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## Reply to comments and questions from SSM concerning Ba-Ra sulphate co-precipitation in canister

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# Contents

1. BACKGROUND AND PROJECT OBJECTIVE .....	1
2. ANSWERS TO COMMENTS AND QUESTIONS.....	3
3. CONCLUSIONS .....	20
4. REFERENCES.....	23



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# 1. Background and project objective

SSM has issued a number of comments and questions concerning the potential uptake of radium released from disposed spent fuel by the formation of Ba-Ra sulphate solid solutions. The formation of such solids leads to a three-order of magnitude decrease in radium solubility according to the calculations by Grandia et al. (2008). This solubility limit is very relevant since  $^{226}\text{Ra}$  is one of the main contributors to radiological dose in some of the scenarios included in the SR-Site safety assessment (SKB, 2011).

One major aspect pointed out by SSM is that SKB considers the formation of Ba-Ra solid solutions when the ratio between radium and barium reaches the highest value ( $2 \times 10^{-4}$  after  $1 \times 10^5$  years of spent fuel alteration; Grandia et al. (2008), p. 36 and SKB, 2010a, p. 108). SSM considers that SKB should include additional data showing that the favourable conditions for the formation of solid solutions are also maintained under canister breaching scenarios at earlier times.

In detail, SSM requires additional comments and deeper explanations on the following questions:

- a. It is not clear whether the most detailed reference given by SKB (Grandia et al, 2008) takes into account transport of barium away from the canister. This can have the largest effect in the case of an early canister failure, when there is more time for Ba to be removed from the interior of the canister.
- b. The availability of barium in the spent fuel matrix is not discussed in Grandia et al. (2008), but the release rate is rather assumed without further explanation to be proportional to the dissolution rate of the spent fuel matrix.
- c. The effects of an early canister failure, and variation in the spent fuel dissolution rate, is not discussed in Grandia et al. (2008). The sensitivity analysis is limited to variation in the sulphate concentration.
- d. Grandia et al. (2008) uses ATM-104 fuel since the inventory for barium had not been specified for the relevant fuel categories. SKB should provide a motivation for this assumption since "Spahiu, pers. comm." is no traceable reference.



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e. Grandia et al. (2008) refers to a study by Ceccarello et al. (2004) that proposes that strontium can inhibit uptake of radium in barite. SKB should investigate if this effect can be important, considering the concentration of strontium in Forsmark groundwaters.

f. As is pointed out by Trivedi (2012), SKB should comment the fact that natural radium in the surrounding groundwater appears to correlated with calcium rather than barium (see Crawford, 2010, page 125).

The objective of this report is to provide detailed answers to all these questions and comments from SSM.



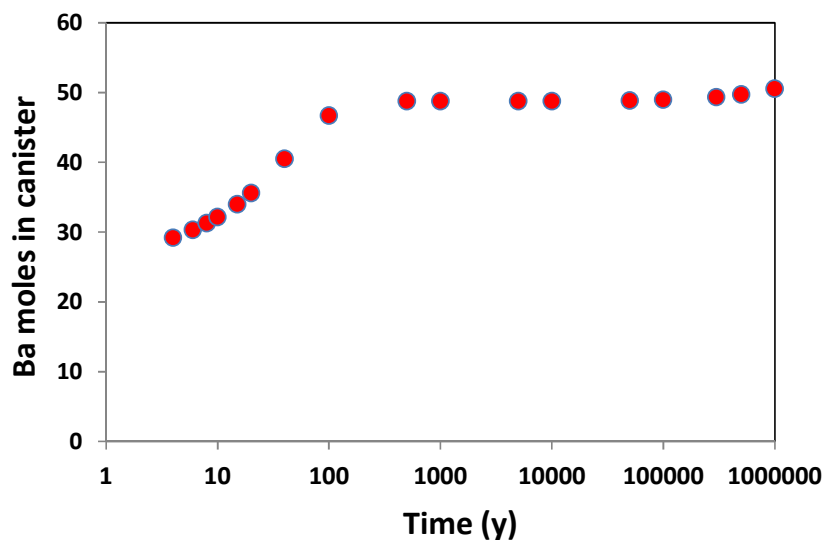
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## 2. Answers to comments and questions

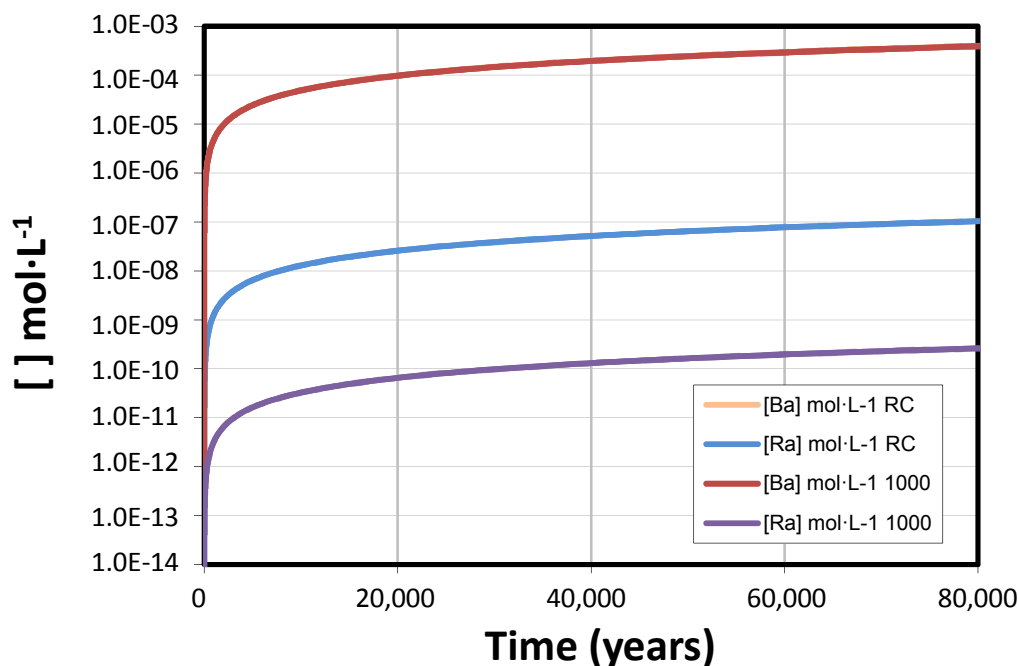
*Questions a and c: Impact of perforation time and barium transport on barium availability.*

The calculations in Grandia et al. (2008) considered the highest Ra/Ba ratio in the canister to assess the radium uptake into barite sulphate solid solutions. The reason behind was because this was judged to be the worst scenario in terms of radium release to gap water. However, the capacity of the chemical system to form solid solutions is independent of the time of canister perforation after the first 100 years since the evolution of dissolved Ba concentration is almost invariable in time after this period (Fig. 1).

Unlike barium, radium inventory increases much slower. Radium concentration in canister void water is very low if the spent fuel is dissolved at early times. As an example, if release takes place after 1000 years from deposition, the concentration of radium in gap water after  $1 \times 10^5$  years of spent fuel dissolution (at  $k = 1 \times 10^{-7} \text{ y}^{-1}$ ) is  $3 \times 10^{-10} \text{ M}$ , assuming no metal sulphate precipitation (Fig. 2).



**Fig. 1.** Evolution of barium mass in the spent fuel in canister through time (from Grandia et al., 2008).



**Fig. 2.** Evolution of Ba and Ra concentrations in canister void considering perforation of canister at 1000 years and 300,000 years (RC, reference case in Grandia et al., 2008) after fuel disposal. The release of barium is independent of the penetration time since the evolution is almost identical. In contrast, radium concentrations are almost 3 orders of magnitude lower in the case of perforation at early times.

According to the calculations of the spent fuel dissolution (Grandia et al., 2008), the amount of barium in each canister after disposal is ~30 moles (Fig. 1). This amount increases in time due to Cs decay and it reaches up to 40-50 moles after 100 years. Even considering an early leakage, Ba dissolution into the void water will be guaranteed if the water is unsaturated in barite. When the sulphate concentration is sufficiently high, Ra and Ba will remain in the canister as co-precipitate and the same holds for UO<sub>2</sub> resulting from fuel dissolution and secondary uranium precipitation in the canister.

In periods with low sulphate concentrations both Ra and Ba will dissolve and potentially could leave the canister, while the total amount of uranium in the fuel and in the precipitate is the same.

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The concentration of Ba released from fuel dissolution is sufficient to co-precipitate the Ra released simultaneously from the fuel if sulphate is present even at quite low concentrations (less than  $1 \times 10^{-4} \text{M}$ ). If concentration of sulphate decreases at early times below the solubility limit of barite, precipitated sulphate could dissolve releasing both Ba and Ra to the void water. If this Ba migrates out from the canister, the lack of barium in the void water could prevent the formation of later Ra-barite that captured the Ra released from the secondary  $\text{UO}_2$ , which could be faster than the rate of Ba release from the spent fuel. Then, the question arising at this point is if all Ba produced before has disappeared, what would be the ratio between Ba produced only by fuel dissolution compared with Ra released from fuel+Ra generated from precipitated  $\text{UO}_2$ ?

Barium in the void water will not “disappear” out from the canister if there is certain concentration of Ba in the groundwater outside the canister. Once in solution in the void water, barium would diffuse out if its concentration is higher than in the external water following the Fick’s law (eq. 1):

$$J = -D \frac{\partial \phi}{\partial x} \quad (\text{eq.1})$$

, where  $J$  is the diffusion flux in  $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ,  $D$  is the diffusion coefficient in  $\text{m}^2 \cdot \text{s}^{-1}$ , and  $\frac{\partial \phi}{\partial x}$  is the ratio of the concentration gradient (in  $\text{mol} \cdot \text{m}^{-3}$ ) and the distance of diffusion (in m).

