European Geothermal Congress 2016
Strasbourg, France, 19-24 Sept 2016

Radium isotope concentrations in deep geothermal fluids as finger prints of the aquifer rocks

Detlev Degering[1], Norman Dietrich[1], Felix Krüger[2], Julia Scheiber[3], Markus Wolfgramm[4], Matthias Köhler[1]

[1] VKTA - Radiation Protection, Analytics & Disposal Rossendorf e. V., P.O. Box 510119, 01314 Dresden, Germany

[2] VacuTec Meßtechnik GmbH Dresden, Dornblüthstraße 14, 01277 Dresden, Germany

[3] GEIE Exploitation Minière de la Chaleur, 67250 Kutzenhausen, France

[4] Geothermie Neubrandenburg GmbH, 17033 Neubrandenburg, Germany

detlev.degering@vkta.de

Keywords: Radionuclides, Geothermal fluid, Radium, α-recoil.

ABSTRACT

The role of α-recoil for the release of Radium isotopes (^{228}Ra, ^{226}Ra) into highly saline deepwaters was investigated by Monte-Carlo simulations focussing on the solid-fluid interface. A close relation between Th/U in the rock and ^{228}Ra/^{226}Ra in the fluid is predicted. Applications on real systems illustrate the importance of the investigated mechanism.

1. INTRODUCTION

Enhanced activity concentrations of the Radium isotopes ^{226}Ra (from ^{238}U decay series), ^{228}Ra and ^{224}Ra (from ^{232}Th) in the order of 10 Bq/l are typical features of highly saline deep geothermal fluids (Degering & Köhler 2015). Since they may produce radioactive scales with specific activities up to some 1000 Bq g^{-1} in components of geothermal plants it is necessary to clarify their origin and to discuss if the selection of the aquifer rock can influence the radionuclide concentration in fluid.

Several processes were identified in literature which contribute to Radium isotope interactions between fluid and solid phase in an aquifer (cf. the overview in IAEA (2014)):

- Mobilisation by weathering and dissolving of rock minerals. It could be proved that this contribution does not contribute to more than 0.01 Bq l^{-1} (Degering & Köhler 2016).

- Release of decay products of the natural decay series by α-recoil processes. Typical energies of recoil nuclei are in the order of 60 ... 100 keV and result in displacements of several 10 nm in solids. In near-surface-regions they can thus enter the aqueous phase.

- Removal by coprecipitation during the formation of secondary minerals. In open pores and faults of the aquifer this process will proceed slowly and does not contribute to an instantaneous and perpetual removal of Radium isotopes from solution.

- Sorption of dissolved species onto mineral surfaces or particles. Under the reducing conditions of deep geothermal aquifers this process plays a major role in the removal of Uranium and Thorium nuclides from solution (Ivanovich & Harmon 1992). The sorption of Radium species is largely hampered in brines of high salinity. Furthermore, Ra is stabilised in solution under these conditions (Zukin et al. 1987).

Thus for highly saline deep geothermal fluids α-recoil is the prevailing mechanism for the release of Radium isotopes into solution. A permanent removal of these species only occurs via radioactive decay. The observed activity concentrations represent a stationary state with balanced α-recoil and decay.

Recently the importance of α-recoils for Radium isotope release could be verified by laboratory experiments using the time dependence of ^{224}Ra (half life 3.6 d) activity concentrations (Dietrich & Degering 2016). They showed a clear increase of the Radium concentration in solution for salinities > 10 g l^{-1}.

In the present paper the general properties of Radium isotope release were investigated by Monte-Carlo simulations. Their findings are applied in a second step onto some examples of geothermally used natural aquifer systems.

2. MONTE CARLO SIMULATIONS

The model used for the simulation of Radium release processes at the solid-fluid interfaces of the aquifer rock included the following features:

- Release of radionuclides exclusively by recoil of product nuclei after α-decay. In the solid phase the initial activity distribution is assumed to be homogeneous and ^{238}U plus ^{232}Th decay series are in radioactive equilibrium.

