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# Activity concentrations of <sup>238</sup>U and <sup>226</sup>Ra in two European black shales and their experimentally-derived leachates

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#### Abstract

The production of gas from unconventional resources became an important position in the world energy economics. In 2012, the European Commission's Joint Research Centre estimate 16 trillion cubic meters (Tcm) of technically recoverable shale gas in Europe. Taking into account that the exploitation of unconventional gas can be accompanied by serious health risks due to the release of toxic chemical components and natural occurring radionuclides into the return flow water and their near-surface accumulation in secondary precipitates, we investigated the release of U, Th and Ra from black shales by interaction with drilling fluids containing additives that are commonly employed for shale gas exploitation.

We performed leaching tests at elevated temperatures and pressures with an Alum black shale from Bornholm, Denmark and a Posidonia black shale from Lower Saxony, Germany. The Alum shale is a carbonate free black shale with pyrite and barite, containing 74.4  $\mu$ g/g U. The Posidonia shales is a calcareous shale with pyrite but without detectable amounts of barite containing 3.6  $\mu$ g/g U.

Pyrite oxidized during the tests forming sulfuric acid which lowered the pH on values between 2-3 of the extraction fluid from the Alum shale favoring a release of U from the Alum shale to the fluid during the short-term and in the beginning of the long-term experiments. The activity concentration of <sup>238</sup>U is as high as 23.9 mBq/ml in the fluid for those experiments. The release of U and Th into the fluid is almost independent of pressure. The amount of uranium in the European shales is similar to that of the Marcellus Shale in the United States but the daughter product of <sup>238</sup>U, the <sup>226</sup>Ra activity concentrations in the experimentally derived leachates from the European shales are quite low in comparison to that found in industrially derived flowback fluids from the Marcellus shale. This difference could mainly be due to missing Cl in the reaction fluid used in our experiments and a lower fluid to solid ratio in the industrial plays than in the experiments due to subsequent fracking and minute cracks from which Ra can easily be released.

Key words: unconventional gas production, black shales, flowback, radioactivity, NOR, batch experiments

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#### 43 **1. Introduction**

Increasing gas production from unconventional shale gas plays in the United States (U.S.) and the 44 related engineering improvements for shale gas production in terms of drilling and hydraulic 45 46 fracturing took also exploitation of European shale gas under consideration. The U.S. Energy 47 Information Administration (U.S. EIA, 2013) estimated that Europe could hold 13.4 Tcm (trillion 48 cubic meters) technically recoverable shale gas. A similar value of 15.9 Tcm was estimated by the 49 European Commission's Joint Research Centre (JRC, 2012). 132 shale gas exploitation and appraisal wells have been drilled in Europe so far, most of them in Poland, Sweden and the UK (AAPG, 2016). 50 Due to commercial viability, political barriers and public concerns, roughly 2/3 of all companies 51 52 relinquished their concessions or let them expire (AAPG, 2016). In Germany, eight wells were drilled 53 since 2008 in the Wealden or in the Posidonia formation (both Lower Saxony) but no details about the gas flow were published. One well was drilled in the Alum shale in Denmark and the drilling of 17 54 shallow wells into the Alum shale of Ostergötland is reported for Sweden from which only some 55 56 showed a gas flow (AAPG, 2016).

The production of unconventional gas is linked with a high-pressure injection of several thousand 57 58 cubic meters of water for each well (Gregory et al., 2011; SEAB, 2011) to create minute cracks in which hydrocarbons can flow to the wellbore. The formation and the operator determine the 59 composition of the suspension for injection that is generally made of 90% water, 9 - 9.5% sand or 60 ceramics and 1 - 0.5% chemical additives (e.g. Arthur et al., 2008; King, 2012; Wood et al., 2011). 61 62 Additives could include small volumes of mainly hydrochloric acid ( $< 10 \text{ m}^3$ ) injected during the 63 initial stage of the gas exploitation to clean perforation tunnels and dissolve carbonate precipitates that seal veins. Chelating agents (e.g. citric, acetic acid) are added to the fracturing fluid to prevent the 64 65 precipitation of iron and manganese compounds. Additional ingredients of the fracturing fluid could be corrosion inhibitors, friction reducers, surfactants, clay stabilizers, biocides and cross-linkers 66 tailored for the specific lithological conditions (e.g. Arthur et al., 2008; Stringfellow et al., 2014). In 67 practice, 10 - 80% of the injected suspension returns to the surface: the so called flowback (Arthur et 68 al., 2008; Wood et al., 2011). The amount of flowback depends on formation characteristics, well 69 70 design and operating parameters.

71 To date, much of the research on the environmental impacts of unconventional gas production is 72 related to the origin of gas leakages during drilling, exploitation and production (e.g. Molofsky et al., 2013), the chemical composition of the flowback (e.g. Barbot et al. 2013; Chermak and Schreiber, 73 74 2014; Dieterich et al., 2016; Gregory et al., 2011; Gordalla et al., 2013; Renock et al., 2016), the release of microbiota and organic molecules from the shales (e.g. Hölzer et al., 2016; Strong et al., 75 2013; Zhu et al., 2015) and the enrichment of toxic trace elements like As, Cd, Co, Cr, Hg, Ni, Zn, U, 76 77 V in the flowback (e.g. Marcon, et al., 2017; Wilke et al., 2015; Chermak and Schreiber, 2014 and 78 references therein). Some studies deal with the release of naturally occurring radionuclides (NORs) of 79 oil- and gas-field produced waters, scales or drill cuttings but these studies cover only very specific