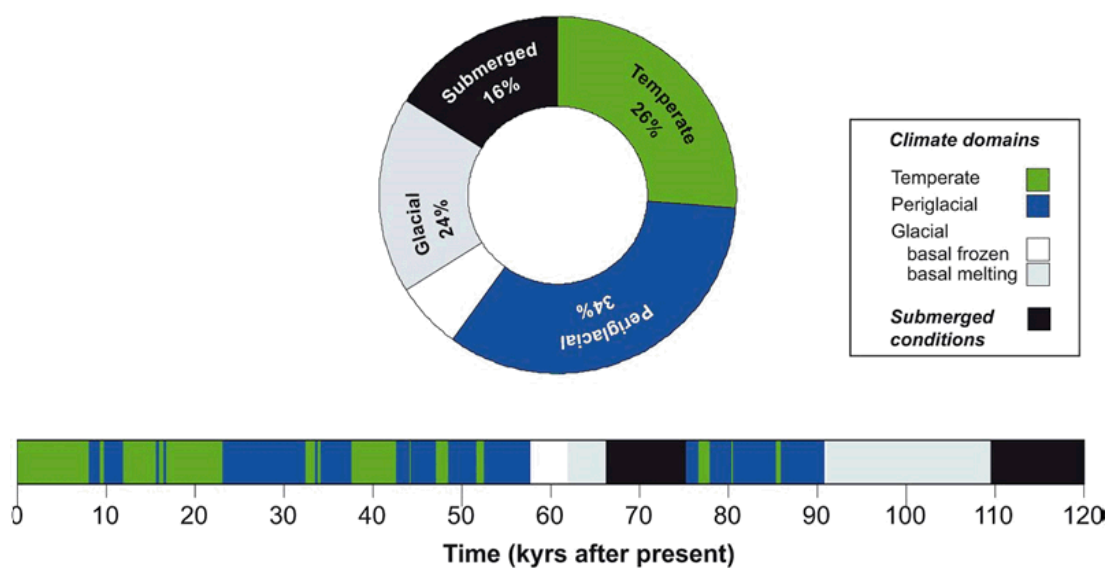
The flux of barium ions would be proportional to the concentration gradient. The concentration of barium in the void water during barite dissolution at early times is expected to be around  $1 \times 10^{-7} \text{M}$ . Grandia et al. (2008) calculated a value of  $7.4 \times 10^{-8} \text{M}$ , which is the concentration in equilibrium with barite. It is assumed that this barite already exists in the void due to initial mixing with sulphate-bearing water prior to the inflow of diluted, sulphate-free water. This Ba concentration is very similar to that expected in the external water intruding after canister failure.

In the scenario in which Ra-Ba co-precipitation is accounted for in SR-Site, it is assumed the presence of bentonite around spent fuel canisters. In this scenario, the



external water is not Ba free since geosphere and bentonite barriers are believed to supply barium to the groundwater via water-rock interaction. In this respect, calculations from Berner and Curti (2002) yields [Ba] around  $9 \times 10^{-8}$  M in the bentonite porewater. This similarity in the Ba concentration in and out of the canister would lead to very small concentration gradients and virtually no diffusion flux.

In addition to Ba, the concentration of sulphate in the void water is not expected to be extremely low at early times since climate models predict the onset of glacial period after 60,000 years of repository closure (SKB, 2011; Fig. 3). Only after these glacial periods, freshwater is “injected” downwards at repository depths. In any case, the duration of these glacial periods is shorter than 15,000-20,000 years, and calcium sulphate in bentonite is high enough (ca. 1%, e.g., Table 3-2 in SKB, 2010b,) to supply  $\text{SO}_4^{2-}$  ions to intruding groundwater, leading to high sulphate concentrations ( $[\text{SO}_4^{2-}] > 1 \times 10^{-2}$  M). The timing for complete removal of sulphate, even considering glacial waters, is predicted not to be shorter than 15,000 years (Arcos et al., 2006).



**Fig. 3.** Duration of climate domains at Forsmark, expressed as percentage of the total time of the modelled period (120,000 years; from SKB, 2011).

In the scenario that bentonite is eroded and glacial water pass through the canister, the ratio Ra/Ba in the fuel is expected to be always lower than the maximal value of



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0.0006, especially at early times since the amount of radium released from secondary  $\text{UO}_2$  is expected to be low. The reason behind the small Ra release is that not all Ra will be immediately available at surface if the precipitated  $\text{UO}_2$  is composed of 1 micrometer sized grains, the Ra contribution will decrease as the ratio of atoms on surface to the total number of U atoms in the grain, i.e. about 1100 times and almost by  $1 \times 10^6$  if the grains are 1 mm in diameter (calculated with a layer thickness for  $\text{UO}_2(\text{s})$  3.68 Å or  $3.68 \cdot 10^{-10}$  m).

*Question b: Ba release from the fuel.*

Poinsot et al. (2001) reviewed the literature on the composition of spent fuel. The spent fuel consists basically of an  $\text{UO}_2$  matrix with a large number of fission products. Kleykamp (1985, 1993), working mainly on FBR fuels and based on a thermodynamic approach for LWR fuels, classed the fission products into four main classes:

- 1.- Soluble in the fluorine matrix: lanthanides, rare earths as Y, as well as Zr, Nb, Sr.
- 2.- Forming oxide precipitates: Rb, Cs, Ba, Zr, Nb, Mo, Te.
- 3.- Forming metallic precipitates: Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sb, Te.
- 4.- Fission gases and volatile elements: Kr, Xe, Br, I.

The presence of metallic precipitates (class 3 above) is common in LWR fuels with Mo, Pd, Tc, Ru and Rh precipitates (Thomas et al., 1992). Class 2 precipitates (oxides) are exceptional in LWR fuels, mainly in cases when fuel has experienced very high temperatures ( $>1500$  °C). The corresponding elements are generally located in the matrix, without distinction of precipitates and are associated with other classes: either in class 1 (Zr, Nb, Ba) or in class 3 (Mo, Te) or in class 4 (Rb, Cs).

Kleykamp (1993) reports that the solubility of solubility of BaO in  $\text{UO}_2$  is 0.58 mol%, i.e. segregation of Ba in fuel would not be due to solubility limits. Even when  $\text{BaZrO}_3(\text{s})$  formation is included, it is calculated to be distributed homogeneously in

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the pellet at grain boundaries with the usual slight enrichment at the rim (Moriyama and Furuya, 1997).

All SKB leaching studies in presence of air confirm this leaching behaviour of Ba, especially two long-term leaching studies of several fuel pins with various burn-up (Forsyth, 1997; Zwicky et al., 2011). Ba behaves very similar to Sr and besides a slight increased release the first samplings, is released at the same rate as the fuel matrix.

In Grandia et al. (2008), the release of both Ba and Ra into the canister void water is coupled since it is considered that the spent fuel matrix dissolves congruently, based on the review in report TR-04-09 (Werme et al., 2004). This report provides a model of long-term spent fuel behaviour from a large number of studies dealing with spent fuel dissolution. In this model, the conditions are highly reducing due to a H<sub>2</sub>-rich atmosphere produced by anaerobic corrosion of iron. Spent fuel matrix dissolves congruently at linear rates in the range of 10<sup>-6</sup> to 10<sup>-8</sup> per year, with a peak at 10<sup>-7</sup> per year. The model also includes the potential formation of secondary U oxides but fission and decay products are clearly released into solution.

*Question c: Variation of rate of fuel dissolution through time.*

Barium is expected to be released at the rates of spent fuel matrix dissolution, which is between 10<sup>-6</sup> and 10<sup>-8</sup> per year. This fuel dissolution rate is considered constant in SR-Site during all times considered in the safety assessment. The effect of time of canister perforation is discussed above (Question a).

*Question d: Use of ATM-104 fuel as analogue of SKB reference spent fuel for inventory calculation.*

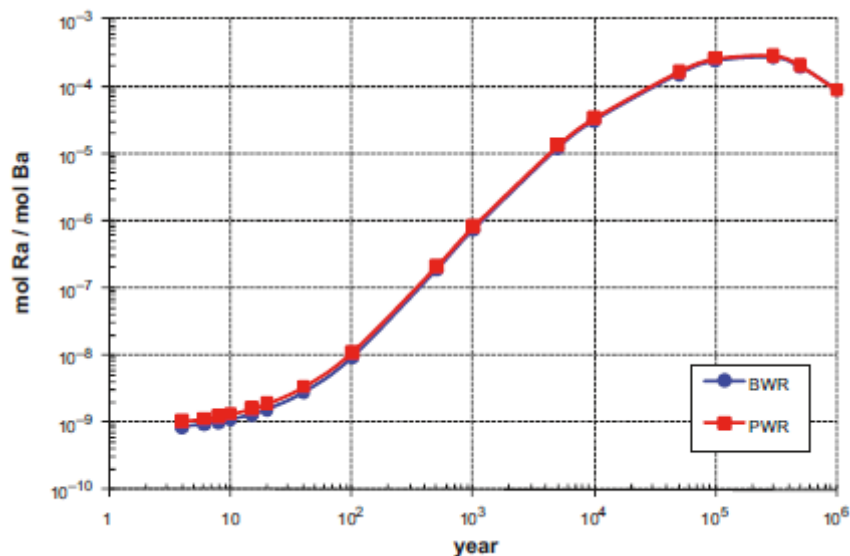
The data used by Grandia et al. (2008) to calculate the evolution of barium and radium in the spent fuel was preliminary and the ATM-104 (Guenther et al., 1991) was used because the lack of barium data on the inventory existing at time of

