/g in (Allard et al., 1979)). Both batch type
86 sorption and column experiments with Hanford sediments (Um and Serne, 2005; Zachara et
87 al., 2007) have revealed that ^{99}Tc is highly mobile and shows virtually no retardation under
88 fully oxidizing conditions. However, under anoxic conditions TcO_4^- is prone to reduction to
89 Tc(IV) and the solubility is limited by the hydrous oxide solid phase $TcO_2 \cdot 1.6H_2O_{(s)}$ (Meyer et
90 al., 1991). As a consequence, distribution coefficients and apparent diffusion coefficients of
91 technetium reported in the literature on natural minerals are scarce and are rarely published
92 together with the respective pe and pH conditions. Tc redox kinetics strongly depend on the
93 availability of reactive Fe(II) in the host rock and the mineral association and speciation on
94 surface (surface complexed, precipitated, and ion exchangeable) (Fredrickson et al., 2009;
95 Heald et al., 2007; Jaisi et al., 2009; Peretyazhko et al., 2008a; Peretyazhko et al., 2008b;
96 Zachara et al., 2007). Äspö *in-situ* and laboratory migration studies (CHEMLAB-2) using Äspö
97 derived natural groundwater revealed $\approx 1\%$ Tc recovery (after 254 days) of the injected
98 Tc(VII) mass (Kienzler et al., 2003; Kienzler et al., 2009). Batch type studies done in parallel
99 revealed surface normalized distribution coefficients, K_a , values of $\approx 2.1 \times 10^{-3}$ m for ^{99}Tc
100 ($t_{\text{contact}} = 14$ d), whereas altered material showed significantly lower values. These results
101 revealed contact/residence time dependent retardation and/or reduction processes. In all
102 studies mentioned above, though carried out under e.g. Ar atmosphere in glove boxes,
103 crystalline rock material used were exposed for a considerable time to air before the
104 experiment. This circumstance might be one of the most important drawbacks in all batch
105 sorption/desorption studies carried out not only on redox sensitive radionuclides but for
106 redox sensitive heavy metals in general. Due to the drastically increased effort in preserving
107 the natural in-situ rock redox capacity during drilling, transporting and storing of the rock

108 material, almost no studies are available using non-oxidized material. In consequence, the
109 distribution coefficients, sorption and reduction properties and behaviour published in
110 numerous studies could be biased and accompanied with high uncertainties. So far, only one
111 study on U interaction with the same un-oxidized Äspö diorite (ÄD) material (provided by
112 KIT-INE) as used in the present study is available (Schmeide et al., 2014). Therefore, the main
113 motivation of this work is to investigate the effect of in-situ rock redox capacity on
114 technetium sorption behaviour by conducting classical batch experiments using non-oxidized
115 and oxidized rock material, respectively.

116

117 **2. Materials and Methods**

118 **2.1. Radionuclides**

119 *2.1.1. ⁹⁹Tc*

120 All Tc batch experiments with Tc concentration $\geq 10^{-9}$ M have been carried out using a ⁹⁹Tc
121 stock solution (13 mM NaTcO₄) produced at the Institute of Hot Chemistry, Nuclear Research
122 Centre (former FZK, now KIT) (Karlsruhe, Germany). The solubility limit of Tc(IV) in a wide
123 range of pH-Eh conditions covering most of the natural systems is about 4.4×10^{-9} M (Duro et
124 al., 2006). The detection limit of low-background liquid scintillation counting (LSC)
125 (Quantulus, PerkinElmer, Inc., LSC cocktail Ultima Gold) for ⁹⁹Tc measurement is $\approx 10^{-10}$ M.

126 *2.1.2. ^{95m}Tc*

127 For experiments with Tc concentrations lower than 10^{-9} M, ^{95m}Tc with a much shorter half-
128 life (61 day) and a main gamma emission line at 204.1 keV was applied. The isotope was
129 produced by proton irradiation of natural Mo foil (50 μ m thickness) containing the natural
130 isotopic composition at ZAG Zyklotron AG (Karlsruhe, Germany). After cooling the foil was
131 transported to the Institute for Nuclear Waste Disposal (KIT-INE) and processed to separate
132 technetium according to the technique of (Boyd et al., 1960). The foil was dissolved in a
133 mixture of concentrated H₂SO₄ and 30% H₂O₂ and afterwards was slowly neutralized with
134 saturated NaOH (up to alkaline pH). The obtained alkaline solution was passed through a
135 column filled with the anion exchanger Dowex 1x8 (100-200 mesh particle size) with a total

136 volume ca. 3 mL. The column was washed first with 20 mL 1 M $K_2C_2O_4$ to remove residues of
137 molybdate and after rinsing with 20 mL of MilliQ water pertechnetate was eluted with 30 mL
138 1 M $HClO_4$. The last fraction was collected into 2 mL vials, which were measured with γ -
139 spectrometry and samples with ca. 90% of ^{95m}Tc were combined and neutralized with
140 concentrated NaOH. The purification level was monitored with ICP-MS and γ -spectrometry.
141 The use of another column filled with Teva[®] Resin (Eichrom Technologies, LLC) prior to
142 Dowex significantly increased chemical purity of Tc. Technetium separation on Teva Resin
143 column was performed from ≈ 1.5 M HNO_3 media and after washing the column with 2 M
144 HNO_3 Tc was eluted with 8 M HNO_3 according to the technique reported by (Tagami and
145 Uchida, 1999). A further separation step on the Dowex column results in the purification
146 from NO_3^- , which may act as undesired oxidizing agent, being absent in natural deep
147 geological anoxic groundwaters. The nitrate concentration was initially controlled with
148 nitrate test strips (Merck) and subsequent ion chromatography (IC) analysis. Detection limit
149 of gamma spectrometric analysis of ^{95m}Tc using a 10 mL vial geometry and a high-purity
150 germanium (HPGe) semiconductor detector was estimated to be $\approx 10^{-14}$ - 10^{-15} M (three hours
151 measurement time) depending on the age of the stock solution.

152 **2.2. Solid materials**

153 *2.2.1. Äspö diorite*

154 Diorite is the dominating rock type in the Äspö area (Kornfält et al., 1997). The general
155 mineralogical characterization of ÄD is presented in Table 1. Fresh Äspö diorite was obtained
156 from a drilling campaign at the Äspö HRL (Sweden) in 2011 within the EU project CP CROCK.
157 Details of the sampling procedure and material characterization were originally published
158 within a CROCK S&T contribution (Schäfer et al., 2012). During the core drilling, special care
159 was taken to minimize the exposure of the solid material to air. Therefore, the drilling
160 procedure was carried out with a double tube technique preserving to the best possible
161 anoxic conditions. Natural Äspö groundwater ($Eh_{SHE} \approx -240$ mV) permanently bubbled with N_2
162 was used as a drilling fluid. After a short visual inspection (max. 5 min) under tunnel
163 atmosphere the cores were directly transferred into a transparent LD-PE bag, which was
164 evacuated three times (≈ -0.4 bar) and purged with nitrogen gas before

165 **Table 1.** Petrographic characterization of Äspö diorite (Byegård et al., 1998; Kornfält et al.,
166 1997).

Material	Rock type	Mineralogical composition, %	Structural characteristic
Äspö diorite	Quartz monzodiorite/ granodiorite	Plagioclase, Quartz, K-feldspar, Biotite, Epidote, Amphibole (mainly hornblende), < 10 Muscovite, titanite, apatite, fluorite, zircon, magnetite	30-50 10-25 10-30 10-25 3-15 Porphyritic, medium-grained

167

168 welding. The same procedure was applied with an Al bag for the second confinement to
169 prevent oxidation during transportation to the KIT-INE laboratories (see Figure A.1, bottom).
170 At KIT-INE the cores were stored in a barrel under Ar atmosphere (≈ 1 bar overpressure).
171 Two Äspö diorite drill cores (borehole KA2368A-01, cores #1.32 and #1.33) were selected for
172 the experiments. Both cores were chosen because of their (maximal) distance to the tunnel
173 wall (13.04 – 13.52 m (core #1.32) and 13.52 – 14.00 m (core #1.33)) and their petrological
174 characterization (fresh Äspö diorite) during the drilling campaign (Figure A.1, top and
175 middle). For preparation of the crushed material, the cores were transferred into an Ar
176 glovebox equipped with a circular diamond saw and cut into small discs (0.5-1 cm in width).
177 These discs were then manually crushed with a hammer and separated into several size
178 fractions by sieving. For the sorption experiments the 1-2 mm size fraction in diameter was
179 chosen. The N_2 -BET surface area of $0.16 \text{ m}^2/\text{g}$ was measured for this size fraction. This un-
180 oxidized crushed material was stored permanently in the glovebox under Ar atmosphere (≤ 1
181 ppm O_2). Part of this crushed diorite material was exposed to air for one week for artificial
182 surface oxidation to investigate the influence of sample preservation and preparation on Tc
183 uptake. The chemical composition of the rock material used was determined at the Institute

184 for Geosciences, Johannes Gutenberg University (Mainz, Germany) by X-Ray fluorescence
185 (XRF) spectrometry (spectrometer MagiXPRO, Philips) with a Rh anode operated at 3.2 kW).
186 In Table A.1 the XRF data for the material studied is compared to the oxidized Äspö diorite
187 used by Huber et al. (2012) and Huber et al. (2010) and to material from (Byegård et al.,
188 1998). A typical granodiorite composition (Nockolds, 1954) is also added in Table A.1 for
189 comparison. The general composition of the ÄD is typical of granitic rocks with high amount
190 of SiO₂ and Al₂O₃ (quartz and feldspar) (Nockolds, 1954). The Fe²⁺ content of the solid phases
191 was measured by cerimetric titration (cerate oximetry) with potentiometric end point
192 determination (Close et al., 1966). The new un-oxidized ÄD shows a much higher amount of
193 ferrous iron ($\approx 39\%$ Fe²⁺/Fe_{tot} vs. $\approx 27\%$ in old ÄD samples) compared to the old oxidized ÄD.
194 This result gives confidence in the approach carried out to preserve the in-situ rock redox
195 capacity. In the work from (Byegård et al., 1998) no information on Fe(II) compounds were
196 reported. In order to estimate the cation exchangeable Fe(II) amount on the mineral
197 surfaces of the Äspö diorite, a method proposed by Heron et al. (1994) was applied using
198 10 mL 1 M CaCl₂ (pH = 7) in contact with 2 g of granite for 24 h. Afterwards, an aliquot was
199 taken for Fe(II) quantification by the ferrozine technique. The analytical procedure of the
200 ferrozine technique is described in Viollier et al. (2000). Additionally, Fe data on the new un-
201 oxidized and old oxidized ÄD material determined by XRF are given in the Table A.1, showing
202 that the overall Fe(II) redox buffer is drastically reduced for the oxidized samples. The ion-
203 exchangeable Fe(II) fraction for the un-oxidized ÄD was quantified at approx. 4–6 µg/g,
204 whereas for the oxidized samples lower values around 1–3 µg/g for ÄD are obtained. The
205 rather high uncertainty in the measurements is attributed to the natural heterogeneity of
206 the rock material. The content of ion-exchangeable Fe(II) is about three orders of magnitude
207 lower than Fe(II) amount in the bulk obtained by XRF (see Table A1). However, the ratio
208 between Fe(II) content in fresh and oxidized materials of the order of three is similar for
209 both types of measurements.

210 **2.3. Groundwater**

211 Different types of groundwater have been used in the experimental program. Besides the
212 natural Äspö groundwater (ÄGW) a synthetic groundwater simulant (ÄGWS) has been
213 prepared to mimic the CROCK drilling site outflow groundwater composition (see Schäfer et

214 al. (2012)). All chemicals used in the preparation of the synthetic groundwater were of
 215 analytical grade. Solutions were prepared with deionized Milli-Q water which was stripped
 216 with Ar prior to use. ÄGWS has a comparable composition to natural Äspö groundwater
 217 sampled *in-situ* from borehole KA3600-F-2 sampled in a Ar pre-flushed 50 L Teflon-coated Al-
 218 barrel at the CP-CROCK site (Heck and Schäfer, 2012). Chemical compositions of the ÄGWS
 219 used and natural groundwater samples from Äspö and Grimsel (GGW) (glacial melting water
 220 analogue with low ionic strength) are presented in Table 2. Relatively high Eh values of
 221 ÄGWS and GGW is explained by the low concentration of the redox couples (e.g.
 222 Fe(II)/Fe(III)) in the solution, which cannot be measured using a Pt-electrode.

