1   **Influence of sediment redox conditions on uranium mobilisation during saline intrusion**

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16   Abstract (word count 212)

17   In the UK, several coastal nuclear sites have been identified as vulnerable to future sea level

18   rise. Legacy contamination at these sites has accumulated in sub-surface sediments at risk of

19   future seawater inundation and intrusion. Porewater salinization, changes in pH and the influx

20   of oxygen into sediments may impact the stability of sediment associated uranium (U). In this

21   study, saturated column experiments were performed to compare the mobilisation of U from

22   oxic and reduced sediments into seawater under environmentally relevant flow conditions.

23   Uranium release profiles were independent of the initial geochemistry of the sediments.

24   Uranium release from the sediments was kinetically controlled, showing relatively slow

25   desorption kinetics, with release initially limited by the impact of the sediments on the pH of

26   the seawater. Significant U release only occurred when the pH was sufficiently high for the

27   formation of U-carbonate complexes (pH_{oxic} 6.3; $pH_{reduced}$ 7.5). Uranium was more strongly

28   bound to the reduced sediments and after 400 pore volumes of seawater flow, release was

29   more extensive from the initially oxic (46%) compared with initially nitrate reducing (27%)

30   and iron reducing (18%) sediments. The products of iron cycling appeared to act as a buffer

31   limiting U mobilisation, but the on-going dissolution of the Fe-phases suggests that they did

32   not form a permanent protective layer.

33   **Highlights**

34   • Seawater intrusion promotes U mobilisation from oxic and reduced sediments

35   • Initially reducing conditions result in stronger binding of U to the sediment

36   • Mobilisation was pH dependent and kinetically controlled

37   • Fe(III) phases formed during Fe(II) oxidation retard U release temporarily

38

39   **Keywords:** *Uranium; porewater salinization; desorption; transport; oxic and reduced*

40   *sediments; oxidation*

41   **1. Introduction**

42   Radioactive waste is generated throughout the nuclear cycle and accidental discharges, and

43   70 years of nuclear activities have resulted in a significant legacy of contaminated soil and

44   sediment at nuclear facilities worldwide (McKenzie and Armstrong-Pope, 2010; Reistad et al.,

45   2008; Zachara et al., 2013). Due to their need for cooling water several nuclear facilities

46   (example.g. in the UK, USA and Japan) are located in low lying coastal areas and this close

47   proximity to the shoreline raises questions regarding their future safety with respect to

48   projected climate change and rising sea levels.

49   Much of the contamination at nuclear sites has accumulated in the sub-surface sediments

50   (McKenzie and Armstrong-Pope, 2010; McKinley et al., 2006) and these will be at risk of

51   seawater inundation and intrusion. Uranium is a long lived radionuclide (^{238}U $t_{1/2} = 4.5$ x10^9

52   years) and is both a persistent and widespread contaminant found at uranium mining and mill

53   tailings sites, nuclear facilities and waste disposal sites worldwide (McKinley et al., 2006;

54   Riley and Zachara, 1992). All of the U isotopes are alpha emitters, chemotoxic and radiotoxic

55   and any remobilisation of U from sediments may lead to human dietary exposure through the

56   consumption of contaminated food (Belles et al., 2013).

57   Localised areas of reduced sediments are found in sub-surface environments at legacy nuclear

58   sites. The redox conditions in sub-surface sediments are variable; therefore uranium is found

59   in both the reduced U(IV) and oxidised U(VI) forms (Sharp et al., 2011; Zhou and Gu, 2005).

60   Uranium(VI) sorbs to a variety of minerals and related phases including clays (Rodriguez et

61   al., 2008; Whicker et al., 2007), iron (oxy)hydroxides (Duquene et al., 2008; Gómez et al.,

62   2006; Martinez et al., 1995; Sherman et al., 2008) and aluminium and silica oxides

63   (Sylwester et al., 2000). Uranium(VI) can also co-precipitate with iron oxy-hydroxides and

64   calcium carbonates (Duff et al., 2002; Reeder et al., 2000) and so its behaviour, at least in

65   some situations, can be influenced by the cycling of other elements in the system.

66   Uranium(IV) species form under reducing conditions, and have a higher affinity for surface

67   binding sites and a lower solubility than U(VI) species (Langmuir, 1978). The product of

68   U(VI) reduction is often uraninite (UO_2) (Campbell et al., 2011; Ginder-Vogel et al., 2006).

69   Additionally, U(VI) that is sorbed to sediments surfaces can be reduced to sorbed U(IV)

70   phases (Begg et al., 2011; Gu et al., 2005).

71 Uranium(VI) mobilisation can be promoted by the formation of U(VI) carbonate complexes,

72 such as $UO_2(CO_3)_2^{2-}$ or $UO_2(CO_3)_3^{4-}$, when the pH is >6 (Choy et al., 2006; Zhou and Gu,

73 2005). Thermodynamic data suggests that carbonate does not complex U(IV) or promote UO_2

74 dissolution under reducing conditions (Guillaumont et al., 2003). However, the production of

75 CO_3^{2-} and HCO_3^{-} during microbial respiration has been shown to promote the formation of

76 stable uranyl carbonate complexes under reducing conditions (Wan et al., 2008).

77 Since sediments can interact with seawater and lower its pH until the sediment's reactive

78 phases are exhausted, column experiments have been shown to be more appropriate than

79 batch experiments for investigating the impact of seawater inundation on U mobilisation from

80 oxic Dounreay sediments (Eagling et al., 2013). In these column experiments, pH changes

81 were monitored as a function of flow volume and U mobilisation, which began when the pH

82 reached 6.9 due to the formation of U-carbonate complexes. As the pH increased further,

83 mobilisation of U was slow and the elution profile was consistent with kinetically slow

84 release processes.