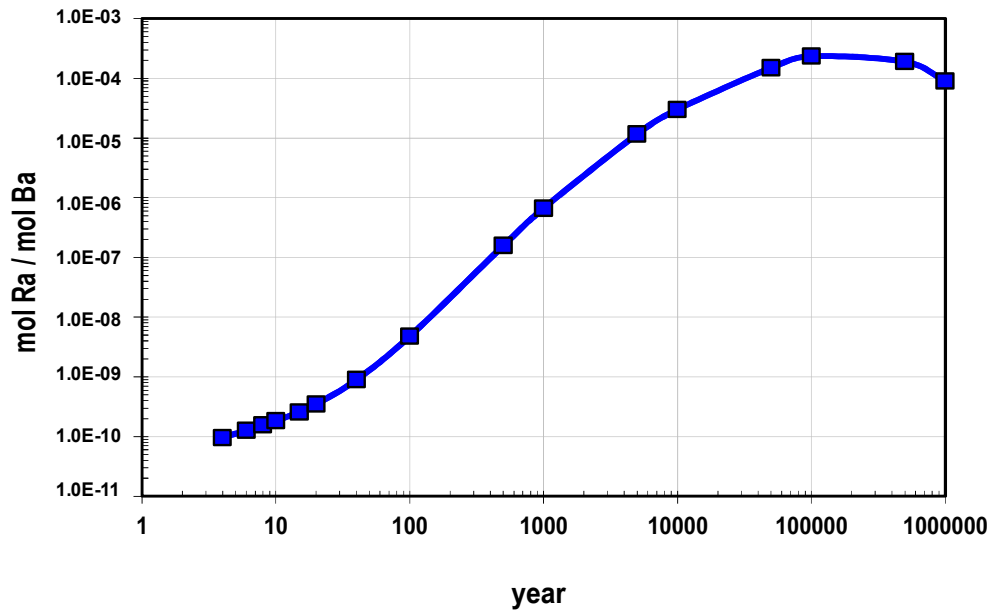
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project development. The fuel used is remarkably similar in terms of radioactivity to those reported later in the SKB report TR-10-13 (SKB, 2010c).

The radionuclide inventory calculations done by Grandia et al. (2008) were used in Sr-Site based on the spent fuels of the two type canisters PWR 1 and BWR 1 by using data in Table C-15 of the report TR-10-13 (*Spent Fuel Report*; SKB, 2010c) and reported in the Data Report TR-10-52 (SKB 2010 a). Ra/Ba ratios (Fig. 4, top, from TR-10-52) were very similar to those previously calculated by Grandia et al. (2008) (Fig. 4, bottom).

Consequently, the use of ATM-104 fuel inventory to quantify the radium uptake by the formation of solid solutions was a temporary solution, which showed up to be quite near the real situation. In any case, in the Sr-Site calculations the real inventories were used.





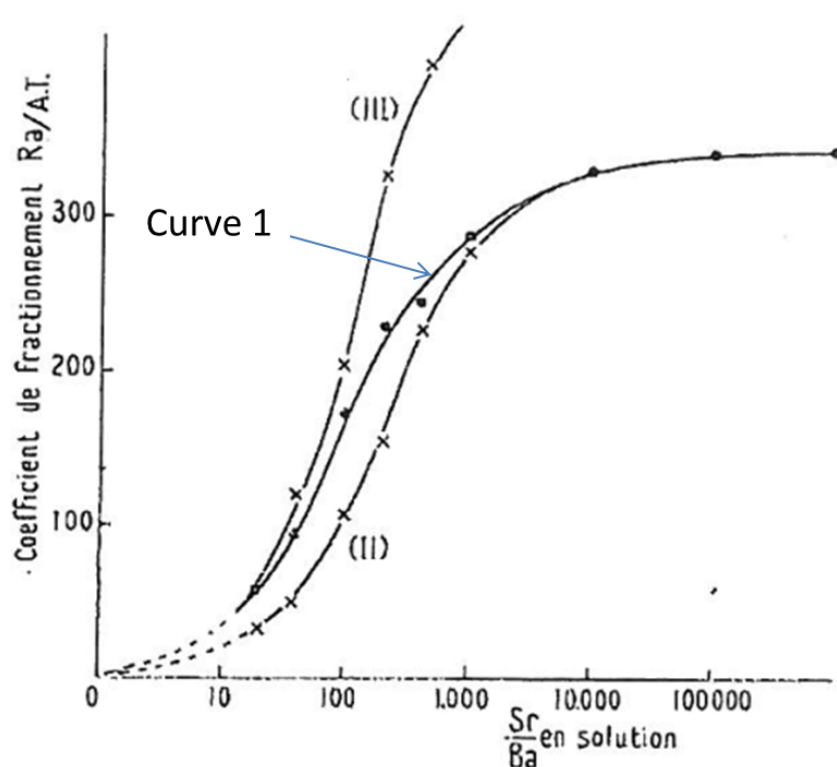
**Fig. 4.** Comparison between Ra/Ba evolution from PWR I and BRW I canisters (from SKB, 2010c), and ATM-104 (Grandia et al., 2008).

*Question e: Impact of dissolved Sr on radium uptake in Ba sulphate solid solutions.*

The influence of Sr into Ra uptake as Ba sulphate solid solution has been treated for long time since the pioneering work of Goldschmidt (1940). This author showed that the radium strongly partitioned into the solid phase considering mixtures of Sr and Ba in solution. Considering the partition coefficient  $D_{Ra}$  as (eq. 2):

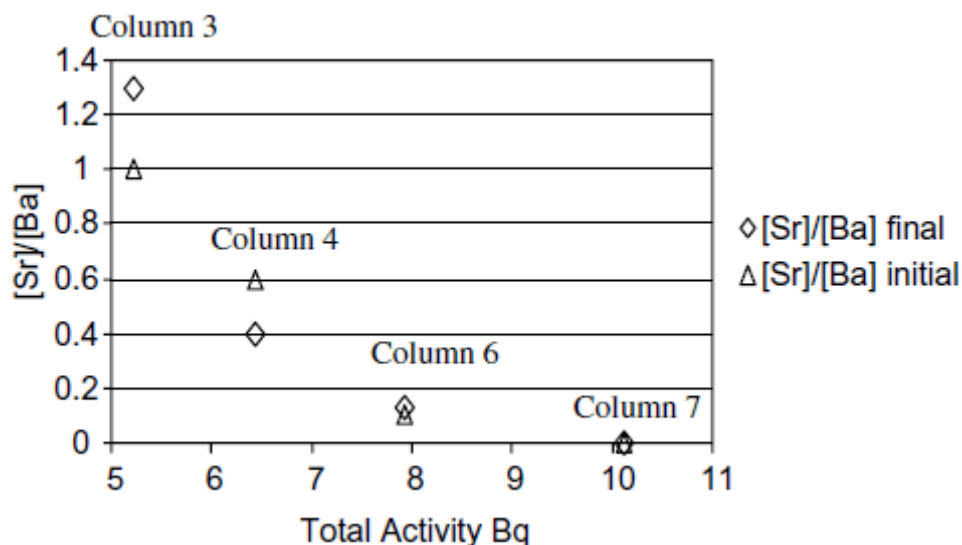
$$D_{Ra} = \frac{\frac{Ra_{ppt}}{Ba_{ppt} + Sr_{ppt}}}{\frac{Ra_{sol}}{Ba_{sol} + Sr_{sol}}} \quad (\text{eq.2})$$

Goldschmidt (1940) found that even at very elevated Sr/Ba ratios, the affinity of radium for the precipitate was very high (curve 1 in Fig. 5). The Ra uptake was expected to be lower compared with co-precipitation in Ba sulphate.



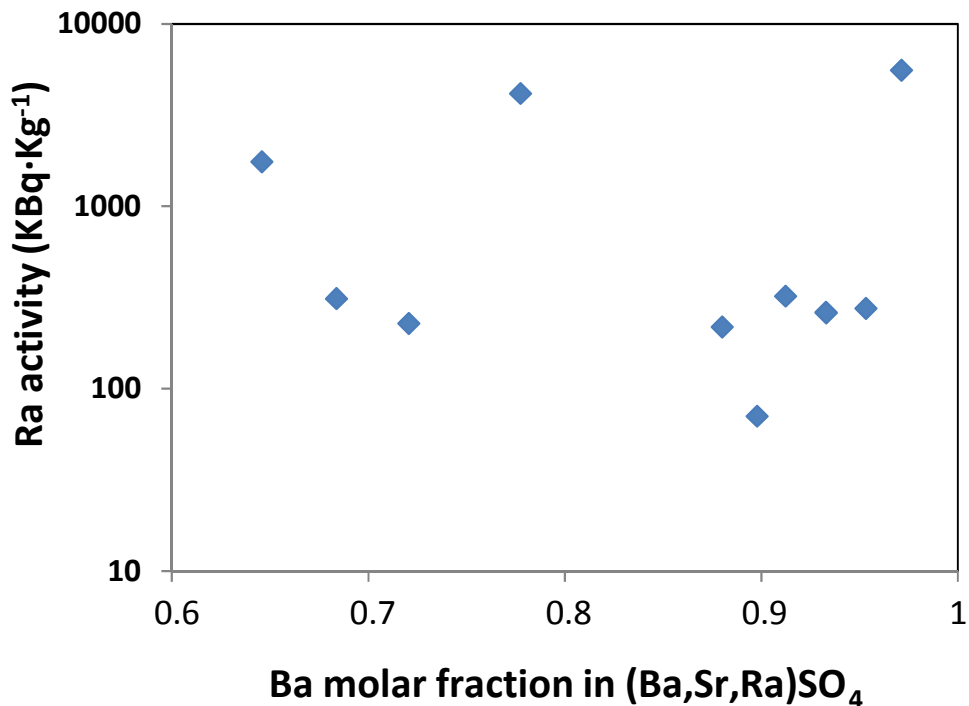
**Fig. 5.** Variation of partitioning coefficient of Ra into a (Ba,Sr,Ra)SO<sub>4</sub> solid solution as a function of initial Sr/Ba in solution (curve 1). Curve II shows the incorporation of radium into the SrSO<sub>4</sub> lattice and curve III is the Ra uptake in pure Sr and Ba sulphates (from Goldschmidt, 1940).