223 **Table 2.** Overview of the chemical compositions of the synthetic Äspö groundwater simulant (GWS),
 224 Äspö groundwater and Grimsel groundwater, respectively.

	synth. Äspö GWS	Synth. Äspö GWS after 122h contact time	Äspö GW (KA-3600-F-2)	Grimsel GW (MI-shear zone)
pH	8.0 ± 0.05	8.0 ± 0.05	7.8 ± 0.05	9.67 ± 0.05
Eh	390 ± 50mV	n.m.	-240 ± 50mV	320 ± 50mV
[Mg ²⁺]	104 ± 1.0 mg/L	104.6 mg/L	69.4 mg/L	12.6 µg/L
[Ca ²⁺]	1109 ± 94 mg/L	1134 mg/L	1135 mg/L	5.3 µg/L
[K ⁺]	19.35 ± 3.86 mg/L	21.56 mg/L	10.5 mg/L	
[Li ⁺]	2.53 ± 0.04 mg/L	2.50 mg/L	6.0 mg/L	
[Fe ^{2+,3+}]	n.m.	n.m.	0.2 mg/L	< D.L.
[Mn]	2.32 ± 3.02µg/L	23.8 µg/L	0.338 mg/L	< D.L.
[Sr ²⁺]	19.68 ± 0.29 mg/L	20.14 mg/L	19.9 mg/L	182 µg/L
[Cs ⁺]	<D.L.	< D.L.		0.79 µg/L
[La ³⁺]	n.m.	n.m.		< D.L.
[U]	0.05 ± 0.01 µg/L	1.70 µg/L	0.11 µg/L	0.03 µg/L
[Th]	0.02 ± 0.01 µg/L	0.07 µg/L	< 0.01 µg/L	< 0.01 µg/L
[Al ³⁺]	182.8 ± 56.3 µg/L	439.6 µg/L	13.3 µg/L	42.9 µg/L
[Na ⁺]	1929 ± 29 mg/L	1905 mg/L	1894 mg/L	14.7 mg/L
[Cl ⁻]	4749 ± 145 mg/L	4895 mg/L	4999 mg/L	6.7 mg/L
[Si]	n.m.	n.m.	4.7 mg/L	5.6 mg/L
[SO ₄ ²⁻]	409 ± 5.0 mg/L	411.88 mg/L	394.4 mg/L	5.8 mg/L
[F ⁻]	1.97 ± 0.09 mg/L	1.98 mg/L	1.41 mg/L	6.3 mg/L
[Br ⁻]	21.17 ± 0.37 mg/L	20.96 mg/L	23.2 mg/L	
[NO ₃ ⁻]	n.m.	n.m.	n.m.	< D.L.

[HCO ₃]	n.m.	n.m.	n.m.	3.0 mg/L
[B]	306.5 ± 212.5 µg/L	146.1 µg/L	885 µg/L	

225 n.m. – not measured; D.L. – detection limit.

226

227 **2.4. Batch experiments**

228 *2.4.1. Sorption experiments*

229 Before the start of the batch sorption kinetic experiments the crushed material was
 230 contacted with relevant groundwater simulant (GWS) for one day and exchanging the water
 231 five times. This step was conducted to remove any remaining fines/colloids from the sieving
 232 procedure. In case of un-oxidized ÄD the last step was performed with natural ÄGW to
 233 establish more realistic conditions. All batch experiments were carried out in 20 mL LSC vials
 234 (HDPE, Zinsser©) inside an Ar glovebox with O₂ concentrations ≤ 1 ppm at room
 235 temperature (20 ± 2° C). The solid-liquid ratio chosen was 2.00g of granitic rock and 8.0mL of
 236 groundwater (250 g/L). Sample duplicates were prepared and kept closed during the
 237 sorption experiments to prevent oxidation of Fe(II) at the mineral surfaces. All sorption
 238 experiments were conducted at pH 8.1 ± 0.05. Tc(VII) concentrations of 1x10⁻⁵M, 1x10⁻⁸M
 239 and 1x10⁻⁹M were used in the experiments. For measurement of ⁹⁹Tc content in the sample
 240 supernatant after the desired contact time 1 mL aliquots were taken and added to 10 mL of
 241 Ultima Gold LSC cocktail for analysis with LSC. To differentiate between potentially formed
 242 colloidal phases (e.g. Tc(IV) eigencolloids) and dissolved species a phase separation by
 243 ultracentrifugation (Beckman Optima XL-90, 90,000 rpm, 694,000 × g) for 1 h was applied.
 244 Redox potential of selected samples was measured in the Ar glovebox by using a Metrohm
 245 (Ag/AgCl, KCl (3 M)) electrode. The measurements were performed directly in the sample
 246 without phase separation. The Eh values were recorded every hour and then corrected for
 247 the standard hydrogen potential (Eh always denotes corrected Eh_{SHE} in this work). The Eh
 248 values were recorded after ca. 1 hour contact time. The redox potential measurements in
 249 the sorption experiments samples were carried out after about two weeks and 1 month
 250 contact time, respectively. Every sample was measured over a period of one day in the open
 251 vial in the Ar glovebox (< 1 ppm O₂) to monitor the Eh evolution. A typical time dependent
 252 Eh evolution is shown in Figure 1. The initial drop in Eh is likely due to the equilibration of

253 the electrode with the solution, whereas the continuous drift to more oxidizing potentials in
 254 the later period might be explained to be a result of oxidation due to traces of oxygen in the
 255 Ar glovebox ($< 1 \text{ ppm O}_2$) that seems to be enough to compensate the redox capacity of the
 256 sample within 24 hours. Therefore, the lowest Eh value detected was used as most
 257 representative for the undisturbed rock/water system in the closed vials.

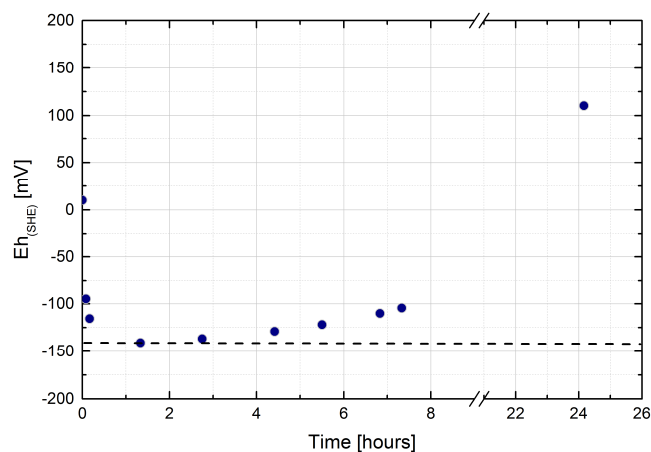


Figure 1: Typical evolution for Eh measurement in synthetic Äspö groundwater simulant with unoxidized diorite sample ($[Tc] = 10^{-10} \text{ M}$). Dashed line marks the Eh value chosen as the final one.

258 2.4.2. Desorption experiments

259 Subsequent to the sorption kinetic experiments, desorption kinetic studies have been
 260 conducted. The Tc containing supernatant of the sorption experiment samples (samples with
 261 3 months contact time in the sorption kinetic experiments) was removed and 8 mL of fresh
 262 Tc-free groundwater added (natural ÄGW and Grimsel groundwater (glacial meltwater
 263 analogue)). For each contact time, the supernatant was always completely removed,
 264 analysed by LSC and substituted with fresh Tc-free groundwater of the same volume. A
 265 subset of the samples was oxidized under air for one month after the sorption experiments.
 266 For this, the initial Tc-containing liquid phase was removed and dry material in the vial was
 267 exposed to air before the fresh Tc-free groundwater was added under aerobic atmosphere.
 268 For this experiment ÄGWS was used instead of natural ÄGW to keep oxidizing conditions.
 269 Desorption experiments cover a time range between a few seconds and 1 month contact
 270 time.

271 **2.5. X-ray spectroscopy**272 *2.5.1. X-ray photoelectron spectroscopy (XPS)*

273 To examine the Tc surface speciation X-ray photoelectron spectroscopy (XPS) was applied.
274 For XPS analysis small un-oxidized Äspö diorite fragments with unpolished faces after cutting
275 by circular saw were contacted with 10^{-5} M Tc(VII) in ÄGWS for two months and washed by
276 MilliQ water for a few seconds to prevent salt precipitation directly before the XPS analysis.
277 All preparation and measurement steps were performed under Ar atmosphere. Transport of
278 the samples from the Ar glovebox to the XPS spectrometer under anoxic atmosphere was
279 achieved by using an O-ring sealed vacuum transfer vessel (PHI model 04-110). XPS
280 measurements were carried out with the XPS system PHI 5000 VersaProbe II (ULVAC-PHI
281 Inc.) equipped with a scanning microprobe X-ray source (monochromatic Al K_{α} (1486.6 eV) X-
282 rays) in combination with an electron flood gun and a floating ion gun generating low energy
283 electrons (1.1 eV) and low energy argon ions (8 eV) for charge compensation at isolating
284 samples (dual beam technique), respectively. The angle between sample surface and
285 analyser was set to 45°. Survey scans were recorded with an X-ray source power of 12 W and
286 pass energy of 187.85 eV. Narrow scans of the elemental lines were recorded at 23.5 eV pass
287 energy. All spectra were charge referenced to C 1s (hydrocarbon) at 284.8 eV. Data analysis
288 was performed using ULVAC-PHI MultiPak program, version 9.5.

289 *2.5.2. X-ray absorption spectroscopy (XAS)*

290 XAS experiments were performed at the INE-Beamline at the ANKA 2.5 GeV synchrotron
291 radiation facility, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. The detailed
292 description of the instrumental setup of the INE-beamline is presented in Rothe et al. (2012).
293 Tc K-edge (21,044 eV) X-ray absorption near edge structure (XANES) spectra were collected
294 in fluorescence mode using one element VITUS Vacuum-Silicon Drift Detector (SDD, Munich,
295 Germany). The uranium mineral meta-schoepite ($\text{UO}_3 \cdot n\text{H}_2\text{O}$) was measured simultaneously
296 with all samples and the Tc(IV) and Tc(VII) references. Pertechnetate solution with
297 concentration of 10^{-2} M was taken as a Tc(VII) reference and $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}_{(s)}$ solid phase was
298 prepared by TcO_4^- reduction in the electrochemical cell and used as Tc(IV) reference. The U
299 L_2 (20,948 eV) edge XANES spectra were used for energy calibration. The set of samples with

300 Tc concentrations of $\approx 10^{-3}$ M contacted with crystalline rock materials was prepared and
 301 mounted in an inert gas cell under argon atmosphere (see Table 3 for an overview of all XAS
 302 samples and references measured). During the measurements, argon continually flowed
 303 through the cell. Data reduction and normalization was performed with the ATHENA
 304 program part of the IFEFFIT software package (Ravel and Newville, 2005).

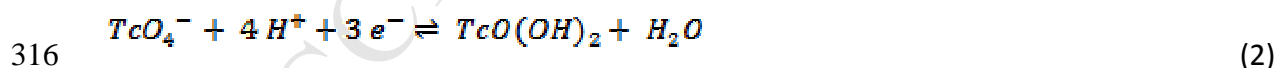
305 **Table 3.** List of samples studied by XAS.

