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Radionuclide Release in Geothermal Aquifers - the Role of Alpha Recoil

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ABSTRACT

The concentration of Ra-226, Ra-228 and Ra-224 in geothermal brines is caused to a high extent by α-recoil processes at the mineral/fluid interface in the aquifer. A Monte Carlo code for the prediction of the activity concentrations and the isotope ratios was developed and tested on single and multi component systems, respectively. The simulations consider the chemical behaviour of released recoil nuclei in the solution as well as the statistical character of the recoil process. Analytical data of Radium isotopes in a geothermal fluid of the North German Basin were well reproduced by this model. Highly radioactive fracture fillings in the granite of Soultz-sous-Forêts could be excluded as a source of the Radium concentration in the associated brine.

1. INTRODUCTION

Geothermal plants in Germany are concentrated in three regions of geothermal potential: the North German Basin, the Upper Rhine Valley and the Molasse Basin. Fluids from the first two regions are characterised by high salinities from 10 to 330 g/l (Wolfgramm et al. 2011, Stober and Jodocy 2011) whereas in the Molasse Basin salinities lie below 12 g/l (Birner et al. 2011). A correlation can be found between high salinity and enhanced radionuclide concentration in the thermal waters of the plants.

This radioactivity content may cause specific activities of precipitated scales in the order of up to some 100 Bq/g and requires the expensive disposal of these radioactive wastes. The prediction of radionuclide concentrations already during the planning phase of a plant would be thus an important issue for a realistic cost estimation.

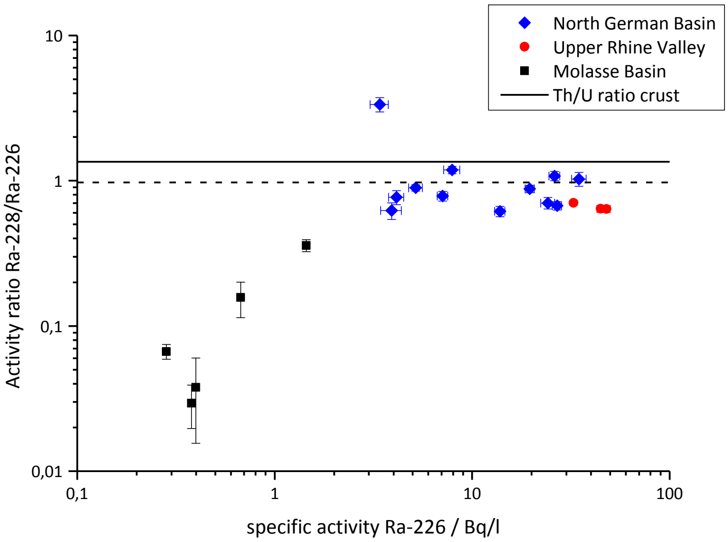

Figure 1: Range of Ra-226 activity concentrations and Ra-228/Ra-226 ratios in thermal waters from geothermal plants in Germany. Also shown is the mean activity ratio of Th-232 and U-238 decay series in the earth crust by a solid line. The dashed line is explained under section 3 (Results of simulation).

Figure 1 gives concentrations of the Radium isotopes Ra-228 and Ra-226 from the Th-232 and U-238 decay series, respectively. The majority of saline waters (North German Basin, Upper Rhine Valley) show a Radium isotope ratio somewhat below the activity ratio of the referring decay series (solid line).

The composition of radionuclides shows characteristic features for all saline waters:

- very low solubility for all Uranium and Thorium isotopes
- highest concentrations belong to the unsupported Radium isotopes Ra-226, Ra-228 and Ra-224
- short living daughter nuclides (Ac-228, Pb-212) of Radium isotopes are formed by Radium decay during water pumping

- Pb-210 occurs at varying concentrations
- K-40 stands for the potassium concentration of some per cent

Figure 2 gives an example for a characteristic fluid from the geothermal plant in Neustadt-Glewe, North German Basin.

