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Replacement of barite by a (Ba,Ra)SO_4 solid solution at close-to-equilibrium conditions: A combined experimental and theoretical study

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Abstract

Solid solution formation between $RaSO_4$ and $BaSO_4$ has long been recognized as a process which potentially controls the Ra concentration in the environment. Here, we have systematically studied the replacement of pure barite by a (Ba,Ra)SO_4 solid solution in 0.1 M NaCl through batch experiments extending up to 883 days at close-to-equilibrium (CTE) conditions, which are relevant to disposal of nuclear waste in a deep geological repository. Kinetic and thermodynamic models were applied to support the interpretation of the experiments, which were carried out at room temperature and at two distinct solid/liquid ratio (0.5 or 5 g/L). Different stages of recrystallization were observed, based on the rate of removal of Ra from aqueous solution. After a first slow kinetic step, a change in the slope of the aqueous Ra concentration vs. time is observed, suggesting nucleation of a new (Ba,Ra)SO_4 phase from supersaturation. If this stage was considered to reflect equilibrium between aqueous and solid solution, one would infer ideality or even negative interaction parameters ($a_0 \leqslant 0$). After this fast nucleation step, in the 0.5 g/L experiments the Ra concentrations in the aqueous solution slowly increase, approaching a concentration close to that required for equilibrium with a regular (Ba,Ra)SO_4 solid solution with an interaction parameter $a_0 = 1.0$. Therefore, these data suggest a non-equilibrium Ra entrapment during the nucleation phase of the replacement, followed by slow recrystallization toward true thermodynamic solid solution equilibrium. Moreover, an interaction parameter value of $a_0 = 1.0$ was inferred from our experiments, which is in good agreement with theoretical predictions from atomistic simulations.

A key result from this study is that aqueous solution and binary (Ba,Ra)SO_4 approach full thermodynamic equilibrium within laboratory time scales (2.5 years). This justifies assuming complete thermodynamic equilibrium for this system in geochemical calculations of processes occurring on geological time scales. This finding is of direct relevance for the safety assessment of radioactive waste disposal, since it may constrain the solubility and thus the mobility of Ra in such environments.

1. INTRODUCTION

The element radium (Ra) with its isotopes ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra is a naturally occurring radioactive material (NORM) of high environmental relevance, which originates from the decay chains of ^{238}U and ^{232}Th. Ra is known to have a high affinity for barium sulfate – leading to its accumulation in barite containing scales connected to technical processes such as oil production or geothermal energy production. The decay of ^{226}Ra produces the gaseous radioactive element radon (Rn) which has an extremely

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short half-life and is thus the largest contributor to an individual's background radiation dose (Keith et al., 2012).

Until recently, the mechanisms leading to structural incorporation into Ra-sulfates have not been studied in detail. After the classical work of Marie Curie, Doerner and Hoskins (1925) and Hahn (1926) in the early decades of the previous century, the focus of research was on technical aspects of Ra enrichment processes (e.g., Rutherford et al., 1996; Stoica et al., 1998; Hamlat et al., 2003).

The mechanism of Ra uptake in these studies was co-precipitation of Ra with $BaSO_4$ from homogenous solutions, which requires a high degree of supersaturation because a critical nucleus needs to be formed before the precipitation starts. This mechanism is relevant to water treatment, the formation of Ra contaminated scales in oil pipes, during unconventional gas extraction or in evaporitic systems and to the prospected formation of a $(Ra,Ba)SO_4$ solid solution following the simultaneous release of Ra and Ba from nuclear waste (Stoica et al., 1998; Grandia et al., 2008; Rosenberg et al., 2011a, 2011b, 2014; Zhang et al., 2014). All these studies have shown that $BaSO_4$ precipitation plays a major role in removing Ra from an aqueous solution compared to other sulfate minerals like gypsum, although these may occur in much larger amounts than barite.