Sample	[Tc], M	Description
Tc(VII) reference	0.01	TcO ₄ ⁻ solution
Tc(IV) reference	-	Solid TcO ₂ covered with supernatant
Tc on ÄD	0.001	Centrifuged suspension

306 2.6. Thermodynamic modelling

307 Geochemical speciation calculations and sorption modelling were conducted with the
 308 geochemical speciation code PHREEQC (version 2) (Parkhurst and Appelo, 1999). The SIT
 309 database provided with PHREEQC is used, in which the thermodynamic constants for Tc
 310 correspond to the ones selected by the NEA Thermochemical Database (Guillaumont et al.,
 311 2003). Pourbaix diagrams were calculated and plotted with “Geochemist’s Workbench”
 312 (version 8.0, Aqueous Solution LLC) code with the default database thermo.dat also modified
 313 for Tc species in accordance with NEA Thermochemical Database (Guillaumont et al., 2003).

314 Under the applied experimental conditions TcO₄⁻ and TcO(OH)₂ are the only relevant
 315 dissolved species for Tc(VII) and Tc(IV), respectively. The redox reaction is:



$$317 \quad K_{\text{VII/IV}} = \frac{[\text{TcO(OH)}_2]}{[\text{TcO}_4^-][\text{H}^+]^4[\text{e}^-]^3} \quad (3)$$

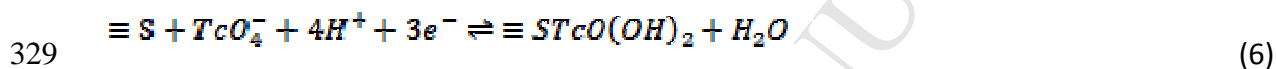
318 where $K_{\text{VII/IV}}$ is the conditional constant of reaction (2) at a given ionic strength. From here
 319 the pe (pe = $-\log a_{\text{e}^-}$ = 16.9×Eh at 25°C) is calculated according to the following equation:

$$pe = \left(\log K_{VII/IV} + \log \left(\frac{[TcO_4^-]}{[TcO(OH)_2]} \right) - 4pH_e \right) / 3 \quad (4)$$

where $pH_c = -\log [H^+]$. The pe corresponding to the 50/50% Tc(VII)/Tc(IV) borderline on a Pourbaix diagram pertaining only to the aqueous species (denoted pe_{aq} or Eh_{aq} for redox potential) is found as follows:

$$pe_{aq} = (\log K_{VII/IV} - 4pH_c) / 3 \quad (5)$$

Sorption of Tc(IV) onto mineral surfaces can also be taken into account. Because this study is restricted to $pH \approx 8$ and low ionic strength for the sorption studies, no surface site protolysis or electrostatics are taken into account. We have considered the following simple reaction (6) to describe sorption onto the mineral surface:



where $\equiv S$ is a generic surface site and $[\equiv S]$ can be calculated using equation (7) with the following parameters: site density: 1 site/nm²; surface area: 0.16 m²/g; S/V: 250 g/L.

$$[\equiv S] = \text{site density} \times \text{surface area} \times (S/V) / N_A = 6.64 \times 10^{-5} \text{ mol/L} \quad (7)$$

where N_A is the Avogadro constant. A similar surface complexation approach was proposed by (Cui and Eriksen, 1996) for Tc uptake by Fe(II)-bearing minerals. According to the reaction (6) the reaction constant is calculated as (8):

$$K_{VII/IV, surf} = \frac{[\equiv STcO(OH)_2]}{[\equiv S][TcO_4^-][H^+]^4[e^-]^3} \quad (8)$$

Tc(IV) uptake on mineral surfaces is high (Westsik Jr et al., 2014), so $[\equiv STcO(OH)_2]$ is expected to be much larger than $[TcO(OH)_2(aq)]$. By contrast, Tc(VII) uptake on minerals can be neglected (Wildung et al., 2004). Using the surface complexation model, the Tc(VII)/Tc(IV) borderline on a Pourbaix diagram accounting for both processes in solution and at the mineral surfaces (denoted pe_{surf} or Eh_{surf}) is calculated as follows:

$$pe = \left(\log K_{VII/IV, surf} + \log \left(\frac{[TcO_4^-]}{[=STcO(OH)_2]} \right) - 4pH_e + \log[=S] \right) / 3 \quad (9)$$

$$pe_{surf} = (\log K_{VII/IV, surf} - 4pH_e + \log[=S]) / 3 \quad (10)$$

In other words, pe_{surf} is the pe value for 50% Tc uptake. Equation (10) applies only for sufficiently low $[Tc]_{tot}$ or high E_h , i.e. where the precipitation of $TcO_2 \cdot 1.6H_2O_{(s)}$ does not occur. Note that, in a modelling study of plutonium (Pu) uptake on kaolinite, (Marsac et al., 2015a) calculated borderlines between two Pu oxidation states pertaining only to the speciation at the kaolinite surface. Such type of calculation cannot be made in our study because Tc(VII) uptake on minerals is unlikely to be quantifiable, in contrast to the relevant Pu oxidation states.

3. Results

3.1. Batch sorption studies

3.1.1. Sorption on Äspö diorite

In the following the term “sorption” implies the total Tc uptake by the solid phase independent of the underlying process (sorption only or reductive sorption). Time dependent sorption of different Tc(VII) concentrations onto oxidized and un-oxidized ÄD are given in Figure 2 for $[Tc]_{tot} = 10^{-5}$ (Figure 2a), 10^{-8} (Figure 2b) and 10^{-9} M (Figure 2c). From the Tc sorption kinetic experiments, it is evident that Tc uptake on un-oxidized material is much higher than the artificially oxidized one. For the sample series of 10^{-8} M and 10^{-9} M $[Tc]_{tot}$ on un-oxidized material plateau values close to 100% sorption are obtained (after 90 days contact time), whereas during the same observation period in experiments with oxidized ÄD only $\approx 40\%$ are removed from solution. Reaching the plateau value for Tc uptake takes more time at lower $[Tc]_{tot}$ concentration. In samples with 10^{-5} M Tc much less relative uptake is observed showing a plateau level for sorbed Tc of around 20 – 25% for the un-oxidized samples and $\approx 10\%$ for the oxidized samples. The steady state is reached after approximately seven days which is much faster than observed for experiments with lower $[Tc]_{tot}$.

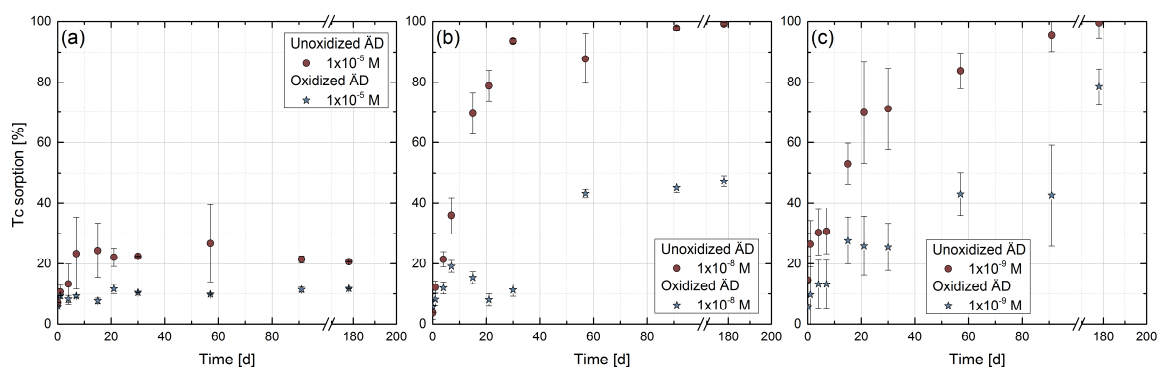


Figure 2. Tc sorption kinetics for different Tc concentrations in presence of oxidized and un-oxidized ÄD (pH 8, $I = 0.2$ M).

367 The formation of colloidal Tc phases (eigencolloids) examined by comparison of Tc
 368 concentration in ultracentrifuged to non-ultracentrifuged samples was not detectable within
 369 the uncertainty limits (± 5 -10%). Either these colloidal phases are not formed or are not
 370 stable under the Äspö GWS conditions chosen (ionic strength ≈ 0.2 M, pH 8).

371 Redox potential measurements of Tc containing ÄGWS after two weeks and 1 month
 372 equilibration time with oxidized and un-oxidized ÄD for three different $[Tc]_{tot}$ are shown in
 373 Figure 3, together with Pourbaix diagrams calculated for the ÄGW composition. For the
 374 oxidized ÄD material the redox potential (E_{SHE}) does not change significantly as a function
 375 of Tc concentration and is within the range of +230 to +280 mV. However, for un-oxidized
 376 ÄD material two trends were observed during the Eh measurements: (a) for low Tc
 377 concentration (up to 10^{-8} M) the Eh value decreases with time from 14 days to one month
 378 and (b) for the highest Tc concentration used (10^{-5} M) the Eh value was unchanged within
 379 the analytical uncertainty. Based on the measured redox potentials in combination with
 380 thermodynamic considerations the following conclusions can be drawn (at least after 2
 381 weeks contact time): (i) for $[Tc] = 10^{-9}$ M Tc(VII) is reduced to a Tc(IV) species in solution
 382 whereas (ii) for $[Tc] = 10^{-8}$ M Tc(IV) precipitates as a solid phase. In case of Tc = 10^{-5} M (iii)
 383 Tc(VII) might not be fully reduced to Tc(IV) since the measured E_{SHE} values are above the
 384 borderline. Nevertheless, a fraction of Tc(VII) might be reduced since the borderline
 385 represents already 50%/50% Tc(VIII)/Tc(IV). In this case the reduced Tc precipitates as a
 386 Tc(IV) solid phase.

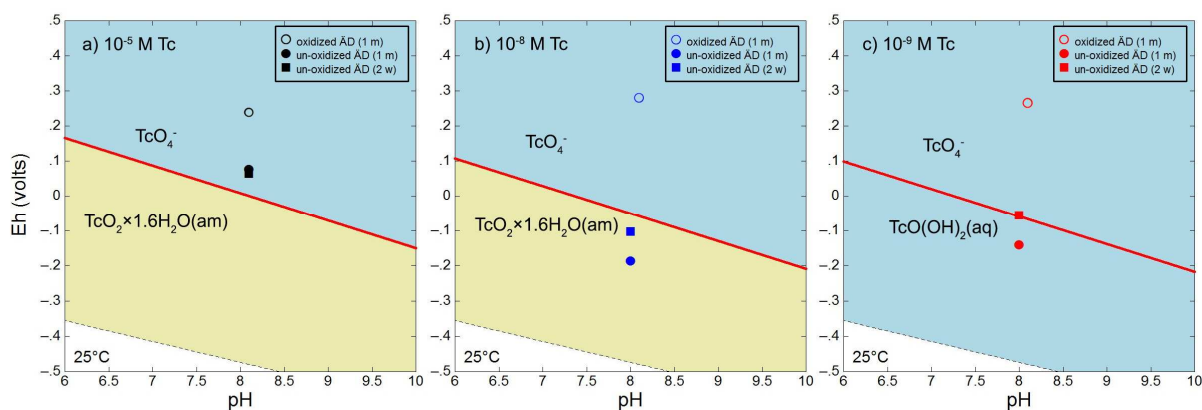


Figure 3. Pourbaix diagrams for ÄGWS containing different Tc concentrations: (a) 10^{-5} M, (b) 10^{-8} M and (c) 10^{-9} M. Data points are given for oxidized (open symbols) and un-oxidized (filled symbols) ÄD for a contact time of two weeks (squares) and one month (circles).

387 3.2. Desorption studies

388 3.2.1. Desorption experiments without artificial oxidation

389 Tc desorption was experimentally monitored over one month using sorption samples for
 390 which Tc had been previously equilibrated with rock material for three months. Very low Tc
 391 desorption was observed in all cases studied irrespective of the nature of the material
 392 (oxidized or un-oxidized) used for sorption. For the case of ÄD samples two types of natural
 393 groundwater were used, namely Äspö and Grimsel GWs (representing glacial melt water
 394 composition with low ionic strength, see Table 2). Tc was detected in the liquid phase only
 395 for samples after contact with 10^{-5} M Tc ÄGWS (Figure 4). After 1 day contact time
 396 desorption achieved values of up to 7% of the Tc amount sorbed after the uptake studies.
 397 This level remained relatively stable up to 30 days of contact time. For lower Tc
 398 concentrations (10^{-8} M and 10^{-9} M initial concentration for sorption experiments) no
 399 desorption was detected with the detection limit of the analytical method.

