

Adsorption of ^{133}Cs and ^{87}Sr on pumice tuff: A comparative study between powder and intact solid phase

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Abstract This study examines the use of intact samples as an alternative to powder in conventional batch sorption studies to determine the distribution coefficient (K_d). Stable cesium (^{133}Cs) and strontium (^{87}Sr) were used under specified geochemical conditions to compare the K_d values of powder and block pumice tuff samples. The aim of the study was to infer any K_d difference under laboratory and field conditions. K_d values for block samples were found to be less than one order of magnitude lower than powder materials for both Cs and Sr on fresh tuff, and more than one order of magnitude lower in oxidized tuff. Destruction of micropores in oxidized tuff was estimated to be mainly responsible for reducing K_d values in oxidized tuff. However, approximately one order of magnitude difference in K_d values indicates that homogeneously prepared intact samples can be used for sorption coefficient measurement at closer to in situ conditions. Pore size distribution analysis using mercury intrusion porosimetry revealed that lower K_d values on block samples result from lower surface area available as sorption sites due to inaccessible closed pores in the intact solid.

Keywords Cesium · Strontium · Pumice tuff · Adsorption

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1 Introduction

This research presents an alternate sample type in the routine laboratory experiment used to measure the distribution coefficient, K_d in in situ field conditions of the solid phase. Batch experiments (also known as static) with powder or crushed materials are the most widely used technique for reliable K_d measurements. However, researchers have two main criticisms of this approach: the difference in solid–liquid (S/L) ratio from in situ conditions (Limousin et al. 2007; Wang et al. 2009), and large sorption values that may not apply to actual flow conditions (Hu and Mao 2012). However, batch experiments are appealing for not requiring much space and for allowing straightforward collection of all parameters of interest, and the named limitations can be overcome using simulations such as thermodynamic sorption models (OECD 2001; Chang and Wang 2002). To more closely approximate the in situ environment, many researchers have compared column experiments (or dynamic systems) with batch-type using intact materials of different sizes (e.g. Widerstand et al. 2010; Lee et al. 2012; Esa 2014; Wu et al. 2015) or making a column with crushed materials (e.g. Xia et al. 2006; Li et al. 2009). As the nuclides travel in the interparticle pores of packed geological substances in the column approach, it should offer a better simulation of the actual environment. Again, this approach has been criticized for its complex experimental set up, requirement of much time and space, homogeneity/inhomogeneity of packed geological substances, consideration of multi-faceted flow dynamics, etc. (MacIntyre et al. 1991; Wise 1993; Allen et al. 1995; Wang et al. 2009). Applying both techniques to minimize those limitations is not always possible due to logistical constraints. Therefore, an approach combining the characteristics of both batch and

column study is necessary, e.g., reduced complexity of the batch system and approximated in situ conditions of the column set-up. The system should also provide reliable K_d data that can be compared with values determined using any other existing method.

K_d values are affected by the chemical and physical conditions of the host rock and of the aqueous phase solution, including surface area, cation exchange capacity, pH, ionic strength, oxidation-reduction potential, and radionuclide concentration (e.g. Iida et al. 2001; Sasaki et al. 2007; Kobayashi et al. 2009; Ohnuki et al. 2009). In addition, as S/L ratio is a major parameter for batch study, selecting a standard quantity of either powder or intact sample material is important. Researchers have studied the effect of different S/L ratios (e.g., Chang and Wang 2002; Du and Hayashi 2006); in nuclear engineering, a 1:10 S/L ratio for powder batch experiments is widely practiced in Japan (JAEA 2014). However, even if the S/L ratio is kept the same, the volume of powder material may differ with sample type depending on particle density. Total surface area, a primary factor affecting sorption/desorption reactions on secondary minerals found in rocks and aquifers, may also differ with density (Rylea et al. 1980). Mineral dissolution/precipitation reactions may change surface area over long periods of time, thereby affecting sorption/desorption capacity. However, particle size (and the corresponding surface area) does not influence sorption behavior until it is smaller than about 63 mm, when it leads to an increase in surface area and sorption values (Rogers and Meijer 1993). Batch experiments are therefore usually conducted with homogenous grain size to keep the particle size effect negligible.