85 As well as inducing pore water salinization and altering the porewater pH, seawater intrusion

86 introduces oxygen into reduced sediments, allowing the re-oxidation of sediment associated

87 U(IV). Uranium re-oxidation has been observed in batch experiments at circumneutral pH

88 where U(IV) was rapidly oxidised to U(VI), followed by mobilisation (Law et al., 2011), and

89 this can be accelerated by bicarbonate complexation (Ulrich et al., 2008). However, sediment

90 re-oxidation may not always lead to the mobilisation of U(VI); e.g. Zhong *et al.*, (2005)

91 found that during re-oxidation U mobilisation from Fe-rich Oak Ridge sediments was limited

92 by sorption of U(VI) to the secondary Fe(III) minerals formed. Additionally, Fe(II) sorbed to

93 the outer surface of sediments may re-oxidise to form an Fe(III) oxide veneer that acts as a

94 diffusional barrier, protecting against U(IV) re-oxidation (Zhong et al., 2005).

95   Relatively few studies have investigated the mobilisation of U(VI)/(IV) from sediments under

96   more environmentally relevant flow conditions (Abdelouas et al., 1999; Komlos et al., 2008a;

97   Komlos et al., 2008b; Moon et al., 2007; Moon et al., 2009). Re-oxidation studies have

98   shown that secondary products formed during Fe reduction did not protect U(IV) from

99   oxidation and mobilisation under flow conditions (Komlos et al., 2008b; Moon et al., 2007).

100 A similar effect resulting from the low solubility of Fe re-oxidation products has been

101 observed during Tc remobilisation from Fe rich sediments, with flow conditions promoting

102 more Tc mobilisation compared with batch systems (Eagling et al. 2012). However, iron

103 sulphide precipitates formed under more extensively reducing conditions have been reported

104 to act as a buffer, preventing U oxidation and/or release under flow conditions (Abdelouas et

105 al., 1999; Moon et al., 2009). Mackinawite was particularly effective and provided long term

106 protection when formed in sufficient quantities (Abdelouas et al., 1999). Uranium oxidation

107 and/or release from geochemically reducing sediments into seawater has not, however, been

108 investigated.

109 The aim of this study was to investigate how the initial geochemical conditions of an Fe-rich

110 sediment affect the mobilisation of U during seawater intrusion. Iron-rich sediments with

111 similar properties to the Sellafield, UK site were contaminated with U and either stored open

112 for six months in the dark, or sealed and stored in the dark for different lengths of time to

113 allow the natural microbial communities to change the geochemical redox conditions to

114 nitrate-reducing and then iron-reducing. The sediments were then used in column

115 experiments simulating seawater intrusion to investigate U cycling and release processes in

116 sub-surface environments under environmentally relevant flow through conditions.

117 **2. METHODS**

2.1. Sediment and water. Sandy, iron rich sediments with a similar mineralogical

composition (quartz, silicates and feldspars) and geochemical characteristics to the

Quaternary alluvial flood plain deposits that underlie the Sellafield site (Cumbria, UK), as

previously characterised by Law et al. (2010), were sampled from Crediton UK (Lat:

50^0.8091'N ; Long: 03^0.6815'W), homogenised and sieved (<2 mm) in a field-moist state.

Seawater was collected from the L4 coastal monitoring station in the Western English

Channel to avoid estuarine influence (see www.westernchannelobservatory.org.uk) and

filtered (0.4 µm Nuclepore^{TM} track edge membrane, Whatman). Characterisation of the

sediments is detailed elsewhere (Eagling et al., 2012). A synthetic groundwater solution (pH

= 7.2) representative of the Sellafield region (Wilkins et al., 2007) was prepared by

dissolving salts in Milli-Q water (the constituents are shown in SI Table 1).

2.2. Contamination of oxic sediments with U. Sieved sediment (< 2 mm) was amended

with simulated groundwater containing U ≈ 25 µM ($UO_2(NO_3)_2.6H_2O$) at a 1(g):1(mL)

sediment to solution ratio. After a 7 day sorption period, the supernatant was separated from

the sediment by centrifugation (10 min at 7500 g). Moist sediments were transferred to a

container and stored in the dark at 21 ^{o}C for a 6 month ageing period. Periodically the

container was opened to allow entry of air and ensure that the sediments did not become

reducing.

2.3. Contamination of anoxic sediments with U. The U-amended synthetic groundwater

was added to sieved sediment to give a 1(g):1(mL) sediment:solution ratio and incubated

anaerobically in 250 mL serum bottles in the dark at 21 ^{o}C. The natural microbial consortium

reduced the sediments over time without the addition of amendments. At pre-selected time

intervals the serum bottles were transferred to an anaerobic chamber (COY Laboratory

Products Inc., MI; 95% N_2, 5% H_2, O_2 < 50 ppm) and the slurries transferred into centrifuge

vessels. The Eh and pH of the slurries were measured using hand held electrodes. Sediments

143   were separated from the porewater by centrifugation and then the U concentration in the

144   supernatant was determined by ICP-MS (Thermo X Series 2, Thermo Scientific). Redox

145   indicators (NO_3^- and SO_4^{2-}) were determined by ion chromatography (Dionex DX-500). Acid

146   (0.5 M HCl) extractable Fe(II) was determined spectrophotometrically (λ_{max} = 562 nm) using

147   ferrozine (Lovely and Phillips, 1986; Stookey, 1970). The incubations were targeted to obtain

148   nitrate-reducing and iron-reducing conditions.