Similar results were later reported by Ceccarello et al. (2004) from a simple set of diffusion experiments. They showed that radium co-precipitation was reduced (up to 40%) when the Sr-Ba ratio increased in the initial solution (Fig. 6). They suggested that high Sr-Ba ratios during barite-celestite solid solution precipitation may reduce the rate of radium uptake into the precipitates. It is worth mentioning that, as previously showed by Goldschmidt (1940), even at very high Sr/Ba, radium is still being clearly uptaken and the fluid in equilibrium is depleted with Ra.



**Fig. 6.** Radium activity in (Ba,Sr,Ra)SO<sub>4</sub> solid solutions as a function of initial Sr/Ba in the solution (from Ceccarello et al., 2004).

The results of Ceccarello et al. (2004) from lab experiments are not well correlated with data from samples formed during oil-field extraction activities. Formation of (Ba,Sr,Ra)SO<sub>4</sub> solid solutions from Sr-rich fluids is clearly evidenced in many examples of radioactive scale. Most of these radioactive scale precipitate from mixing of fluids involving seawater, which contains high Sr concentration. For instance, Gazineu et al. (2005) analysed scale and slurry from oil activities in Brazilian fields and found radioactive, Sr-bearing barite (up to 0.64 Sr molar fraction). They found no correlation between radium activity and Sr molar fraction (Fig. 7).



**Fig. 7.** Radium activity of radioactive scale from Brazilian oil fields with corresponding Ba molar fraction in the precipitate. The remaining mole fraction is Sr. From Gazineu et al. (2005).

The results of Ceccarello et al. (2004) and Goldschmidt (1940) are also apparently in contradiction with more recent experimental works by Rodríguez-Galán et al. (2013) and Hedström et al. (2013). Rodríguez-Galán et al. (2013) considered Pb as a proxy of Ra to assess the effect of Sr on the radium sorption. They used (Ba,Sr)SO<sub>4</sub> solid solutions with relative high contents of Sr (up to 15%Sr) in a reactor with dissolved lead, and the conclusion was that Pb was uptaken at greater extent into the solid solution compared to pure BaSO<sub>4</sub>. On the other hand, Hedström et al. (2013) performed experiments with equal concentrations of Sr, Ba and Ra in solution and concluded that radium is also co-precipitated in a (Ba,Sr,Ra)SO<sub>4</sub> solid solution.

Numerical modelling considering ternary (Ba,Sr,Ra)SO<sub>4</sub> solid solution also supports the radium uptake in presence of strontium. Shao et al. (2009) predicted the radium retardation due to multiple solid solution formation in the near field of a nuclear waste repository using Gibb Energy Minimization (GEM) approach. They included

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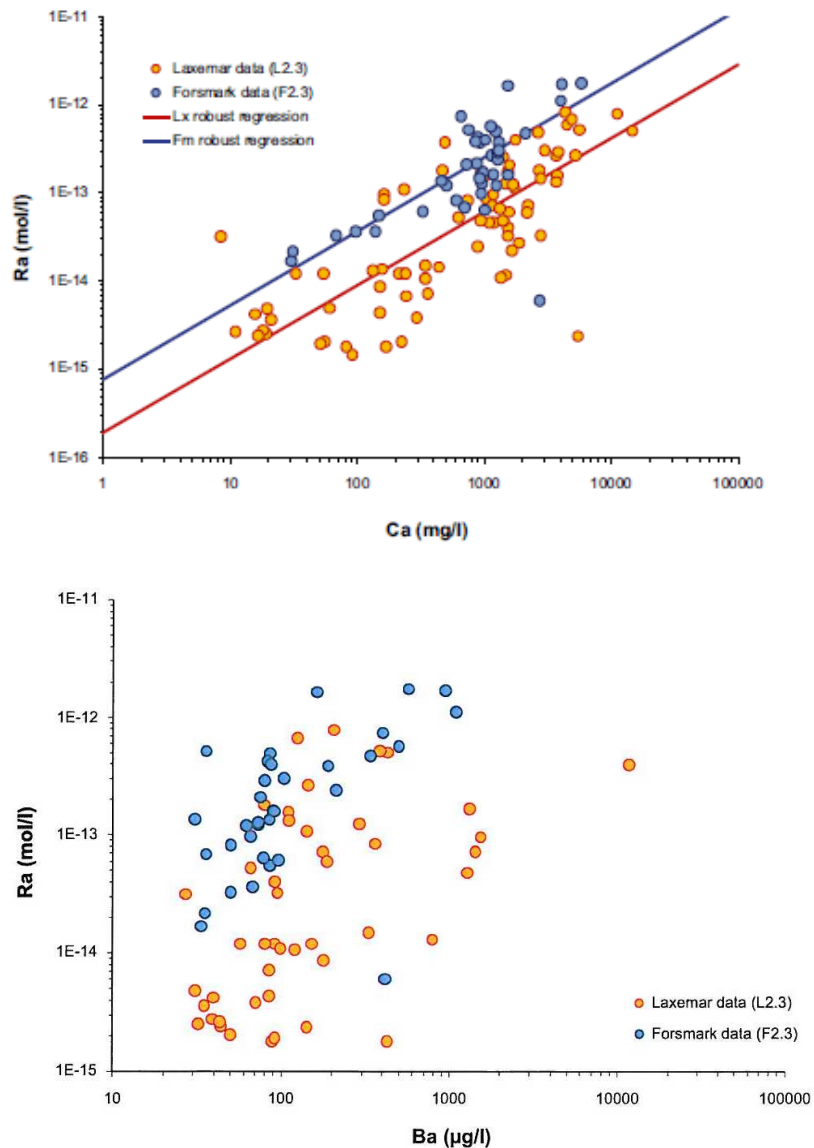
both solid solutions and pure phases of the Ba-Sr-Ra-Ca-SO<sub>4</sub>-CO<sub>3</sub> system. The numerical results predicted that Ra will eventually be fixed as ternary (Ba,Sr,Ra)SO<sub>4</sub> solid solution as a result of sulphate input into the system. The sulphate supply for the solid solution formation is ensured due to the dissolution of gypsum from bentonite.

*Question f: Role of barium sulphate as a solubility-limiting phase in present-day waters in Forsmark and Laxemar. Possible correlation between Ca and Ra.*

The uptake of radium in a Ba-sulphate solid solution is considered as a very relevant geochemical process to limit the Ra leakage from the spent fuel in view of three groups of evidences: (1) lab experiments, (2) formation of radioactive scale in industrial facilities (e.g., oil industry), and (3) natural waters. The first two are already detailed in question e. The third group of evidences comes from radium and barium data from natural aquifers (see review in Grandia et al., 2008).

Crawford (2010) presented concentration plots showing apparent correlation between Ra and Ba, and Ra and Ca in present-day waters from Forsmark and Laxemar (Fig. 8). From the SR-Site assessment, the model estimation of unknown concentrations of trace solutes to fill data gaps in the repository hydrochemical evolution used simple empirical correlations (Salas et al., 2010). The major groundwater components (including Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>/Fe<sup>2+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>/HS<sup>-</sup>, and HCO<sub>3</sub><sup>-</sup>) were computed deterministically in the groundwater simulations, although trace solutes such as Ba and Ra were not included. In the SDM Site data, statistical correlations were identified between paired data sets of Ra and Ca concentration as well as between Ra and Ba. Since Ba was not calculated deterministically in modelling works (Salas et al., 2010), a direct correlation with dissolved Ca was considered to be a more reliable predictor of Ra background levels for the purpose of filling data gaps in simulations than the corresponding correlation with Ba via barite equilibrium.





**Fig. 8.** Radium vs. calcium (top) and radium vs barium (bottom) concentration plot from Forsmark and Laxemar groundwaters (from Crawford, 2010).

A detailed analysis of the chemical data of Forsmark deep groundwaters (from the official Chemnet file "Forsmark\_2\_3\_updated\_Dec30\_2007.xls, SKB, 2010a) shows a good correlation between Ba and Ra (Fig. 9). This correlation is interpreted as equilibrium with Ba-Ra sulphate solid solutions with variable Ba/Ra ratio, since the equilibrium of Forsmark deep groundwaters with barite is clearly observed (Figs. 10

and 11; see Annex 1 for a detailed explanation). The Ba-Ra-SO<sub>4</sub> system appears to be unrelated to the Ca-Sr association since the later solutes are strongly correlated each other (Fig. 12) whereas Ca and Ba (and Ra) are not much coupled (Fig. 13).