The powder batch-sorption approach can produce variable and even negative sorption values for weakly sorbing chemicals or in a low-concentration experiment (Hu and Mao 2012). The reason is the method depends on subtracting two numbers (initial and final aqueous concentration), which sometimes become similar. To minimize these problems, studies of chemical sorption using intact (non-powder) rock specimens under conditions that approximate the prevailing field situation (e.g., in saturation and contact time) is suggested.

Tuff is a potential host rock for disposal of radioactive waste in different places in the world (OECD 2001) where rhyolitic pumice tuff is selected as a generic repository site for low- and intermediate-level radioactive waste in Japan (Sasaki 2005). Recently, the present authors have conducted several studies with the same pumice tuff regarding the adsorption mechanism of cesium (Cs) and iodide (I) ions (Rajib et al. 2011), the effect of stable strontium (Sr) dissolution on adsorption behavior (Rajib et al. 2015), and the effects of solid phase oxidation and ionic strength on Cs adsorption (Rajib et al. 2016). In consequence of those

studies, pumice tuff blocks were prepared and used for parallel batch experiments with powder samples to investigate the potentiality for K_d measurement using intact samples. Because of its highly porous nature, the intact pumice tuff blocks should provide access to comparable surface area as powder samples within the short contact time.

Cs and Sr are important for the sorption study as components of radioactive waste with significant environmental effects. Some radionuclides of Cs and Sr are considered to be among the most harmful elements due to their long half-life, mobility, and contribution to heat and radiation generation (Xiao et al. 2014; Xiao and Zhang 2016). The mobility and chemical retention of Cs^+ and Sr^{2+} in geologic environments is critical to safety analyses of various concepts for storage of radioactive waste. As the removal of these elements by chemical methods is difficult, adsorption on different rocks and mineral surfaces through water-rock interaction can provide valuable data.

2 Experimental methods

Pumice tuff samples were collected from a potential radioactive waste repository in northern Japan where underground construction work has been ongoing. An actively migrating redox front zone of 2.5 to 10 m thick at 50 m below the surface was identified by oxidation of the surrounding rock (Oyama et al. 2007). Oxidized rock can be easily distinguished from fresh pumice tuff by its yellowish brown color. During the batch study with the intact samples, in addition to traditional experimental parameters like pH, ionic strength, and initial nuclide concentration, in situ oxidation effect was observed. Details of solid phase analysis and batch experimental minutes can be found in previous studies (Rajib et al. 2011, 2015, 2016). Porosity and pore size distribution (PSD) of intact pumice tuff samples were measured using mercury intrusion porosimetry (MIP) following standard operating procedure of the equipment. Some important features of experimental methods different from previous studies are described below.

After crushing and sieving pumice tuff, powder of 150 to 300 μm was used to keep the effect of particle size negligible; whereas blocks were prepared at an equal size of 1 cm^3 (Fig. 1). Conventional batch technique was carried out with a S/L ratio of 1:10. However, as the ratio cannot be kept fixed for block samples (the weight of blocks varied from 1.090 to 1.456 g; Table 1), adjusting to 1:10 ratio was necessary to recalculate K_d values. Considering negligible dependency on ionic strength and pH as well as saturation concentration (Rajib et al. 2015, 2016), 10^{-4} mol/L ^{133}Cs (from CsCl) and ^{87}Sr (from SrCl_2) was selected as the initial experimental concentration at acidic, neutral, and alkaline pH regions. Results from stable nuclides of Cs and Sr are expected to be