149   **2.4. Column experiments.** Column experiments were used to simulate the intrusion of

150   seawater into the sediment in order to investigate the release of U from contaminated

151   sediments. Each contaminated sediment (i.e. oxic, nitrate reducing and iron reducing) was

152   packed into a separate polyetheretherketone (PEEK) self-pack column (50 mm x 10 mm;

153   Applied Biosciences) according to Eagling et al. (2012). In order to avoid re-oxidation,

154   reduced sediments were packed into the columns within the anaerobic chamber. The columns

155   were then removed from the anaerobic chamber and oxic seawater was pumped through at a

156   constant flow rate of 1.2 mL h^{-1} using an HPLC pump. The eluate was collected in fractions

157   using a fraction collector at 1.2-3.6 mL intervals. Pre-weighed vessels were placed after every

158   10 sample vials to check the flow rate (uncertainties associated with the flow rate were < 5%).

159   Experiments involving oxic sediment were shorter (400 pore volumes) than those with

160   initially nitrate-reducing and iron-reducing sediments (1000 pore volumes). Flow was

161   stopped for 2 weeks after approximately 765 pore volumes to investigate whether the U in the

162   eluate was in equilibrium with sorbed uranium in the nitrate- and iron-reducing sediment

163   columns (Qafoku et al., 2005; Yin et al., 2011). At the end of each experiment, the column

164   porosity was characterised using a conservative Br$^-$ tracer injected as a pulse onto the column.

165   At the end of each experiment, the column porosity was characterised using a conservative

166   Br$^-$ tracer injected as a pulse onto the column. There was only minor variation in Br$^-$

167   breakthrough (SI Figure S1), which indicates that there was only minor variability in column

168 packing and hence in the column porosity. The linear column flow velocities were 268 m y^{-1}

169 (oxic aged), 235 m y^{-1} (nitrate-reducing) and 262 m y^{-1} (iron-reducing). These flow velocities

170 are within the range of flow velocities observed in sandy aquifers under natural

171 hydrogeological conditions (Mackay et al., 1985). The pH and Eh of the eluate were

172 measured as soon as practically possible after elution and the concentrations of U, Fe and Br

173 were determined by ICP-MS with collision cell technology to eliminate $^{40}Ar^{16}O$ interference

174 on the ^{56}Fe signal. Standards were matrix matched (10 % seawater) and ^{115}In and ^{209}Bi were

175 used as internal standards to account for instrumental drift. Independent standard checks were

176 used to ensure both quality control and consistency between runs. All results were blank

177 corrected to account for U and Fe naturally present in seawater. The limits of detection for Fe

178 and U were 3.0 nM and 0.09 nM respectively.

179 **3. RESULTS AND DISCUSSION**

180 **3.1. Sediment characterisation.** Sediment from the same location has been described

181 previously (Eagling et al. 2012) and characterisation data are shown in SI Tables 2 and 3. The

182 sediment mineralogy was dominated by quartz but also contained silicates, feldspars and

183 hematite, with a high proportion of sand (61 %) and silt (36 %) and a low clay content (3 %).

184 The sediments were iron rich (420 ± 6 mmol Fe kg^{-1}), had a surface area of 6.57 m^{-2} g^{-1}, a

185 cation exchange capacity of the 9.3 ± 1 cmol kg^{-1} and a pH of 3.9 ± 0.3 (measured in Milli-Q

186 water using a 1:1 sediment: solution ratio). The total organic carbon content of the sediment

187 was 2% w/w.

188 **3.2. U immobilisation under oxic conditions.** Uranium sorbed rapidly to the oxic sediments,

189 with 96 ± 2 % of the uranium sorbed after the 7 day period. There was no significant change

190 in the percentage of U sorbed during the subsequent 6 month ageing period and, because

191   conditions remained oxic throughout this time, U was expected to be associated with the

192   sediments as U(VI).

193   **3.3. U immobilisation during reduction.** The conditions in the sealed serum bottles became

194   increasingly reducing over time (Table 1). After 30 days, pore water nitrate concentrations

195   had decreased significantly, indicating that nitrate reduction had been the dominant

196   respiration process. The pH of the sediment had increased, which is consistent with the

197   generation of CO_3^{2-} during nitrate reduction (Law et al., 2010). In these sediments, 99 ± 0.5 %

198   of U(VI) had been removed from solution. In general U(VI) reduction does not occur

199   alongside nitrate reduction (Finneran et al., 2002), and it is likely that U remained in the

200   oxidised form, i.e. as U(VI).

201   After a 120 day reduction period, the nitrate concentration was below the limit of

202   detection. Iron reduction had started by this time, as indicated by ingrowth of 0.5 M HCl

203   extractable Fe(II) (16 ± 1 mmol kg^{-1}). Porewater SO_4^{2-} concentrations increased over the 120

204   day reduction period, evidence that sulfate reduction had not occurred in the sediments. In

205   these sediments 98 ± 1 % of the U had become associated with the sediments. Abiotic or

206   microbial reduction of U(VI) to U(IV) is generally observed in sediments alongside Fe(III)

207   reduction (Begg et al., 2011; Finneran et al., 2002; Gu et al., 2005; Senko et al., 2002).

208   However, in our experiments, there was no significant change in the percentage of U sorbed

209   to the sediments as conditions changed from nitrate- to iron-reducing, which suggests that the

210   oxidation state of U did not change. Calculations performed with the Hydra hydrochemical

211   database with MEDUSA software (Puigdomenech, 2004) also predicted that U(VI) species

212   would dominate. Therefore it is likely that U remained as U(VI) throughout the experiments.