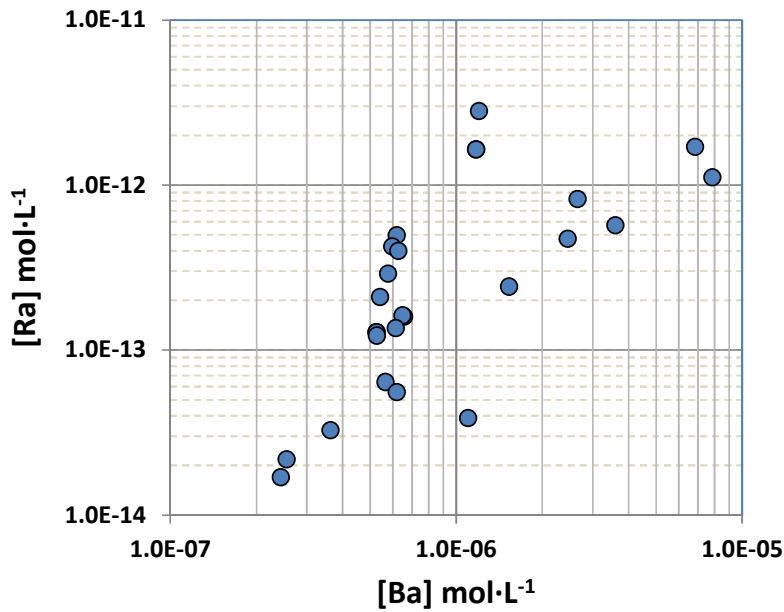
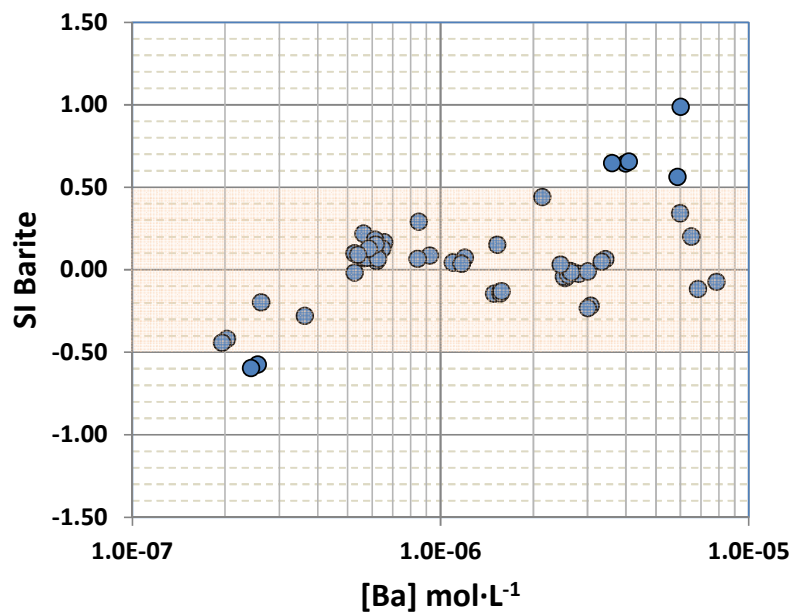
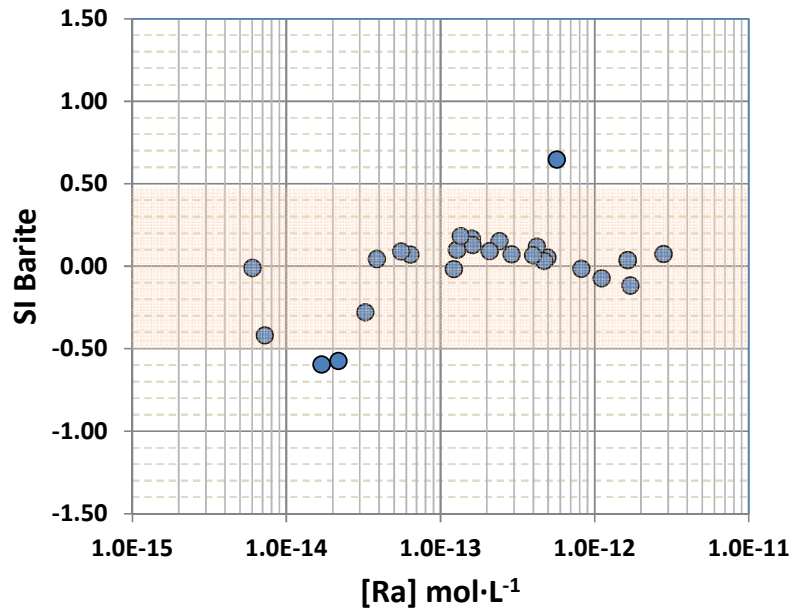


Fig. 9. Radium vs. barium concentration in Forsmark deep groundwaters.

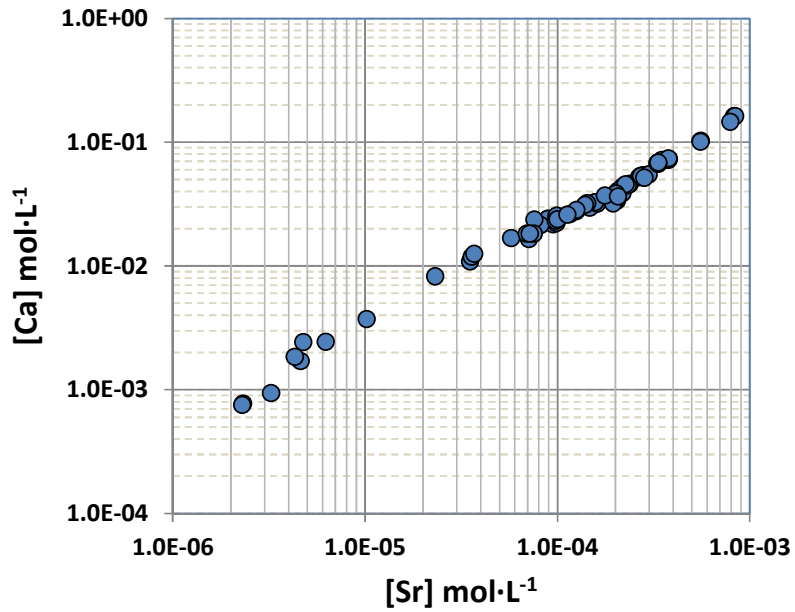


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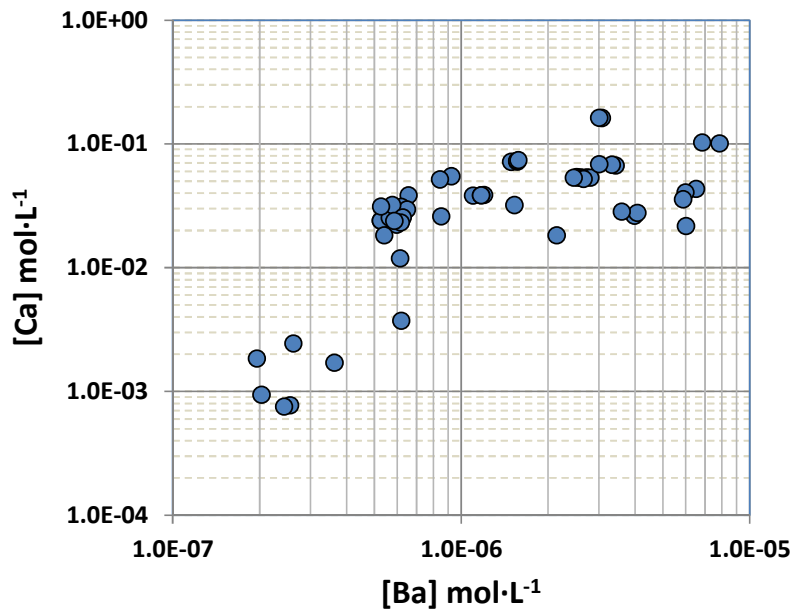
**Fig. 10.** Saturation index (SI) of barite vs. barium concentration in Forsmark deep groundwaters. The pinkish area indicates the SI considered as actual equilibrium (calculated with PHREEQC v.3.0, and WATEQ database).



**Fig. 11.** Saturation index (SI) of barite vs. radium concentration in Forsmark deep groundwaters. The pinkish area indicates the SI considered as actual equilibrium (calculated with PHREEQC v.3.0, and WATEQ database).



**Fig. 12.** [Ca] vs. [Sr] plot in Forsmark deep groundwaters. Note the strong correlation of both solutes, pointing to a common solubility-limiting phase.



**Fig. 13.** [Ca] vs. [Ba] plot in Forsmark deep groundwaters.

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At this point, it is worth mentioning that the solid solution-aqueous solution equilibrium depends on the relative concentration in water of ions, and different solid solution composition leads to distinct ion concentration in solution at equilibrium. Considering that the studied waters at Forsmark have variable concentration of sulphate and low [Ra], the solid solution-aqueous solution equilibrium may result in a range of Ba/Ra ratios both in the solid and in the aqueous phase, explaining that the correlation between Ba and Ra is not apparently strong (see Annex 1 in this report).

As a conclusion, the more relevant information that can be extracted from groundwater composition analysis is that barium and radium concentration in all these waters are in equilibrium with barite (Figs. 11 and 12). Due to the very trace amounts of radium, the solubility product of any solid solution involving barium, radium and sulphate is expected to be very close to the solubility product of pure barite. Therefore, it can be stated that Ra solubility limit phase in the deep groundwaters at Forsmark is likely a set of Ba-Ra sulphate solid solutions.

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### 3. Conclusions

This report provides the answer to the questions by SSM. To sum up:

Question **a**: *It is not clear whether the most detailed reference given by SKB (Grandia et al, 2008) takes into account transport of barium away from the canister. This can have the largest effect in the case of an early canister failure, when there is more time for Ba to be removed from the interior of the canister.*

Answer: Barium transport out of the canister is proved to be limited by the small diffusion rates since the concentration differences between the inside and the outside of the canister would be small. In addition, barite equilibrium is ensured at early times since intrusion of very diluted glacial waters are not expected in the first 50 ky. Also, these periods are likely too short to remove all gypsum in the bentonite, and, therefore, high sulphate concentration in the external water is guaranteed and the formation of Ra-barite as well.