Within spent fuel, the location and the occurrence of Ba and ^{226}Ra with time are different. Stable Ba isotopes are already present as a fission product in fresh spent fuel (SF) after unloading and is contained in oxide precipitates (gray phase). Ba is also formed as fission product from ^{137}Cs and ^{135}Cs. During power plant operation, volatile elements like Cs can migrate to grain boundaries, fractures and the gap region which separates spent fuel and cladding. ^{226}Ra will slowly build up from the decay of ^{238}U and ^{234}U. In contrast to Ba, ^{226}Ra produced in the uranium decay series will be located either in the UO_2-matrix which corrodes rather slowly under repository relevant conditions or may be retained in secondary uranium phases. Therefore, a likely scenario with respect to the disposal of spent nuclear fuel will be an earlier release of stable Ba isotopes compared to ^{226}Ra because Ba produced from the decay of Cs will be more easily accessible during spent fuel corrosion than ^{226}Ra. Due to the presence of sulfate in many ground waters, a formation of barite is likely in case of spent fuel corrosion. Formation of a mixed $(Ba,Ra)SO_4$ phase will then take place under close-to equilibrium (CTE) conditions via replacement of previously formed barite, not by co-precipitation from a highly oversaturated solution (Grandia et al., 2008). In a recrystallization process, also called replacement, a newly formed secondary phase grows at the expense of a dissolving primary phase (Putnis, 2009). In the present study, the primary phase is pure barite whereas the secondary phase is a $(Ba,Ra)SO_4$ solid solution. A thorough understanding of the mechanisms leading to Ra-barite formation in aqueous solutions and the careful quantification of related thermodynamic data (non-ideality parameters, end-member solubility products) is a prerequisite to reliably predict the contribution of ^{226}Ra to radiological doses in safety assessment calculations.

Deriving thermodynamic information from co-precipitation experiments is difficult. The dependence of trace element partitioning on precipitation rate has been amply demonstrated on other systems. Specifically, elements compatible with the host structure – like Ra in barite – have significantly lowered partition coefficients when precipitated at high rates from highly supersaturated solutions, compared to mixed solids grown under CTE conditions (Lorens, 1981; Davis et al., 1987; Dromgoole and Walter, 1990; Tesoriero and Pankow, 1996; Rimstidt et al., 1998; Prieto, 2009). Since recrystallization experiments are typically carried out under CTE conditions, the highest partition coefficients are observed during such replacement processes, as shown e.g., for Cd in calcite by Davis et al. (1987).

Recent experimental and modeling studies have attempted to obtain thermodynamic data relevant for the $(Ra,Ba)SO_4$ solid solution by following the uptake of ^{226}Ra or ^{223}Ra and ^{133}Ba by initially ^{133}Ba free barite (Bosbach et al., 2010; Curti et al., 2010; Vinograd et al., 2013; Klinkenberg et al., 2014; Torapava et al., 2014). These batch and modeling studies have shown that, within a time scale of about 440 days, Ra entered the barite crystal structure during a surprisingly fast recrystallization-like process – indicating partial or even complete replacement of barite by a $(Ba,Ra)SO_4$ solid solution under CTE conditions. The recent micro-analytical study by Klinkenberg et al. (2014) fully supports these results, providing the basis and justification for applying the thermodynamic and kinetic modeling presented here. Klinkenberg et al. (2014) for the first time demonstrated the uptake of Ra into the barite crystal volume and thus provided direct support for the assumption of full recrystallization.

The new experimental data presented here extend the time scale of the experiments to 883 days and are complementary to the microscopic and microanalytical data of Klinkenberg et al. (2014) that were obtained under the same experimental conditions with comparable solid samples – thus allowing a direct link between macroscopic and microscopic observation. In contrast to earlier studies, we focus here on the transient kinetics of $(Ba,Ra)SO_4$ phase formation and on the comparison with solid solution thermodynamic models, taking into account the uncertainty of the key solubility product of $(RaSO_4)$, which is necessary to quantify these models. Using this approach and a careful data analysis, we were able to deduce both recrystallization rates and interaction parameters for mixed phase formation. In particular, the extension of reaction times to more than 800 days allowed us to distinguish between kinetically-driven and close-to-equilibrium mixed phase formation, allowing us to derive the thermodynamically relevant interaction parameter for the binary $(Ba,Ra)SO_4$ solid-solution.

2. MATERIALS, METHODS AND MODELING

2.1. Sample preparation and experimental setup

The solid samples were two commercial barite powders, Sachtleben® (SL) and Aldrich® (AL), which were carefully selected based on their different grain size and morphology. Both raw products were pretreated before the experiment to