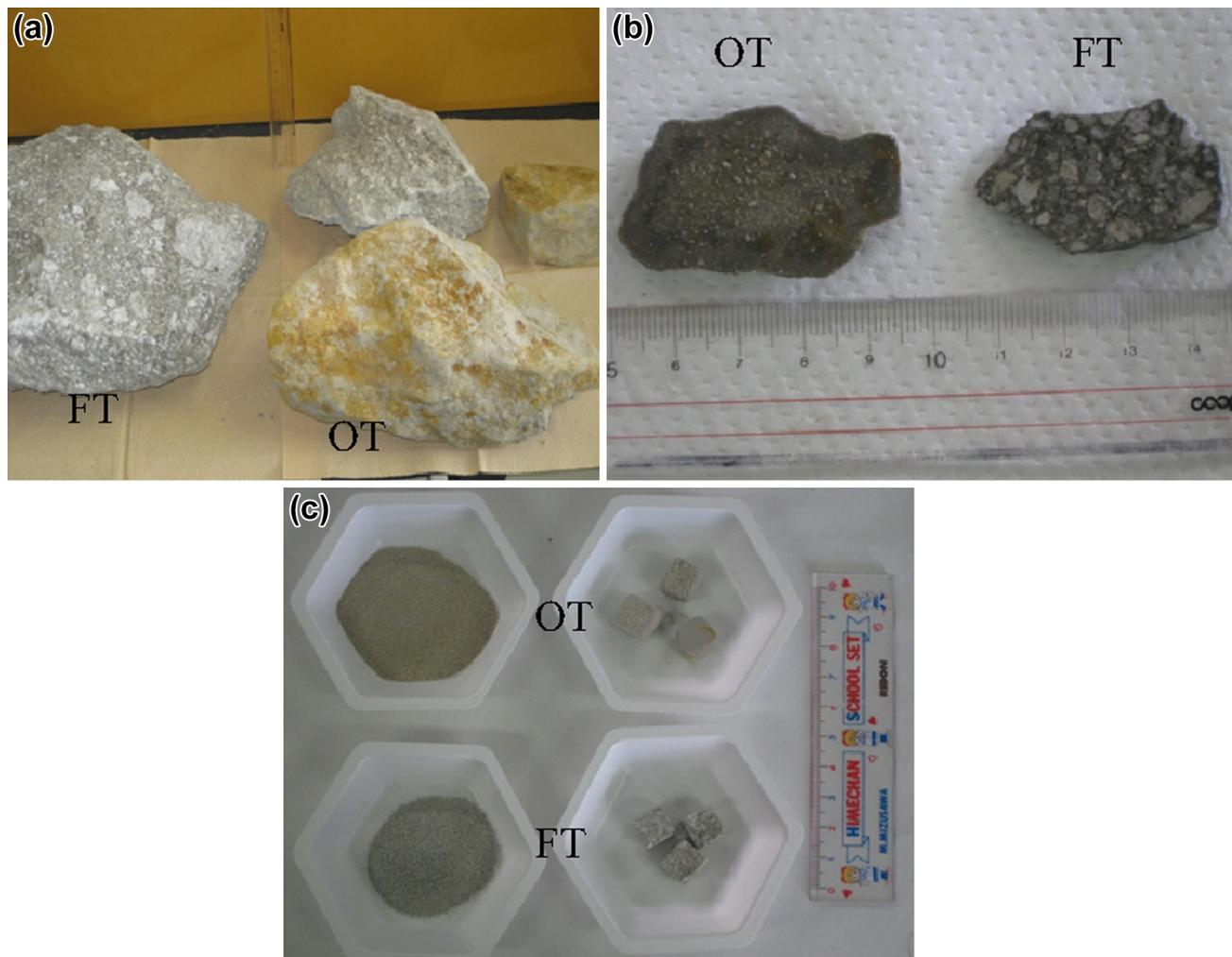


Fig. 1 Pumice tuff samples: **a** Grey fresh tuff (FT) and brownish oxidized tuff (OT); **b** Cross-section of both rocks shows larger grains of pumice are contained in fresh tuff whereas smaller grains contained in oxidized sample; **c** 150–300 µm powder and 1 cm³ blocks prepared for batch adsorption experiment

similar to radio-cesium and -strontium (Igarashi et al. 1998). Since ionic strength (Na^+ concentrations from NaHClO_4) significantly influenced K_d of Cs at less than 1.0 mol/L on pumice tuff (Rajib et al. 2011, 2016), a higher ionic strength of 1.0 and 3.0 mol/L were used (even though such high salt concentration is rarely expected under natural conditions). Natural dissolution of Cs and Sr during the contact time was considered during K_d calculation according to the following modified equation (Rajib et al. 2015):