213   Begg et al. (2011) used sequential extractions to show that U(IV) sorbed to reduced iron rich

214   sediments was bound more strongly than U(VI) sorbed to oxic sediments. Sequential

215   extraction data from our experiments however showed no significant change in the

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216 fractionation of U in the three sediments (SI Figure 2), providing further evidence that there

217 was no change in the oxidation state of U in the systems reported here.

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219 **3.4. Changing geochemical conditions within the column during seawater intrusion.**

220   The pH of the eluent from all three columns was initially low (3.4-5.9), and increased

221 with flow volume, reaching the pH of the inflowing seawater (7.8) after 33-160 pore volumes.

222 The nitrate-reducing and iron-reducing sediments showed a similar pH elution profile, but

223 with a slower increase in the oxic sediment column due to the lower initial pH (Table 1). The

224 pH of the outflow was comparable with that of the other two columns after $\approx$ 160 pore

225 volumes of seawater had been eluted. The pH then remained relatively constant (7.2 - 8.0)

226 over the remainder of each experiment. A similar rapid reduction in pH has been observed

227 previously in column experiments (Eagling et al., 2012). The low initial pH of the eluents in

228 all cases is probably due to the high ionic strength of seawater displacing protons sorbed to

229 the sediments, hence decreasing the pH (Wong et al., 2010), coupled with the high sediment

230 to solution ratios at the start of the column experiments. The 2 week stop-start event applied

231 to the initially nitrate-reducing and iron-reducing columns had no effect on the pH.

232   The Eh of the outflow from the oxic columns remained relatively constant (370 - 440

233 mV). In contrast, the Eh of the nitrate-reducing and iron-reducing columns increased rapidly,

234 suggesting that the sediments were re-oxidised as seawater flowed through the column. It is

235 interesting to note that despite re-oxidation, the Eh remained lower in the oxic column

236 throughout the experiment and the redox conditions in the initially oxic and initially anoxic

237 columns were not the same at any point. The initially Fe-reducing sediments re-oxidised

238 more quickly than the nitrate-reducing sediments, and the Eh remained relatively constant

239 throughout the experiment. The stop-start event had no effect on the Eh of the initially iron

240   reducing sediments. In contrast, the Eh of the nitrate-reducing column was variable, which

241   may be due to flow path modifications and channeling resulting from oxidative mineral

242   dissolution and precipitation (Eagling et al., 2012; Moon et al., 2009). The Eh decreased in

243   the initially nitrate-reducing sediments when the flow was stopped but the reason for this is

244   unclear.

245   In the first 10 pore volumes eluted from the column there was a pulse of Fe (3.3 µM)

246   mobilised from the oxic column, suggesting that a limited pool of labile or exchangeable Fe

247   was readily desorbed (Figure 1). Release of Fe from the initially iron-reducing sediments was

248   also immediate and significant (188 µM) and was due to Fe(II) in the pore waters. After the

249   initial release, Fe leached steadily from the oxic and iron-reducing sediments over the course

250   of the experiment. In contrast, the onset of flow did not result in the initial mobilisation of Fe

251   from the nitrate-reducing sediments. In these columns Fe release was variable and increased

252   between 20 and 120 pore volumes but did not correlate with changes in Eh or pH, supporting

253   the flow path modification hypothesis. After the 2 week stop-start flow event Fe was

254   mobilised from both the nitrate-reducing and iron-reducing sediments within the first pore

255   volume when flow was resumed. The concentration of Fe released rapidly decreased to pre-

256   stop/start flow concentrations, suggesting that this pool of labile Fe was limited.

257

258   **3.5. Uranium cycling during inundation and intrusion**

259   In the first 10 pore volumes, there was a pulse release of U from the oxic sediments

260   which was not seen from the initially reduced sediments (both nitrate-reducing and iron-

261   reducing). This suggests that a limited (0.3 %) but rapidly exchangeable fraction of U(VI)

262   was sorbed to the surface of the oxic sediments. The U pulse was concurrent with the low pH

263   and Fe pulse release observed. After this, in the early period (< 40 pore volumes) in every

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264   column profile, no measurable U was mobilised from the sediments. The eluent pH was also

265   low throughout this period (< 6.3), suggesting that the increased ionic strength of the pore

266   waters alone had a limited effect on U mobilisation. Uranium release was only observed after

267   the pH of the eluted seawater increased above 6.3. This is consistent with the desorption of

268   surface associated U(VI) promoted by the formation of soluble U(VI) species such as

269     $UO_2(CO_3)_2{}^{2-}$ and $UO_2(CO3)_3{}^{4-}$ (Dong et al., 2005; Duff et al., 2002; Fox et al., 2006; Zhong

270   et al., 2005). Uranyl carbonate complexes are less likely to be sorbed to sediment surfaces

271   and therefore will increase U mobility in sub-surface environments (Wazne et al., 2003).

272   Uranium was mobilised after fewer pore volumes of seawater had flowed through the initially

273   nitrate-reducing (38 pore volumes) and iron-reducing (22 pore volumes) sediments compared

274   with the oxic sediments (46 pore volumes). However, U was released at a lower pH from the

275   oxic sediments (pH 6.3) compared with the initially reduced sediments (pH ~7.5).