Question **b**: *The availability of barium in the spent fuel matrix is not discussed in Grandia et al. (2008), but the release rate is rather assumed without further explanation to be proportional to the dissolution rate of the spent fuel matrix.*

Answer: The release of both Ba and Ra into the canister void water is considered congruent with the spent fuel matrix, based on the review in report TR-04-09 (Werme et al., 2004). This report provides a model of long-term spent fuel behaviour from a large number of studies dealing with spent fuel dissolution.

Question **c**: *The effects of an early canister failure, and variation in the spent fuel dissolution rate, is not discussed in Grandia et al. (2008). The sensitivity analysis is limited to variation in the sulphate concentration.*

Answer: Barium is expected to be released at the rates of spent fuel matrix dissolution, which is between  $10^{-6}$  and  $10^{-8}$  per year. This fuel dissolution rate is considered constant in SR-Site during all times considered in the safety

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assessment. The effect of time of canister perforation is discussed above (Question a).

Question d: *Grandia et al. (2008) uses ATM-104 fuel since the inventory for barium had not been specified for the relevant fuel categories. SKB should provide a motivation for this assumption since "Spahiu, pers. comm." is no traceable reference.*

Answer: The fuel used is remarkably similar in terms of radioactivity to those reported later in the SKB report TR-10-13 (SKB, 2010c). Ra/Ba ratios calculated later by SKB and reported in TR-10-52, provided very similar values to those previously calculated by Grandia et al. (2008).

Question e: *Grandia et al. (2008) refers to a study by Ceccarello et al. (2004) that proposes that strontium can inhibit uptake of radium in barite. SKB should investigate if this effect can be important, considering the concentration of strontium in Forsmark groundwaters.*

Answer: The impact of Sr in solution on the Ra uptake in sulphate solid solutions should be minor even considering large Sr concentrations in the void water. Experimental and field examples show that Ra concentration in water is clearly limited by Ba-Ra sulphate solid solutions even in the presence of ion competition. Barite is proved to readily fix radium.

Question f: *As is pointed out by Trivedi (2012), SKB should comment the fact that natural radium in the surrounding groundwater appears to correlated with calcium rather than barium (see Crawford, 2010, page 125).*

Answer: The clearer correlation between Ra and Ca does not imply that the solubility-limiting phase for radium is a carbonate or clay mineral (via ion exchange). Equilibrium between a trace solute and a solid solution usually leads to non-linear major-trace ratio trends. The more significant aspect of the Forsmark groundwaters

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is that equilibrium with barite is attained in most analysed samples, which is the only requirement for radium uptake.





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## 4. References

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# Annex 1. Aqueous solution-Solid solution equilibrium: What does solute correlation mean? The case of Ba-Ra in Forsmark

## 1. Introduction

In groundwater studies correlation between solutes is commonly used to determine sources and solubility-limiting phases. For major ions, almost pure phases control the equilibrium with groundwater but for trace elements, sorption on mineral surfaces and uptake forming non-pure mineral phases (i.e., dilute solid solution) are the predominant processes. In the latter case, the concentration of trace element does not necessarily correlate with that of major (or mineral-forming) solute even existing thermodynamic equilibrium.

A well-known example of coupled solubility limit is the formation of  $\text{BaRaSO}_4$  solid solutions which control the concentration of both Ba and Ra in many groundwaters (e.g., Beaucaire et al., 1987; Sturchio et al., 1993; Grundl and Cape, 2006). However, in many instances, no clear correlation between the measured concentration of these elements is observed. In Forsmark, the correlation is quite good but not strong (see Fig. 6, below). Where it occurs, the apparent poor correlation can be misinterpreted as absence of solubility control of Ra by barium-radium sulphate solid phases. In this document, the reason behind the Ba-Ra correlation is explained following the aqueous solution-solid solution equilibrium theory, along with the prediction of the measurements done in the Forsmark area.

## 2. Aqueous solution-solid solution theory

From the solid solution theory, the equilibrium between the aqueous electrolyte and a solid solution (B,C)L can be expressed by two law-of-mass action (LMA) equations:

$$\{B^+\}\{L^-\} = K_{BL}a_{BL} = K_{BL}x_{BL}f_{BL}$$

$$\{C^+\}\{L^-\} = K_{CL}a_{CL} = K_{CL}x_{CL}f_{CL}$$

where  $\{L^-\}, \{B^+\}, \{C^+\}$  are the aqueous activities of  $L^-, B^+, C^+$  (or  $L^{2-}, B^{2+}, C^{2+}$ );  $K_{BL}$  and  $K_{CL}$  are the solubility products of pure BL and CL end-members with activities  $a_{BL}, a_{CL}$ , mole fractions  $x_{BL}, x_{CL}$ , and activity coefficients  $f_{BL}, f_{CL}$ , respectively. Using the Lippmann's *total solubility product*  $\Sigma\Pi$  defined as

$$\Sigma\Pi = \{L^-\}(\{B^+\} + \{C^+\})$$

the equilibrium  $\Sigma\Pi$  value can be alternatively expressed as

$$\Sigma\Pi_{eq} = K_{BL}x_{BL}f_{BL} + K_{CL}x_{CL}f_{CL}$$

defining the so-called *solidus* curve. The Lippmann *solutus* curve equation is

$$\Sigma\Pi_{eq} = 1 / \left( \frac{x_{B,aq}}{K_{BL}f_{BL}} + \frac{x_{C,aq}}{K_{CL}f_{CL}} \right)$$

where the *aqueous activity fractions* of B and C are defined as

$$x_{B,aq} = \frac{\{B^+\}}{\{B^+\} + \{C^+\}}; \quad x_{C,aq} = \frac{\{C^+\}}{\{B^+\} + \{C^+\}}$$

Concerning the radium and barium equilibrium with a BaRaSO<sub>4</sub> solid solution of variable composition, the equilibrium is:

$$\{Ba^{2+}\}\{SO_4^{2-}\} = K_{Barite}a_{Barite} = K_{Barite}x_{Barite}f_{Barite}$$

$$\{Ra^{2+}\}\{SO_4^{2-}\} = K_{RaSO_4}a_{RaSO_4} = K_{RaSO_4}x_{RaSO_4}f_{RaSO_4}$$

Since the amount of Ra in the environment is always very small compared to barium and sulphate, in all BaRaSO<sub>4</sub> solid solutions  $x_{Barite} \gg x_{RaSO_4}$ . Therefore, small changes in solid solution composition will dramatically change  $\{Ra^{2+}\}$ , leaving unaltered  $\{Ba^{2+}\}$  and  $\{SO_4^{2-}\}$ .

### 3. Examples of aqueous solution-solid solution equilibrium in the BaRaSO<sub>4</sub> system

Let's illustrate the impact of the aqueous solution-solid solution equilibrium in trace element concentration and correlation with major solutes using a simple PHREEQC calculation. Two sets of equilibrium are used (Table 1). The first one shows the [Ra] in equilibrium with variable  $x_{RaSO_4}$  in solid solution. This large variability in  $x_{RaSO_4}$  is not expected in nature since the amounts of Ra are typically low but it could be possible in the canister and near-field environments. The second set shows the equilibrium of a BaRaSO<sub>4</sub> solid of fixed composition (that could be possible in Forsmark) with groundwater with changing relative concentrations of Ba<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> in solution. In all cases, the groundwaters are Na and Cl-rich (around 0.02 M).

Table 1: Input and output data of PHREEQC calculations of different examples of groundwater-solid solution equilibrium.

Set 1: Changing solid composition

	Ba fraction solid solution	Ra fraction solid solution	initial [Ba]	initial [Ra]	initial [SO <sub>4</sub> ]	intial SI barite	final [Ba]	final [Ra]	final [SO <sub>4</sub> ]	final SI barite
1	0.9999999	0.0000001	1.00E-07	1.00E-11	1.00E-03	-0.48	3.05E-07	1.61E-14	1.00E-03	0.00
2	0.9999999	0.0000001	1.00E-07	1.00E-11	1.00E-03	-0.48	3.05E-07	1.61E-13	1.00E-03	0.00
3	0.999999	0.000001	1.00E-07	1.00E-11	1.00E-03	-0.48	3.05E-07	1.61E-12	1.00E-03	0.00
4	0.99999	0.00001	1.00E-07	1.00E-11	1.00E-03	-0.48	3.05E-07	1.61E-11	1.00E-03	0.00
5	0.999	0.001	1.00E-07	1.00E-11	1.00E-03	-0.48	3.05E-07	1.61E-10	1.00E-03	0.00

Set 2: Changing barium and sulfate composition

	Ba fraction solid solution	Ra fraction solid solution	initial [Ba]	initial [Ra]	initial [SO <sub>4</sub> ]	intial SI barite	final [Ba]	final [Ra]	final [SO <sub>4</sub> ]	final SI barite
1	0.9999999	0.0000001	1.00E-05	1.00E-11	1.00E-05	-0.39	1.57E-05	8.09E-12	1.57E-05	0.00
2	0.9999999	0.0000001	5.00E-06	1.00E-11	5.00E-05	0.01	4.94E-06	2.55E-12	4.99E-05	0.00
3	0.9999999	0.0000001	1.00E-06	1.00E-11	1.00E-04	-0.4	2.46E-06	1.27E-12	1.02E-04	0.00
4	0.9999999	0.0000001	1.00E-07	1.00E-11	1.00E-03	-0.48	3.05E-07	1.61E-13	1.00E-03	0.00

The results of the calculations (Table 1), considering an ideal solid solution show that no [Ba]-[Ra] correlation is possible even existing equilibrium with BaRaSO<sub>4</sub>

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mineral if variable compositions are present in the Forsmark rocks (Fig. 1). This is because [Ba] is not significantly affected but [Ra] is strongly modified by the equilibrium.