$$K_d = \frac{(\text{Conc.}[ini] + \text{Conc.}[diss]) - \text{Conc.}[fin]}{\text{Conc.}[fin]} \times \frac{V}{W} \quad (1)$$

where $\text{Conc.}[ini]$, $\text{Conc.}[fin]$ and $\text{Conc.}[diss]$ are the initial, final, and dissolved concentrations of nuclide in solution, respectively; and V and W are volume of liquid and weight of solid, respectively. All the samples were kept in an argon-filled desiccator to avoid carbonate contamination, especially for the alkaline condition. Such

experimental conditions were selected to obtain reliable K_d values from intact samples without significant influence of other parameters.

The differences of K_{dS} were calculated by subtracting powder and block sample values on the logarithmic scale (in m³/kg) and are expressed as a percentage with respect to the higher value. For example, considering K_d of powder and block samples are K_dP and K_dB , in m³/kg, respectively, the difference was calculated as

$$[(K_dB - K_dP) \times 100]/K_dP \quad (2)$$

Both fresh and oxidized tuff samples were used for such calculations at similar pH, ionic strength, and initial concentrations of nuclides. Being redox inactive elements, Cs and Sr are suitable for observation of the water–rock interaction in oxidized or reducing conditions. Finally, the average of all the differences were considered as standard lower values for block samples compared to powder. The

Table 1 Variation of weight of blocks from fresh and oxidized pumice tuff to indicate differences in S/L ratio

Sample	Weight (g)	Sample	Weight (g)
BFC-414	1.109	BFS-414	1.370
BFC-418	1.265	BFS-418	1.135
BFC-412	1.183	BFS-412	1.367
BFC-434	1.247	BFS-434	1.350
BFC-438	1.217	BFS-438	1.227
BFC-432	1.269	BFS-432	1.158
BOC-414	1.151	BOS-414	1.205
BOC-418	1.239	BOS-418	1.381
BOC-412	1.244	BOS-412	1.187
BOC-434	1.403	BOS-434	1.427
BOC-438	1.344	BOS-438	1.364
BOC-432	1.143	BOS-432	1.385

Weight of all powder samples is 1 g and volume of liquid is 10 mL for all samples. Sample number explanation: B-Block; F-Fresh or O-Oxidized; C-Cesium or S-Srontium; 4-Nuclide initial concentration of 10^{-4} mol/L; 1 or 3-ionic strength of 1.0 or 3.0 mol/L, respectively; and 4,8, and 2 are pH 4, 8, and 12, respectively

average includes K_d values under all nuclide concentrations, ionic strengths, and pH levels.

3 Results and discussion

The pumice tuff samples were characterized by low density and high porosity, averaging 0.87–1.22 g/mL and 51%–52%, respectively, as measured by MIP. Fresh tuff was of lower density and higher porosity (0.87 g/mL and 52%, respectively) compared to oxidized tuff (1.22 g/mL, 51% porosity) (Table 2). The low density and high porosity of fresh tuff reflected the presence of larger pumice grains, which have a lower density (0.75 g/mL) and higher porosity (around 60%). Although pumice grains were also present in oxidized tuff samples, they were too small to

Table 2 Pore size distribution (PSD) data summary of fresh (FT) and oxidized (OT) tuff by MIP before and after batch experiment

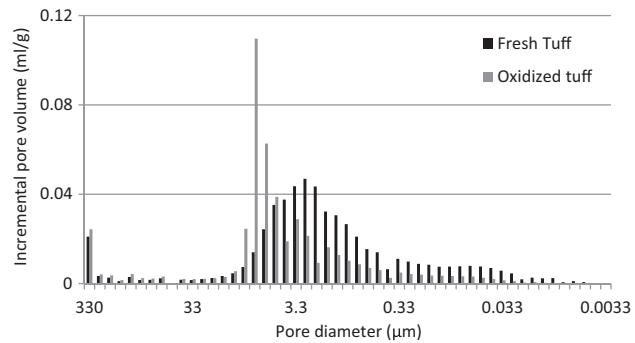
	Before experiment		After experiment	
	FT	OT	FT	OT
Total pore area (m^2/g)	8.310	2.202	7.513	2.249
Average pore diameter (μm)	0.366	0.931	0.266	0.798
Bulk density (g/mL)	0.865	1.215	1.124	1.136
Porosity (%)	51.87	50.76	51.81	50.84