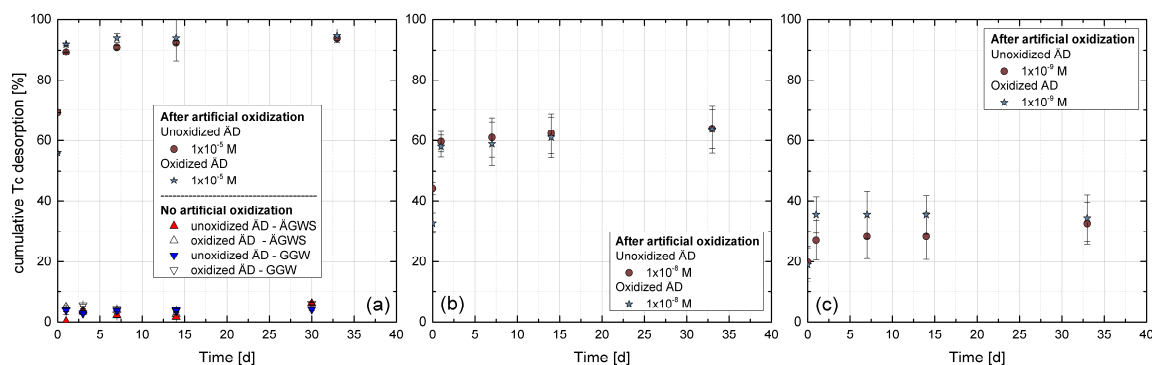


Figure 4. Desorption of Tc sorbed to oxidized and un-oxidized ÄD material by ÄGWS after 1 month pre-oxidation under atmospheric conditions. Results of the experiment after artificial oxidation and contact with ÄGWS and GGW are additionally included in (a). Please note, that these data points have the unit “% desorbed”.

400 3.2.2. Desorption experiments with artificial oxidation

401 Desorption kinetics for ÄD with different $[Tc]_{initial}$ after sample pre-oxidation is given in Figure
 402 4. Pre-oxidation of the ÄD samples under aerobic conditions for 1 month before addition of
 403 ÄGWS changed the Tc desorption behaviour drastically (Figure 4). Both sorption experiments
 404 with originally oxidized and un-oxidized materials revealed the same desorption behaviour.
 405 Desorption is fast with the main part of technetium being released after a few seconds
 406 contact time and after one day a concentration plateau value was reached.

407 3.3. Spectroscopic analyses

408 3.3.1. X-ray photoelectron spectroscopy (XPS)

409 XPS analysis of an un-oxidized ÄD disc fragment after contacting with 10^{-5} M Tc(VII) in ÄGWS
 410 for 2 months under Ar atmosphere in the glovebox revealed that Tc is associated to mafic
 411 (dark) minerals only (see Figure A.2), whereas on felsic (light) minerals no Tc was found.
 412 Figure 5 (left) shows the measured Tc 3d XPS spectra with the characteristic $3d_{3/2}$ and $3d_{5/2}$
 413 peak

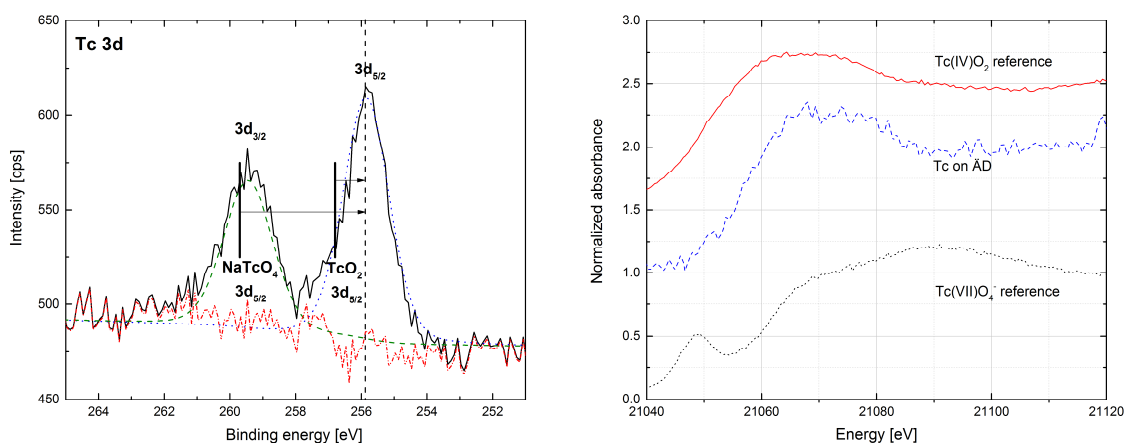


Figure 5. (left) Tc 3d XPS narrow scan spectrum of an ÄD sample after contacting with Tc(VII)-containing ÄGWS. The green (dashed) and blue (dotted) curves show the fits to the $3d_{3/2}$ and $3d_{5/2}$ XPS elemental lines, respectively, the red line represents the residuum. (right) Normalized Tc K-edge XANES spectra of a sample after sorption of Tc onto ÄD and of Tc(IV) and Tc(VII) references.

414 positions. Due to the rather low Tc concentration used in the sorption experiment on the ÄD
 415 disc the spectra is quite noisy. Both Tc(VII) and Tc(IV) should have two 3d peaks ($3d_{5/2}$ and
 416 $3d_{3/2}$) for each oxidation state. Since there are only two peaks in the area of interest, the
 417 conclusion is that there is only one Tc oxidation state present at the mineral surface, and the
 418 position of Tc(IV) $3d_{5/2}$ (TcO_2) at 256.8 eV reference line is closer to the experimental data
 419 (255.9 eV) than the Tc(VII) $3d_{5/2}$ (NaTcO_4) 259.7 eV reference line. It was therefore
 420 concluded that Tc found on the ÄD surface is in the tetravalent oxidation state. Binding
 421 energy reference lines for TcO_2 and NaTcO_4 were taken from (Wester et al., 1987).

422 3.3.2. X-ray absorption near-edge structure (XANES)

423 XANES analysis provides bulk information on the Tc oxidation states after interaction of 10^{-3}
 424 M Tc with ÄD. Normalized Tc K-edge XANES spectra are presented in Figure 5 (right) for Tc
 425 on ÄD together with Tc(IV) and Tc(VII) references. The Tc K-edge XANES spectra of the TcO_2
 426 and TcO_4^- reference materials have characteristic spectral features, which readily allow Tc
 427 oxidation state characterization. For example, the spectrum of the Tc(VII) reference, where
 428 Tc is surrounded by four oxygen atoms in tetrahedral conformation, exhibits a pre-edge
 429 absorption resonance at about 21,050 eV generated by the $1s \rightarrow 5p/4d$ transition (Altmaier

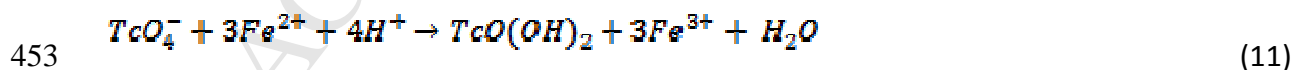
430 et al., 2011b). Since Tc(IV) generally possesses octahedral coordination, this transition is
 431 forbidden and the pre-edge feature cannot be seen in the spectrum of the Tc(IV) reference
 432 compound. The overall shape and energy position of the rising absorption edge of the Tc K-
 433 edge XANES spectrum of Tc on Äspö diorite is similar to the TcO₂ reference without the pre-
 434 edge feature of Tc(VII). These fingerprint approach allows to identify Tc(IV) as dominating Tc
 435 species on ÄD in line with the XPS results.

436 4. Discussions

437 4.1. Tc uptake mechanisms

438 The spectroscopic investigations described above together with the batch
 439 sorption/desorption experimental results and the thermodynamic calculations demonstrate
 440 that Tc retention in a reducing condition is always coupled to a reduction process from
 441 Tc(VII) to Tc(IV). Tc(VII) shows no or only very weak sorption. Thus, the mechanism leading
 442 to the removal of Tc from solution may be attributed to (i) a sorption/surface complexation
 443 of a Tc(IV) species after reduction in solution by e.g. dissolved Fe(II) and/or (ii) precipitation
 444 of poorly soluble TcO₂·1.6H₂O_(s) again due to Tc(VII) reduction in solution by e.g. dissolved
 445 Fe(II) species. Especially in those experiments with the highest Tc concentration a
 446 reduction/precipitation process might occur, as the Tc(IV) solubility limit of 4.4×10⁻⁹ M (Duro
 447 et al., 2006) should be significantly exceeded in case of reduction. A third possible
 448 mechanism of Tc retention could be (iii) the Tc(VII) reduction by structurally bound or
 449 surface bound Fe(II) species. A general scheme of the processes potentially involved into
 450 Tc(VII) immobilization is shown in Figure 6.

451 Considering only Fe(II) as a potential reducing agent for Tc(VII)/Tc(IV) the transformation
 452 follows according to equation (11):



454 In a first attempt we simply tried to assess whether the available amount of Fe(II) is
 455 sufficient to reduce added Tc(VII). The ion-exchangeable Fe(II) content was taken as an
 456 approximation for the readily “available Fe(II)” and decreases from (2.2±0.5)×10⁻⁵ M in un-
 457 oxidized ÄD to (9±5)×10⁻⁶ M in oxidized ÄD. Based on the solid to liquid ratio chosen (250

458 g/L) these values give $(1.8 \pm 0.4) \times 10^{-7}$ mol/vial Fe(II) for un-oxidized ÄD and $(7 \pm 4) \times 10^{-8}$
 459 mol/vial Fe(II) for oxidized ÄD. Thus, it is obvious that the material extracted and transferred
 460 under normal ambient atmospheric conditions (oxidized ÄD) possesses a lower redox
 461 capacity. From the comparison of the Fe(II) content ($(7 \pm 4) \times 10^{-8}$ mol/vial Fe(II)) with the total
 462 amount of added Tc (8×10^{-8} mol/vial (10^{-5} M Tc), 8×10^{-11} mol/vial (10^{-8} M Tc) and 8×10^{-12}
 463 mol/vial (10^{-9} M Tc)) and taking into account that three electrons are required to reduce
 464 Tc(VII) to Tc(IV) oxidized ÄD still provides enough ion-exchangeable Fe(II) to reduce
 465 $29.1 \pm 16.7\%$ of total Tc in the sample containing 10^{-5} M Tc, which is close to the experimental
 466 observation of $12 \pm 1\%$ Tc being reduced. Furthermore, un-oxidized ÄD does not provide
 467 enough Fe(II) for the complete reduction of 10^{-5} M Tc. These estimations are supported by
 468 the finding that Eh values in the granite/water suspensions increase significantly when 10^{-5}

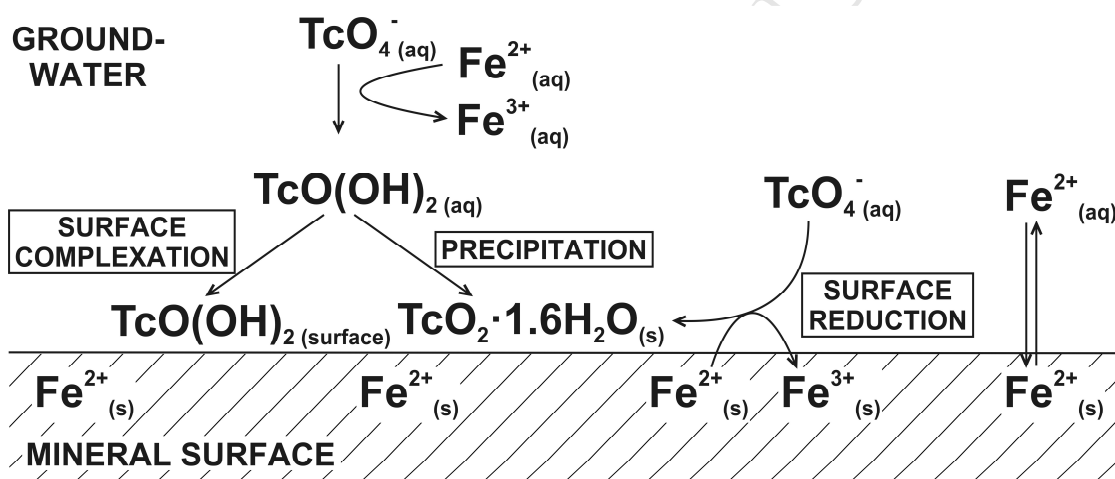


Figure 6. General scheme of Tc(VII) sorption and reduction processes.