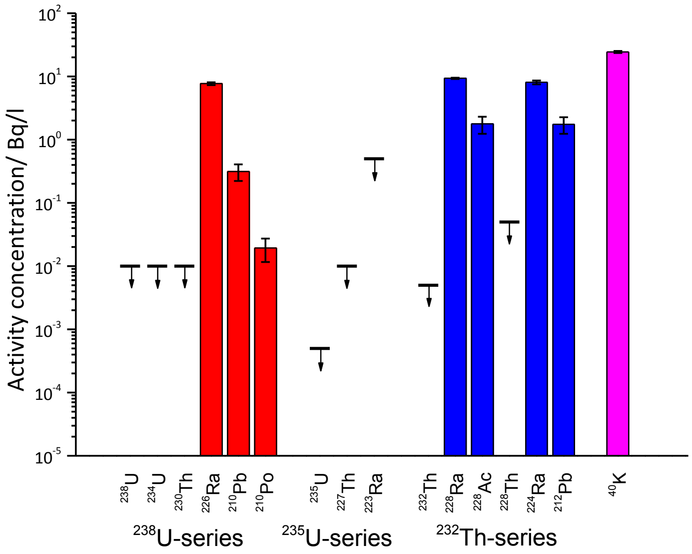

Figure 2: Radionuclide concentrations in thermal water from the geothermal plant in Neustadt-Glewe, North German Basin. Arrows indicate the detection limit for this nuclide. (after Degering et al. 2011a)

The dominating Radium isotopes represent a wide range of half lifes: Ra-226 (1600 y), Ra-228 (5.75 y) and Ra-224 (3.63 d). Especially the occurrence of Ra-224 indicates that – in contrast to the "eternal" stable isotopes – only a short time period elapsed since the radionuclide release. Therefore, the Radium concentration must be the result of a presently ongoing process. Main processes controlling the nuclide concentrations are weathering and α-recoil (e.g. Porcelli 2008) but weathering must be excluded because of the very low disintegration rate of the aquifer rock. In the present paper we investigate the ability of an α-recoil model for explaining the observed radionuclide concentrations in saline geothermal fluids.

2. APPLIED MODEL

As a consequence of the conservation of momentum a nucleus experiences a recoil when emitting an α-particle. The recoil energy is in the order of some ten keV and causes a displacement of the product nucleus in the crystal lattice of a mineral grain. α-decays in the surface region near the solid/liquid interface may therefore result in the release of nuclei into the fluid phase. The fate of these nuclei in solution depends on their physical and chemical properties.

Both parameters displacement range and direction are of statistical nature and an analytical solution of the recoil process is possible just for special cases. An earlier paper by Sun and Semkow (1998) uses this analytical approach for the calculation of "emanation rates" from mineral surfaces by α-recoil.

Displacement range distributions of the recoil nuclei were determined by applying the ion implantation code SRIM (www.srim.org). Recoil energies and resulting mean recoil ranges are listed in Table 1 for all α-decays leading within the decay chains to the observed Radium isotopes.

Table 1: Typical recoil parameters for α-decays leading to the observed Radium isotopes

α-decay		Main α-energy E_α/ MeV	Recoil energy E_R/ keV	Mean recoil range R/ nm
Mother nuclide	Daughter nuclide			
U-238	Th-234	4.20	71.8	36.2
U-234	Th-230	4.78	83.1	39.2
Th-230	Ra-226	4.69	83.0	39.2
Th-232	Ra-228	4.01	70.4	35.5
Th-228	Ra-224	5.42	96.9	43.0

The simulation of isotope release from mineral surfaces of the aquifer rock by α–recoil was implemented by means of a statistical attempt using a specially developed Monte-Carlo code ARECOIL. The code uses the randomly distributed input parameters to generate the rate of nuclei releasing the surface per area (release flux).

The behaviour of the daughter nuclides in the fluid takes into account their chemical properties:

- Under the reducing conditions in the aquifer all Uranium and Thorium isotopes (Th-234, U-234, Th-230, Th-228) are insoluble and will be sorbed onto the mineral surfaces immediately after ejection by α-recoil.
- Radium isotopes (Ra-226, Ra-228, Ra-224) are well soluble and stabilised by the formation of chloride complexes in solution and by hindered surface sorption (Herczeg et al. 1988, Langmuir and Riese 1985). They are assumed to be homogeneously dispersed in the total pore volume of the aquifer by diffusion and convection processes.
- The decay of Ra-228 in solution forms the isotope Th-228 which is instantly attached to all available surfaces by sorption.

