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Influence of sediment redox conditions on uranium mobilisation during saline intrusion

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Abstract (word count 212)

In the UK, several coastal nuclear sites have been identified as vulnerable to future sea level rise. Legacy contamination at these sites has accumulated in sub-surface sediments at risk of future seawater inundation and intrusion. Porewater salinization, changes in pH and the influx of oxygen into sediments may impact the stability of sediment associated uranium (U). In this study, saturated column experiments were performed to compare the mobilisation of U from oxic and reduced sediments into seawater under environmentally relevant flow conditions. Uranium release profiles were independent of the initial geochemistry of the sediments. Uranium release from the sediments was kinetically controlled, showing relatively slow

desorption kinetics, with release initially limited by the impact of the sediments on the pH of the seawater. Significant U release only occurred when the pH was sufficiently high for the formation of U-carbonate complexes (pH_{oxic} 6.3; $\text{pH}_{\text{reduced}}$ 7.5). Uranium was more strongly bound to the reduced sediments and after 400 pore volumes of seawater flow, release was more extensive from the initially oxic (46%) compared with initially nitrate reducing (27%) and iron reducing (18%) sediments. The products of iron cycling appeared to act as a buffer limiting U mobilisation, but the on-going dissolution of the Fe-phases suggests that they did not form a permanent protective layer.

Highlights

- Seawater intrusion promotes U mobilisation from oxic and reduced sediments
- Initially reducing conditions result in stronger binding of U to the sediment
- Mobilisation was pH dependent and kinetically controlled
- Fe(III) phases formed during Fe(II) oxidation retard U release temporarily

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

1. Introduction

Radioactive waste is generated throughout the nuclear cycle and accidental discharges, and 70 years of nuclear activities have resulted in a significant legacy of contaminated soil and sediment at nuclear facilities worldwide (McKenzie and Armstrong-Pope, 2010; Reistad et al., 2008; Zachara et al., 2013). Due to their need for cooling water several nuclear facilities (example.g. in the UK, USA and Japan) are located in low lying coastal areas and this close

proximity to the shoreline raises questions regarding their future safety with respect to projected climate change and rising sea levels.

Much of the contamination at nuclear sites has accumulated in the sub-surface sediments (McKenzie and Armstrong-Pope, 2010; McKinley et al., 2006) and these will be at risk of seawater inundation and intrusion. Uranium is a long lived radionuclide (^{238}U $t_{1/2} = 4.5 \times 10^9$ years) and is both a persistent and widespread contaminant found at uranium mining and mill tailings sites, nuclear facilities and waste disposal sites worldwide (McKinley et al., 2006; Riley and Zachara, 1992). All of the U isotopes are alpha emitters, chemotoxic and radiotoxic and any remobilisation of U from sediments may lead to human dietary exposure through the consumption of contaminated food (Belles et al., 2013).

Localised areas of reduced sediments are found in sub-surface environments at legacy nuclear sites. The redox conditions in sub-surface sediments are variable; therefore uranium is found in both the reduced U(IV) and oxidised U(VI) forms (Sharp et al., 2011; Zhou and Gu, 2005). Uranium(VI) sorbs to a variety of minerals and related phases including clays (Rodriguez et al., 2008; Whicker et al., 2007), iron (oxy)hydroxides (Duquene et al., 2008; Gómez et al., 2006; Martinez et al., 1995; Sherman et al., 2008) and aluminium and silica oxides (Sylwester et al., 2000). Uranium(VI) can also co-precipitate with iron oxy-hydroxides and calcium carbonates (Duff et al., 2002; Reeder et al., 2000) and so its behaviour, at least in some situations, can be influenced by the cycling of other elements in the system.

Uranium(IV) species form under reducing conditions, and have a higher affinity for surface binding sites and a lower solubility than U(VI) species (Langmuir, 1978). The product of U(VI) reduction is often uraninite (UO_2) (Campbell et al., 2011; Ginder-Vogel et al., 2006). Additionally, U(VI) that is sorbed to sediments surfaces can be reduced to sorbed U(IV) phases (Begg et al., 2011; Gu et al., 2005).