276   After the onset of mobilisation, U release was most rapid from the oxic sediments and

277   maximum concentrations of U were eluted after fewer pore volumes of seawater had flowed

278   through the column (85 pore volumes) compared with the initially anoxic sediments (nitrate-

279   reducing 140 pore volumes; iron-reducing 150 pore volumes). Additionally, higher

280   concentrations of U were mobilised from the oxic sediments (U_{max} 220 nM) compared with

281   the anoxic sediments (nitrate-reducing 115 nM; iron-reducing 72 nM). These observations,

282   together with the higher pH associated with the onset of U mobilisation from the anoxic

283   sediments suggest that the U was more strongly bound to the anoxic sediments. This is

284   consistent with the physico-chemical changes that take place in the sediments during

285   reduction and/or during re-oxidation in seawater. Despite the differences in the maximum

286   concentration released, a similar fraction of the U ($\approx 6\%$) initially associated with the

287   sediments was released between time zero and the time at which maximum concentrations of

288   U were observed. This shows that although U was mobilised at different rates and was

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289   associated with different binding sites in the three sediments, a similar fraction of U was

290   readily mobilised from each sediment during this period.

291   After the peak U release (85-150 pore volumes), there was a slower on-going release,

292   producing a tail in all of the elution profiles (Figure 1a). This tailing is indicative of

293   kinetically controlled release, which involves U release from a range of binding sites with

294   different desorption kinetics and/or a re-distribution between slow and fast reactive sites

295   (Handley-Sidhu et al., 2009; Liu et al., 2008; Qafoku et al., 2005). The differences in the

296   shape of the release profiles during the tailing section (Figure 2) suggests that more than one

297   release process was occurring. The majority of the U mobilised (83-90 %) was released

298   during the tail section (i.e. after the peak in U concentration was observed). Therefore

299   relatively slow desorption kinetics dominated the mobilisation of U from all of the sediments.

300   Flow was stopped for 2 weeks in the initially nitrate-reducing and iron-reducing

301   columns. During this period U was mobilised from the nitrate- reducing and iron-reducing

302   sediments (Figure 1a), which provides further evidence that U release was kinetically

303   controlled. The highest concentrations of U were mobilised in the first pore volume after flow

304   resumed; U concentrations then decreased rapidly and only a small fraction of the U

305   originally associated with the sediments was released from the nitrate-reducing (1.4 %) and

306   iron-reducing (0.9 %) sediments respectively. Uranium mobilisation correlated with Fe

307   release in the first 10 pore volumes when flow was resumed ($r = 0.875$ (nitrate-reducing),

308   0.970 (iron-reducing); $p=0.000$, $n=12$); evidence that Fe phases play a role in controlling U

309   mobility, with desorption/dissolution of Fe phases promoting U release. The association and

310   cycling of U with Fe (oxy)hydroxides has also been observed in marine sediments (Barnes

311   and Cochran, 1993; Morford et al., 2007).

312   After 400 pore volumes of seawater had flowed through each column, more U had

313   been released from the oxic sediments (46 % of the total U initially associated with the

314   sediments) compared with the nitrate-reducing sediments (27 %) and iron-reducing sediments

315   (18 %). Release from the reduced sediments occurred throughout the experiment and in total

316   53 % was released from nitrate-reducing sediments and 38 % from initially iron-reducing

317   sediments ($\approx$1000 pore volumes). The lower U release from the iron-reducing sediment is

318   consistent with the hypothesis that low solubility Fe(III) phases form during the re-oxidation

319   of Fe(II) and these phases provide effective surfaces for U sorption and/or a physical barrier

320   preventing U mobilisation. The stop-start events showed that kinetically slow Fe mobilisation

321   correlated with U mobilisation, supporting this hypothesis. Although slow, the release of both

322   U and Fe continued throughout the experiment, which suggests that U mobilisation was only

323   retarded, rather than prevented by these phases. Similar results have been reported in

324   freshwater sediments (Moon et al., 2009; Zhong et al., 2005) where Fe(II) containing

325   minerals did not permanently protect U from mobilisation.

326   The results from the oxic sediment columns show similarities with those obtained in a

327   similar experiment conducted using sediment from the nuclear site at Dounreay (Scotland)

328   (Eagling et al., 2013). These two sediments have several common characteristics; they are

329   both iron rich, acidic, sandy loams with a low clay content and similar cation exchange

330   capacities (SI Tables S2 and S3). Uranium was mobilised at a similar pH from the two

331   sediments (this study pH 6.3; Dounreay pH 6.9), and both peak profiles showed long tailing

332   sections (Figure 2). There were differences in the elution volume before U began to be

333   released (85 pore volumes in this study compared with 160 pore volumes for Dounreay

334   sediment), however a similar fraction ($\approx$ 47 %) of sorbed U was mobilised from each

335   sediment over 400 pore volumes, with the majority of the U mobilised during the tail section.

336   The fact that these two sediments show similar U remobilisation behavior supports the view

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337   that these trends can be extrapolated to predict the impact of future sea level rise on other

338   legacy nuclear sites with similar geochemical conditions.

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340   **3.6. Conclusions and Environmental Implications**

341   Seawater intrusion into U-contaminated sediments causes U mobilisation by introducing

342   oxygen into reduced sediments and increasing the pH of the sediment pore waters. However,

343   U release from the sediment was kinetically controlled, showing relatively slow desorption

344   kinetics. The profiles differed according to the initial geochemical conditions and there was

345   evidence that Fe-phases play an important role in retarding U release. However, the on-going

346   dissolution of the Fe-phases suggests that they do not form a permanent protective layer.