- areas such as the Marcellus shale in the Appalachian Basin (U.S.) (e.g. Chem and Sharma, 2016; Phan
- 81 et al., 2015; Nelson et al., 2015 & 2014; Haluszczak et al., 2012; Rowan et al., 2011; NYSDEC,
- 82 2009), the Bowland shale in the UK (Environment Agency, 2011) or one shale in Pomerania, Poland
- 83 (Mykowska et al., 2015; Mykowska and Hupka, 2014). Therein, the focus is on alpha particle emitter
- 84 of the <sup>238</sup>U -, <sup>235</sup>U and <sup>232</sup>Th decay series e.g. <sup>226</sup>Ra (Fig.1).
- $^{238}$ U series nuclides are often enriched in TOC-rich shales when U was scavenged as U(IV) under
- reducing conditions (e.g. Chen and Sharma, 2016; Chermak and Schreiber, 2014; Schovsbo, 2002;
  Stetten et al., 2018; Raiswell and Berner, 1985). It can be assumed that the reservoir of leachable U-
- series nuclides initially relates dominantly to scavenging and/or chemical precipitation of uranium
- 89 from weathering fluids whereas the proportion of U<sup>238</sup>- and Th<sup>232</sup>-series nuclides re-mobilized from
- 90 weathering resistant minerals (e.g. zircon) is negligible. Uranium may be initially co-precipitated with
- 91 Fe(Mn)OOH (Muller et al., 1995 and references therein) or hosting in biogenic calcite (Russell et al.,
- 1994) and may be initially or post-depositional immobilized as U(IV) to form, e.g. secondary uraninite (UO<sub>2</sub>), coffeinite (U(SiO<sub>4</sub>)<sub>1-x</sub>(OH)<sub>4x</sub>) or autunite (Ca[(UO<sub>2</sub>)(PO<sub>4</sub>)]<sub>2</sub> · 10 - 12 H<sub>2</sub>O), depending on the
- 94 composition of the coexisting fluids during early stages of sediment burial (Duff et al., 2002;
  95 Fredrickson et al., 2000; Cumberland et al., 2016; Lecomte et al., 2017).
- 96 The release of U into the drilling fluid may depend on the amount of leachable U available from the 97 shale deposits processed for gas exploitation but also from the carbonate and sulfide contents of the shale (e.g. Nelson et al., 2015; Wilke et al., 2015). Interaction of pyrite-rich shales with oxic fluids 98 99 generates sulfuric acid that dissolves carbonates and can generate fluids with low pH when the 100 buffering capacity of the carbonate gets exhausted (Chermak and Schreiber, 2014; Wilke et al., 2015). Decrease in pH favors the release of weakly bound cations from cation exchange sites and the 101 102 solubility of minerals hosting uranium. If acids are present, either as ingredient in the fracturing fluid 103 or formed by fluid-rock interactions during the course of shale gas production, U(IV) would be mobile 104 even under reducing conditions (Garrels and Christ, 1965). Oxygen-containing fluids force the formation of easily soluble U(VI)-oxyanions. U(VI) or U(IV) release due to pH decrease during solid-105 fluid interactions may be associated with the formation of less soluble secondary U(VI) or U(IV) 106 precipitates with CO<sub>3</sub><sup>2-</sup> or PO<sub>4</sub><sup>3-</sup> that may counteract uranium increase in the return fluids (Sandino & 107 Bruno, 1992; Stetten et al., 2018). 108
- $^{226}Ra$  (T\_{1/2}= 1600 a;  $^{238}U$  series) and  $^{228}Ra$  (T\_{1/2}=5.76 a;  $^{232}Th$ -series) behave less mobile in natural 109 environments (e.g. Vengosh et al., 2014), though they frequently show slightly enhanced activities in 110 groundwater compared to their activities in surface waters (Schettler et al., 2015 and references 111 therein). <sup>226</sup>Ra and <sup>228</sup>Ra are preferentially sorbed to ion-exchange sites of particle surfaces (Ames et 112 al., 1983), get co-precipitated with BaSO<sub>4</sub> or BaCO<sub>3</sub> (Langmuir and Riese, 1985) or may be taken up 113 by plants (Bettencourt et al., 1988). Moreover, Ra is efficiently scavenged by Mn(IV)-hydroxides 114 which finds analytical application as a pre-concentration step for Ra (Charette et al., 2015 and 115 references therein). These reactions will lower the concentration of dissolved Ra in the drilling fluid 116

- and can yield substantial accumulative enrichments of Ra and its decay products (<sup>210</sup>Pb, <sup>210</sup>Po) in
   coexisting solids at near-surface compartments (e.g. Nelson et al., 2015 and references therein).
- 119 In this study, we determine and assess the activity concentrations of <sup>238</sup>U, and <sup>232</sup>Th from one Alum

120 and one Posidonian black shale and, furthermore, the activity concentration of <sup>238</sup>U and the radioactive

- 121 decay product <sup>226</sup>Ra from the experimentally derived black shale leachates. We intend to increase the
- 122 knowledge about the amount of radioactive elements that might be enclosed in the drill cutting waste
- 123 and that may become mobilized from black shales into the fluids, the radioactivity they produce and 124 how European shales prospected for gas production differ in this topic from shales used for
- 125 unconventional gas production in the U.S. (e.g. the Marcellus shales).

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### 127 **2. Experimental settings**

128 2.1 Black shales

A black shale sample from the Upper Cambrian Alum shale of Scandinavia (Skelbro-2, Bornholm, 129 Denmark) and one from the lower Jurassic Posidonia shale of central Europe (Haddessen, NW-130 Germany) were chosen to simulate temporal changes in the composition of flow back water by 131 solid/fluid interaction in lab experiments under defined conditions (Table 1; Fig. 2; see Wilke et al., 132 2015 for details). The selection of shales was done in accordance with a perspective shale gas 133 production (Horsfield et al., 2010). Both samples were taken from cores (not from cuttings) in 134 lithologies suitable for industrial gas production. Samples have been milled to < 2 mm grain size and 135 136 were not sieved to preserve different grain size fractions.