469 M Tc(VII) are added. This amount is apparently sufficient to exceed the redox capacity of the
 470 diorite material at a solid to liquid ratio of 250 g/L. In all batch experiments the granite
 471 material should provide enough Fe(II) for the Tc(VII) reduction at lower $[\text{Tc}]_{\text{tot}}$.

472

473 4.2. Sorption parameters

474 The temporal change in Tc concentration during the batch sorption experiment can be
 475 described with an exponential decay equation (13):

$$476 \quad C_t = (C_0 - C_{eq})e^{-kt} + C_{eq} \quad (13)$$

477 where C_0 and C_{eq} are the initial and equilibrium Tc concentrations (M), respectively, and k is
 478 the sorption rate coefficient (time⁻¹). Hence, calculating sorption S_t as (14)

$$479 \quad S_t = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (14)$$

480 time dependent sorption data can be fitted with the rate equation (15):

$$481 \quad S_t = S_{eq}(1 - e^{-kt}) \quad (15)$$

482 where S_t and S_{eq} are the sorption percentages at the moment t and at equilibrium (6 months
 483 contact time), respectively. Sorption rate coefficients obtained from this fitting are
 484 presented in Table 4. The uptake rates (k) are significantly higher for the experiments with
 485 high total Tc concentration, which is a general observation in chemical reaction kinetics. A
 486 closer inspection shows that fitting of experimental data obtained with highest Tc
 487 concentrations to the kinetic rate model provides a better correlation when two exponential
 488 functions (rate constants) are taken. For instance, the sorption of 10^{-5} M Tc onto oxidized ÄD
 489 can be fitted with two exponential functions with k values of 0.017 ± 0.008 and 0.265 ± 0.056
 490 d^{-1} . This might be an indication of the existence of more than one retention mechanism, e.g.
 491 surface sorption and precipitation, respectively. We have to emphasize, however, that the

492 **Table 4.** Main parameters obtained by Tc (VII) sorption experiments onto ÄD.

Mate-rial	Fe(II) available, mg/g	Initial Tc concentration, mol/L	Eh, 1-2 months *, mV	k , d^{-1}	K_d , L/kg	K_a , m	Tc sorbed after 6 months, %
ÄD un-oxidized	4-6	1.07×10^{-5}	76	0.24 ± 0.100	1.1 ± 0.200	$(6.80 \pm 0.80) \times 10^{-6}$	21 ± 2.0
		$(1.05 \pm 0.05) \times 10^{-8}$	-187	0.075 ± 0.009	500 ± 200	$(2.90 \pm 1.30) \times 10^{-3}$	99.2 ± 0.6
		$(1.10 \pm 0.10) \times 10^{-9}$	-142	0.036 ± 0.004	900 ± 800	$(5.30 \pm 4.90) \times 10^{-3}$	99.5 ± 6.0
ÄD ox-	1-3	1.07×10^{-5}	238	0.15 ± 0.040	0.53 ± 0.050	$(3.30 \pm 0.30) \times 10^{-6}$	12 ± 1.0
		$(1.05 \pm 0.05) \times 10^{-8}$	280	0.017 ± 0.010	3.6 ± 1.000	$(2.20 \pm 0.60) \times 10^{-5}$	47 ± 8.0

dized

 $(1.10 \pm 0.10) \times 10^{-9}$

264

 0.007
 ± 0.001

22±8

 $(1.40 \pm 0.5) \times 10^{-4}$

84±6.0

493 * values in Fig. 3; N/A – not applicable.

494

495 system consists of highly coupled redox, precipitation and surface interaction phenomena. A
 496 simple interpretation of sorption mechanisms just based on reaction rate analysis is certainly
 497 not feasible. This becomes obvious when looking to literature data. Exponential fitting of Tc
 498 sorption data from Bondietti and Francis (1979) gives a k value of around $1.1 \pm 0.4 \text{ d}^{-1}$ for an
 499 initial Tc concentration of $1.1 \times 10^{-7} \text{ M}$ with Westerly granite as a solid material (167 g/L
 500 solid/liquid ratio). The pH/Eh values for this material were also comparable (pH 8, Eh -100
 501 mV) to the conditions used in present work, but neither Fe(II) content nor specific surface
 502 area of the material were specified in the paper, which could significantly contribute to the
 503 enhanced rates found in Bondietti and Francis (1979).

504 Distribution coefficients (K_d in L/kg) obtained for Tc sorption onto Äspö material were
 505 calculated using the following equation (16):

$$506 \quad K_d = \frac{C_l}{C_s} = \frac{A_0 - A_t}{A_t} \times \frac{V}{m_{\text{solid}}} \quad (16)$$

507 where C_l and C_s are the equilibrium concentrations of solutes in aqueous and solid phases,
 508 respectively, A_0 and A_t are the initial and final aqueous radionuclide activities at equilibrium
 509 (Bq/mL), respectively, V is the volume of the aqueous phase (mL) and m_{solid} is the solid
 510 mass (g). Typical K_d values obtained within the present work are presented in Table 4
 511 together with measured initial Tc concentrations, amount of ion-exchangeable Fe(II) and
 512 redox potentials. From a thermodynamic point of view the K_d approach assumes a fully
 513 reversible sorption process, but in most papers it is used even when irreversible
 514 reduction/precipitation processes are involved (Albinsson et al., 1991; Allard et al., 1979;
 515 Kaplan and Serne, 1998). In the report of USEPA (1999) authors describe “conditional” K_d
 516 values for the interpretation of experimental data in cases when the rigorous application of
 517 the K_d approach is prohibited (e.g. in non-equilibrium, irreversible, or solubility controlled
 518 systems). In the present work K_d values are considered as conditional distribution

519 coefficients. For a better comparison of the retention behaviour with literature data, K_d
520 should be normalized to the specific surface area of the solid material used in the
521 experiments according to the equation (17):

$$K_a = \frac{K_d}{S_{BET}} (\times 10^{-6}) \quad (17)$$

523 where K_a is the surface area normalized distribution coefficient (m) and S_{BET} is the specific
524 surface area of the solid determined by N_2 -BET (m^2/g). K_a values for the ÄD material are
525 shown in Table 4. Since the surface area of oxidized and un-oxidized ÄD remains the same,
526 this normalization does not affect the comparison between them. The K_d values obtained for
527 the oxidized material (see Table 4; 10^{-5} M Tc) in this study with 0.53 ± 0.05 L/kg for oxidized
528 ÄD are in good agreement with recently published data of Videnska and Havlova (2012) who
529 reported a K_d value of 0.3 L/kg under oxidizing conditions for 1.6×10^{-4} M ^{99}Tc on granitic rocks
530 from Melechov Massive, Centre Bohemian Massive, Czech Republic (> 0.8 mm size fraction).
531 Since the surface area was not mentioned in the publication, K_a values cannot be calculated
532 for these results. Batch-type studies on Tc uptake with well-preserved un-oxidized crushed
533 granitic rocks can hardly be found in the literature. We have compared the data obtained
534 with experiments performed under artificial reducing conditions. Ito and Kanno (1988) have
535 published the Tc distribution between solution and granitic rocks (0.49 – 0.83 mm size
536 fraction, 10^{-12} M [^{95m}Tc]) together with a number of other minerals under oxidizing and
537 reducing conditions. Under oxidizing conditions (in 0.16 M $NaNO_3$) K_d values of 0.1 L/kg ($K_a =$
538 4.8×10^{-7} m) were obtained, while under reducing conditions (0.1 M $NaBH_4$ and 0.16 M
539 $NaNO_3$) values of 45.6 L/kg ($K_a = 2.2 \times 10^{-4}$ m) increasing up to 68 L/kg ($K_a = 3.2 \times 10^{-4}$ m) with
540 decreasing NO_3^- concentration down to 0.016 M could be determined. The paper by
541 McKinley and Scholtis (1993) summarized the data on K_d values of Tc on different materials
542 including granitic rocks used for the safety assessment of waste disposal at that time. Here
543 the values range from 0 to 250 L/kg depending on the experimental conditions and the
544 origin of the rocks. The authors emphasize that Tc sorption under oxidizing conditions is
545 normally very low or zero, and for reducing conditions K_d values increase by 1–2 orders of
546 magnitude.

547 **4.3. Tc desorption**

548 As was shown in the results section, Tc desorption without artificial oxidation of the material
 549 is almost negligible. We suppose that the relatively rapid establishment of a steady state
 550 for the Tc concentration after only 1 day desorption is the consequence of washing out
 551 residual Tc(VII) in the porewater rather than desorption of sorbed or precipitated Tc(IV). For
 552 the desorption experiments after artificial oxidation, the general trend of the fast desorption
 553 up to a plateau value might be explained by the rapid oxidation of surface associated Tc(IV)
 554 to the heptavalent oxidation state and thus to the (almost) non-sorbing pertechnetate anion
 555 whereas strongly sorbing un-oxidized Tc(IV) does not have any significant contribution to the
 556 desorption process. The same observations were made by numerous investigators (Begg et
 557 al., 2008; Burke et al., 2006; Morris et al., 2008), where Tc(IV) oxidation to Tc(VII) was found
 558 to be a driving force for the Tc desorption process. Taking into account Tc uptake
 559 mechanisms discussed in section 4.1, one can assume two different mechanisms, namely
 560 predominantly surface complexation for $\log [Tc]_{\text{tot}} = -8$ and -9 and $TcO_2 \cdot 1.6H_2O_{(s)}$
 561 precipitation for $\log [Tc]_{\text{tot}} = -5$ governing the Tc sorption process. Consequently, for the
 562 same initial Tc concentration, a similar Tc desorption behaviour can be expected for oxidized
 563 and un-oxidized systems, which is in a good agreement with the experimental data observed
 564 for the ÄD. A higher degree of desorption observed for the samples with higher $[Tc]_{\text{initial}}$
 565 might be explained by the relatively easier oxidation of the surface associated $TcO_2 \cdot 1.6H_2O_{(s)}$
 566 phase in comparison to the surface complexed Tc(IV) species (see Table 5) which are
 567 probably more recalcitrant to remobilization during oxidation. Similar presumptions were
 568 expressed (Begg et al., 2008; Burke et al., 2006; Morris et al., 2008), but the mechanical
 569 nature of this resistance is still a matter of further research.

570 **Table 5.** Comparison of the sorption/desorption values for the oxidized and un-oxidized ÄD for the
 571 artificially oxidized sample series. Desorption time of 1 month.

Material	$-\log [Tc]_{\text{initial}}$	Tc sorption, %	Tc desorption, %
	5	21±2	93.7±0.6
ÄD (un-oxidized)	8	99.2±0.6	64±7
	9	99.5±6	33±7
ÄD (oxidized)	5	12±1	94±3

8	47±8	64±8
9	84±6	35±8

572

573 **4.4. Spectroscopic analyses**

574 According to the XPS results (see Figure 5 left), the Tc signal was detected only on dark mica-
575 type mineral surface (most likely biotite or magnetite), which contains structural Fe(II). It is
576 well known that Tc(VII) is concentrated on Fe(II)-containing minerals (Burke et al., 2010;
577 Fredrickson et al., 2009; McBeth et al., 2011) as “hotspots” due to surface (heterogeneous)
578 reduction into insoluble Tc(IV) oxide phase or/and homogeneous reduction in the solution
579 into soluble Tc(IV) species with subsequent sorption on the mineral surface. According to the
580 results of Peretyazhko et al. (2008a) heterogeneous Tc(VII) reduction on the surface
581 associated Fe(II) is orders of magnitude faster than the homogeneous reduction by aqueous
582 Fe²⁺ and may occur on the Fe(II)-containing mineral surfaces. XANES analysis of the Äspö
583 diorite contacted with Tc-containing ÄGWS indicated the presence of Tc(IV) as well.