A total 4 and 12 samples before and after the experiment, respectively, were measured to obtain average values

affect the pore properties. The smaller pumice grains in the oxidized tuff likely resulted from dissolution accompanying oxidation. MIP analysis of original pumice tuff samples before the batch experiment showed that fresh tuff mostly has pores ranging from 0.6–10 μm , whereas a large fraction of pores in oxidized tuff are in the narrower range of 3.9–9.5 μm (Fig. 2). The average pore area greatly varies from $\sim 8.3 \text{ m}^2/\text{g}$ in fresh tuff to $\sim 2.2 \text{ m}^2/\text{g}$ in oxidized tuff, a result of reduction in smaller sized pores in the oxidized sample, as revealed by PSD.

PSD data are informative in the comparison of K_d values between powder and block samples of similar solid phase. Both Cs and Sr sorb significantly on the pumice tuff surface under different geochemical conditions (Rajib et al. 2011, 2015, 2016). Therefore, the present experiment was conducted under specific experimental environments to minimize the effect of variations in pH, ionic strength, and initial concentration. To keep the weight of blocks close to that of powder samples, 1 cm^3 size blocks were used. Because of the low density of the materials, 1 cm^3 blocks weighed 1.09–1.45 g. The variation did not have a large impact on the surface area. As it was not possible to keep exactly same weight for all the blocks, the recalculation to 1:10 S/L ratio was carried out, allowing for the comparison of K_d values with those of similar S/L ratio of powder samples. Natural dissolution of nuclides was incorporated by adding the dissolved amount of Cs (5.5×10^{-9} mol/L for fresh tuff and 5.9×10^{-9} mol/L for oxidized tuff) and Sr (8.27×10^{-7} mol/L for fresh tuff and 4.76×10^{-6} mol/L for oxidized tuff) to initial concentrations. Such high Sr dissolution considerably affects the K_d values (Rajib et al. 2015) and was incorporated. Dissolved Cs was found at the background level and could be neglected.

An initial concentration of 10^{-4} mol/L is the saturated or near-saturated concentration for Cs sorption on pumice tuff (Rajib et al. 2016). At this concentration, Cs K_d values showed little variation with ionic strength change from 1.0

**Fig. 2** Pore size distribution of fresh and oxidized tuff obtained from MIP study (adopted from Rajib et al. 2016). Accumulation of larger pores in a narrow margin and reduction of micro-pores are the main differences between them

to 3.0 mol/L or pH 4, 8, and 12. Batch experiments with Cs and Sr showed similar nature of K_d values in both the powdered and block tuffs, e.g. no pH dependency and similar K_d values at similar ionic strength (Figs. 3, 4). This suggests the use of available surface sites in equal quantity for both block and powder solid phases. The K_d values for block samples were found to be less than one order of magnitude lower than powders, as calculated using Eq.(2). Almost all the samples showed a similar tendency with the average values 8.79% lower for Cs (from a range of 6.26% to 10.98%) and 4.94% lower for Sr (from a range of 0.33% to 12.41%) in block samples of fresh tuff. In oxidized tuff, the difference increased to more than one order of magnitude as the block samples showed differences of 14.58% (from a range of 4.38% to 19.97%) and 13.65% (from a range of 4.39% to 20.05%) for Cs and Sr, respectively. The lower K_d values on block samples might be due to the use of lower surface area as sorption sites since many closed pores in intact solids cannot be accessed. The destruction