137

#### 138 2.2 Extraction experiments

We designed two experimental set-ups consisting of A) 250 ml Erlenmeyer flasks connected with a 139 140 reflux condenser for short-term experiments (24 h) under atmospheric pressure and at 100°C and B) of 800 ml autoclaves made of a Ni-Cr-Mo-W alloy (Hastelloy<sup>TM</sup>) coated inside with 141 polytetrafluoroethylene (PTFE), for long-term studies of 2 and 6 month at 100 bar and 100 °C. Latter 142 conditions roughly simulate the target formation in Damme 3 well (Lower Saxony, Germany), where 143 144 hydraulic fracturing was performed in a shale at ca. 1-1.5 km depth at a pressure of 110-150 bar and a temperature of ca. 80 °C (Olsson et al., 2013). Both experimental set-ups run under oxidizing 145 146 conditions. A solid to liquid ratio of 1:12.5 was applied for both experimental set-ups. Fluids in the autoclaves were O2-saturated and overlaid by headspace containing 1% O2 at the beginning of the 147 experiment and 0.2% O<sub>2</sub> at the end. About 3 ml fluid was sampled at each sampling time for HR-ICP-148 MS measurements and the pH measured instantaneously before degassing to avoid a change in pH. 149 After sampling, the pressure in the autoclave was re-adjusted to 100 bar by adding N<sub>2</sub> from the gas 150 pressure bottle. Further experimental details are given in Wilke et al. (2015). 151

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153 2.3 Analytical methods

We determined the initial mineralogical compositions of both shales using X-ray diffraction analysis 154 (XRD) using a PANalytical Empyrean (Table 1). Elemental concentrations in the shales were 155 determined by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS, 156 157 THERMO ELEMENT XR) following HF-aqua regia (1/1) digestion, fuming with HClO<sub>4</sub> and dilution 158 by 1/1000 with 2% HNO<sub>3</sub> (Table 2, Supplement 1). Reaction fluids from the experiments were filtered 159 using a 0.45 µm Nylon membrane filter and diluted by 1/10 with 2% HNO<sub>3</sub> before HR-ICP-MS 160 analyses. For all measurements, calibration solutions with concentrations of 0.25 and 10 µg/l were applied and at least three aliquots of the reaction fluids were analyzed. The uncertainty for all ICP-MS 161 analyses is about 2-5%. The detection limits of the applied analytical routine using ICP-MS in the high 162 resolution mode typically ranged between 0.5 and 1 ng/g depending on the element. 163

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165 2.4 Gamma-spectrometry

An amount of 4 ml out of 30-50 ml reaction fluid of the two short-term and on the beginning and the end of both long-term experiments was used for gamma spectrometry. Special treatment was needed for the reaction fluid from the short-term experiment using Alum. 40 ml fluid were diluted to 50 ml with 5% HNO<sub>3</sub> prior analysis to dissolve precipitations from the fluid. Fluid activities were measured using a high purity well-type germanium detector of Canberra (cryostat model: 7915-30-ULB). 4 ml of the fluids were filled in PE tubes (d= 15 mm, h = 45 mm) for gamma measurements (Table 2).

Our measurements aimed on the quantification of Ra activity concentrations of the <sup>238</sup>U- and <sup>232</sup>Thdecay series. The Ra release of <sup>238</sup>U and <sup>232</sup>Th-decay series into the extraction fluids could be in similar order of magnitude due to Th and U concentrations of the shales.

Presumed <sup>226</sup>Ra equilibrium with <sup>238</sup>U, the theoretical number of counts for <sup>214</sup>Pb (<sup>238</sup>U-series nuclide) at 351.92 keV exceeds the sum of counts for <sup>226</sup>Ra and <sup>235</sup>U 3.5-fold. Nonetheless, we decided to perform the <sup>226</sup>Ra determinations at 186 keV for the following arguments: a) Background peaks of <sup>214</sup>Pb at 295.21 keV and 351.92 keV may vary over time due to changes in the <sup>222</sup>Rn concentration of the lab-air b) we cannot be sure about the impermeability to <sup>222</sup>Rn of the PE-tubes used and c) the efficiency calibrations that considered the <sup>222</sup>Rn distribution between the headspace and the 4 ml fluid in the PE tubes were not available when we performed the measurements.

182 The 186 keV peak is affected by  $^{226}$ Ra at 186.211 keV (3.64%) and  $^{235}$ U at 185.715 keV (57.0%)

183 (NuDat2.7 Database (NNDC) 2017). Interferences by <sup>234</sup>Pa at 186.15 keV with a recommended

intensity of 0.00325 (Huang and Wang, 2011) and by  $^{234m}$ Pa at 184.7 keV with an intensity of 0.00168

185 (<u>NuDat2.7</u> Database (NNDC) 2017) are neglectable. Detector calibration based on the measurement of

a dilution of 4 ml NIST4966 Standard (289.1 Bq/ml) in the PE tube (41071 counts, uncertainty 0.53%, t<sub>meas</sub>= 1919 s) yielded an efficiency of 0.49 at 186 keV. The inferred detector efficiency might be an

- $t_{meas}$  = 1919 s) yielded an efficiency of 0.49 at 186 keV. The inferred detector efficiency might be an overestimation if the standard includes impurities of <sup>235</sup>U. An efficiency calibration using solid powder
- overestimation if the standard includes impurities of <sup>235</sup>U. An efficiency calibration using solid powder
   of Nussloch loess which considered <sup>235</sup>U interference corrections for assumed <sup>238</sup>U-<sup>226</sup>Ra equilibrium
- 190 with the same fill height in the PE tube (IAG reference material data sheet) yielded a detector

- efficiency of 0.47 at 186 keV that supports the plausibility of the efficiency calibration for the 4 mlfluid aliquots.
- 193 Uncertainty values for  $\gamma$ -counting at 186 keV of the fluid samples from the lab experiments varied

between 5.4 and 16.8% (Table 2). Calculations followed the equations given in Supplement 2.

195 Corrections for interferences by <sup>235</sup>U are based on <sup>238</sup>U concentration measurements using ICP-MS

- 196 (Table 2). We considered an  $^{238}U/^{235}U$  ratio of  $137.818 \pm 0.045$  (Hiess et al., 2012) which corresponds
- to an activity ratio of 21.709.
- Long-term background measurements did not yield significant photopeaks at 186 keV above the background scatter. We did not consider spectral coincidences for photopeak measurements at 186 keV which are minor (e.g. Yücel et al., 2010). A slight photopeak at 351.92 keV of  $^{214}$ Pb (35.6%) (t<sub>meas</sub>= 13 days, 153 counts, uncertainty 26.4%) mostly represents the  $^{222}$ Rn activity in the measuring room and is not related to a significant  $^{226}$ Ra blank of the detector. Otherwise, it would be related to a
- $203 \quad ^{226}$ Ra activity blank concentration of 0.3 mBq/ml.
- The <sup>232</sup>Th-decay series includes <sup>224</sup>Ra and <sup>228</sup>Ra. The most intense photopeak of <sup>224</sup>Ra at 240.98 keV (4.1%) was not strong enough to be measurable in the extraction fluids of our experiment. Less intense photopeaks of <sup>228</sup>Ra occur in the low-energy range, outside of our measuring span. Alternatively, the short-lived <sup>212</sup>Pb of the <sup>224</sup>Ra decay is detectable by its strong photopeak at 238.62 keV (43.6%) which is inferred by <sup>224</sup>Ra at 240.98 keV (4.1%). We only obtained a photopeak at 238.62keV (t<sub>meas</sub>= 1208830 s, 235 counts) in the fluid sampled at the beginning of the long-term experiment using Alum Shale.
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#### 212 **3. Results**