347   Despite the differences in the initial geochemistry of the sediments prior to pore water

348   salinization and quantitative differences in U release, the general trends in the U release

349   profiles were broadly similar. The oxic column data showed excellent agreement with results

350   from similar column experiments using Dounreay sediments. This suggests that, regardless of

351   the geochemical redox conditions, U(VI) release is; (a) dependent on pH, (b) kinetically slow,

352   and (c) on-going from iron rich, sandy loam sediments with a low clay content.
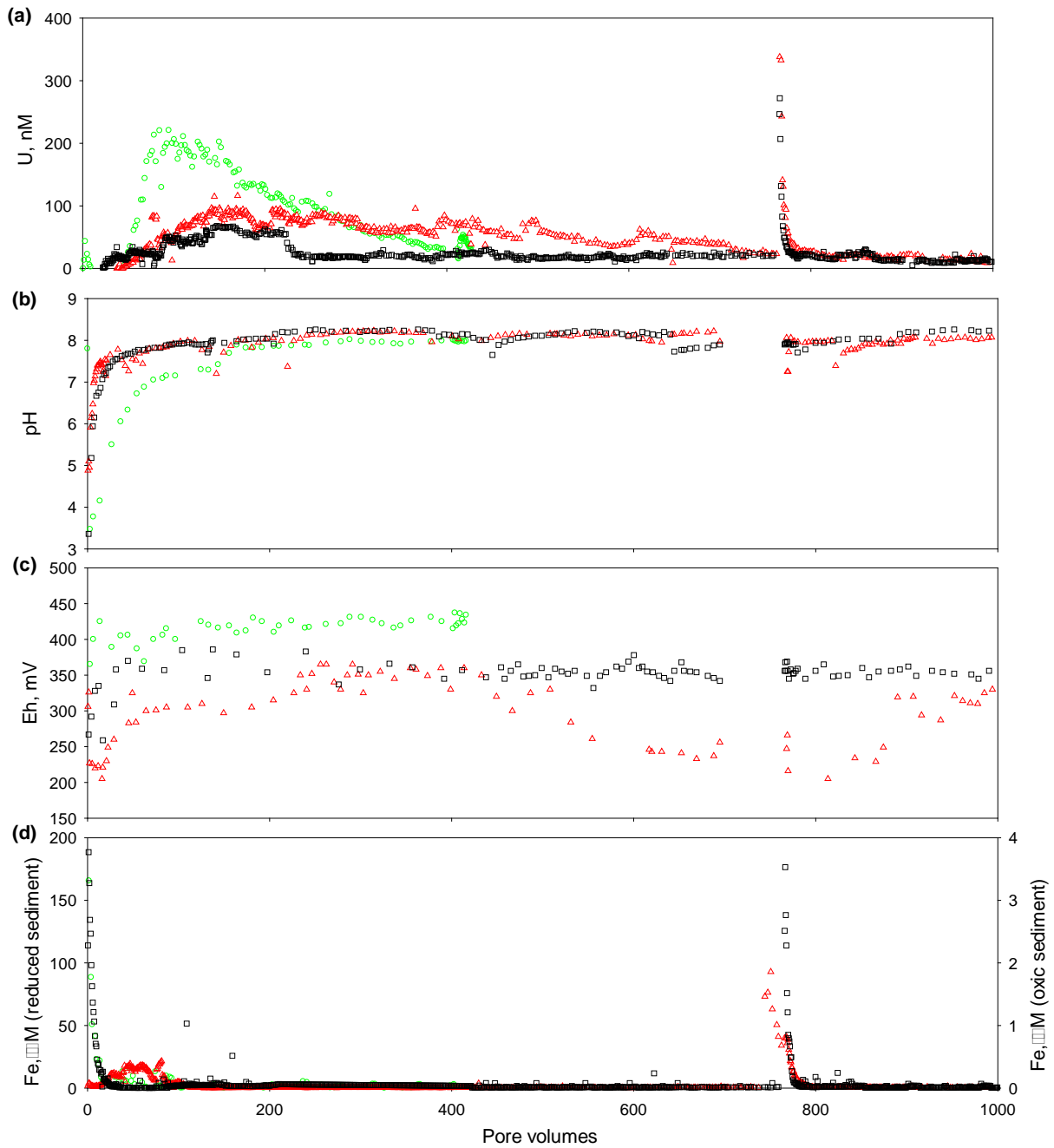
353

358   **Appendix A. Supplementary data**

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359   Supplementary data to this article can be found online at

360   http://dx.doi.org/10.1016/j.chemgeo.2013.08.030.