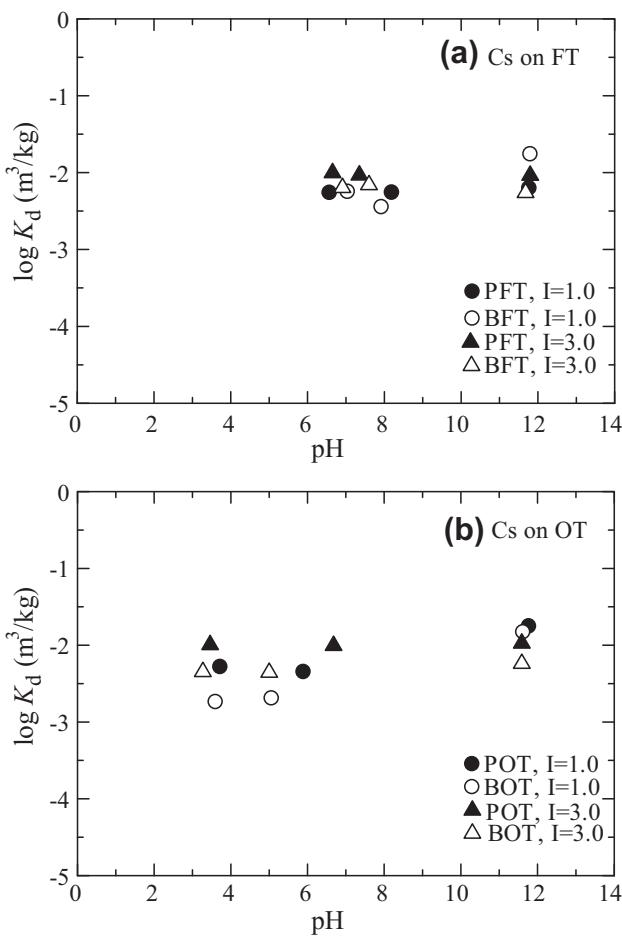


Fig. 3 Influence of pH on K_d values of cesium (Cs) at initial nuclide concentration of 10^{-4} mol/L and ionic strength of 1.0 and 3.0 mol/L, where, B, P, OT, FT indicate block, powder, oxidized tuff, and fresh tuff samples, respectively; **a** fresh tuff and **b** oxidized tuff

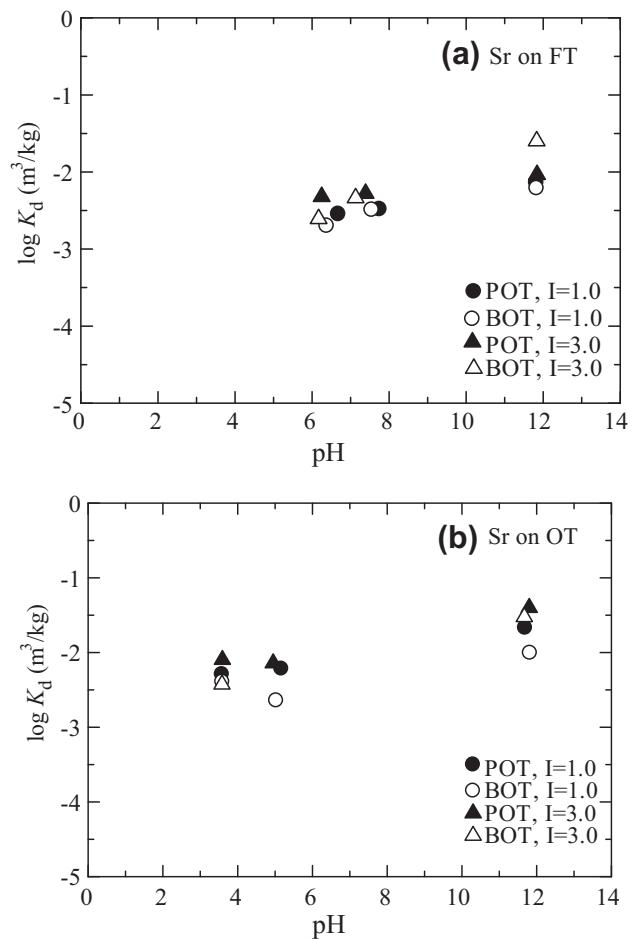


Fig. 4 Influence of pH on K_d values of strontium (Sr) at initial nuclide concentration of 10^{-4} mol/L and ionic strength of 1.0 and 3.0 mol/L, where, B, P, OT, FT indicate block, powder, oxidized tuff and fresh tuff samples, respectively; **a** fresh tuff and **b** oxidized tuff