213 3.1 Shales

The XRD data show significant differences in mineralogy between the Alum shale from Bornholm, Denmark and from the Posidonia shale from Lower Saxony, Germany (Table 1). The Alum shale is non-calcareous and contains high amounts of pyrite whereas the Posidonia shale is carbonate rich and contains a lower amount of pyrite. ICP-MS data show a more than 20-times higher U content in the Alum shale (74.4  $\mu$ g/g) compared to the Posidonia shale (3.6  $\mu$ g/g; Table 2). 11.1  $\mu$ g/g of <sup>232</sup>Th was obtained from the Alum shale and 6.6  $\mu$ g/g from the Posidonia shale.

- 220
- 221 3.2 Fluids

Due to pyrite oxidation and the formation of sulfuric acid during the course of the experiment the pH in the reaction fluid of the Alum shale declined to 2-3 (Table 2, Suppl. Table 1, Fig. 3), whereas the reaction fluid in contact with the Posidonia shale increased up to 7-8. Under oxidizing but neutral conditions during the short-term experiment with the carbonate-rich Posidonia shale ca. 0.2% of the uranium was mobilized from the shale (Table 2, Fig. 3). Under oxidizing and acidic conditions during

227 the short-term and at the beginning of the long-term experiments using the pyrite-rich Alum shale and

- EF ca. 32% and 22% of the uranium was mobilized, respectively (Fig. 3). <sup>232</sup>Th was released from the
  Alum shale to the fluid with ca. 22% at the beginning of the long-term experiments and with ca. 0.8 %
  during the short-term experiment using the Alum shale and EF (Table 2, Fig. 3).
- 231 The activity concentration of <sup>238</sup>U is as high as 23.9 mBq/ml in the fluids of the short-term experiment with the Alum shale. During the long-term experiment with the Alum shale <sup>238</sup>U-activity 232 233 concentrations, calculated on the basis of the ICP-MS analyses, decreased from 16 mBq/ml to 0.0006 234 mBq/ml. For all Posidonia shale extracts the activity concentration of  $^{238}$ U is very low ( $\leq 0.0075$ mBq/ml) or below detection limit. The activity concentrations for <sup>226</sup>Ra lie between 3.5 and 235 5.0 mBq/ml in Alum shale experiments (Table 2). The activity concentrations of dissolved <sup>226</sup>Ra 236 remained unchanged at 4.1 mBq/ml between the beginning and the end of the long-term experiment 237 238 with the Posidonia shale using the extraction fluid (EF).
- 239

## 240 **4. Discussion**

A study of the International Atomic Energy Agency (IAEA, 2003), which compiles the current knowledge about the characteristics, occurrence in various compartments, and activity concentration ranges of natural radionuclides at oil and gas exploitation sites (Chapter 5.3; page 55 and Chapter 5.5; page 56), states that <sup>238</sup>U and <sup>232</sup>Th are not mobilized and largely remain in the reservoir (IAEA, 2003).

- The U content of the Alum shale from Denmark used in our experiments (74.4  $\mu$ g/g) is a little lower 245 than the mean values of the two upper Cambrian Alum shales in Bornholm, namely from the Olenus 246 and Peltura zones with 92 µg/g and 100 µg/g, respectively, and is similar to the lower-most 247 Ordovician Alum shale from Denmark with 73 µg/g (Schovsbo, 2002) and an Alum black shale from 248 Sweden (72.6 µg/g; Lavergren et al., 2009). It is shown that the primary enrichment of U in the upper 249 Cambrian Alum shale has likely been taken place by the diffusion of ions through the seafloor along 250 sulfate reductions horizons at or above the sediment-water interface (Schovsbo, 2002). During the 251 middle Cambrian, scavenging of uranium onto organic particles lead primarily to the uranium 252 enrichment in the Alum shales (Lecomte et al., 2017). The Posidonia shale contains 3.6 µg/g U. 253 Comparing both European shales with the Marcellus shale in the U.S., the investigated shales show 254 comparable contents in U whereas the experimentally derived leachates show a much lower <sup>226</sup>Ra 255 256 activity (Table 2) than published Ra activities of the flowback water from the Marcellus shale. The 257 Devonian Marcellus shale is known for particularly high U contents compared to those of other shales in the U.S., such as Eagle Ford, Utica or Antrim (Chermak and Schreiber, 2014; Kargbo et al., 2010). 258 259 Whole rock ICP-MS analyses show 13.5±0.3 µg/g U for a Marcellus shale from the Chenago County, NY (Renock et al., 2016), between 0.6 and 72.3  $\mu g/g U$  for a Marcellus shale from Greene County, PA 260 (Chen and Sharma, 2016) and 2-47  $\mu$ g/g for Marcellus shale from the Tioga and Greene Counties, NY 261
- and PA respectively (Phan et al., 2015).