Uranium(VI) mobilisation can be promoted by the formation of U(VI) carbonate complexes, such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ or $\text{UO}_2(\text{CO}_3)_3^{4-}$, when the pH is >6 (Choy et al., 2006; Zhou and Gu, 2005). Thermodynamic data suggests that carbonate does not complex U(IV) or promote UO_2 dissolution under reducing conditions (Guillaumont et al., 2003). However, the production of CO_3^{2-} and HCO_3^- during microbial respiration has been shown to promote the formation of stable uranyl carbonate complexes under reducing conditions (Wan et al., 2008).

Since sediments can interact with seawater and lower its pH until the sediment's reactive phases are exhausted, column experiments have been shown to be more appropriate than batch experiments for investigating the impact of seawater inundation on U mobilisation from oxic Dounreay sediments (Eagling et al., 2013). In these column experiments, pH changes were monitored as a function of flow volume and U mobilisation, which began when the pH reached 6.9 due to the formation of U-carbonate complexes. As the pH increased further, mobilisation of U was slow and the elution profile was consistent with kinetically slow release processes.

As well as inducing pore water salinization and altering the porewater pH, seawater intrusion introduces oxygen into reduced sediments, allowing the re-oxidation of sediment associated U(IV). Uranium re-oxidation has been observed in batch experiments at circumneutral pH where U(IV) was rapidly oxidised to U(VI), followed by mobilisation (Law et al., 2011), and this can be accelerated by bicarbonate complexation (Ulrich et al., 2008). However, sediment re-oxidation may not always lead to the mobilisation of U(VI); e.g. Zhong *et al.*, (2005) found that during re-oxidation U mobilisation from Fe-rich Oak Ridge sediments was limited by sorption of U(VI) to the secondary Fe(III) minerals formed. Additionally, Fe(II) sorbed to the outer surface of sediments may re-oxidise to form an Fe(III) oxide veneer that acts as a diffusional barrier, protecting against U(IV) re-oxidation (Zhong et al., 2005).

Relatively few studies have investigated the mobilisation of U(VI)/(IV) from sediments under more environmentally relevant flow conditions (Abdelouas et al., 1999; Komlos et al., 2008a; Komlos et al., 2008b; Moon et al., 2007; Moon et al., 2009). Re-oxidation studies have shown that secondary products formed during Fe reduction did not protect U(IV) from oxidation and mobilisation under flow conditions (Komlos et al., 2008b; Moon et al., 2007).

A similar effect resulting from the low solubility of Fe re-oxidation products has been observed during Tc remobilisation from Fe rich sediments, with flow conditions promoting more Tc mobilisation compared with batch systems (Eagling et al. 2012). However, iron sulphide precipitates formed under more extensively reducing conditions have been reported to act as a buffer, preventing U oxidation and/or release under flow conditions (Abdelouas et al., 1999; Moon et al., 2009). Mackinawite was particularly effective and provided long term protection when formed in sufficient quantities (Abdelouas et al., 1999). Uranium oxidation and/or release from geochemically reducing sediments into seawater has not, however, been investigated.

The aim of this study was to investigate how the initial geochemical conditions of an Fe-rich sediment affect the mobilisation of U during seawater intrusion. Iron-rich sediments with similar properties to the Sellafield, UK site were contaminated with U and either stored open for six months in the dark, or sealed and stored in the dark for different lengths of time to allow the natural microbial communities to change the geochemical redox conditions to nitrate-reducing and then iron-reducing. The sediments were then used in column experiments simulating seawater intrusion to investigate U cycling and release processes in sub-surface environments under environmentally relevant flow through conditions.

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° .8091'N ; Long: 03° .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™ 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 (UO₂(NO₃)₂·6H₂O) 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 °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 °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% N₂, 5% H₂, O₂ < 50 ppm) and the slurries transferred into centrifuge vessels. The Eh and pH of the slurries were measured using hand held electrodes. Sediments

were separated from the porewater by centrifugation and then the U concentration in the supernatant was determined by ICP-MS (Thermo X Series 2, Thermo Scientific). Redox indicators (NO_3^- and SO_4^{2-}) were determined by ion chromatography (Dionex DX-500). Acid (0.5 M HCl) extractable Fe(II) was determined spectrophotometrically ($\lambda_{\text{max}} = 562 \text{ nm}$) using ferrozine (Lovely and Phillips, 1986; Stookey, 1970). The incubations were targeted to obtain nitrate-reducing and iron-reducing conditions.