- Prompt and complete sorption of all released U- and Th-isotopes at the solid-fluid interface.

- Long-term and complete stabilisation of all released Radium isotopes in solution. Thorium isotopes formed by decay of dissolved Radium are sorbed as described above.

- Application of the model along the decay series starting with ^{238}U (for ^{226}Ra) and ^{232}Th (for ^{228}Ra and ^{224}Ra), respectively.

This model, especially the inclusion of all Radium isotope precursors in the decay series can no longer be solved analytically. Monte-Carlo simulations use instead a randomised selection of parameters like (i) the position of the α-decay, (ii) the emission direction and (iii) the range of the recoil nucleus, which will be repeated for a given event number n. Such a procedure was implemented as a small program code for PC application. The code is able to calculate activity concentrations for aquifer systems containing up to 100 different rock components. Input parameters are the Th- and U-contents and the specific surface area of each constituent as well as the porosity of the overall system.

Figure 1 shows after the simulation of 10^7 decay events the near-surface depth distribution in the solid as well as the surface flux of α-decay product nuclei. The model system contained a single component of a fine grained material (“clay”) with a specific ^{238}U activity of 100 Bq/kg and a specific surface area of 10 m² g^{-1}.

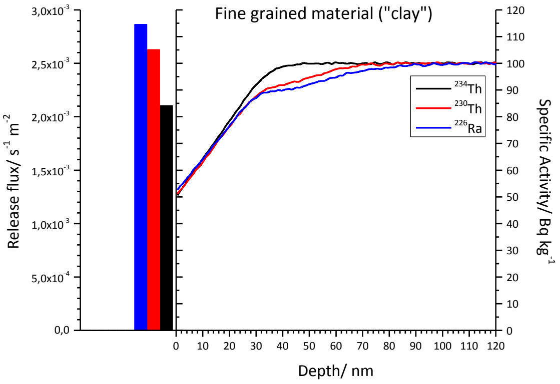

Figure 1: Near-surface depth distribution of the specific activity of α-recoil products (lines) and the corresponding release fluxes at the surface.

Obviously, the activity profiles change when progressing along the ^{238}U decay series (^{238}U ⇨ ^{234}Th ... ⇨ ^{230}Th ⇨ ^{226}Ra). A depletion layer is formed with increasing depth whereas the formation of a surface layer containing ^{234,230}Th results in a “backfire” profile recognisable by the shoulders at ≈ 35 nm in the ^{230}Th and ^{226}Ra distribution.

Besides the activity profiles, several general conclusions could be drawn from a number of simulations:

- The release fluxes of a certain radionuclide, i.e. the number of nuclei leaving the surface per time and area depend only from the activity concentration of the first nuclide of the decay series in the rock. They can thus be normalised to this activity concentration, as summarised in Table 1 for silicate rocks.

Normalised release flux / (s^{-1} m^{-2})/ (Bq m^{-3})				
^{234}U	**^{230}Th**	**^{226}Ra**	**^{228}Ra**	**^{224}Ra**
$9{,}1 \cdot 10^{-9}$	$11{,}3 \cdot 10^{-9}$	$12{,}3 \cdot 10^{-9}$	$8{,}9 \cdot 10^{-9}$	$12{,}1 \cdot 10^{-9}$

Table 1: Normalised fluxes for the release of radionuclides by α-recoil from silicate rock.

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

$$\left.\frac{c_A(^{228}\text{Ra})}{c_A(^{226}\text{Ra})}\right|_{\text{fluid}} = 0.720 \cdot \left.\frac{A(^{232}\text{Th})}{A(^{238}\text{U})}\right|_{\text{rock}}$$

- This ratio establishes a correlation between the composition of fluid and rock, respectively. It offers the possibility to derive the Th/U ratio of the source rock from the Radium isotope signature of the deepwater (and vice versa) and can therefore be utilised for clarifying the fluid’s origin.