In our experiment, the non-calcareous U-rich Alum shale behaves differently than the calcareous 263 Posidonia shale. The reaction fluid of the calcareous Posidonia shale had a pH of 7-8 during the course 264 of the experiments and only 0.2% of the U was mobilized from the solids. The pyrite-rich and 265 carbonate-free Alum shale leads to an acid reaction fluid with a pH of 2-3 containing max. 32% of the 266 267 U that the shale initially contained (Fig. 3). One has to take into account that the Alum shale has no 268 carbonate that could counteract the pH decrease in the fluid due to oxidizing of pyrite. The actual 269 uranium concentrations in the shale and the substantially higher pyrite concentrations in the Alum shale compared to the Posidonia shale are the driving prerequisites to generate the high U-content in 270 the extraction fluids. <sup>238</sup>U is detectable for all extracts except for the beginning of the long-term 271 experiment using the Posidonia shale. We obtained enhanced <sup>238</sup>U activities, calculated on the basis of 272 273 the ICP-MS analyses, in the reaction fluids during the short-term (23.9 mBq/ml) and at the beginning of the long-term (16.0 mBq/ml) experiment using the Alum shale. 274

Compiled Marcellus shale flowback data show a max <sup>238</sup>U activity concentration of 5.6 mBq/ml with a 275 median (N=16) of 0.012 mBq/ml but there is no information about the sampling time after hydraulic 276 fracturing (e.g. Abualfaraj et al., 2014; Haluszczak et al. 2012 and references therein). Following 277 278 hydraulic fracturing, an increase in the U concentration of the produced water was observed during the first week in the Marcellus shale (Phan et al., 2015) and in the Niobrara formation, NE-Colorado 279 (Rosenblum et al., 2017) whereas in later stages of the gas exploitation the U concentration dropped. 280 This is similar to the results of our long-term experiment using the Alum shale (Fig. 3). After U(IV) is 281 282 oxidized to the soluble and hence readily mobile U(VI) it could scavenged by FeOOH precipitates or reduced again inorganically by  $Fe^{2+}$  or  $Mn^{2+}$  species (via e.g.  $Fe^{2+} \Leftrightarrow Fe^{3+} + e^{-}$ ) that are either present 283 284 dissolved in the aqueous phase or structurally sorbed to phyllosilicates, phosphates or oxides (e.g. 285 Stetten et al., 2018 and references therein). Oxidation of pyrite, present in the Marcellus, Alum and Posidonia shales (Table 1) yields reactive Fe<sup>2+</sup> that was leached in our experiments. 286

Due to their age, the <sup>226</sup>Ra activity concentrations of both shales leached in our experiments can be assumed to be in secular equilibrium with <sup>238</sup>U. The <sup>226</sup>Ra activities of the low-pH Alum shale extracts slightly exceeded those of the Posidonia shale (Table 2) in the long-term experiments. Obtained <sup>226</sup>Ra activity concentrations from the Alum shale extracts seem to increase during the course of that experiment but are similar taken the given count uncertainties into account. Therefore, our findings do neither support nor oppose results of produced waters from the Marcellus shale by Rowen et al. 2011 in which the total Ra activities have been found to be higher in later production stages.

A rough Ra release estimation from the shales into the extraction fluids, taken into account the U concentration of the solids determined by ICP-MS, the ratio of solids and liquids used during the experiments and the presupposed equilibrium between  ${}^{238}$ U and  ${}^{226}$ Ra show that ca. 80% of the solidbound  ${}^{226}$ Ra was released from the Posidonia shale but only <5% from the Alum shale. We suggest that the detectable minor percentages of Ra released from the Alum shale into the fluid could point to co-precipitation of Ra with secondary sulfates (Fisher, 1998) like moorhousite and bianchite that were evident using X-ray diffraction (see Wilke et al., 2015 for details) or to a recrystallisation of barite (Grandia et al., 2008). The Ba concentrations in the Posidonia extractions increased during the course of the long-term experiment, whereas the increase of dissolved sulphate associated with the oxidation of pyrite for the Alum shale experiment might have counteracted a Ba increase in the coexisting fluid by the precipitation of Ba-rich sulfates (Supplement 1).

- Ra can be remobilized from particle surfaces by replacement with other similar cations such as Ca, 305 306 depending on their concentration in the extraction fluid and/or released by dissolution of chemical 307 precipitates. Radiation damage may favor Ra liberation from solids but is unlikely. Secondary precipitates of U less strongly bind <sup>226</sup>Ra than detrital minerals such as zircons that also host <sup>232</sup>Th. At 308 the beginning of the short-term experiment using Alum shale we measured weak <sup>224</sup>Ra and <sup>212</sup>Pb 309 photopeaks, indicating very low <sup>228</sup>Ra activity concentrations. The dominance of <sup>226</sup>Ra versus <sup>228</sup>Ra in 310 the experimental fluids is likely related to differences in the solid substrates hosting <sup>238</sup>U and <sup>232</sup>Th. 311 <sup>226</sup>Ra-bearing solids may be dominantly represented by chemical precipitates hosting U from which 312 313 <sup>226</sup>Ra is easily released, whereas <sup>228</sup>Ra should be predominantly hosted in fluvial or aeolian debris that more strongly embeds the <sup>232</sup>Th-series nuclides. Substantial <sup>226</sup>Ra/<sup>228</sup>Ra fractionation associated with 314 315 precipitation from the fluid or due to cation exchange is unlikely.
- The Pennsylvania Department of Environmental Protection (PA DEP, 2009; unpublished) analyzed 25 316 flowback fluids from Devonian Marcellus shale typically using gamma-spectrometry and obtained a 317 <sup>226</sup>Ra activity concentration as high as 625 mBq/ml (median A<sup>[226</sup>Ra]: 22 mBq/ml; max. total 318 (226Ra+228Ra): 667 mBq/ml; median total (226Ra+228Ra): 35 mBq/ml). The New York State 319 Departments of Environmental Conservation (NYSDEC, 2009) detected a <sup>226</sup>Ra activity concentration 320 as high as 593 mBq/ml out of 13 flowback fluids (median A[<sup>226</sup>Ra]: 203.1 mBq/ml) from the 321 Marcellus shale. Since there is no information about the analytical method, the data need to be handled 322 with care (Nelson et al., 2014). Latter study observed 670±26 mBq/ml in Marcellus shale flowback 323 water. The United States Geological Survey (USGS) analyzed 14 production waters from Devonian 324 Marcellus shale in Bradford County, PA and obtained a <sup>226</sup>Ra activity concentration as high as 201 325 mBq/ml (median A<sup>[226</sup>Ra]: 64 mBq/ml; max. total (<sup>226</sup>Ra+<sup>228</sup>Ra): 231 mBq/ml; median total 326 (<sup>226</sup>Ra+<sup>228</sup>Ra): 91 mBq/ml Rowen et al., 2011). Here, Ra was co-precipitated with Ba and the 327 precipitate measured by gamma-spectrometry. All studies revealed median activities that are higher 328 329 than the industrial effluent discharge limit of 2.2 mBq/ml for <sup>226</sup>Ra (U.S. Nuclear Regulatory Commission, 2011). 330
- For comparison, the Environment Agency of UK published a report in 2011 about the Bowland shale.
   The flowback of the Preese Hall well showed <sup>226</sup>Ra activity concentrations between 14±2.1 and 90±12