2.4. Column experiments. Column experiments were used to simulate the intrusion of seawater into the sediment in order to investigate the release of U from contaminated sediments. Each contaminated sediment (i.e. oxic, nitrate reducing and iron reducing) was packed into a separate polyetheretherketone (PEEK) self-pack column (50 mm x 10 mm; Applied Biosciences) according to Eagling et al. (2012). In order to avoid re-oxidation, reduced sediments were packed into the columns within the anaerobic chamber. The columns were then removed from the anaerobic chamber and oxic seawater was pumped through at a constant flow rate of 1.2 mL h^{-1} using an HPLC pump. The eluate was collected in fractions using a fraction collector at 1.2-3.6 mL intervals. Pre-weighed vessels were placed after every 10 sample vials to check the flow rate (uncertainties associated with the flow rate were $< 5\%$). Experiments involving oxic sediment were shorter (400 pore volumes) than those with initially nitrate-reducing and iron-reducing sediments (1000 pore volumes). Flow was stopped for 2 weeks after approximately 765 pore volumes to investigate whether the U in the eluate was in equilibrium with sorbed uranium in the nitrate- and iron-reducing sediment columns (Qafoku et al., 2005; Yin et al., 2011). At the end of each experiment, the column porosity was characterised using a conservative Br^- tracer injected as a pulse onto the column. At the end of each experiment, the column porosity was characterised using a conservative Br^- tracer injected as a pulse onto the column. There was only minor variation in Br^- breakthrough (SI Figure S1), which indicates that there was only minor variability in column

packing and hence in the column porosity. The linear column flow velocities were 268 m y⁻¹ (oxic aged), 235 m y⁻¹ (nitrate-reducing) and 262 m y⁻¹ (iron-reducing). These flow velocities are within the range of flow velocities observed in sandy aquifers under natural hydrogeological conditions (Mackay et al., 1985). The pH and Eh of the eluate were measured as soon as practically possible after elution and the concentrations of U, Fe and Br were determined by ICP-MS with collision cell technology to eliminate ⁴⁰Ar¹⁶O interference on the ⁵⁶Fe signal. Standards were matrix matched (10 % seawater) and ¹¹⁵In and ²⁰⁹Bi were used as internal standards to account for instrumental drift. Independent standard checks were used to ensure both quality control and consistency between runs. All results were blank corrected to account for U and Fe naturally present in seawater. The limits of detection for Fe and U were 3.0 nM and 0.09 nM respectively.

3. RESULTS AND DISCUSSION

3.1. Sediment characterisation. Sediment from the same location has been described previously (Eagling et al. 2012) and characterisation data are shown in SI Tables 2 and 3. The sediment mineralogy was dominated by quartz but also contained silicates, feldspars and hematite, with a high proportion of sand (61 %) and silt (36 %) and a low clay content (3 %). The sediments were iron rich (420 ± 6 mmol Fe kg⁻¹), had a surface area of 6.57 m² g⁻¹, a cation exchange capacity of 9.3 ± 1 cmol kg⁻¹ and a pH of 3.9 ± 0.3 (measured in Milli-Q water using a 1:1 sediment: solution ratio). The total organic carbon content of the sediment was 2% w/w.

3.2. U immobilisation under oxic conditions. Uranium sorbed rapidly to the oxic sediments, with 96 ± 2 % of the uranium sorbed after the 7 day period. There was no significant change in the percentage of U sorbed during the subsequent 6 month ageing period and, because

conditions remained oxic throughout this time, U was expected to be associated with the sediments as U(VI).

3.3. U immobilisation during reduction. The conditions in the sealed serum bottles became increasingly reducing over time (Table 1). After 30 days, pore water nitrate concentrations had decreased significantly, indicating that nitrate reduction had been the dominant respiration process. The pH of the sediment had increased, which is consistent with the generation of CO_3^{2-} during nitrate reduction (Law et al., 2010). In these sediments, $99 \pm 0.5 \%$ of U(VI) had been removed from solution. In general U(VI) reduction does not occur alongside nitrate reduction (Finneran et al., 2002), and it is likely that U remained in the oxidised form, i.e. as U(VI).