- In an undisturbed stationary fluid system the activity concentration ratio of ^{224}Ra and ^{228}Ra (both from the ^{232}Th decay chain) is given by

$$\left.\frac{c_A(^{224}\mathrm{Ra})}{c_A(^{228}\mathrm{Ra})}\right|_{\mathrm{fluid}} = 1.36$$

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 ^{224}Ra the ratio decreases.

3. APPLICATIONS

To get an overview of typical geological formations used in deep geothermal plants of Germany using highly saline fluids (located in the North German Basin and the Upper Rhine Valley), about 150 samples from drilling cores and analogue outcrops were taken and analysed. The resulting database formed the basis for comparisons with radium analyses on brines from deep geothermal plants and other sources.

In the subsequent chapter we present a few examples of the application of simulation results onto real systems.

3.1. Fluid samples

A lot of Radium isotope analyses were performed in the last decade on deepwaters used for geothermal as well as for e.g. balneological purposes. In Figure 2 the ^{228}Ra/^{226}Ra activity ratios of these fluids are plotted vs. the total activity concentration of ^{226}Ra.

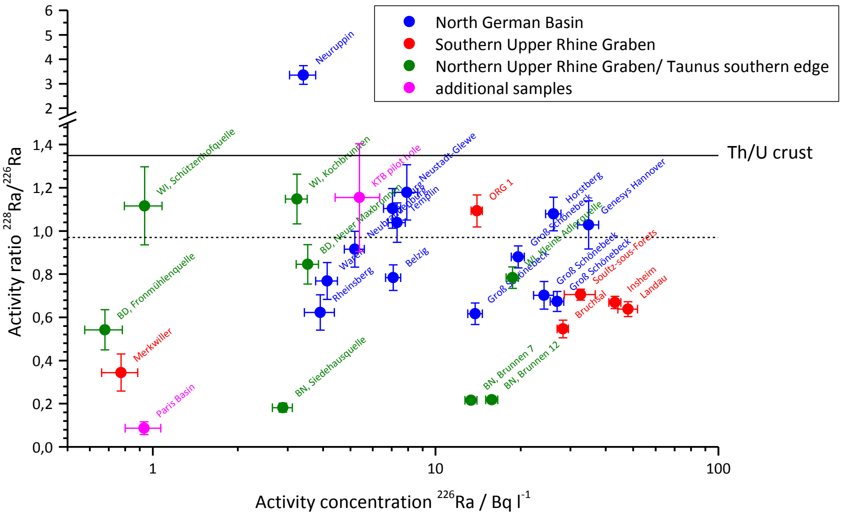

Figure 2: Summary of Radium isotope analyses performed on fluid samples mainly from Germany. The solid line gives the mean ^{232}Th/^{238}U activity ratio of the earth's crust. The dashed line is explained in the text.

The absolute ^{226}Ra activity concentrations cover a wide range of two orders of magnitude (0.7 ... 50 Bq l^{-1}). Concentrations > 1 Bq l^{-1} are generally associated with salinities > 10 g l^{-1}.

^{228}Ra/^{226}Ra activity ratios vary as well in a wide range (0.09 ... 3.4). The lowest values (< 0.5) were determined in waters from limestone aquifers. This fact is explained by the low solubility of Thorium leading to low Th/U ratios in sedimentary formations.

The mean ^{232}Th/^{238}U activity ratio of the earth's crust can be calculated from the average Th and U contents (Wedepohl 1995) to $\left.\frac{A(^{232}\mathrm{Th})}{A(^{238}\mathrm{U})}\right|_{\mathrm{rock}} = 1.35$. This value (solid line in Figure 2) is obviously higher than the majority of the ^{228}Ra/^{226}Ra ratios in fluids. The contradiction is resolved by applying the scaling factor of 0.72 between Th/U rock ratio and Radium isotope fluid ratio (cf. chapter 2). It leads to a mean ^{228}Ra/^{226}Ra activity ratio of 0.97 in fluids which is much closer to the data points (see dashed line in Figure 2).