584 **4.5. Thermodynamic modelling**

The general scheme of the modelling applied is described in Section 2.6. A similar calculation approach was applied in previous studies related to the modelling of Pu sorption to kaolinite (Marsac et al., 2015a) and Np sorption on illite (Marsac et al., 2015b) with respect to the differences in chemistry. Figure 7 shows the Tc(IV) fraction in the aqueous phase modelled with PHREEQC for $\log [\text{Tc}]_{\text{tot}} \leq -8$ as a function of the redox potential. For pH = 8.0 and I = 0.1 M, Eh of the $[\text{Tc(VII)}]_{\text{aq}}/[\text{Tc(IV)}]_{\text{aq}}$ borderline is -53 mV (E_{haq} , calculated from equation (5)), as highlighted in Figure 7. To account for sorption processes (see equation (9)), $\log K_{\text{VII/IV,surf}}$ is determined as follows. The site density is arbitrarily set equal to 1 site/nm², which is the same order of magnitude as commonly observed for several minerals (Burlakov et al., 2000; Jeppu and Clement, 2012). The value for $\log K_{\text{VII/IV,surf}}$ is strongly dependent on this arbitrarily chosen site density. At Eh values ≤ -90 mV almost all Tc is calculated to be Tc(IV) (see Figure 8). Such conditions prevail in the experiments with un-oxidized ÄD and $\log [\text{Tc}]_{\text{tot}} \leq -8$. Taking these experimental data, $\log K_{\text{VII/IV,surf}}$ is deduced by a fitting procedure and is found to be equal to 35.7 (see equation (8)). This value is kept constant for all the following calculations.

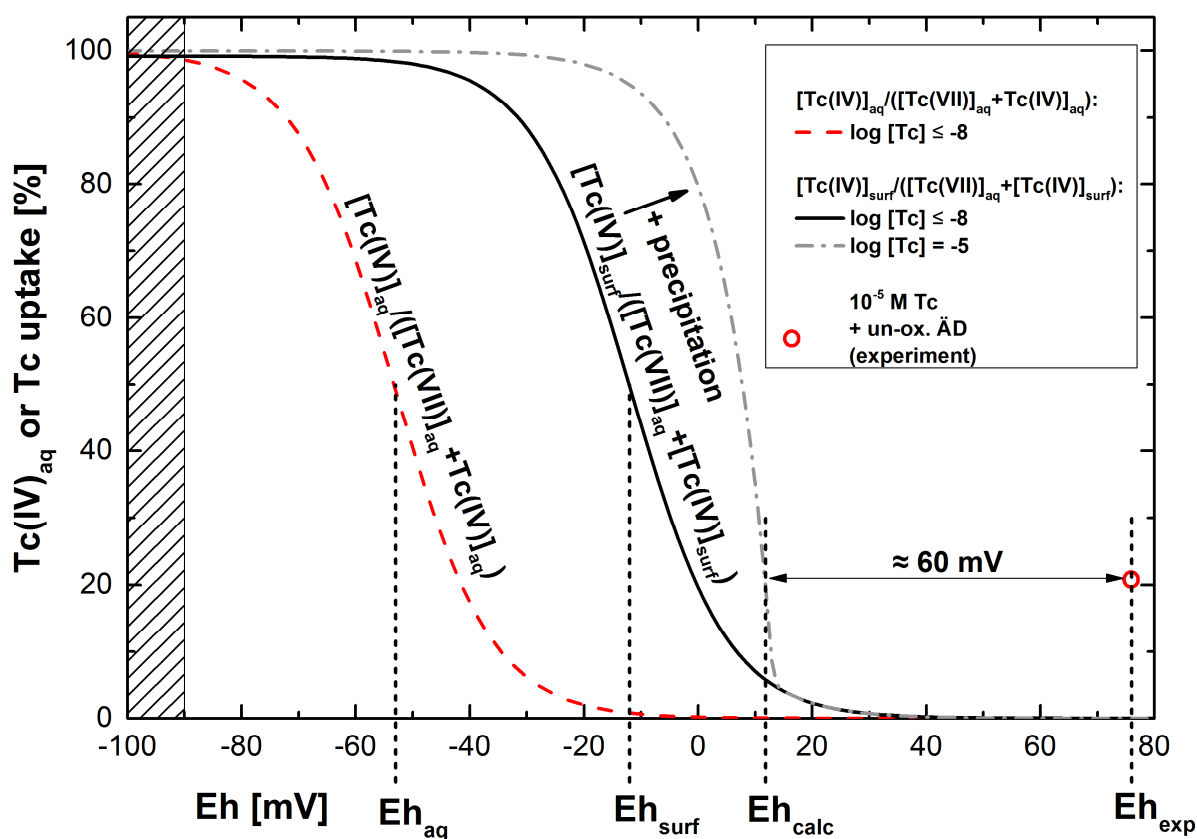


Figure 7. Tc(IV) fractions depending on the redox potential (pH 8, $I = 0.1$ M) calculated according to the equations (4) and (9), respectively. Eh_{exp} corresponds to the measured redox potential; Eh_{calc} relates to the calculated redox potential where 21% of Tc is removed from solution in the experiment with $\log [Tc]_{tot} = -5$; $[Tc(VII)]_{aq}^{yellow}/[Tc(IV)]_{aq}^{yellow}$ and $[Tc(VII)]_{aq}^{yellow}/[Tc(IV)]_{surf}^{yellow}$ borderline redox potentials are as well marked by vertical dashed lines; the shaded area at the left side shows the Eh region where model calculations predict quantitative uptake.

585 The borderline redox potential where $[Tc(IV)]_{surf}$ and $[Tc(VII)]_{aq}$ exist in equimolar
 586 concentrations, Eh_{surf} , is found equal to -12 mV in accordance to the equation (10). In
 587 agreement with the findings of Marsac et al. (Marsac et al., 2015a; Marsac et al., 2015b) for
 588 Np and Pu sorption to clays, the strong sorption behaviour of Tc(IV) shifts the borderline Eh
 589 to higher values as compared to that for the $[Tc(IV)]_{aq}/[Tc(VII)]_{aq}$ ratio, Eh_{aq} , in aqueous
 590 solution in the absence of mineral surfaces. For $\log [Tc]_{tot} = -5$ precipitation of $TcO_2 \cdot 1.6H_2O_{(s)}$
 591 is predicted, which represents the 2nd retention mechanism, and extends the stability field of
 592 Tc(IV) further. In the respective experiment the measured Eh value (Eh_{exp}) is $76 \text{ mV} \pm 50 \text{ mV}$,

593 where the model predicts insignificant uptake in disagreement with the experimentally
594 observed $\approx 21\%$ uptake. Actually, the model is very sensitive to the redox potential. For
595 instance, a change in Tc uptake from 2% to 80% is predicted by assuming a slight decrease in
596 $E_{h_{calc}}$ from +20 to 0 mV for $\log [Tc]_{tot} = -5$. Regarding the uncertainties of experimental Eh
597 data in a range of ± 50 mV (Altmaier et al., 2011a) and the uncertainty of model parameters,
598 our simulation results are not so different from experimental data. The discrepancy of Tc
599 uptake in simulation and experiment can easily be explained by uncertainties in redox
600 potential measurements. According to model calculations, the dominating uptake
601 mechanism at $\log [Tc]_{tot} = -5$ is precipitation of $TcO_2 \cdot 1.6H_2O_{(s)}$. This is in agreement with
602 XANES measurements performed with a 1 mM Tc-containing solution contacted with the
603 crushed material. The model predicts almost 100% Tc uptake for $Eh \leq -90$ mV in accordance
604 with the experimental results for un-oxidized $\ddot{A}D$ at $\log [Tc]_{tot} \leq -8$ (see Table 4). However,
605 relatively high Tc uptake ($> 30\%$, see Table 4 & 5) of the oxidized materials at $\log [Tc]_{tot} \leq -8$
606 and rather high Eh values (> 200 mV) cannot be explained by the thermodynamic model. No
607 Tc reduction and no uptake is calculated above $Eh \geq \approx 30$ mV (see Figure 7). Nevertheless, Tc
608 uptake by the oxidized materials is significant but is lower as compared to that by the un-
609 oxidized $\ddot{A}D$ (see Figure 2). This finding may suggest that, although oxidized, a redox partner
610 for the reduction of Tc(VII) to Tc(IV) is present in significant amounts, which, however, is not
611 detected by the Eh measurements using a Pt-electrode. Another aspect relates to the
612 concentration of redox partners required for reproducible and thermodynamically defined
613 redox potential measurements using a Pt-electrode, which is proposed to be $\geq \approx 10^{-6}$ M
614 (Grenthe et al., 1992). The ion-exchangeable ferrous iron concentration in the oxidized rock
615 materials lie very close to that minimum value of $(9 \pm 5) \times 10^{-6}$ M Fe(II) for oxidized $\ddot{A}D$. It
616 seems likely that Fe(II) content available is quantitatively consumed during the Tc reduction
617 process by oxidization to Fe(III) inhibiting a precise Eh determination by the platinum
618 electrode. Thus a higher uncertainty in the Eh measurements and in the interpretation of the
619 results needs to be considered for the higher $[Tc]_{tot}$ series and the oxidized $\ddot{A}D$.

620

621 5. Conclusions

622

623 A batch type sorption/desorption study on Tc interaction with crushed granitic rock material
624 from the generic URL in Sweden (Äspö HRL) was performed. Part of the crushed material
625 from Äspö HRL used in the experiments has been obtained and handled under anoxic
626 conditions before and during the experiments thus representing to a great extent natural *in-*
627 *situ* rock material conditions (e.g. redox capacity) relevant to the far-field environment of a
628 repository in crystalline rock. According to the experimental findings, Tc(VII) is reduced
629 under natural anoxic conditions to Tc(IV) followed by either precipitation of $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}_{(s)}$
630 or/and surface complexation of soluble Tc(IV) species on the rock surface. Comparison of
631 samples after ultracentrifugation shows no detectable amount of Tc colloidal phase under
632 simulated groundwater conditions applied. After contact of Tc(VII)-containing groundwater
633 simulants with crystalline rock materials, Tc(IV) species were detected on mafic mica-type
634 Fe-containing minerals. Apparently, the Tc(VII) concentration directly influences the amount
635 of Tc uptake on un-oxidized and oxidized material, which can be correlated with the ion-
636 exchangeable Fe(II) buffer available (4 – 6 $\mu\text{g/g}$ for un-oxidized ÄD and 1 – 3 $\mu\text{g/g}$ for
637 oxidized ÄD). Tc behaviour on oxidized ÄD differs dramatically compared to un-oxidized ÄD
638 samples. In general, artificially oxidized rock material could retain approx. 2 times less Tc
639 compared to un-oxidized material. Distribution coefficients (K_d) and surface area normalized
640 distribution coefficients (K_a) were determined for artificially oxidized and original un-oxidized
641 ÄD which serve as parameters for transport modelling or performance assessment modelling
642 purposes. Technetium desorption from the ÄD is insignificant under anoxic conditions, but
643 after artificial oxidation technetium mobility is increased due to re-oxidation of Tc(IV) to
644 Tc(VII). Such reactions might become relevant in scenarios where oxidized glacial melt water
645 intrusion into a repository is considered. The similar Tc desorption behaviour from the
646 initially oxidized and un-oxidized ÄD samples indicates the same retention mechanism for
647 both types of the material even taking into account the difference in the total uptake
648 capacity. Samples from the batch sorption studies with high $[\text{Tc}]_{\text{tot}}$ show increased
649 desorption most probably due to faster re-oxidation of the $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}_{(s)}$ precipitate in
650 comparison to surface complexed Tc(IV) species. According to the thermodynamic
651 calculations, for $\log [\text{Tc}] \leq -8$ Tc(IV) surface complexation is a predominant process of Tc
652 immobilization, while at higher Tc concentration $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}_{(s)}$ precipitation plays the main

653 role. This work clearly highlights the importance of using well-preserved (un-oxidized)
654 natural materials for the reliable estimation of the interaction of redox sensitive elements
655 with these solid phases. The difference in retention capacity between artificially oxidized and
656 un-oxidized material is highly significant. The data obtained gives important implications on
657 the prediction of Tc behaviour under natural conditions for safety assessment of deep
658 geological disposals of SNF and HLW in undisturbed and disturbed crystalline environments.