- mBq/ml. This is three to twenty-times higher to our experimental findings of 3.5 5.0 mBq/ml using 333 the Alum shale but in the range of median <sup>226</sup>Ra activities for Marcellus shale flowback fluids derived 334 by PA DEP (2009) and Rowen et al. (2011). In a recent publication from Jodłowski et al. (2017), 335 returned frackturing fluids, drilling mud and proppants as well as drill cuttings were subject to activity 336 337 measurements from multiple rigs from either the Baltic basin or the Lublin Trough in north-eastern 338 Poland. The returned fracturing fluids were sampled after a set a solid-fluid separators on-site. The 339 <sup>238</sup>U activity concentrations (< 30 mBq/ml) and the <sup>226</sup>Ra activity concentrations (2-70 mBq/ml; median 43 mBq/ml) of the Polish sites cover our experimental data. 340
- 341 In contrast to the U concentration in flowback fluids at shale gas production sites, the activity 342 concentration of Ra was found to be higher in late stage production waters of active industrial shale 343 gas production (e.g. Haluszczak et al., 2012) but kept quite constant in both long-term experiments. 344 The main reason for elevated Ra activities in flowback fluids from production sites compared to those from our reaction fluids could be seen in the fluid itself because our experimental fluids do not have 345 elevated Cl concentrations (e.g. Kraemer and Reid, 1984; Fisher, 1998; Vengosh et al., 2014; Nelson 346 et al., 2015) and our experiments do not simulate connected intra-and intergranular pores filled with 347 348 reservoir water (Dresel and Rose, 2010) from which Ra can easily release. Furthermore, a smaller fluid to solid ratio due to minute cracks in grains after subsequent hydraulic fracturing in industrial 349 drills would also explain the differences in the activity concentrations of <sup>226</sup>Ra. 350

#### 351 5. Conclusions

The Posidonia shale from Germany and the Alum shale from Denmark, both differ in their 352 353 mineralogical and chemical composition were chosen to quantify the release of U, Th and Ra by solid/water interaction in long-term lab experiments under defined experimental conditions. 354 Temperature, pressure, and initial fluid composition roughly simulated the target formation in Damme 355 3 well, Lower Saxony, Germany. The flow through character regarding the solid/fluid interaction, 356 however, could not be simulated in the static lab experiments, which probably underestimated the 357 solid/fluid ratio during the real gas exploitation. The release of U into the extraction fluid appears to be 358 independent from pressure and independent from the pH of the initially applied fluid during gas 359 exploitation (Wilke et al., 2015) but depends on the carbonate and sulfide contents of the shales and 360 361 therewith also from the pH of the resulting fluid as well as the amount of leachable U in the shale. Our 362 findings point to a preferential Ra release from U-hosting solids.

The carbonate-rich Posidonia shale which contains less U and Th than the non-calcareous and pyriterich Alum shale also releases comparably low amounts of U and Th whereas the Ra release from the shales into the extraction fluid was similar. Both European shales show comparable contents in U than reported by the USGS for the Marcellus shale. However, the experimentally derived flowback samples show much lower Ra activity concentrations than the flowbacks from the Marcellus shale. The main

reasons could be a) the missing Cl in our reaction fluid that is naturally present in the reservoir fluids,

b) that in industrial plays the fluid to solid ratio is most probably smaller c) minute cracks and well 369 connected intra-and intergranular pore spaces facilitate the release of Ra in industrial drills and d) co-370 precipitation of Ra or recrystallization of barite. 371

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#### **Figure Captions** 563

Fig. 1 Upper radioactive decay chains for A) <sup>238</sup>U and B) <sup>232</sup>Th. Half-lives are given: a=years, d=days, 565 h=hours, m=minutes, s=seconds. Half-lives from the international nuclear structure and decay data 566 network under the auspices of the IAEA. https://www-nds.iaea.org/relnsd/NdsEnsdf/QueryForm.html. 567 Radionuclides marked by a green background were quantitatively determined for this study. 568

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Fig. 2 Geographic map showing the location of described black shales in Europe. The map was 570 adapted from the Esri World Geocoder. The Alum shale distribution is modified from Buchardt et al., 571 1997 and the Posidonia shale distribution adapted from the BGR (2016). Red circles show our sample 572 573 locations.

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Fig. 3 ICP-MS analyses of U and Th of fluids sampled during the course of long-term experiments 575 using both shales and the extraction fluid (EF). The uncertainty is approx. 5%. On the secondary axis,







Reference	Name	Location	Stratigraphy	Age	Depth [m]	Minerals [decresing amount]	TOC
	Alum 18	Bornholm (DK)	Alum shale	Upper Cambrian	18.2	Ms/IIt, Qz, Py, Or, Brt	9.0
Wilke et al., 2015	Posidonien 103	Haddessen (D)	Posidonia shale	Lower Jurassic	50.8	Cb, Qz, Ms/Ilt, Kln, Py, Ab	5.6
Renock et al., 2016		Chenago County	-		571	Qz, Ilt, Chl, Cb, Py, Brt	-
Chen and Sharma, 2016, Marcon et al., 2017		Whipkey State#1 Greene County	- Marcellus Shale	Middle Devonian	2375-2406	Qz, Cb, Ms/llt, Py	5.2-5.7
Dhon at al. 2015		G1-G8, Greene County	-		2374-2407		1.0-79.7
Phan et al., 2015		T1-T7, Tioga County			901-1434		1.1-52.4

#### Table 1. Description and composition of black shales from europe and the US for comparison. Mineral abbreviations after Whitney and Evans, 2010.

