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Tracing U mobility in deep groundwater using Ra isotopes

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Abstract

The mobility of natural U is compared among four boreholes in a fractured granite using Ra isotopes and geochemical modelling. $^{222}\text{Rn}/^{226}\text{Ra}$ activity ratios (ARs) spanning an order of magnitude underline differences in reactive surface area. $(^{224}\text{Ra}/^{228}\text{Ra})_{\text{ARs}}$ up to 9 indicate recent changes in hydrogeochemistry, and $(^{226}\text{Ra}/^{228}\text{Ra})_{\text{ARs}}$ 0.6–30 indicate variable deposition of U. Dissolved U is related to dissolution of a solid U(VI) phase by groundwater with $\text{HCO}_3^- > 20 \text{ mg}\cdot\text{L}^{-1}$. U reduction is hindered by $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$.

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1. Introduction

The Swedish Nuclear Fuel and Waste Management Co. (SKB) has applied to construct a spent nuclear fuel repository ~500 meters below sea level (m.b.s.l.) in Forsmark, Sweden¹. The mobility of natural U at the site must be understood to assess the performance of a repository. Elevated ($>10 \mu\text{g}/\text{L}$) dissolved natural U in Fe(II) containing Forsmark groundwaters (~500 m.b.s.l.) with $>20 \text{ mg}/\text{l} \text{HCO}_3^-$ has prompted an investigation of U and its nuclides².

Forsmark is dominated by fractured calc-alkaline crystalline bedrock (~1.85 Ga). Groundwaters evolved from five endmembers: current meteoric and minor present Baltic Sea (20–200 m.b.s.l.), post-glacial Littorina Sea (9000–

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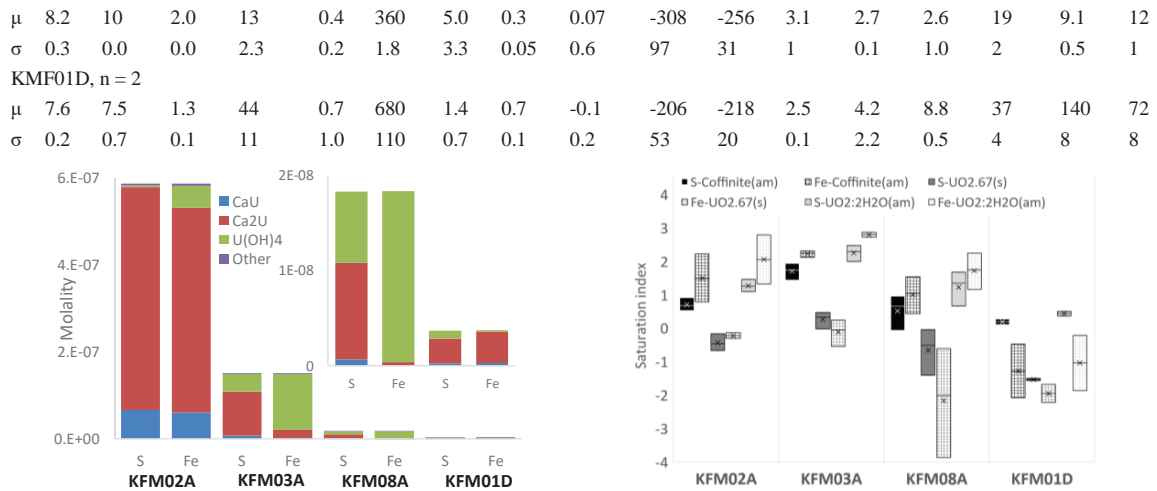


Fig. 2. Calculated (a) aqueous speciation and (b) saturation indexes of U solid phases using Fe and S redox couples.