ARECOIL can consider systems composed of different components. Besides the already mentioned recoil characteristics and chemical behaviour of the isotopes further input parameters are the effective porosity of the aquifer rock and for each component its specific surface area, density and its (assumed to be homogeneous) U- and Th-concentration.

3. RESULTS OF THE SIMULATION

Applying the ARECOIL code to single component systems it was possible to clarify some basic consequences of α-recoil:

- A close relation exists between the Th-232/U-238 activity ratio $\left.\frac{A(\mathrm{Th}-232)}{A(\mathrm{U}-238)}\right|_{\mathrm{rock}}$ in the source rock and the Ra-228/Ra-226 activity ratio $\left.\frac{A(\mathrm{Ra}-228)}{A(\mathrm{Ra}-226)}\right|_{\mathrm{fluid}}$ in the brine:

  $$\left.\frac{A(\mathrm{Ra}-228)}{A(\mathrm{Ra}-226)}\right|_{\mathrm{fluid}} = 0.72 \cdot \left.\frac{A(\mathrm{Th}-232)}{A(\mathrm{U}-238)}\right|_{\mathrm{rock}} \qquad (1)$$

  The dashed line in Figure 1 which is much closer to the data points corresponds to the Ra-228/Ra-226 fluid ratio resulting from the Th-232/U-238 ratio of the crust.
- In an undisturbed stationary fluid system the activity ratio of Ra-224 and Ra-228 (both from the Th-232 decay chain) is given by

  $$\left.\frac{A(\mathrm{Ra}-224)}{A(\mathrm{Ra}-228)}\right|_{\mathrm{fluid}} = 1.36 \qquad (2)$$

  Any deviation from this value indicates a disturbance of the stationary state. For example, during pumping of thermal water both isotopes are no longer supplied and because of the lower half life of Ra-224 the ratio decreases.
- The fluid concentrations of the Radium isotopes depend linearly from the specific surface area. Thus the fine grained components like silt or clay determine the radionuclide concentration of the fluid.

In a next step a more realistic situation was investigated by performing simulations on a two component system containing a coarse grain as well as a fine grain fraction. This model system was derived from the well investigated aquifer system at Neustadt-Glewe (cf. Degering and Köhler 2009)

Table 2: Two component model system for the test of α-recoil simulations

Description	Relative mass fraction	Specific surface area/ m²/g	Density/ g/cm³	Specific activity/ Bq/kg		Effective porosity
				U-238 series	Th-232 series	
Sandstone	95 %	0.3	2.3	10	12	0.2
Clay	5 %	10	2.5	80	95	

The model aquifer rock consists of a sandstone component with low specific area and low U/Th-content and a clay phase charaterised by large surface area and enhanced radionuclide content (Table 2).

Table 3: Resulting release fluxes of α-recoil nuclei from the surface of the components

Description	Release flux/ nuclei/s/m²		
	Ra-226	Ra-228	Ra-224
Sandstone	$2.8 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$	$9.0 \cdot 10^{-4}$
Clay	$2.5 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$

The resulting release rate of α-recoil nuclei from the surface of each component amounts to several nuclei per m² and h (Table 3) and seems to be very low; but one has to consider a total surface of about $2 \cdot 10^6$ m² per m³ aquifer rock in this case. Note that the contribution of the clay phase is about one order of magnitude higher than that for the sandstone.

Activity depth distributions of α-recoil products near the solid/liquid interface of the sandstone component are presented in Figure 3. The upper profile shows a depletion zone whose depth is progressing along the U-238 decay chain. The shoulders in the Th-230 and Ra-226 curves around 40 nm are decay products of surface sorbed species (Th-234 and Th-230). In the lower plot a superposition of two effects is visible: again a depletion zone is formed by the decays of Th-232 and Th-228. On the other hand Ra-228 released at a higher flux from clay surfaces is distributed in the whole pore volume until its decay product Th-228 is sorbed onto all surfaces. This additional surface fraction of Th-228 causes in the sandstone fraction the enhanced Ra-224 concentration up to 50 nm depth.