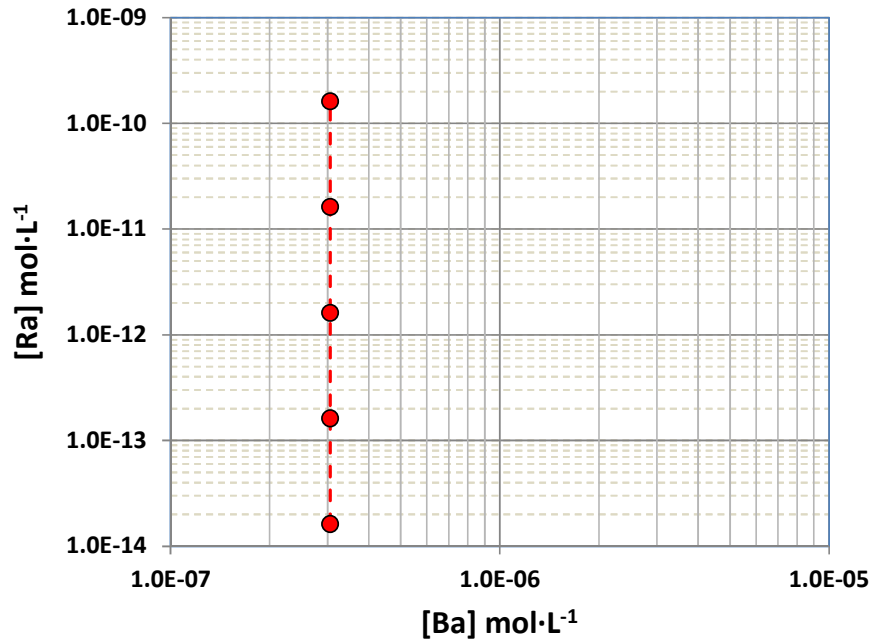


Fig. 1. Predicted [Ba] and [Ra] in equilibrium with solid solutions of variable composition.

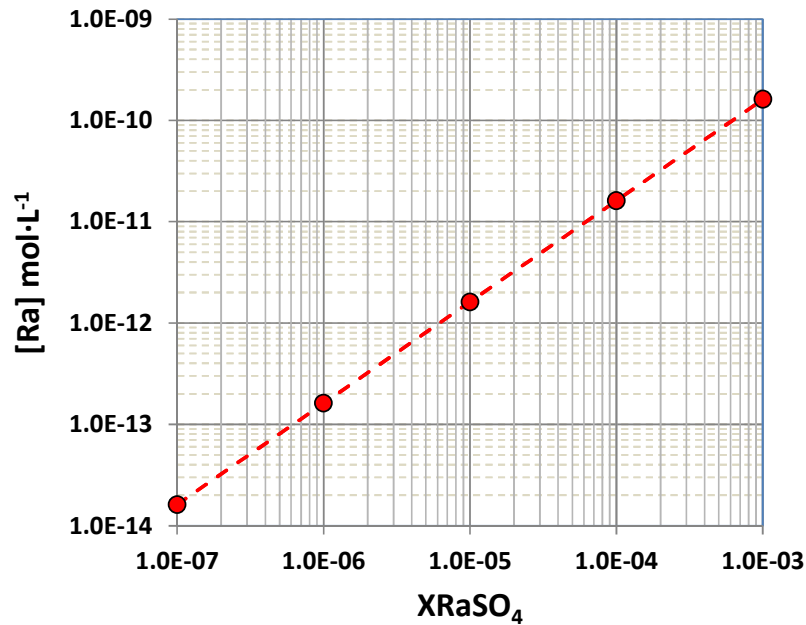


Fig. 2. Predicted [Ra] in groundwater and  $X_{\text{RaSO}_4}$  in solid solution from equilibrium calculations with solid solutions of variable composition.

In contrast, a perfect correlation exists between final [Ra] and  $x_{\text{RaSO}_4}$  in solid solution (Fig 2). In all cases, the final solution is saturated in barite.

As mentioned above, this scenario is not realistic in a natural environment. Instead, if the solid solution composition in equilibrium with groundwaters is fixed (Table 1, set 2), a perfect correlation is predicted (Fig. 3) and total equilibrium with barite is computed (Fig. 4).



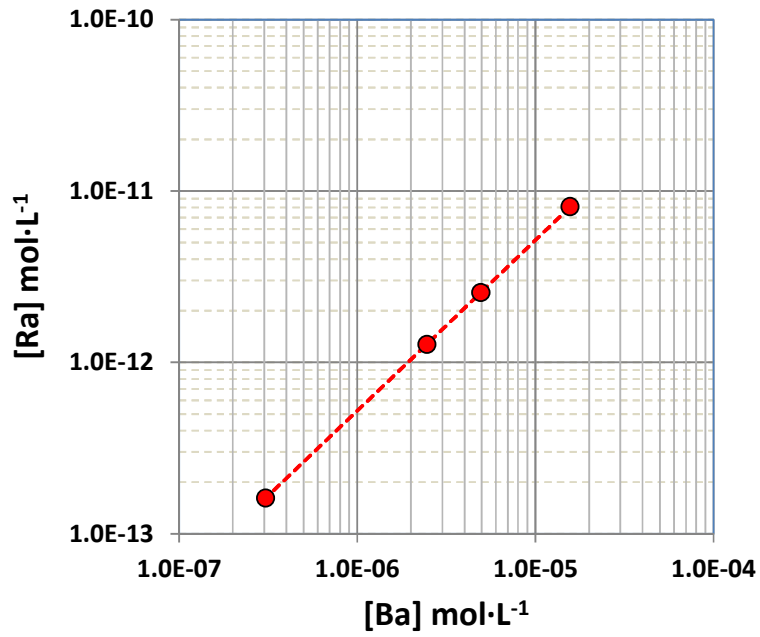


Fig. 3. Predicted [Ba] and [Ra] in equilibrium with a solid solution of fixed composition.

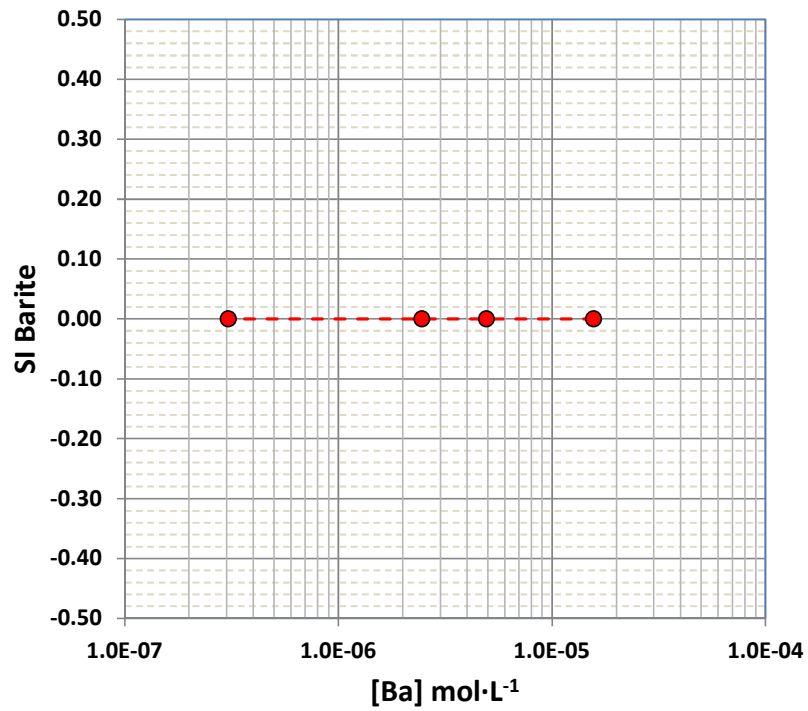


Fig. 4. Saturation index of equilibrated waters in set 2.

The ideality or non-ideality of the solid solution has not much to do with the final Ra-Ba correlation. In Fig. 5, the [Ba] and [Ra] concentration in equilibrium with a solid solution of fixed composition has been computed considering a non-ideality behavior of the solid solution. A Guggenheim parameter  $W_0$  of 1.5 KJ/mol has been considered following Brandt et al. (2013). The final solute concentration is slightly different but the correlation is kept.

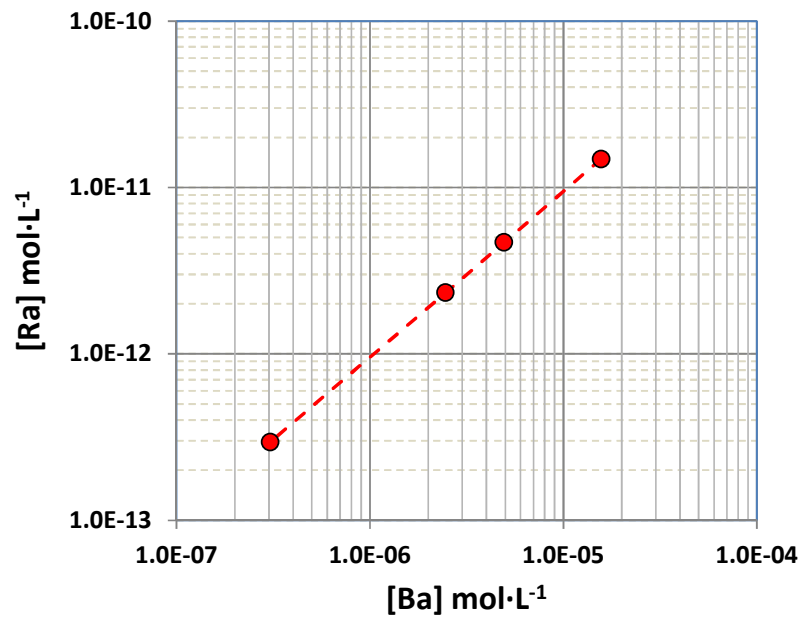


Fig. 5. Predicted [Ba] and [Ra] in equilibrium with a solid solution of fixed composition considering a non-ideal behavior of the Ra uptake.

