Retention of ^{226}Ra by Montmorillonite

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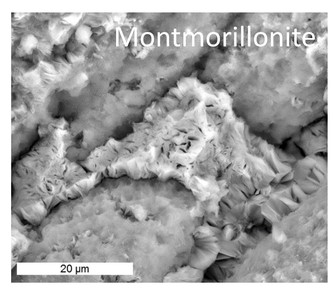
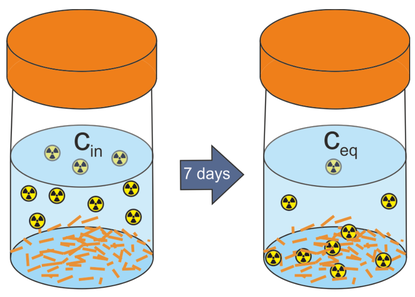
Introduction

Although ^{226}Ra is a critical radionuclide in the safety analysis for deep geological disposal of spent nuclear fuel, adsorption data for ^{226}Ra onto clay minerals are sparse. So far, the retention of ^{226}Ra by clay minerals is assumed similar to that of Sr and Ba, based on chemical analogy. Montmorillonite as a major constituent of bentonite (up to 90 wt.-%) is an important sink for potentially released radionuclides. This study presents new adsorption data of Ba and ^{226}Ra on montmorillonite. Is Ba a good analogue for Ra?



Materials & Methods

- Homo-ionic Na form of Wyoming montmorillonite (SWy-2)
- **Batch adsorpion experiments:**
  - ^{226}Ra and Ba adsorption edges in the pH range 5 to 10 at different ionic strengths (0.01 - 0.3 M NaCl)
  - ^{226}Ra and Ba adsorption isotherms (pH 7, 10^{-9} M < [Ra,Ba] > 10^{-2} M)



$$R_d = \frac{C_{solid}}{C_{liquid}} = \frac{C_{in} - C_{eq}}{C_{eq}} \frac{V}{M}$$

- **Modelling:**
  - Two site Protolysis Non Electrostatic Surface Complexation and Cation Exchange adsorption model (2SPNE SC/CE) [1].

Results: Modelling

Experiment	Kinetics		Edges				Isotherms
NaCl concentration (M)	0.02	0.1	0.01	0.02	0.14	0.3	0.02
Cation exchange reaction	**log K_c**						
2Na-SWy + Ba^{2+} ⇔ Ba-SWy + $2Na^+$	-	-	-	0.70	-	0.90	0.70
2Na-SWy + Ra^{2+} ⇔ Ra-SWy + $2Na^+$	0.84	1.34	0.70	0.70	1.14	1.34	0.70

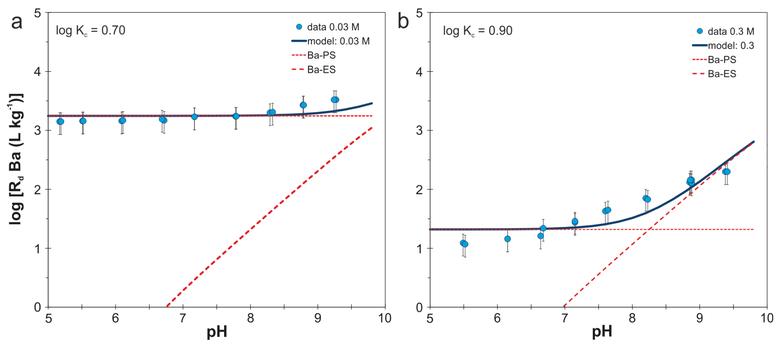
Low ionic strength: Cation exchange reactions between Ba^{2+}–Na^+ and Ra^{2+}–Na^+ on the planar sites of Na-SWy with corresponding selectivity coefficients (K_c) quantitatively describe all experimental data. Similar K_c for Ba and ^{226}Ra.