3.2. Aquifer of Soultz-sous-Forêts

The aquifer of the geothermal plant in Soultz-sous-Forêts is based on a fault system in the granitic basement (Scheiber & Cuenot 2014). Pumped fluids show a salinity of about 100 g l^{-1} and Radium concentrations of 33 Bq l^{-1} ^{226}Ra and 23 Bq l^{-1} ^{228}Ra, respectively. Fracture fillings of distinctly enhanced radioactivity could be excluded as source of the fluid radioactivity because of their non-matching Th/U ratios (Degering et al. 2015).

To examine the responsibility of α-recoil processes at mineral surfaces in open fault zones of the granite samples from the EPS-1 core were investigated. This drilling core reaches down to a depth of about 2230 m and is situated in close proximity to the currently used wells GPK-1 ... -4. Especially one zone of highly altered rock around 2175 m depth was in the centre of interest, although it was only partly preserved in the core. This fault zone is an active one since the outflow of hot native brine was recorded during drilling.

Analyses were performed not only with respect to the radionuclide content of the rock but also on the porosity and specific surface area of the sampled material.

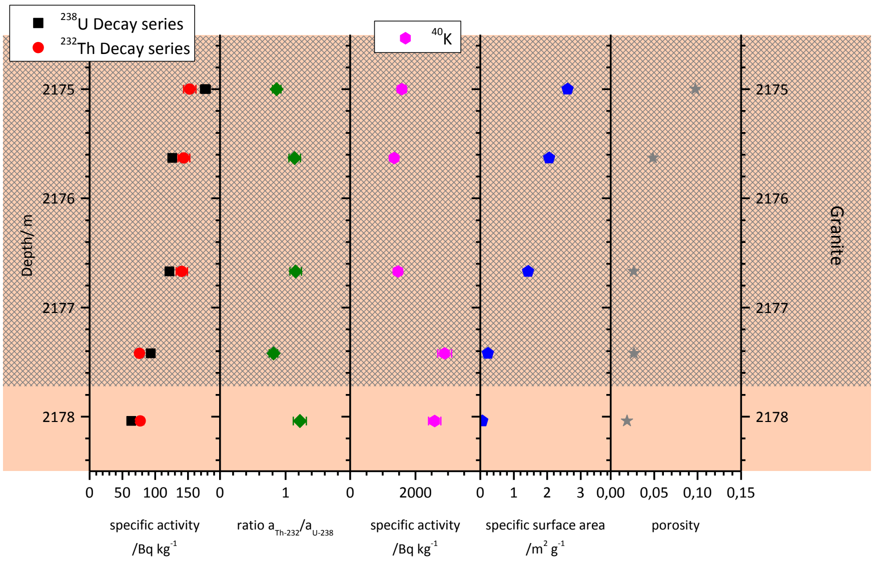

Figure 3: Analytical results of the investigated lower fault zone in core EPS-1, Soultz-sous-Forêts. The open fault zone is marked by hatching.

The investigated fault zone comprises the evolution from a permeable fluid conducting zone towards the low permeable host rock. As shown in Figure 3, this transition is characterised by a decrease of specific activities, specific surface areas and porosities. The Th/U ratio remains in contrast nearly constant, the ^{40}K activity increases in the edge region.

For testing the contribution of this part of the granite body to the overall activity concentration of the Soultz fluid the analysed sequence of different rock samples was considered as a completed aquifer system. Each data point in the permeable regions shown in Figure 3 was treated as one component of an aquifer and on this basis Monte-Carlo simulations of this “pseudo-aquifer” was performed.