#### 4. Interpretation of the measured data at Forsmark

The calculations reported in section 3 allow us explaining what we see today in Forsmark groundwaters. There, two different [Ba]-[Ra] trends are measured (Fig. 6). Remarkably, almost all groundwaters are well-equilibrated with barite (Fig. 7). All these data are interpreted as equilibrium with different solid solution compositions. Small changes of solid solution composition, as a result of long geological history of water-rock interaction, are very plausible.

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It is clear that a perfect correlation between measured [Ba] and [Ra] at Forsmark is not expected, even having an equilibrium with solid solution that limits their solubility, since a fixed-composition of a solid solution in the whole area is not expected. Consequently, a poor [Ba]-[Ra] correlation does not mean lack of equilibrium with BaRaSO<sub>4</sub> solid solution.

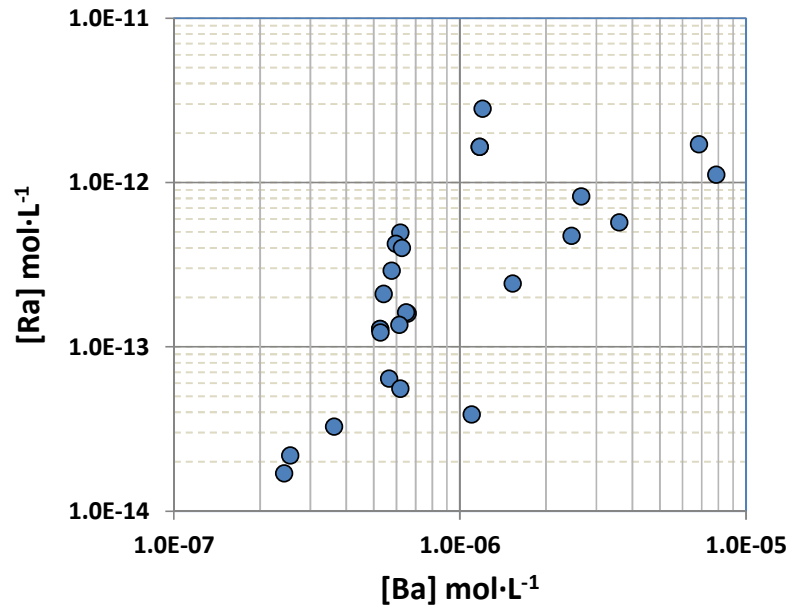


Fig. 6. [Ba] and [Ra] in deep groundwaters in Forsmark area.

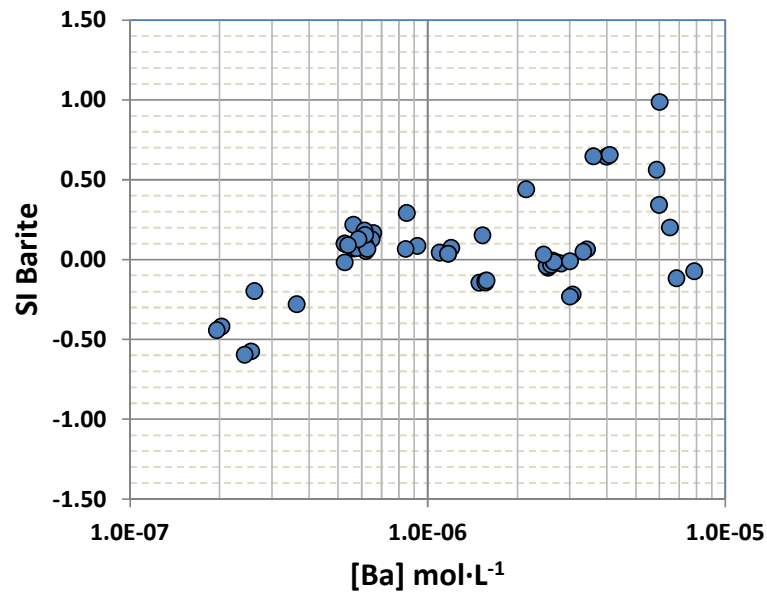


Fig. 7. Saturation index of barite in the deep groundwaters from Forsmark area.

Following the calculations in the previous section, the trend of lower slope can be predicted by considering equilibrium with BaRaSO<sub>4</sub> solid solutions of composition between  $X_{\text{RaSO}_4} = 0.00000015$  and  $0.00000045$  (red and green dashed lines in Fig.

8). However, if we take into account that salinity in Forsmark groundwater is variable, with an inverse correlation between  $[Cl^-]$  and  $[SO_4^{2-}]$  at higher salinities (Fig. 9), the data can be predicted by using one single solid solution composition ( $X_{RaSO_4} = 0.00000015$ ) and inverse  $[Cl^-]$  with  $[SO_4^{2-}]$  (orange dashed line in Fig. 8). The formation of  $RaCl^+$  aqueous complexes limits the  $Ra^{2+}$  availability to equilibrate with the solid solution.

On the other hand, the trend with higher slope can be explained by a combination of solid solution compositions higher in  $X_{RaSO_4}$  and variable salinities.

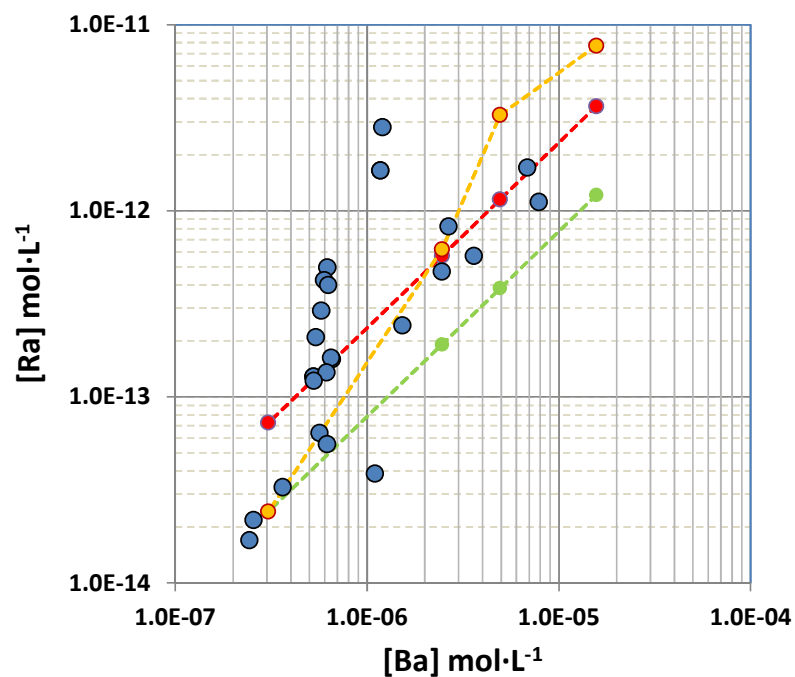


Fig. 8.  $[Ba]$  and  $[Ra]$  in deep groundwaters in Forsmark area, and model predictions of  $[Ba]$  and  $[Ra]$  in equilibrium with fixed solid solution composition. Green dashed line is the Ba-Ra correlation in equilibrium with a solid solution of  $X_{RaSO_4} = 0.00000015$ ; red dashed line is the Ba-Ra correlation in equilibrium with a solid solution of  $X_{RaSO_4} = 0.00000045$ ; and orange dashed line is the Ba-Ra correlation in equilibrium with a solid solution of  $X_{RaSO_4} = 0.00000015$  considering variable salinity ( $Na^+$  and  $Cl^-$ ).

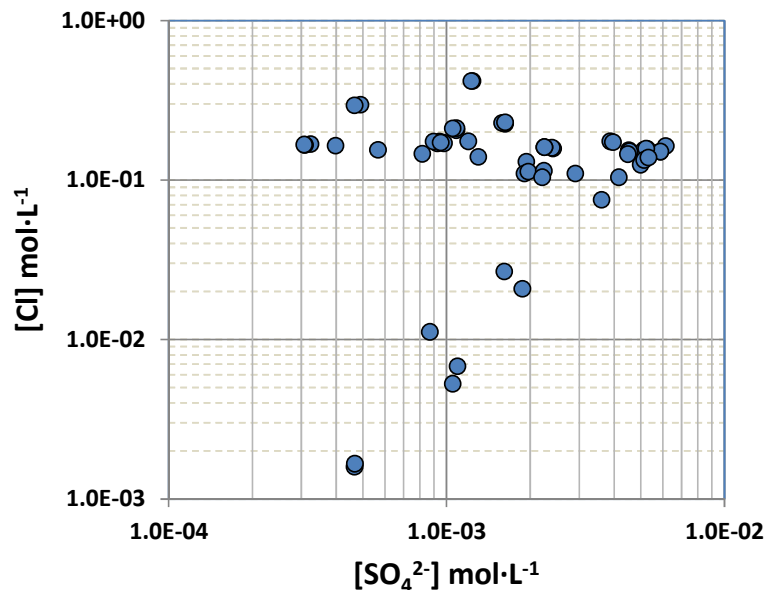


Fig. 9. [Cl] and [SO<sub>4</sub>] in deep groundwaters in Forsmark area.

## 5. Conclusions

From the aqueous solution-solid solution theory, the Ba-Ra concentration in deep groundwaters in Forsmark can be fully explained considering equilibrium with BaRaSO<sub>4</sub> phase of variable composition. The scatter observed in a [Ra]-[Ba] plot is interpreted as equilibrium with different solid composition; also, effects of ionic strength can add more dispersion. Therefore, the observation of poor correlation does not mean lack of equilibrium with BaRaSO<sub>4</sub> at Forsmark.

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