Figures and captions
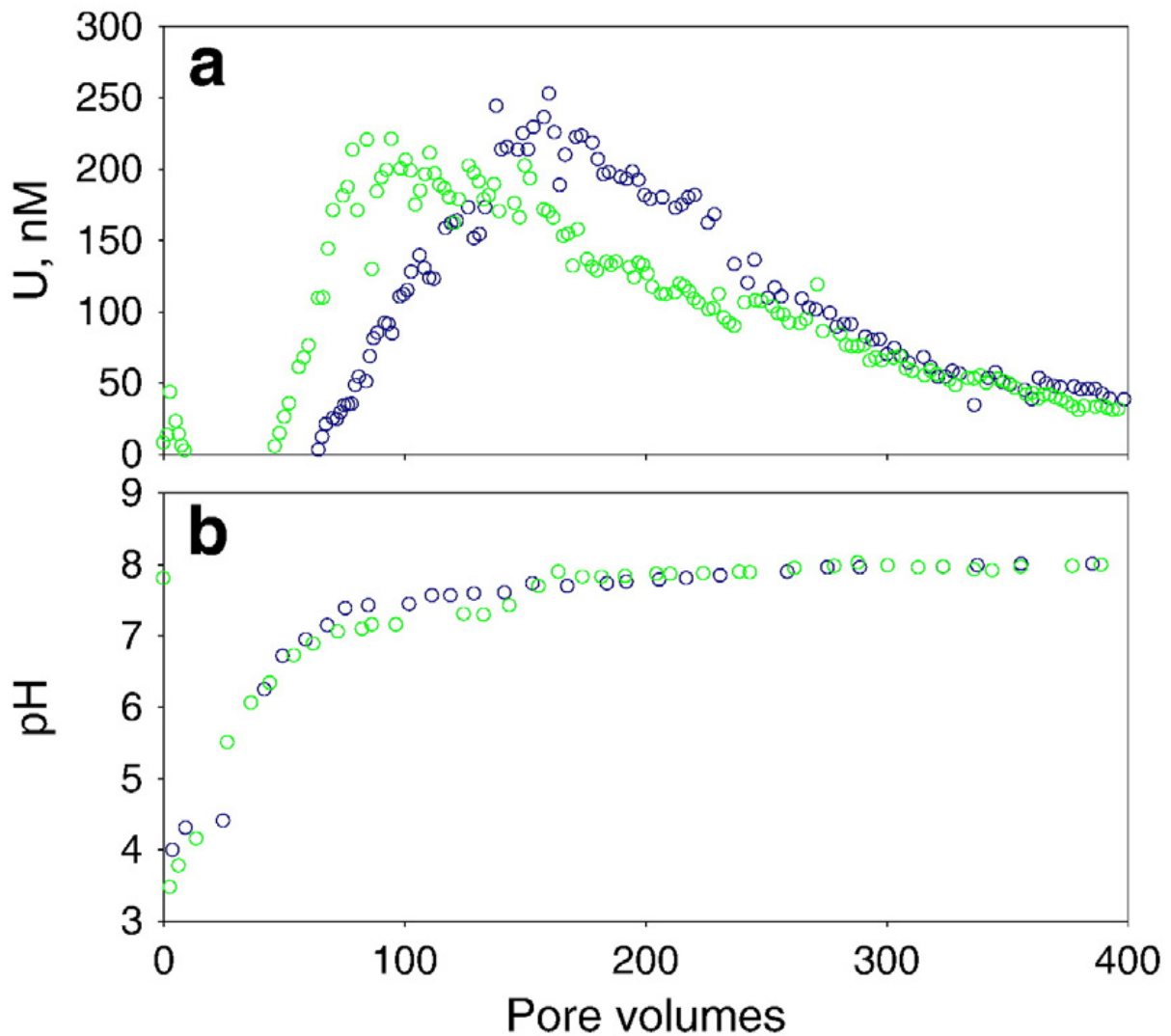
364   Figure 1. Concentration of (a) uranium and (d) iron mobilised from sediments with

365   corresponding changes in (b) pH and (c) Eh in the eluate during saturated flow through

366   column experiments. Columns were packed with; (○) oxic sediments that had been aged for 6

367   months; (Δ) nitrate-reducing sediments and (□) iron-reducing sediments. Seawater was used

368   as the mobile phase. All values were above the limit of detection for the respective techniques

369   throughout the run. Figure 1(d) shows Fe mobilised from columns packed with reduced

370   sediments (nitrate-reducing and iron-reducing) on the primary axis and Fe mobilised from

371   columns packed with oxic sediments (aged 6 months) on the secondary axis.

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Fig. 2. Concentration of (a) uranium from sediments with corresponding changes in (b) pH in the eluate during saturated flow through column experiments. Columns were packed with ( ) oxic sediments (this study) and ( ) oxic Dounreay sediments that had been aged for 6 months; using seawater as the mobile phase. All values were above the limit of detection throughout the run for the respective techniques used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

381   Table 1. Conditions in the sediments and porewaters prior to use inmobilisation experiments.

382   Data show means ± 1 standard deviation (n = 10). LOD is the limit of detection — shown in

383   brackets.

	Oxic (aged)	Nitrate reducing	Extensively iron reducing
385 Time	6 months	30 days	120 days
386 Eh, mV	469 ± 30	170 ± 1	15 ± 5
387 pH	3.9 ± 0.3	6.4 ± 0.6	7.0 ± 0.5
388 % U associated with sediments			
389	96 ± 2	99 ± 1	98 ± 1
390 NO_3^-, μM	4800 ± 300	4.4 ± 0.6	<LOD (2.5)
391 Acid extractable Fe(II), nmol kg^{-1}			
392	<LOD(0.55)	<LOD (0.55)	16 ± 1.0
393 SO_4^{2-}, μM	3.8 ± 0.7	4.2 ± 0.9	4.8 ± 0.1

394   Appendix A   **Supplementary Information**

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396   **Influence of initial sediment redox conditions on U mobilisation during saline intrusion**

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413   Table S1: Constituents of synthetic groundwater (Wilkins et al., 2007).

Salt	Concentration, $g\ L^{-1}$
KCl	0.0066
$MgSO_4.7H_2O$	0.0976
$MgCl_2.6H_2O$	0.0810
$CaCO_3$	0.1672
Na_2SiO_3	0.0829
$NaNO_3$	0.0275
NaCl	0.0094
$NaHCO_3$	0.2424

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422   Table S2. Sediment characteristics

Composition	Crediton	Dounreay
Sand (%)	61	52
Silt(%)	36	43
Clay (%)	3	5
Specific surface area ($m^2 g^{-1}$)	6.57	5.92
Cation exchange capacity (CEC)	(9.3 ± 1 mEq/100 g	12 ± 1 mEq/100 g
total organic carbon (% by mass)	2.0	4.0
pH	3.9 ± 0.3	4.4 ± 0.2