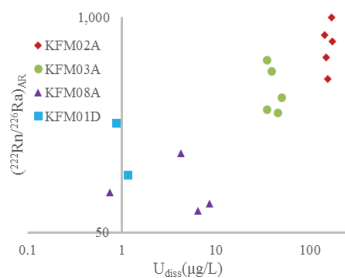


Fig. 3. $(^{222}\text{Rn}/^{226}\text{Ra})_{\text{AR}}$ versus total dissolved U (Sicada)

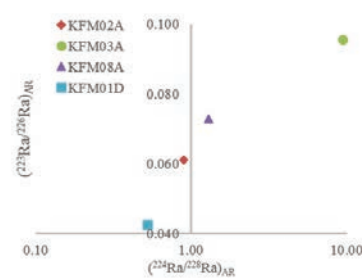


Fig. 4. $(^{223}\text{Ra}/^{226}\text{Ra})_{\text{AR}}$ versus $(^{224}\text{Ra}/^{228}\text{Ra})_{\text{AR}}$

3.1. Speciation-solubility calculations

In each section, barite was slightly over-saturated and calcite was in equilibrium. Total dissolved solids were $\sim 10 \text{ g}\cdot\text{L}^{-1}$. Redox potentials (Eh) were calculated from the $\text{Fe}(\text{OH})_{3(\text{s})}/\text{Fe}^{+2}$ (Fe^8) and the $\text{S}(-2)/\text{SO}_4^{2-}$ (S) redox couples. Resulting potentials agreed well with the in-situ Eh measurements⁹. Redox potentials are more negative and also more sensitive to the selected couple in KFM03A and KFM08A than in KFM02A and KFM01D.

The speciation of U, particularly between $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ and $\text{U}(\text{OH})_4$, was sensitive to the redox selection (Fig. 2a). Irrespective of the selected couple, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ predominated in KFM02A. In KFM03A, the speciation was more complex, resulting in $\sim 25\%$ and 90% $\text{U}(\text{OH})_4$ for the S and Fe couples, respectively. It appears unlikely that so high a proportion U(IV) is present in a solution with such high dissolved U.

Saturation indices (SI) of the U-bearing solid phases were less sensitive to the redox selection (Figure 2b). An amorphous UO_{2+x} was in equilibrium in KFM02A and KFM03A. Amorphous coffinite and an amorphous hydrous U(IV) ($\text{UO}_2\cdot 2\text{H}_2\text{O}(\text{am})$) phase are oversaturated in all except KFM01D. All samples were under-saturated with respect to uranophane ($-6 < \text{SI} < -3$), whose SI was more dependent on alkalinity than on redox.

3.2. Ra and Rn ARs

$^{222}\text{Rn}/^{226}\text{Ra}$ ARs can be used to attribute elevated U_{Diss} to a low adsorption potential (i.e. reactive surface area) of the local aquifer solids or to the aqueous speciation of U, i.e. the presence of low-sorbing $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$. $^{226}\text{Ra}_{\text{Diss}}$ alone does not indicate a reactive surface area because the $^{226}\text{R}_{\text{tot}}$, which depends on $^{226}\text{Ra}_{\text{Ads}}$, is unknown. However, ^{222}Rn , sourced by $^{226}\text{Ra}_{\text{Diss}}$ and $^{226}\text{Ra}_{\text{Ads}}$, is unreactive so principally available as $^{222}\text{Rn}_{\text{Diss}}$ (Fig. 1). Linking $^{222}\text{Rn}_{\text{Diss}}$ to $^{226}\text{Ra}_{\text{tot}}$, $^{226}\text{Ra}_{\text{Ads}}$ can be inferred from the $(^{222}\text{Rn}/^{226}\text{Ra})_{\text{AR}}$, which is proportional to the reactive surface area⁵.

A relationship is observed between $(^{222}\text{Rn}/^{226}\text{Ra})_{\text{AR}}$ and U_{Diss} (Fig. 3). This suggests that the reactive surface area is actually greater where U_{Diss} is elevated than where U_{Diss} is low, which is likely a result of the high fracture frequency around the KFM02A and KFM03A zones relative to the KFM08A and KFM01D zones. It appears that, particularly in KFM02A, U adsorption is hindered by aqueous speciation rather than by a low reactive surface area.