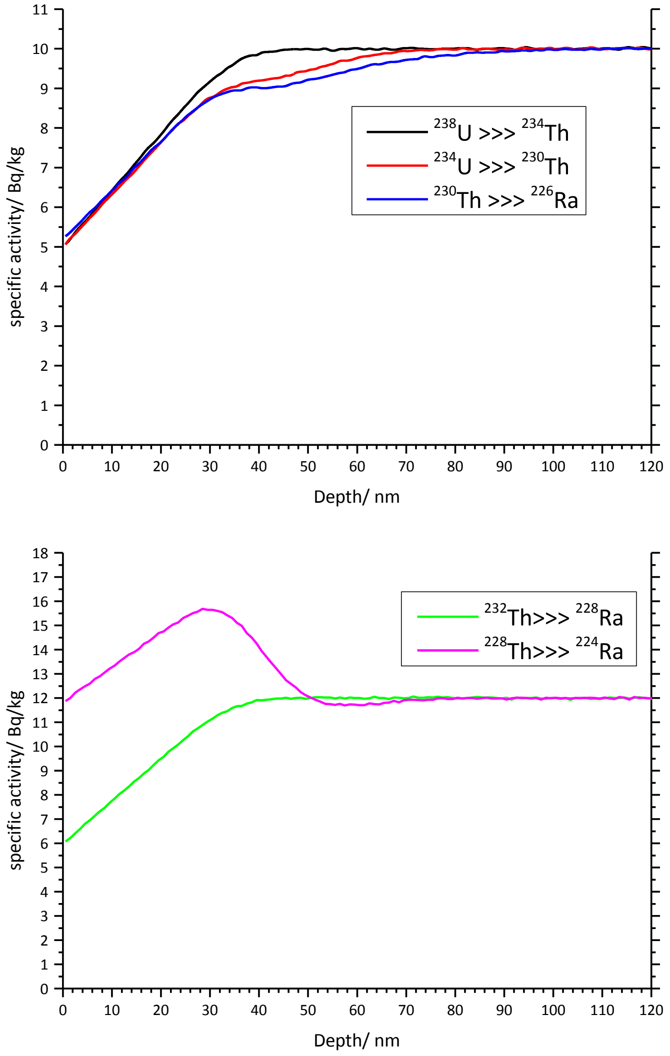

Figure 3: Near-surface depth distribution of the specific activity of α-recoil products. Shown is the sandstone component. The corresponding decays are listed in the legends. Above: U-238 decay series; Below: Th-232 decay series

A stationary situation will be reached when the decay rate (the activity) of a Radium isotope in solution equals the total production rate by α-recoil. The consequent Radium activity equilibrium concentrations for the model system are 12.1 Bq/l (Ra-226), 10.4 Bq/l (Ra-228) and 14.1 Bq/l (Ra-224) and comparable to those found generally for the North German Basin brines (cf. Figure 1).

4. APPLICATIONS

4.1. Fracture filling by secondary mineral formation

The EGS plant at Soultz-sous-Forêts, France in the Upper Rhine Valley produces fluids from a fault system in the granitic basement. Radionuclide concentrations of these highly saline waters (≈ 100 g/l) were determined by gamma spectrometry applying an elaborated measuring program as described in Degering and Köhler (2011). The results (Table 4) showed elevated levels of the activity concentrations.

Table 4: Results of radionuclide analyses on waters from the geothermal plant at Soultz-sous-Forêts

	activity concentration/ Bq/l			
	Ra-226	Pb-210	Ra-228	Ra-224
Soultz-sous-Forêts	33 ± 4	7.6 ± 1.3	23 ± 3	21.3 ± 1.2

In preceding investigations (Merleau 2012) of the Soultz granite several fracture fillings of distinctly enhanced radioactivity were detected. The question arised, if secondary mineralisation of this type could be the source of the radionuclides in the brine. To clarify this, samples of these mineral fillings were analysed regarding their U- and Th-concentration. The sample masses were partly in the sub-gram range, even below 100 mg. Analyses were performed in a well-type gamma detector at the underground laboratory Felsenkeller in Dresden, Germany (Niese et al. 1998). Additionally, bulk granite samples from different depth were analysed for comparison.