Ra i	nk. 226	bla 1.	t 2 fi ient	nent vlem	plen upp e frc	enc subl	ind s, st	in equilibrium to <sup>238</sup> U in the fluids. bdl: below detection limit. ° Values below detection limit and therefore less confidential but applied because it's statistical difference from the blank.	specifications of the radiometric analyses and for further calculation details. #) <sup>238</sup> U concentration value considered for <sup>238</sup> U-activity concentration calculations, see Supplement 1. <sup>226</sup> F	Table 2. <sup>222</sup> Th and <sup>238</sup> U concentrations of shales used for leaching experiments and data for coexisting fluid compositions during the experiments. See text and supplement 2 for	
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	<sup>232</sup> Th	HR-ICP-MS	pH in experiment	amount of shale unit in experiment [g]	Rock used	Fluid used				
3.6	6.6			used				Posidonia 103	Sol	
74.4	11.1							Alum 18	ids	
bdl	bdl		7.0					water		REAC
bdl	bdl							biocide		CTION EDU
bdl	bdl		5.					surfactant	Extraction	CTS
bdl	bdl		9					friction reducer	fluid (EF)	
bdl	bdl							clay stabilizer		
0.001	bdl		7.6	(5	Posidonia 103	deionize		Short-term		
0.549	0.0005°		2.6	01	Alum 18	ed water	24 H	experiments:		
0.001	0.0001°		7.6		Posidonia 103		nours	100°C/ 1bar		
1.917	0.007		2.2	01	Alum 18			with oxygen		RE
							-		Fluids	ACTION PR
bdl	bdl		7.7		Posidonia 103 Day1	Ē	2 m	Long-term e		ODUCTS
0.00005°	bdl		7.6	64	Posidonia 103 Day64	Ŧ	Ionth	xperiments: 100		
1.283	0.197		 3.0		Alum 18 Day1	띢	6 n	°C/ 100bar v		
0.00005°	bdl		3.0		Alum 18 Day184	Π	nonth	vith oxygen		

<sup>35</sup> U] (mBq/ml)	A[ <sup>226</sup> Ra] (mBq/ml)	Uncertainty (%)	Counts (186 keV)	Δt <sub>meas</sub> (s)	A[ <sup>238</sup> U] (mBq/ml)	<sup>238</sup> U[ICP-MS] (ng/ml) <sup>#</sup>	
3.48x10-4	4.2	9.7	1236	4087195	0.01	0.6°	
1.1	3.5	7.4	718	607731	23.9	1917	G
							amma-spe
							- Cfr
bdl	4.1	12.9	879	2998580	bdl	bdl	ctrometry
bdl 2.80x10-5	4.1 4.1	12.9 16.0	879 485	2998580 1644805	bdl 6,2x10-4	bdl 0.05°	ctrometry
bdl 2.80x10-5 0.74	4.1 4.1 4.2	12.9 16.0 5.4	879 485 1358	2998580 1644805 1208830	bdl 6,2x10-4 16.0	bdl 0.05° 1283	ctrometry