After a 120 day reduction period, the nitrate concentration was below the limit of detection. Iron reduction had started by this time, as indicated by ingrowth of 0.5 M HCl extractable Fe(II) ($16 \pm 1 \text{ mmol kg}^{-1}$). Porewater SO_4^{2-} concentrations increased over the 120 day reduction period, evidence that sulfate reduction had not occurred in the sediments. In these sediments $98 \pm 1 \%$ of the U had become associated with the sediments. Abiotic or microbial reduction of U(VI) to U(IV) is generally observed in sediments alongside Fe(III) reduction (Begg et al., 2011; Finneran et al., 2002; Gu et al., 2005; Senko et al., 2002). However, in our experiments, there was no significant change in the percentage of U sorbed to the sediments as conditions changed from nitrate- to iron-reducing, which suggests that the oxidation state of U did not change. Calculations performed with the Hydra hydrochemical database with MEDUSA software (Puigdomenech, 2004) also predicted that U(VI) species would dominate. Therefore it is likely that U remained as U(VI) throughout the experiments. Begg et al. (2011) used sequential extractions to show that U(IV) sorbed to reduced iron rich sediments was bound more strongly than U(VI) sorbed to oxic sediments. Sequential extraction data from our experiments however showed no significant change in the

fractionation of U in the three sediments (SI Figure 2), providing further evidence that there was no change in the oxidation state of U in the systems reported here.

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

The pH of the eluent from all three columns was initially low (3.4-5.9), and increased with flow volume, reaching the pH of the inflowing seawater (7.8) after 33-160 pore volumes. The nitrate-reducing and iron-reducing sediments showed a similar pH elution profile, but with a slower increase in the oxic sediment column due to the lower initial pH (Table 1). The pH of the outflow was comparable with that of the other two columns after $\approx$ 160 pore volumes of seawater had been eluted. The pH then remained relatively constant (7.2 - 8.0) over the remainder of each experiment. A similar rapid reduction in pH has been observed previously in column experiments (Eagling et al., 2012). The low initial pH of the eluents in all cases is probably due to the high ionic strength of seawater displacing protons sorbed to the sediments, hence decreasing the pH (Wong et al., 2010), coupled with the high sediment to solution ratios at the start of the column experiments. The 2 week stop-start event applied to the initially nitrate-reducing and iron-reducing columns had no effect on the pH.

The Eh of the outflow from the oxic columns remained relatively constant (370 - 440 mV). In contrast, the Eh of the nitrate-reducing and iron-reducing columns increased rapidly, suggesting that the sediments were re-oxidised as seawater flowed through the column. It is interesting to note that despite re-oxidation, the Eh remained lower in the oxic column throughout the experiment and the redox conditions in the initially oxic and initially anoxic columns were not the same at any point. The initially Fe-reducing sediments re-oxidised more quickly than the nitrate-reducing sediments, and the Eh remained relatively constant throughout the experiment. The stop-start event had no effect on the Eh of the initially iron

reducing sediments. In contrast, the Eh of the nitrate-reducing column was variable, which may be due to flow path modifications and channeling resulting from oxidative mineral dissolution and precipitation (Eagling et al., 2012; Moon et al., 2009). The Eh decreased in the initially nitrate-reducing sediments when the flow was stopped but the reason for this is unclear.

In the first 10 pore volumes eluted from the column there was a pulse of Fe (3.3 μM) mobilised from the oxic column, suggesting that a limited pool of labile or exchangeable Fe was readily desorbed (Figure 1). Release of Fe from the initially iron-reducing sediments was also immediate and significant (188 μM) and was due to Fe(II) in the pore waters. After the initial release, Fe leached steadily from the oxic and iron-reducing sediments over the course of the experiment. In contrast, the onset of flow did not result in the initial mobilisation of Fe from the nitrate-reducing sediments. In these columns Fe release was variable and increased between 20 and 120 pore volumes but did not correlate with changes in Eh or pH, supporting the flow path modification hypothesis. After the 2 week stop-start flow event Fe was mobilised from both the nitrate-reducing and iron-reducing sediments within the first pore volume when flow was resumed. The concentration of Fe released rapidly decreased to pre-stop/start flow concentrations, suggesting that this pool of labile Fe was limited.