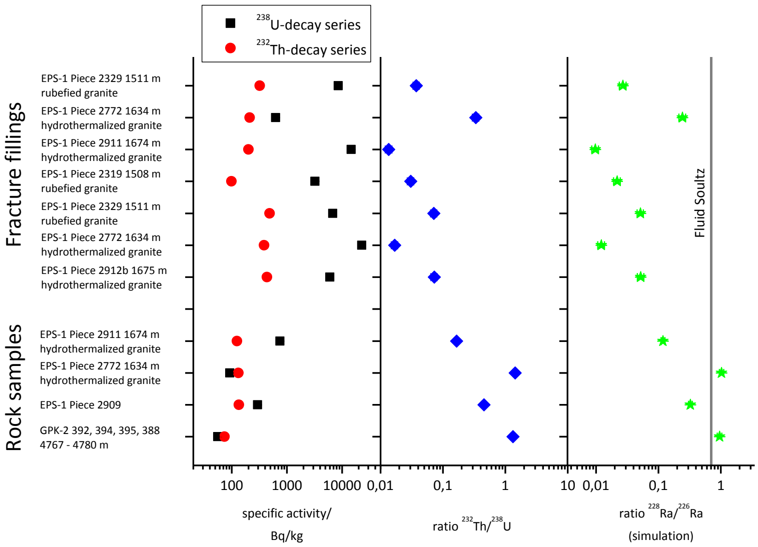

Figure 4: U- and Th-content of fracture fillings and bulk rock samples, the activity ratio of both decay series and theoretical Radium isotope ratios of the fluid

Values for the specific activities of the U-238 and Th-232 decay series are summarised in Figure 4 together with the Th-232/U-238 activity ratios of these mineral and rock samples. For the fracture fillings high specific activities up to > 10 000 Bq/kg were found for the U-238 decay series; the data for the Th-232 chain are in general at least one order of magnitude smaller. The specific activities of both decay series and their differences are distinctly lower for the rock samples.

By applying the presented α-recoil model (see section 3, formula (1)) theoretical Ra-228/Ra-226 ratios can be derived from these values under the assumption that each single sample is solely responsible for the Radium content in solution. These calculated values are plotted in the right part of Figure 4. Also shown is the Radium isotope ratio in the geothermal fluid from Soultz-sous-Forêts.

It is clearly visible that α-recoil release of Radium nuclei from secondary minerals would result in too low Ra-228/Ra-226 ratios, much below the fluid value. Hence highly active fracture fillings can be excluded as possible sources of the radioactivity in the Soultz brine. Only granite material from the bulk produces theoretical Radium ratios comparable to the observed level.

4.2. Geothermal system Neubrandenburg, North German Basin

The geothermal plant at Neubrandenburg utilises an aquifer in the Postera sandstone formation (Wolfgramm and Seibt 2006). The aquifer rock is characterised by an alternation of porous sandstone and claystone/clastic clay. Typical material from each subsection of the whole aquifer region was sampled at the drilling core GtN 2/85. Thereby in every subsection coarse grained and fine grained material was taken separately and their relative mass fractions in the subsection and in the whole aquifer were estimated. Specific activities of the U-238 and the Th-232 decay series in samples were analysed by gamma spectrometry. The specific surface area of each sample was determined by polythermal N_2 gas adsorption (BET method). Porosity data were taken from the drilling documentation.

Analytical results on core samples are summarised in Figure 5. The geological situation was highly simplified for the sake of clarity. Top and bottom sealing layer consists of fine grained clayey material as shown by the large specific surface area. In the aquifer region the four sandstone samples have low specific activities < 15 Bq/kg for both decay chains as well as small areas < 1 m²/g. In contrast, the U/Th-content as well as the surface area is distinctly larger for the four claystone/ clastic clay samples. The clayey material should therefore dominate the Radium input by α-recoil, as stated above.