659 **6. Acknowledgements**

660
661 The research leading to these results has received funding from the Federal Ministry of
662 Economics and Technology (BMW_i) collaborative project VESPA (Behavior of long-lived
663 fission and activation products in the near field of a repository and possible retention
664 mechanisms) under contract № 02 E 10800 and the European Union's European Atomic
665 Energy Community's (Euratom) 7th Framework Programme FP7/2007-2011 under grant
666 agreement № 269658 (CP CROCK).

667

668

669 **7. References**

670

671 Albinsson, Y., Christiansensatmark, B., Engkvist, I., Johansson, W., 1991. Transport of
672 actinides and Tc through a bentonite backfill containing small quantities of iron or
673 copper. *Radiochim Acta* 52-3, 283-286.

674 Allard, B., Kigatsi, H., Torstenfelt, B., 1979. TECHNETIUM - REDUCTION AND
675 SORPTION IN GRANITIC BEDROCK. *Radiochemical and Radioanalytical Letters*
676 37, 223-229.

677 Altmaier, M., Gaona, X., Fellhauer, D., Buckau, G., 2011a. Intercomparison of redox
678 determination methods on designed and near-natural aqueous systems, FP 7
679 EURATOM Collaborative Project "Redox Phenomena Controlling Systems". KIT
680 Scientific Publishing.

681 Altmaier, M., Kienzler, B., Duro, L., Grivé, M., Montoya, V., 2011b. 3rd Annual Workshop
682 Proceedings of the Collaborative Project "Redox Phenomena Controlling Systems"
683 (7th EC FP CP RECOSY). KIT INE.

684 Begg, J.D.C., Burke, I.T., Charnock, J.M., Morris, K., 2008. Technetium reduction and
685 reoxidation behaviour in Dounreay soils. *Radiochim Acta* 96, 631-636.

686 Bodin, J., Delay, F., de Marsily, G., 2003. Solute transport in a single fracture with negligible
687 matrix permeability: 2. mathematical formalism. *Hydrogeology Journal* 11, 434-454.

688 Bondietti, E.A., Francis, C.W., 1979. Geologic Migration Potentials of Technetium-99 and
689 Neptunium-237. *Science* 203, 1337-1340.

690 Boyd, G.E., Larson, Q.V., Motta, E.E., 1960. Isolation of milligram quantities of long-lived
691 technetium from neutron irradiated molybdenum. *J Am Chem Soc* 82, 809-815.

692 Burke, I.T., Boothman, C., Lloyd, J.R., Livens, F.R., Charnock, J.M., McBeth, J.M.,
693 Mortimer, R.J.G., Morris, K., 2006. Reoxidation behavior of technetium, iron, and
694 sulfur in Estuarine sediments. *Environmental Science & Technology* 40, 3529-3535.

695 Burke, I.T., Livens, F.R., Lloyd, J.R., Brown, A.P., Law, G.T.W., McBeth, J.M., Ellis, B.L.,
696 Lawson, R.S., Morris, K., 2010. The fate of technetium in reduced estuarine
697 sediments: Combining direct and indirect analyses. *Applied Geochemistry* 25, 233-
698 241.

699 Burlakov, V.M., Sutton, A.P., Briggs, G.A.D., Tsukahara, Y., 2000. Simulation of Porous Si
700 and SiO_x Layer Growth, in: MSM (Ed.), *Technical Proceedings of the 2000*
701 *International Conference on Modeling and Simulation of Microsystems*, University of
702 Oxford, UK, pp. 95-97.

703 Byegård, J., Johansson, H., Skålberg, M., Tullborg, E.-L., 1998. The interaction of sorbing
704 and non-sorbing tracers with different Äspö rock types. Sorption and diffusion
705 experiments in the laboratory scale.

706 Close, P., Hornyak, E.J., Baak, T., Tillman, J.F., 1966. Potentiometric titration of micro
707 amounts of iron(II) with very dilute cerium(IV) sulfate. *Microchemical Journal* 10,
708 334-339.

709 Cui, D., Eriksen, T.E., 1996. Reduction of Pertechnetate in Solution by Heterogeneous
710 Electron Transfer from Fe(II)-Containing Geological Material. *Environmental Science*
711 *& Technology* 30, 2263-2269.

712 Duro, L., Grivé, M., Cera, E., Gaona, X., Domènech, C., Bruno, J., 2006. Determination and
713 assessment of the concentration limits to be used in SR-Can. SKB.

- 714 Fredrickson, J.K., Zachara, J.M., Plymale, A.E., Heald, S.M., McKinley, J.P., Kennedy,
715 D.W., Liu, C., Nachimuthu, P., 2009. Oxidative dissolution potential of biogenic and
716 abiogenic TcO₂ in subsurface sediments. *Geochimica et Cosmochimica Acta* 73,
717 2299-2313.
- 718 Grambow, B., 2008. Mobile fission and activation products in nuclear waste disposal. *Journal*
719 *of Contaminant Hydrology* 102, 180-186.
- 720 Grenthe, I., Stumm, W., Laaksuharju, M., Nilsson, A.C., Wikberg, P., 1992. Redox potentials
721 and redox reactions in deep groundwater systems. *Chemical Geology* 98, 131-150.
- 722 Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D.A., Rand, M.H.,
723 2003. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium,
724 Americium and Technetium. Elsevier.
- 725 Heald, S.M., Zachara, J.M., Jeon, B.H., McKinley, J.P., Kukkadapu, R., Moore, D., 2007.
726 XAFS study of the chemical and structural states of technetium in Fe(III) oxide Co-
727 precipitates. *X-Ray Absorption Fine Structure-XAFS* 13 882, 173-175.
- 728 Heck, S., Schäfer, T., 2012. Short Note: CP CROCK groundwater sample characterization
- 729 Heron, G., Crouzet, C., Bourg, A.C.M., Christensen, T.H., 1994. Speciation of Fe(II) and
730 Fe(III) in contaminated aquifer sediments using chemical extraction techniques.
731 *Environ. Sci. Technol.* 28, 1698-1705.
- 732 Huber, F., Enzmann, F., Wenka, A., Bouby, M., Dentz, M., Schäfer, T., 2012. Natural micro-
733 scale heterogeneity induced solute and nanoparticle retardation in fractured crystalline
734 rock. *Journal of Contaminant Hydrology* 133, 40-52.
- 735 Huber, F., Seher, H., Kunze, P., Bouby, M., Banik, N.L., Hauser, W., Geckeis, H., Kienzler,
736 B., Schäfer, T., 2010. Laboratory study on colloid migration and colloid-radionuclide
737 interaction under Grimsel groundwater conditions simulating glacial melt-water
738 intrusion in the Äspö system. KIT INE.
- 739 IAEA, 2001. The use of scientific and technical results from underground research laboratory
740 investigations for the geological disposal of radioactive waste. IAEA, Vienna.
- 741 Ito, K., Kanno, T., 1988. Sorption behavior of carrier-free technetium-95m on minerals, rocks
742 and backfill materials under both oxidizing and reducing conditions. *J Nucl Sci*
743 *Technol* 25, 534-539.
- 744 Jaisi, D.P., Dong, H.L., Plymale, A.E., Fredrickson, J.K., Zachara, J.M., Heald, S., Liu, C.X.,
745 2009. Reduction and long-term immobilization of technetium by Fe(II) associated
746 with clay mineral nontronite. *Chemical Geology* 264, 127-138.
- 747 Jeppu, G.P., Clement, T.P., 2012. A modified Langmuir-Freundlich isotherm model for
748 simulating pH-dependent adsorption effects. *Journal of Contaminant Hydrology* 129-
749 130, 46-53.
- 750 Kaplan, D.I., Serne, R.J., 1998. Pertechetate exclusion from sediments. *Radiochim Acta* 81,
751 117-124.
- 752 Kienzler, B., Vejmelka, P., Römer, J., Fanghänel, E., Jansson, M., Eriksen, T.E., Wikberg, P.,
753 2003. Swedish-German actinide migration experiment at ÄSPÖ hard rock laboratory.
754 *Journal of Contaminant Hydrology* 61, 219-233.
- 755 Kienzler, B., Vejmelka, P., Römer, J., Schild, D., Jansson, M., 2009. Actinide migration in
756 fractures of granite host rock: laboratory and in situ investigations. *Nuclear*
757 *Technology* 165, 223-240.
- 758 Kornfält, K.A., Persson, P.O., Wikman, H., 1997. Granitoids from the Äspö area, southeastern
759 Sweden - geochemical and geochronological data. *GFF* 119, 109-114.
- 760 Kratz, J.V., Lieser, K.H., 2013. Nuclear and Radiochemistry: Fundamentals and Applications.
761 Wiley.

- 762 Marsac, R., Banik, N.L., Lützenkirchen, J., Buda, R.A., Kratz, J.V., Marquardt, C.M., 2015a.
763 Modeling plutonium sorption to kaolinite: Accounting for redox equilibria and the
764 stability of surface species. *Chem Geol* 400, 1-10.
- 765 Marsac, R., Banik, N.L., Lützenkirchen, J., Marquardt, C.M., Dardenne, K., Schild, D., Rothe,
766 J., Diascorn, A., Kupcik, T., Schafer, T., Geckeis, H., 2015b. Neptunium redox
767 speciation at the illite surface. *Geochimica et Cosmochimica Acta* 152, 39-51.
- 768 McBeth, J.M., Lloyd, J.R., Law, G.T.W., Livens, F.R., Burke, I.T., Morris, K., 2011. Redox
769 interactions of technetium with iron-bearing minerals. *Mineralogical Magazine* 75,
770 2419-2430.
- 771 McKinley, I.G., Scholtis, A., 1993. A comparison of radionuclide sorption databases used in
772 recent performance assessments. *Journal of Contaminant Hydrology* 13, 347-363.
- 773 Meyer, R.E., Arnold, W.D., 1991. The Electrode Potential of the Tc(IV)-Tc(VII) Couple,
774 *Radiochim. Acta*, p. 19.
- 775 Meyer, R.E., Arnold, W.D., Case, F.I., Okelley, G.D., 1991. Solubilities of Tc(IV) Oxides.
776 *Radiochim Acta* 55, 11-18.
- 777 Morris, K., Livens, F.R., Charnock, J.M., Burke, I.T., McBeth, J.M., Begg, J.D.C., Boothman,
778 C., Lloyd, J.R., 2008. An X-ray absorption study of the fate of technetium in reduced
779 and reoxidised sediments and mineral phases. *Applied Geochemistry* 23, 603-617.
- 780 Neretnieks, I., 1980. Diffusion in the rock matrix - An important factor in radionuclide
781 retardation. *Journal of Geophysical Research* 85, 4379-4397.
- 782 Nockolds, S.R., 1954. Average Chemical Compositions of Some Igneous Rocks. *Geol Soc*
783 *Am Bull* 65, 1007-1032.
- 784 Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (Version 2) - A Computer
785 Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse
786 Geochemical Calculations, p. 312.
- 787 Peretyazhko, T., Zachara, J.M., Heald, S.M., Jeon, B.H., Kukkadapu, R.K., Liu, C., Moore,
788 D., Resch, C.T., 2008a. Heterogeneous reduction of Tc(VII) by Fe(II) at the solid-
789 water interface. *Geochimica Et Cosmochimica Acta* 72, 1521-1539.
- 790 Peretyazhko, T., Zachara, J.M., Heald, S.M., Kukkadapu, R.K., Liu, C., Plymale, A.E., Resch,
791 C.T., 2008b. Reduction of Tc(VII) by Fe(II) sorbed on Al (hydr)oxides.
792 *Environmental Science & Technology* 42, 5499-5506.
- 793 Rard, J.A., Rand, M.H., Anderegg, G., Wanner, H., 1999. *Chemical Thermodynamics of*
794 *Technetium*. Elsevier.
- 795 Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-
796 ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat* 12, 537-541.
- 797 Rothe, J., Butorin, S., Dardenne, K., Denecke, M.A., Kienzler, B., Loble, M., Metz, V.,
798 Seibert, A., Steppert, M., Vitova, T., Walther, C., Geckeis, H., 2012. The INE-
799 Beamline for actinide science at ANKA. *Rev Sci Instrum* 83.
- 800 Schäfer, T., Stage, E., Büchner, S., Huber, F., Drake, H., 2012. Characterization of new
801 crystalline material for investigations within CP CROCK. 1st Workshop Proceedings
802 of the Collaborative Project „Crystalline Rock Retention Processes“ (7th EC FP CP
803 CROCK), 63-72.
- 804 Schmeide, K., Gürtler, S., Müller, K., Stuedtner, R., Joseph, C., Bok, F., Brendler, V., 2014.
805 Interaction of U(VI) with Äspö diorite: A batch and in situ ATR FT-IR sorption study.
806 *Applied Geochemistry* 49, 116-125.
- 807 SKB, 2011. Äspö Hard Rock Laboratory: Annual report.