3.5. Uranium cycling during inundation and intrusion

In the first 10 pore volumes, there was a pulse release of U from the oxic sediments which was not seen from the initially reduced sediments (both nitrate-reducing and iron-reducing). This suggests that a limited (0.3 %) but rapidly exchangeable fraction of U(VI) was sorbed to the surface of the oxic sediments. The U pulse was concurrent with the low pH and Fe pulse release observed. After this, in the early period (< 40 pore volumes) in every

column profile, no measurable U was mobilised from the sediments. The eluent pH was also low throughout this period (< 6.3), suggesting that the increased ionic strength of the pore waters alone had a limited effect on U mobilisation. Uranium release was only observed after the pH of the eluted seawater increased above 6.3. This is consistent with the desorption of surface associated U(VI) promoted by the formation of soluble U(VI) species such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Dong et al., 2005; Duff et al., 2002; Fox et al., 2006; Zhong et al., 2005). Uranyl carbonate complexes are less likely to be sorbed to sediment surfaces and therefore will increase U mobility in sub-surface environments (Wazne et al., 2003). Uranium was mobilised after fewer pore volumes of seawater had flowed through the initially nitrate-reducing (38 pore volumes) and iron-reducing (22 pore volumes) sediments compared with the oxic sediments (46 pore volumes). However, U was released at a lower pH from the oxic sediments (pH 6.3) compared with the initially reduced sediments (pH ~ 7.5).

After the onset of mobilisation, U release was most rapid from the oxic sediments and maximum concentrations of U were eluted after fewer pore volumes of seawater had flowed through the column (85 pore volumes) compared with the initially anoxic sediments (nitrate-reducing 140 pore volumes; iron-reducing 150 pore volumes). Additionally, higher concentrations of U were mobilised from the oxic sediments (U_{max} 220 nM) compared with the anoxic sediments (nitrate-reducing 115 nM; iron-reducing 72 nM). These observations, together with the higher pH associated with the onset of U mobilisation from the anoxic sediments suggest that the U was more strongly bound to the anoxic sediments. This is consistent with the physico-chemical changes that take place in the sediments during reduction and/or during re-oxidation in seawater. Despite the differences in the maximum concentration released, a similar fraction of the U ($\approx 6\%$) initially associated with the sediments was released between time zero and the time at which maximum concentrations of U were observed. This shows that although U was mobilised at different rates and was

associated with different binding sites in the three sediments, a similar fraction of U was readily mobilised from each sediment during this period.

After the peak U release (85-150 pore volumes), there was a slower on-going release, producing a tail in all of the elution profiles (Figure 1a). This tailing is indicative of kinetically controlled release, which involves U release from a range of binding sites with different desorption kinetics and/or a re-distribution between slow and fast reactive sites (Handley-Sidhu et al., 2009; Liu et al., 2008; Qafoku et al., 2005). The differences in the shape of the release profiles during the tailing section (Figure 2) suggests that more than one release process was occurring. The majority of the U mobilised (83-90 %) was released during the tail section (i.e. after the peak in U concentration was observed). Therefore relatively slow desorption kinetics dominated the mobilisation of U from all of the sediments.

Flow was stopped for 2 weeks in the initially nitrate-reducing and iron-reducing columns. During this period U was mobilised from the nitrate-reducing and iron-reducing sediments (Figure 1a), which provides further evidence that U release was kinetically controlled. The highest concentrations of U were mobilised in the first pore volume after flow resumed; U concentrations then decreased rapidly and only a small fraction of the U originally associated with the sediments was released from the nitrate-reducing (1.4 %) and iron-reducing (0.9 %) sediments respectively. Uranium mobilisation correlated with Fe release in the first 10 pore volumes when flow was resumed ($r = 0.875$ (nitrate-reducing), 0.970 (iron-reducing); $p=0.000$, $n=12$); evidence that Fe phases play a role in controlling U mobility, with desorption/dissolution of Fe phases promoting U release. The association and cycling of U with Fe (oxy)hydroxides has also been observed in marine sediments (Barnes and Cochran, 1993; Morford et al., 2007).