of smaller pores in oxidized tuff due to oxidation phenomena might cause higher reducing K_d values. These pores may reduce the adsorption of nuclides in oxidized tuff as micro-porous structures are reported to be responsible for nuclide retardation (Wu et al. 2015).

Cesium and strontium are usually sorbed in the interlayers of phyllosilicate minerals or clay minerals such as micas (Lee et al. 2012; Qin et al. 2012; Wu et al. 2015). In pumice tuff, such minerals were rarely found and so the adsorption showed low values, with a few exceptions at high pH (near 12). The high values were due to carbonate contamination as the samples were removed from the argon-filled desiccator for pH adjustment every two weeks. Salt precipitation around the cap of the solution-containing test tubes supports the assumption of contamination in higher pH samples. For contaminated surface sites at high pH only, fresh and oxidized tuff showed little difference in K_d values at acidic to neutral pH. Lack of appropriate mineral surface caused less adsorption in present

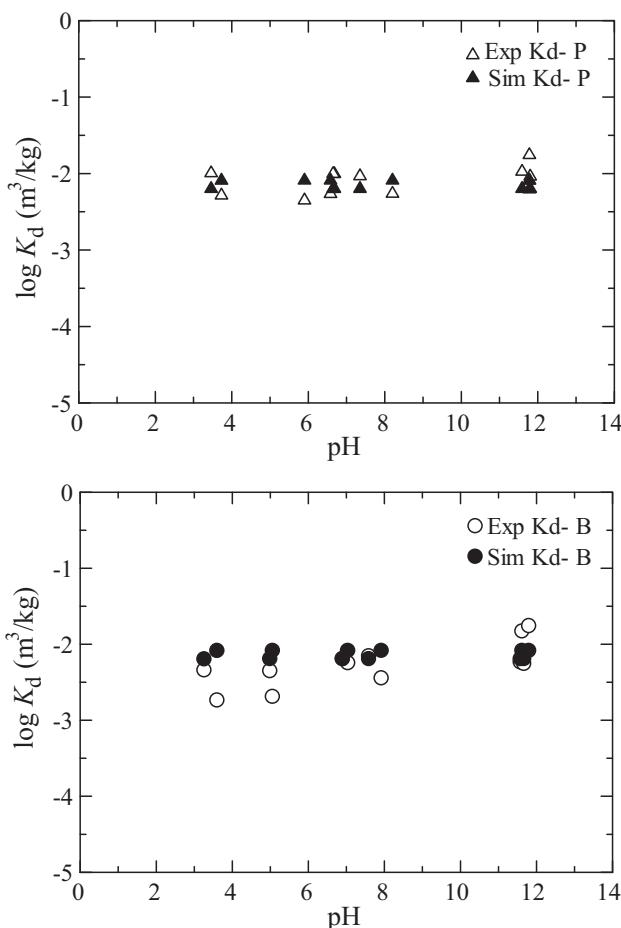


Fig. 5 Fitting of experimental K_d data for Cs by one site surface complexation model; Exp and Sim indicate experimental and simulated data, respectively; *P* and *B* indicate powder and block samples, respectively

experimental conditions despite having much variation in surface area.

Although block samples are rarely used in static batch sorption experiment, as documented in the literature, they were used in the present study with the assumption that the blocks more closely represent the ‘natural condition’: compact with intact PSD. However, there might be disturbances during block preparation (changes in pores, fractures, compactness, etc.) including the possibility of fragmenting, the effect of shaking, and the long aging period. The K_d difference between block and powder is expected to be caused by these changes in physical properties of fractures during the experiment. Changes of pore properties may change pore connectivity—either reducing or increasing—affecting the solution’s ability to access the surface sites and eventually changing sorption quantities.