Site type	Capacity
≡S^{W2}OH	$4.0 \cdot 10^{-2}$ mol·kg^{-1}
Surface complexation reactions	**Constants**
≡S^{W2}OH + H^+ ⇔ ≡$S^{W2}OH_2^+$	log K^+ = 6.0
≡S^{W2}OH ⇔ ≡$S^{W2}O^-$ + H^+	log K^- = -10.5
≡S^{W2}OH + Ba^{2+} ⇔ ≡$S^{W2}OBa^+$ + H^+	log K_1 = -5.0
≡S^{W2}OH + Ra^{2+} ⇔ ≡$S^{W2}ORa^+$ + H^+	log K_1 = -5.0

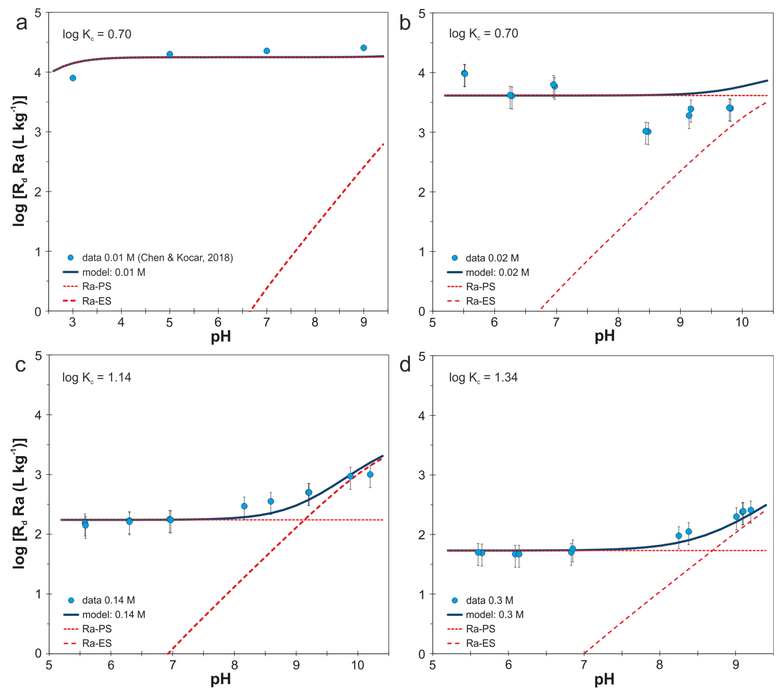
High ionic strength, high pH: an additional surface complexation reaction on the amphoteric edge sites of Na-SWy needs to be considered, reproducing the experimental data for both elements quite well. Different K_c for Ba and ^{226}Ra at high ionic strength.

Results: Experiments

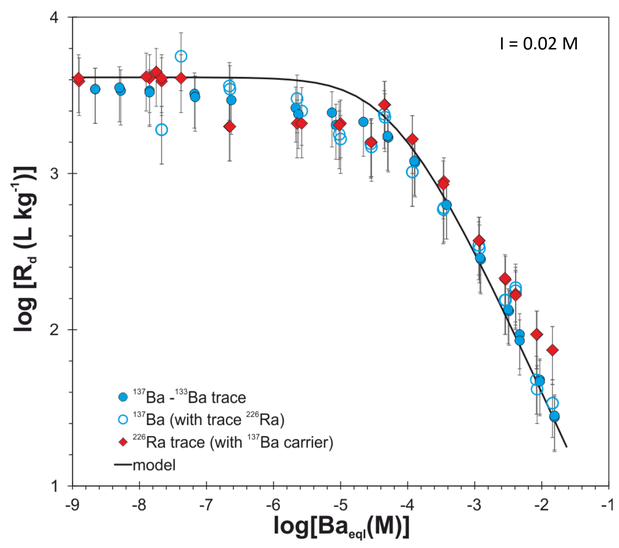
Barium adsorption edges:



Radium adsorption edges:



Barium and radium adsorption isotherms:



Download the paper with all results here:

Klinkenberg et al. 2021 Appl. Geochem. (open access)

Conclusions

- Ba is good analogue for ^{226}Ra regarding the adsorption on montmorillonite at ionic strengths < 0.1 M and pH < 8
- ^{226}Ra deviates in its behaviour at higher ionic strength
- A plausible explanation for this observation: larger ionic radius of ^{226}Ra compared to Ba → favours its selectivity behaviour on Na-montmorillonite
- The contribution of surface complexation to the overall adsorption is the same for Ba and Ra and is independent of ionic strength

References & Acknowledgements

[1] Bradbury & Baeyens, 1997. J. Contam.Hydrol. 27, 223-248; [2] Chen & Kocar, 2018. Environ. Sci. Technol. 52, 4023–4030.

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