After 400 pore volumes of seawater had flowed through each column, more U had been released from the oxic sediments (46 % of the total U initially associated with the sediments) compared with the nitrate-reducing sediments (27 %) and iron-reducing sediments (18 %). Release from the reduced sediments occurred throughout the experiment and in total 53 % was released from nitrate-reducing sediments and 38 % from initially iron-reducing sediments (≈ 1000 pore volumes). The lower U release from the iron-reducing sediment is consistent with the hypothesis that low solubility Fe(III) phases form during the re-oxidation of Fe(II) and these phases provide effective surfaces for U sorption and/or a physical barrier preventing U mobilisation. The stop-start events showed that kinetically slow Fe mobilisation correlated with U mobilisation, supporting this hypothesis. Although slow, the release of both U and Fe continued throughout the experiment, which suggests that U mobilisation was only retarded, rather than prevented by these phases. Similar results have been reported in freshwater sediments (Moon et al., 2009; Zhong et al., 2005) where Fe(II) containing minerals did not permanently protect U from mobilisation.

The results from the oxic sediment columns show similarities with those obtained in a similar experiment conducted using sediment from the nuclear site at Dounreay (Scotland) (Eagling et al., 2013). These two sediments have several common characteristics; they are both iron rich, acidic, sandy loams with a low clay content and similar cation exchange capacities (SI Tables S2 and S3). Uranium was mobilised at a similar pH from the two sediments (this study pH 6.3; Dounreay pH 6.9), and both peak profiles showed long tailing sections (Figure 2). There were differences in the elution volume before U began to be released (85 pore volumes in this study compared with 160 pore volumes for Dounreay sediment), however a similar fraction (≈ 47 %) of sorbed U was mobilised from each sediment over 400 pore volumes, with the majority of the U mobilised during the tail section. The fact that these two sediments show similar U remobilisation behavior supports the view

that these trends can be extrapolated to predict the impact of future sea level rise on other legacy nuclear sites with similar geochemical conditions.

3.6. Conclusions and Environmental Implications

Seawater intrusion into U-contaminated sediments causes U mobilisation by introducing oxygen into reduced sediments and increasing the pH of the sediment pore waters. However, U release from the sediment was kinetically controlled, showing relatively slow desorption kinetics. The profiles differed according to the initial geochemical conditions and there was evidence that Fe-phases play an important role in retarding U release. However, the on-going dissolution of the Fe-phases suggests that they do not form a permanent protective layer. Despite the differences in the initial geochemistry of the sediments prior to pore water salinization and quantitative differences in U release, the general trends in the U release profiles were broadly similar. The oxic column data showed excellent agreement with results from similar column experiments using Dounreay sediments. This suggests that, regardless of the geochemical redox conditions, U(VI) release is; (a) dependent on pH, (b) kinetically slow, and (c) on-going from iron rich, sandy loam sediments with a low clay content.

Acknowledgments

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Appendix A. Supplementary data

359 Supplementary data to this article can be found online at
360 <http://dx.doi.org/10.1016/j.chemgeo.2013.08.030>.

361 Figures and captions

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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 immobilisation experiments.
 382 Data show means $\pm$ 1 standard deviation (n = 10). LOD is the limit of detection — shown in
 383 brackets.

384		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

Appendix A **Supplementary Information**

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).

<i>Salt</i>	<i>Concentration,</i>
	<i>g L⁻¹</i>
<i>KCl</i>	<i>0.0066</i>
<i>MgSO₄·7H₂O</i>	<i>0.0976</i>
<i>MgCl₂·6H₂O</i>	<i>0.0810</i>
<i>CaCO₃</i>	<i>0.1672</i>
<i>Na₂SiO₃</i>	<i>0.0829</i>
<i>NaNO₃</i>	<i>0.0275</i>
<i>NaCl</i>	<i>0.0094</i>
<i>NaHCO₃</i>	<i>0.2424</i>

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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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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) $\pm$ 1 standard deviation.

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

degassed with N₂ and the centrifuge tubes were sealed with parafilm and double bagged during shaking and centrifugation to prevent entry of air.

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