Fluid samples corresponding to the described aquifer were taken from the geothermal well 4 of the plant in Neubrandenburg and analysed by gamma spectrometry as described above. Results for the activity concentrations of Ra-226 and Ra-228 are given in Table 5.

Table 5: Results of gammaspectrometric analysis of the brine from Neubrandenburg and result of the simulation by ARECOIL

	activity concentration/ Bq/l		activity ratio
	Ra-226	Ra-228	Ra-228/Ra-226
Fluid sample	5.2 ± 0.4	4.74 ± 0.20	0.89 ± 0.04
Simulation	6.6	5.5	0.85

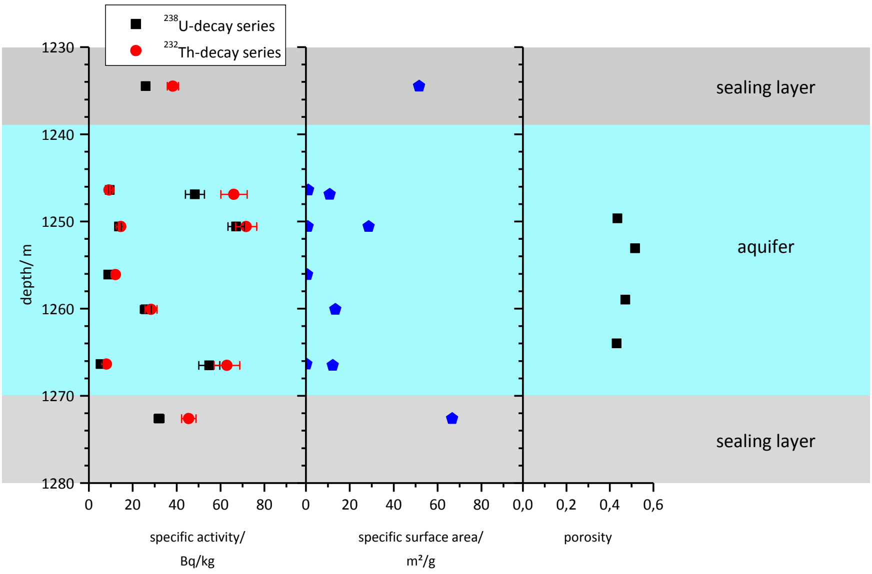

Figure 5: Analytical results on rock samples from core GtN 2/85

The data gained from the typical aquifer samples were used as input parameters for the simulation of an eight component system by ARECOIL. As shown in Table 5 a good agreement was obtained both for the activity concentrations and for the isotope ratio. Because the clay fraction of the whole aquifer was deduced from the stratification of a single core the value of the total Radium concentration is relatively uncertain and therefore somewhat overestimated. On the other hand, the Radium isotope ratio is well reproduced.

5. CONCLUSIONS

The α-recoil process at the mineral/fluid interface is a promising candidate for the explanation of the activity concentrations of Ra-226, Ra-228 and Ra-224 in highly saline geothermal fluids. A model must include all α-decays in the natural decay chains prior to the observed Radium isotopes, the statistical character of the recoil nuclei release from mineral surfaces and their chemical behaviour in the brine. The code ARECOIL was developed for the implementation of this model to real situations. Tests showed close relations between Th/U-ratio of aquifer rock and the Ra-228/Ra-226 activity ratio of the geothermal fluid. Fine grained aquifer constituents like clay material play a dominant role in Radium release because of their large specific surface area.

Simulations by ARECOIL clarified the role of fracture fillings in the granite of the EGS plant at Soultz-sous-Forêts, France. Their responibility for the enhanced Radium contents of the Soultz brine could be excluded. Obviously, a broader view on the geological situation in the Upper Rhine Valley is necessary to understand the origin of dissolved Radium isotopes.

As a more complex system the sandstone aquifer of the geothermal plant at Neubrandenburg, Germany was investigated. Data from the drilling core lead to the simulation of an eight component system. The agreement between calculated Radium concentrations and the analytical fluid data is satisfying, especially the Ra-228/Ra-226 isotope ratio is well reproduced.

The model approach realised by the code ARECOIL is obviously suited for the prediction of Radionuclide concentrations in geothermal fluids on the base of geological parameters of the aquifer rock.

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