Supplementa	Ca	A Co Fe Ma Co < ㄷ 큐 B ㅋ	La Bab Bab Bab Bab Bab Bab Bab Bab Bab Ba	рH	day	Ca	P ⊟ Cr Fe S	Li Srbb Sg La	рH
y Table 1: Shown	24760	N 4 20 72 - 1 4 4 4 4 4	4 8 4 4 <sup>22</sup> 4 86 <sub>2 8</sub> 62 <u>-</u>	7.7	long-term exper	64285	7 197 1283 577 338 3165 764955 764955 1220 1404	50 131 <i>27</i> 6691 269 277 591 185 2777 591 183 35 32 35 32 32	3.0
are all analyse	38760	7 5 10 9 1 2 4 4 3	5 4 5 5 4 3 185 5 4 3 185 5 185	7.5	iment using P	81421	11 14 193 1437 681 681 409 3728 904177 1413 1503	60 15123 2144 7728 2231 2231 329 616 516 516 516 313 33 37	2.9
s for the discus	52760	8 6 8 9 - 2 5 5 5 6	321 826 718 826 718 826 718	7.4	osidonia shale 1	110962	29 9 156 1598 800 477 4299 1170817 1170817 1911	17087 1880 1888 129 226 404 710 237 6 237 237 404 710 237 237 238	2.8
sed experimen	65760	2 7 8 8 4 3 4 4 7	12 370 26 370 26 806 806 806 41 753 47	7.4	and extractio	218017	71 17 1689 1105 912 5092 1641740 2437 3460	1 13 195 16 100 32 275 4 80 5 31 103 3 264 12 12 18 62	2.5
ts. Detection lin	75760	≅∼&&&∆∆∞∆∆∆∞	587 983 13 4 29 83 13 4 29	7.5	n fluid (EF) 1	255037	97 2 20 1571 1153 764 5193 1740414 2321 3813	150 17157 10161 398 475 264 1266 284 1266 284 12 284 475 284	2.4
nits (DL) are 1n	93760	∷∞92	20 537 949 118 63 118 63 118	7.4		414712	95 1 698 249 5765 249 5765 4839 2258	214 10831 10032 501 179 583 154 178 178 178 178	2.5
ng/g and better	198760	539 106 26	44 13 25 23 21 23 21 24 25 3 25 3 25 3 25 3 25 3 25 3 26 4 4 326 4 326 5 326 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	7.3	2	289322	110 2 3 17 399 1122 5541 1926009 4872 2325	204 11370 35 9803 536 145 561 145 561 145 561 156 52 2	2.4
Columns and	206760	107 2 1 1 3 7 6 6 7 2 2 1 1 1 3	46 1257 2373 24 2373 25 25 25 25 25 25 25 25 25 25 25 25 25	7.4	22	295314	101 1 1 69 583 5760 1948600 9674 617	229 10776 611 45 569 65 84 84 84 84 84 84	2.4
Th and U valu	215760	169 5	49 194 194 1194 1194 1194 1194 1194 119	72	22	301528	97 <1 1 38 594 5814 1953576 14439 58	263 9934 10545 620 521 72 42 42 44	2.5
es in a frame n	219760	908 00 × × 4 4 ×	49 118 12500 137 157 157 157 157 157 157 157 157 157 15	7.3	2	311172	102 1 1 1 122 5246 1865044 15143 32	271 9915 10555 657 52 52 485 52 406	2.7
nark the discus	245760	21 7 7	55 116 2748 2748 2748 47 47	7.1	ω	318908	74 1 29 4220 6057 1906633 18080 5	263 15007 9696 586 441 75 24 441 75 75 441 75 75	2.9
sed experimen	240760	13 109 3 1 1 1 1 1 5 5 5 5 5 5 5 5 5 5 5 5 5 5	11 85 2745 88 48 48	7.0	ω	295833	53 <1 <1 <1 2164341 22057 1	262 21872 2 7254 580 285 286 286 285 285 285 212 285 212 285 213 21872 21872 2 580 21872 2 580 580 580 580 580 581 581 582 582 582 582 582 582 582 582 582 582	3.2
tal results.	246760	19 5	56 11 2750 2750 94 11 27 2750 94 94 94 94 94 94 94 94 94 94 94 94 94	7.1	ω	213612	60 <1 <1 <1 6 62 1 62 7 162 527 909 16309 1	217 13573 134 5855 579 579 149 200 20 20 20 20 275 272 21	3.1
	249760	41 4172 7	55 126 2789 2789 45 45	7.2	з	215878	60 <1 <1 5 7169 521414 13964 <1	227 11740 502 1 590 147 117 12 12 12 12 12 12	3.1
	253760	2067 24 2 2 3 4 2 3 4 3 3 4 2 3 4 3 4 3 5 4 5 5 5 5 5 5 5 5 5 5 5 5 5	113 113 2907 1386 127 2907 1386 2	7.2	4	221029	58 41 5 457 7296 526838 14425	11838 11838 4310 596 129 129 129 129 129 129	3.1
	264760	3777 8	1360 4065 4563 4563 4563	7.0	cn	220620	54 53 183 4 53 183 4 53 183 4 54 55 5 54 5 54 5 54 5 54 5 54 5 54	241 12191 3669 600 21 112 112 112 40	3.1
	276760	9 9 82 9 10 5 10 5 10 5 10 5 10 5 10 10 10 10 10 10 10 10 10 10 10 10 10	12 29 12 12 12 13 5 5 2 2 5 3	7.3	60	219025	55 -1 -1 -1 -1 -1 -1 -2027 -7589 -531948 -531948 -15058 -1	249 13130 688 33552 616 122 101 128 128 128 128 128 128 128	3.1
	276760	3783 4 4	73 31 3050 1252 13 125 1252 13 118	7.3	10	216845	52 <1 <1 <1 363 7159 516713 15170 <1	2 31 120 83 2 690 5 90 2 22 8 5 8 5 11 8 5 8 5 11 8 5 11 1 8 5 3 9 4 1	3.1
	277760	422 9	74 29 29 29 47 12 39 84 112 34 119 114	7.3	11	213705	52 3 <1 <1 300 7074 507414 15182 1	231 12063 2378 585 585 22 24 14 86 14 86 14 22 24	3.1
	280760	5208 4 4	74 29 3057 1228 1424 21 124 21	7.3	12	212157	53 4 <1 285 7069 506359 15503 <1	1 1988 1 1988 2 250 591 22 22 82 11 1 1 82 22 2 11 1 2 2 2 2 2 2 3 4 3 4 3 4 3 4 3 4 3 4 3 4	3.0
	280760	4130 5 2 0	77 27 3041 1213 14 122 14 22	7.3	15				
	278760	¥ ∞ ≈ 80 7 ≈ ≏ ≏ ≏ 5 5	78 24 2988 2988 2988 2988 2988 2988 2988	7.4	19				
	275760	311 311 311 311 311 311 311 311 311 311	77 2822 2822 2822 2822 282 282 282 282 2	7.4	26				
	270760	40 8 2 2 3	91 25 61 1048 18 111 2800 7 1048 18	7.4	33				
	259760	3020 2 1	93 2800 907 106 41	7.5	\$				
	258760	2847 2 1	96 20 2800 2800 854 113 2 2	7.5	47				
	255760	N 3 8 8 N 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	2700 2700 819 2700 57 41 41 41 41 41	7.5	\$2				
	249760	767 &	2700 732 118	7.6	64				



Supplement 2: Specifications of the radiometric analyses and calculation formula

## Variables used

Eff (186 keV)= 0.49	Detector efficiency at 186 keV
Ab[ <sup>235</sup> U (185.715keV)]= 57.0%	Intensity
Ab[ <sup>226</sup> Ra (186.21keV)]= 3.64%	Intensity
counts (186 keV)	
$\Delta t_{meas}(s)$	Measuring time
$A_v = 6.02 \times 10^{23} \text{ mol}^{-1}$	Avogadro constant
<sup>238</sup> U <sub>meas</sub> (ng/ml)	ICP-MS results
$A[^{238}U]_{calc}$ (mBq/ml)	calculated on the basis of ICP-MS analyses
$T_{1/2}[^{238}U] = 4.47 x 10^9 a$	Half-life <sup>238</sup> U
$T_{1/2}[^{235}U] = 7.04 \times 10^8 a$	Half-life <sup>235</sup> U
$^{238}\text{U}/^{235}\text{U} = 137.818 \pm 0.045 \ (2\sigma)$	after Hiess et al. (2012)
$A[^{238}U]/A[^{235}U] = 21.709$	Reciprocal is 0.04606
$V_{meas} = 4 ml$	Volume aliquot for y-measurement

$$A[^{238}U](mBq/ml) = \frac{\left(^{238}U_{[meas]}(ng/mL) \times 10^{-6} \times A_v \times \ln^{10}(2)\right)}{238 \times T_{1/2}[^{238}U] \times 365.2422 \times 24 \times 3600}$$

$$A[^{235}U](mBq/ml) = \frac{A[^{238}U]}{21.709}$$

$$A\left[^{226}Ra\right]\left(\frac{Bq}{ml}\right) = \left[\frac{counts[186keV]}{V_{meas} \times t_{meas} \times Eff[186keV]} - A\left[^{235}U\right] \times 0.57\right] \times \frac{1}{0.0364}$$