	Activity concentration c_a/ Bq/l						Activity ratio R_a			
	^{226}Ra		^{228}Ra		^{224}Ra		^{228}Ra/^{226}Ra		^{224}Ra/^{228}Ra	
	c_a	Δc_a	c_a	Δc_a	c_a	Δc_a	R_a	ΔR_a	R_a	ΔR_a
Simulation	277		204		279		0.74		1.36	
Fluid	33	4	23	3	21.2	1.2	0.71	0.03	0.88	0.06

Table 2: Results of Monte-Carlo-simulations on the investigated subsystem in the core EPS-1 and analytical results of the real fluid at the site Soultz-sous-Forêts.

The results of these simulations together with the actual fluid data are summarised in Table 2. Obviously the absolute values of the activity concentrations are overestimated by a factor of ≈ 8. But one has to remind that just a very small section of the total aquifer served as basis of the simulation which cannot be representative for the hole granite body. Nevertheless, some valuable conclusions can be drawn from the simulation:

- The properties of the investigated fault zone are sufficient to explain the order of magnitude of the Radium isotope activity concentrations found in solution. Common specific activities of Th and U in granite together with the determined specific surface areas and porosity provide enough α-reoil nuclei to achieve enhanced Ra concentrations.

- The observed ^{228}Ra/^{226}Ra activity ratio in solution is in good agreement with that of the simulation. This fact indicates that a typical Th/U ratio of the granite is reflected by the Radium isotope ratio in fluid.

- The ^{224}Ra/^{228}Ra ratio in the fluid is lower than the expected value and gives a mean time period between last Radium release from rock and sampling at the well head of about 2 days.

Similar results (overestimation of the absolute concentrations and good agreement of the Radium ratios) were found also for aquifers of the North German Basin which were investigated by sampling of drilling cores and simulation of the overall system by the Monte-Carlo code.

3. CONCLUSIONS

Monte-Carlo simulations of α-recoil processes at the solid/fluid interface reveal a close relation between the Th/U activity ratio in an aquifer rock and the ^{228}Ra/^{226}Ra activity ratio in fluids.

The occurrence of enhanced activity levels of Radium isotopes in saline deepwaters can be explained only with common specific U and Th activities and does not require enhanced levels of these sources.

REFERENCES

Degering, D., Köhler, M.: Natural radionuclides in deep geothermal heat and power plants of Germany, *FOG - Freiberg Online Geoscience* **40** (2015) 178-185.

Degering, D. et al.: Radionuclide release in geothermal aquifers – the role of alpha recoil, *Proceedings World Geothermal Congress*, Melbourne, Australia (2015)

Degering, D., Köhler, M.: Prognose und Monitoring natürlicher Radionuklide in Anlagen der tiefen Geothermie (ProRad), Bundesministerium für Wirtschaft und Energie, Förderkennzeichen 0325571, *Abschlussbericht* (2016).

Dietrich, N., Degering, D.: Experimental study for the release of radium isotopes into saline water, *International Conference on Radioanalytical and Nuclear Chemistry RANC-2016*, Budapest, Hungary (2016), paper 492, 190 – 191.

IAEA: The Environmental Behaviour of Radium: Revised Edition, *Technical Report Series 476*, Vienna International Atomic Energy Agency (2014).

Ivanovich, M., Harmon, R.S. (eds.): Uranium-series disequilibrium: Applications to earth, marine, and environmental sciences, 2. ed., *Oxford Clarendon Press* (1992).

Scheiber, J., Cuenot, N.: Reservoir Characteristics of the Soultz EGS Site, *„First Year Progress" Report*, GEIE Exploitation Minière de la Chaleur, Kutzenhausen (2014).

Wedepohl, K. H.: The composition of the continental crust, *Geochim. Cosmochim. Acta* **59** (1995) 1217-1232.

Zukin, J.G. et al.: Uranium-thorium series radionuclides in brines and reservoir rocks from two deep geothermal boreholes in the Salton Sea Geothermal Field, southeastern California, *Geochim. Cosmochim. Acta* **51** (1987) 2719 – 2731.

Acknowledgement

The present work is a part of the funded project BMWi 0329937C. The authors wish to thank the Federal Ministry for Economic Affairs and Energy of the Federal Republic of Germany for this financial support.