- 808 Tagami, K., Uchida, S., 1999. Comparison of the TEVA center dot Spec resin and liquid-
809 liquid extraction methods for the separation of technetium in soil samples. *J Radioanal*
810 *Nucl Ch* 239, 643-648.
- 811 Um, W., Serne, R.J., 2005. Sorption and transport behavior of radionuclides in the proposed
812 low-level radioactive waste disposal facility at the Hanford site, Washington.
813 *Radiochim. Acta* 93, 57-63.
- 814 USEPA, 1999. The Kd model, methods of measurement, and application of chemical reaction
815 codes, Understanding variation in partition coefficient, Kd values. United States
816 Environmental Protection Agency, Office of Air and Radiation, p. 212.
- 817 Videnska, K., Havlova, V., 2012. Retention of Anionic Species on Granite: Influence of
818 Granite Composition, Waste Management 2012, Phoenix, Arizona, USA.
- 819 Viollier, E., Inglett, P.W., Hunter, K., Roychoudhury, A.N., Van Cappellen, P., 2000. The
820 ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Applied*
821 *Geochemistry* 15, 785-790.
- 822 Wester, D.W., White, D.H., Miller, F.W., Dean, R.T., Schreifels, J.A., Hunt, J.E., 1987.
823 Synthesis and characterization of technetium complexes with phosphorus-containing
824 ligands - the homoleptic trimethylphosphite, dimethylmethylphosphonite and
825 methyl-diethylphosphinite technetium(I) cations. *Inorg Chim Acta* 131, 163-169.
- 826 Westsik Jr, J.H., Cantrell, K.J., Serne, R.J., Qafoku, N.P., 2014. Technetium Immobilization
827 Forms. Literature Survey.
- 828 Wildung, R.E., Li, S.W., Murray, C.J., Krupka, K.M., Xie, Y., Hess, N.J., Roden, E.E., 2004.
829 Technetium reduction in sediments of a shallow aquifer exhibiting dissimilatory iron
830 reduction potential. *Fems Microbiol Ecol* 49, 151-162.
- 831 Xu, S., Wörman, A., 1999. Implications of sorption kinetics to radionuclide migration in
832 fractured rock. *Water Resources Research* 35, 3429-3440.
- 833 Zachara, J.M., Heald, S.M., Jeon, B.-H., Kukkadapu, R.K., Liu, C., McKinley, J.P.,
834 Dohnalkova, A.C., Moore, D.A., 2007. Reduction of pertechnetate [Tc(VII)] by
835 aqueous Fe(II) and the nature of solid phase redox products. *Geochimica et*
836 *Cosmochimica Acta* 71, 2137-2157.
- 837
838
839
840

841
842
843

Supplementary Material



Figure A.1. (Top and middle) Cores used in the batch experiments directly after drilling. (Bottom) Two-layers packing of the cores, sealed into LD-PE and Al bags.

844
845
846
847

848 **Table A.1.** XRF data on Äspö diorite (material used in this study, old oxidized ÄD samples
 849 used in (Huber et al., 2010 & 2012), oxidized ÄD from (Byegård et al., 1998)), and typical
 850 granodiorite (Nockolds, 1954) composition.

Element (RMS _{rel})	Äspö diorite (this study), wt. %	Äspö diorite, (Huber et al., 2010 & 2012), wt. %	Äspö diorite (Byegård et al., 1998), wt. %	Typical granodiorite (Nockolds, 1954), wt. %
SiO ₂	62.71	66.06	60.1	66.88
(0.4%) Al ₂ O ₃	17.27	16.89	18.1	15.66
(0.7%) Fe ₂ O ₃	4.39	2.6	5.1	1.33
(0.8%) FeO	2.51	0.87	-	2.59
(0.8%) MnO	0.08	0.05	0.1	0.07
(1.8%) MgO	1.76	0.8	2.2	1.57
(0.3%) CaO	3.75	2.41	4.4	3.56
(0.5%) Na ₂ O	4.55	4.91	4.7	3.84
(1.3%) K ₂ O	3.05	4.38	3.2	3.07
(0.8%) TiO ₂	0.66	0.35	0.8	0.57
(1.0%) P ₂ O ₅	0.24	0.12	0.3	0.21
(1.1%) Loss on ignition (LOI)	0.67	1.37	1.0	0.65
<i>Sum</i>	<i>99.1</i>	<i>99.4</i>	<i>100</i>	<i>100</i>
Trace element (LLD)	Concentration, ppm	Concentration, ppm	Concentration, ppm	
Ba (10.5ppm)	1162	n.d.	1770	
Co	11	5	n.d.	
(2.2ppm) Cr	24	6	n.d.	
(5.3 ppm) Cu	2	1	n.d.	
(1.6 ppm) Ga	23	19	n.d.	
(1 ppm) Nb	15	9	n.d.	
(1.1 ppm) Ni	18	6	n.d.	
(3.7 ppm) Pb	17	16	89	
(2.7 ppm)				

Sc	6	4	n.d.
(2.7 ppm)			
Sr	1052	770	1300
(1.5 ppm)			
Th	9.5	5.7	5.2
(1.7 ppm)			
U	4.4	1.8	2.1
(1.1 ppm)			
V	62	36	n.d.
(6.1 ppm)			
Y	22	16	18.1
(1.3 ppm)			
Zn	76	43	n.d.
(1.1 ppm)			
Zr	168	139	256
(0.9 ppm)			

851 n.d. – not detected, RMS_{rel} – relative root square mean, LLD – lower limit of detection;
852 RMS_{rel} and LLD are taken from the \ddot{A} D XRF analysis.

853

854

855

856

857

858 **Table A.2.** List of samples from the batch sorption studies and long-term sorption
 859 experiments on un-oxidized and oxidized ÄD.

Material	Contact time, days	Tc uptake, %		log [Tc] = -5		log [Tc] = -6		log [Tc] = -7		log [Tc] = -8		log [Tc] = -9		log [Tc] = -10		log [Tc] = -11	
		%	±. %	%	±. %	%	±. %	%	±. %	%	±. %	%	±. %	%	±. %	%	±. %
un-oxidized ÄD	0.04	7.10	0.06							3.57	2.16	14.51	8.08				
	1	8.38	0.06							13.42	2.00	25.14	7.59				
	1	12.80	0.06							10.82	2.02	27.94	7.59				
	4	19.94	0.06							19.04	1.95	33.15	7.40				
	4	6.47	0.06							23.95	1.89	27.54	7.54				
	7	35.15	0.05							41.64	1.67	35.55	7.33				
	7	11.54	0.06							29.96	1.82	25.95	7.59				
	15	15.37	0.08							76.46	1.15	52.74	6.85				
	15	33.37	0.07							62.74	1.38	53.14	6.83				
	21	25.12	0.08							83.88	1.00	53.14	6.83				
	21	19.14	0.08							73.74	1.20	86.73	5.76				
	30	22.43	0.08							93.48	0.77	71.13	6.28				
	57	13.90	0.09							79.66	1.09	70.35	6.31				
	57	39.59	0.07							95.86	0.70	97.14	5.41				
	91	20.26	0.08							97.56	0.65	96.34	5.43				
	91	22.63	0.08							97.90	0.64	94.34	4.98				
	141	44.76	0.12	48.19	0.19	48.70	0.24	53.83	0.23	90.85	0.51	81.65	1.73	95.06	4.15		
	141	46.67	0.12	25.49	0.16	41.41	0.21	85.39	0.40	90.34	0.49	76.36	0.99	95.65	4.66		
	178	20.70	0.08							99.44	0.58	100.00	5.12				
178									98.88	0.60	99.54	5.12					
oxidized ÄD	0.04	5.69	0.09							7.61	2.06	-3.45	8.35				
	0.04									4.02	2.10	8.15	8.06				
	1	9.40	0.09							7.65	2.06	18.96	7.78				
	1	9.31	0.09							8.59	2.05	-5.84	8.39				
	4	7.08	0.09							12.12	2.02	9.76	8.01				
	4	9.45	0.09							11.74	2.02	10.56	7.99				
	7	8.83	0.09							23.04	1.90	5.35	8.11				
	7	9.69	0.09							15.23	1.98	14.95	7.87				
	15	6.75	0.09							14.51	1.99	25.36	7.61				
	15	8.59	0.09							16.21	1.97	24.95	7.61				
	21	13.09	0.09							2.57	2.11	33.35	7.40				
	21	10.08	0.09							13.49	2.00	13.36	7.92				
	30	10.38	0.09							11.23	2.03	22.96	7.68				
	57	9.90	0.09							76.91	1.14	39.35	7.23				
	57	9.82	0.09							43.11	1.66	42.55	7.14				
	91	10.51	0.09							53.55	1.52	23.37	7.66				
	91	12.21	0.09							36.51	1.74	57.77	6.71				
	141	3.07	0.71	13.79	0.15	17.12	0.17	18.52	0.17	77.49	2.29	80.46	2.51	67.14	1.23		
	141	1.64	0.09	8.56	0.15	16.69	0.17	16.96	0.17	24.18	1.11	63.70	1.17	60.10	1.02		

Material	Contact time, days	Tc uptake, %													
		log [Tc] = -5		log [Tc] = -6		log [Tc] = -7		log [Tc] = -8		log [Tc] = -9		log [Tc] = -10		log [Tc] = -11	
		%	±. %	%	±. %	%	±. %	%	±. %	%	±. %	%	±. %	%	±. %
	178							54.83	1.82	90.15	5.67				
	178	11.69	0.09					39.70	1.82	77.75	6.07				

860

861

862

863

864



Figure A.2. ÄD sample for XPS after contacting with Tc(VII)-containing ÄGWS. Red circle indicates the region where Tc(IV) was found.

865
866
867
868
869
870
871
872
873

Paper highlights:

- Tc sorption/desorption kinetics investigation was performed on both oxidized and un-oxidized Äspö diorite (Sweden) on different Tc concentrations.
- The difference between artificially oxidized and well-preserved natural rock material is shown.
- Tc colloidal phase formation was not detected under simulated natural conditions.
- Spectroscopic investigations shown the accumulation of Tc(IV) species on mafic (e.g. mica, magnetite) minerals
- Tc sorption parameters on the rock material studied (distribution coefficient, sorption rate) were derived.