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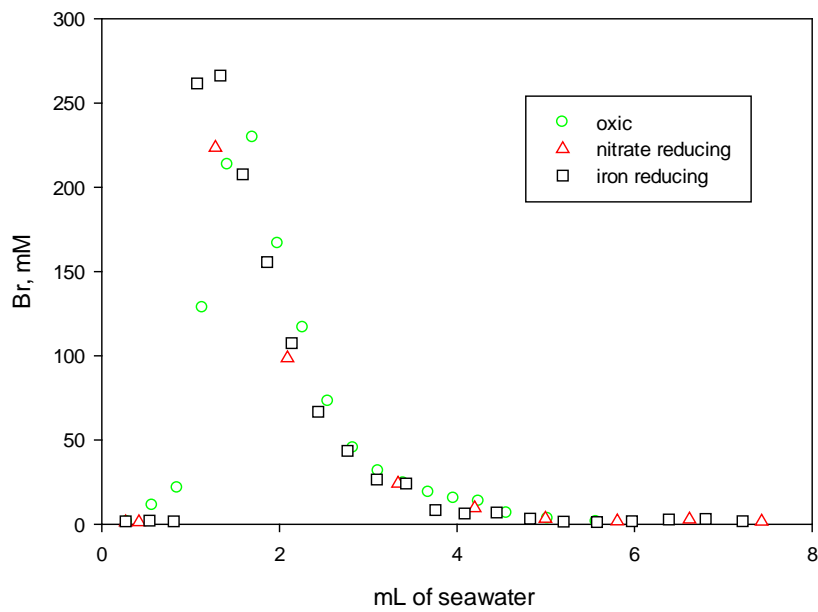
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432 Table S3. Major elemental composition of the sediments determined using inductively

433 coupled plasma mass spectrometry (ICP-MS) following aqua regia digestion. Means shown

434 (n=3) ± 1 standard deviation.

	Crediton, mmol kg^{-1}	Dounreay, mmol kg^{-1}
Al	670 ± 20	300 ± 9
Ca	38 ± 1	33 ± 3
Fe	420 ± 6	280 ± 8
Mg	120 ± 4	140 ± 4
Mn	16 ± 0.1	5.0 ± 0.3
Si	25 ± 2	25 ± 1
Sr	0.15 ±0.01	0.10 ± 0.01

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438   Figure SI 1. Characterisation of column experiments using a conservative Br⁻ tracer. Columns

439   were packed with (○) oxic sediments that had been aged for 6 months; (Δ) nitrate-reducing

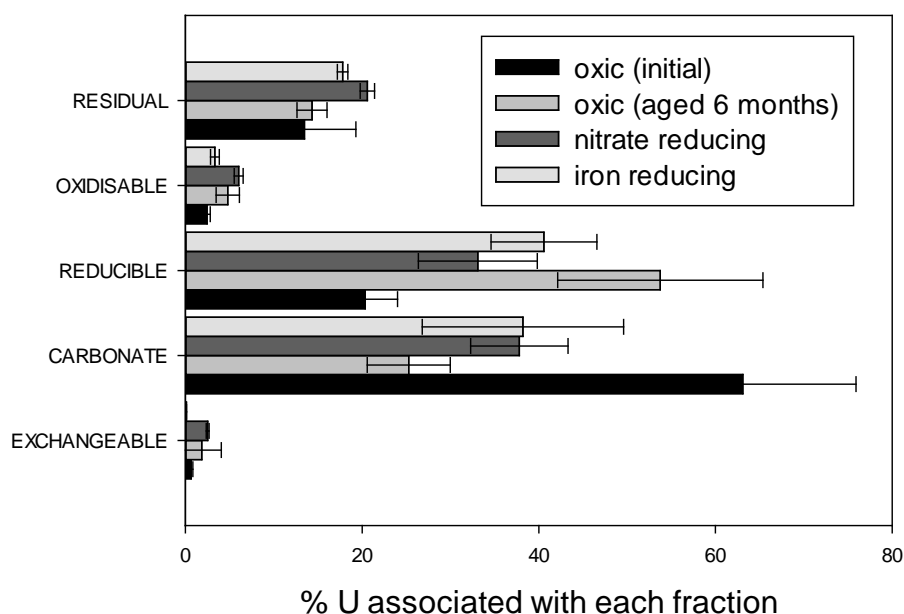440   and (□) iron-reducing sediments, with seawater as the mobile phase.

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% U associated with each fraction

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Figure SI 2. Sequential extraction data for U extracted from initially oxic sediment

(immediately after the sorption experiments), sediment aged for 6 months, nitrate-reducing

and iron-reducing sediments. Each bar represents the mean of three separate extractions ± 1

standard deviation. Sequential extractions were carried out using a modified 5 step Tessier

sequential extraction procedure suitable for use in anaerobic environments (Keith-Roach et

al., 2003; Tessier et al., 1979). Oxic (6month aged) and reduced (nitrate-reducing and iron-

reducing) sediments were progressively leached to determine (1) the exchangeable fraction (1

M $MgCl_2$ / pH 7 /1 h), (2) carbonate fraction (1 M sodium acetate/ pH 5/ 5 h), (3) reducible

fraction (0.1 M ammonium oxalate/ pH 2/ 16 h), (4) oxidisable fraction (H_2O_2/ followed by 1

M ammonium acetate/ 6% HNO_3/ 16 h) and (5) the residual fraction (aqua regia/ 2 h). In

order to maintain anaerobic conditions, approximately 1.00 g of reduced sediment was

accurately weighed into each centrifuge tube within the anaerobic chamber. To prevent

oxidation of samples, all manipulations during steps 1-3 (i.e. those prior to the oxidising

leach) were also carried out in the anaerobic chamber. Leachate solutions for these steps were

462   degassed with N_2 and the centrifuge tubes were sealed with parafilm and double bagged

463   during shaking and centrifugation to prevent entry of air.

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