K_d values from powder samples have been found to be approximately one order of magnitude higher than intact samples using dynamic or through-diffusion methods (e.g. Xia et al. 2006 for sedimentary rocks; Lee et al. 2012 for

igneous rocks). The present results with batch experiments using block samples provide similarly different values. However, there is a significant difference between the solid phase of the present study compared with the literature, especially in terms of surface area and PSD, which may affect adsorption behavior considerably.

It is worth mentioning that the K_d values presented in this experiment were obtained from individual samples only. This may produce some uncertainties in measurement of the K_d values. As K_d depends on the initial nuclide concentration, pH, ionic strength, etc., the uncertainties could come from preparation of the initial nuclide concentration and ionic strength, measurement of final nuclide concentration in aqueous form by ICP-MS, or measurement of sample weight for S/L ratio. While preparing the initial nuclide concentration, slight changes in weight of CsCl or SrCl₂ powder could change the initial Cs/Sr concentration. The weight of pumice tuff powder or blocks also could change the S/L ratio. However, in the present case, the weight was measured with an electronic balance with 0.0001 g accuracy. Accuracy to the ten thousandth’s place prevents changes in K_d values at more than one thousandth mL/g, which could not affect the final values on the logarithmic scale. For example, a change of sample weight from 1.1515 to 1.1516 g yielded K_d change from 5.49826 to 5.49778 mL/g, resulting in no significant difference on the logarithmic scale. For ICP-MS measurement, the detection range was between 10^{-4} and 10^{-8} mol/L and the counts per second for each sample were obtained from the average of three acquisitions of the data in the machine, usually within 10% deviation. If any value was larger than 10%, the sample was measured again. Therefore, uncertainty from ICP-MS in determining nuclide concentration in solution can be considered to have a negligible impact on K_d values in the present experiment.

3.1 Evaluation of experimental K_d data with model simulation

To evaluate the experimental data, K_d values were analyzed through one site surface complexation model as previously applied with Cs on similar samples (details are referred to Rajib et al. 2011). Igor Pro 6.37 simulation software was used for the fitting of experimental K_d values and determining a model parameter like dissociation constants for Cs and Na. These parameters can be used to predict K_d values for similar types of rocks for which sorption data are lacking (Sasaki et al. 2007). However, unlike the previous study, the present experimental conditions include high initial Cs concentration and ionic strength, and low sample quantity. Despite such limitations, using some parameters from previous studies, the fitting of K_d data was done successfully and a dissociation

constant for Cs for the present experimental conditions was obtained (Fig. 5). It can be concluded that the surface complexation model can be applied to high ionic strength and high initial concentration as well.

From simulated data at present experimental conditions (high Cs concentration of 10^{-4} M and high ionic strength of 1.0, 3.0 M), the dissociation constant of Cs for pumice tuff was found to be 6.546 ± 0.213 . This value is considerably higher than the values obtained with Cs on separated tuff (5.79) and pumice (5.92) in Rajib et al. (2011). The lower constants were due to the use of low initial Cs concentrations (10^{-5} , 10^{-6} and 10^{-7} mol/L) and very low ionic strength (0.003 and 0.1 mol/L).

Therefore, the Cs K_d data can be considered valid for further reference. Although the same fitting analysis was not applicable for Sr K_d data due to a difference in its valency state, considering the similar order K_d values relative to Cs at similar experimental condition, Sr K_d s are expected to be valid as well.

4 Conclusions

Cubic block shaped intact samples were successfully used to determine the distribution coefficient, K_d , of Cs and Sr on fresh and oxidized pumice tuff. The K_d values were compared with powder samples under similar experimental conditions. Intact samples from fresh tuff returned K_d less than one order of magnitude smaller, and over one order of magnitude smaller for oxidized tuff. Reduction of micro-pores of less than 0.6 μm was found to be the main factor in lowering the K_d values in intact samples. The reduced values can be compared with the literature where intact samples were used. Experiments with more samples with variable geochemical conditions should be conducted to confirm the use of block samples as substitutes for powder materials.

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