$^{224}\text{Ra}/^{228}\text{Ra}$ ARs and $^{223}\text{Ra}/^{226}\text{Ra}$ ARs indicate whether the system has returned to steady state after a change in the hydrologic regime. ^{224}Ra and ^{223}Ra are produced and recoiled into solution, and arrive at a constant groundwater activity more rapidly than ^{228}Ra and ^{226}Ra . Similarities between ^{223}Ra and ^{226}Ra production through their respective decay chains should result in a steady state $^{223}\text{Ra}/^{228}\text{Ra}$ AR of .046 after ~8000 y. Similarly, ^{224}Ra is replenished by local ^{228}Th more rapidly than ^{228}Ra by ^{232}Th , so $(^{224}\text{Ra}/^{228}\text{Ra})_{\text{ARs}} > \sim 1\text{--}2$ indicate recent disruption in groundwater flow⁵.

The positive relationship between $(^{223}\text{Ra}/^{226}\text{Ra})_{\text{AR}}$ and $(^{224}\text{Ra}/^{228}\text{Ra})_{\text{AR}}$ (Fig. 4) demonstrates that these ARs are driven by the state of the Ra systems, rather than by e.g. sorption kinetics. No relationship between AR and alkalinity or dissolved U has been observed (Table 1). KFM01D is in steady state with respect to both $^{226}\text{Ra}_{\text{diss}}$ and $^{228}\text{Ra}_{\text{diss}}$. $^{226}\text{Ra}_{\text{diss}}$ is not in steady state in KFM02A and KFM08A. Therefore, these groundwaters were replenished within the past 8000 y. KFM03A has not reached steady state with respect to $^{228}\text{Ra}_{\text{diss}}$, so this groundwater in this borehole section was replenished < 10 years ago.

$^{226}\text{Ra}/^{228}\text{Ra}$ ARs can be used to determine the U/Th ratio of the local fracture surfaces because ^{226}Ra and ^{228}Ra are progeny of ^{238}U and ^{232}Th , respectively. The average $(^{238}\text{U}/^{232}\text{Th})_{\text{AR}}$ of the upper crust is ~0.8. $(^{226}\text{Ra}/^{228}\text{Ra})_{\text{ARs}}$ in groundwater should be similar but may increase where U has been mobilized⁵. The maximum $(^{226}\text{Ra}/^{228}\text{Ra})_{\text{AR}}$ was observed in KFM03A (~30). Although KFM02A had the highest HCO_3^- and dissolved U contents, the $(^{226}\text{Ra}/^{228}\text{Ra})_{\text{AR}}$ was only ~2, which suggests that the extent of secondary U deposition on the fracture surface near KFM02A is low relative to KFM03A. In KFM01D, an AR ~0.6 is similar to the average crust and thus indicative of low U mobility.

4. Conclusions

Integrated speciation-solubility calculations and Ra-Rn systematics support the following working hypotheses:

- In borehole section KFM02A, U_{Diss} is driven by HCO_3^- -rich Littorina groundwaters. ARs were disrupted around the time of seawater intrusion. Uranophane is under-saturated, and elevated U_{Diss} is maintained by $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ complexation.
- Borehole section KFM03A, with lower HCO_3^- and lower redox potential alongside $(^{226}\text{Ra}/^{228}\text{Ra})_{\text{ARs}} \sim 30$, is a zone of U deposition. Destabilization of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, elevated UOH_4 , and disruption of $^{228}\text{Ra} < 10\text{a}$ suggests geochemical disequilibrium.
- Major U oxidation by hydrothermal fluids did not occur in the zone around borehole section KFM01D, given the $(^{226}\text{Ra}/^{228}\text{Ra})_{\text{AR}}$ of ~0.6. Thus, a $\text{U(VI)}_{\text{solid}}$ phase is not available for dissolution by the HCO_3^- -containing groundwater.

Acknowledgments

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