



Se(IV) uptake by Äspö diorite: Micro-scale distribution



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ARTICLE INFO

Article history:

Available online 27 June 2014

ABSTRACT

Risk assessment of deep geological repositories (DGR) for high level radioactive waste demands radionuclide (RN) sorption data, with minimised uncertainties, on repository barriers. Sorption data in crystalline rocks, are principally obtained on crushed material and reported as distribution coefficients, relative to the mass of solid (K_d in m^3/kg). Main sources of uncertainty on available sorption data are due to differences in experimental approach (comparison of crushed and intact material), groundwater and rock composition, redox conditions or the high heterogeneity of crystalline rock.

In this study, the effect of rock mineral heterogeneity on selenium(IV) surface distribution on diorite crystalline rock was analysed under oxic and anoxic conditions. The micro-Particle Induced X-ray Emission (μPIXE) ion beam technique was selected because it allows quantifying tracer distribution directly on intact rock samples, at mineral micro-scale.

Diorite samples were extracted from the Äspö underground research laboratory (Sweden), handled and transported under anoxic conditions. Maintaining controlled redox conditions during the whole experiment is considered particularly relevant to preserve real repository conditions.

Selenite distribution on Äspö diorite surface was heterogeneous, its retention being higher under anoxic conditions. By μPIXE analyses the main Se retentive regions were identified, equivalent in both oxic/anoxic conditions, and surface distribution coefficients (K_d) were determined on main diorite minerals. Sorption values ranged from near zero, on quartz or K-feldspars, to higher values on Fe-bearing minerals like biotite ($K_a \sim 7 \times 10^{-5}$ m) under anoxic conditions. Experimental K_a values determined here are compared to reported distribution coefficients (K_d).

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1. Introduction

Performance assessment calculations, carried out to verify the long-term safety of deep geological repositories (DGR) for high-level radioactive waste (Chapman, 2006; Pusch, 2008) demand radionuclide (RN) sorption/retention data sets, with minimised uncertainties, within the engineered and natural barriers, like crystalline host rock.

Radionuclide sorption is a surface mediated process sensitive to the geochemical properties of constituent minerals and to the available surface area. In a real case, radionuclide sorption can take place directly on minerals at surface of flow-bearing fractures, on grain boundaries and micro-fractures in the rock matrix. Crystalline rocks exhibit an average negative surface charge almost over the whole range of pH since most minerals have net negative

charge. Aqueous ionic species will preferably sorb on mineral surfaces with a net charge of opposite sign.

Most radionuclide sorption databases used for performance assessment of crystalline rock considered radionuclide distribution coefficients (K_d) obtained on crushed material, under specific conditions (Crawford, 2010; Crawford et al., 2006; McKinley and Scholtis, 1993). A great variability of radionuclide sorption values in crystalline rock is reported, mainly due to differences in groundwater or rock composition, experimental approach, contact times or redox conditions (Crawford et al., 2006). There is also difference between K_d values obtained with crushed material or with intact rock samples, since crushing induces formation of new surfaces (Carbol and Engkvist, 1997; Missana et al., 2006). It has been proposed that usual K_d values, reported per mass of solid, should be measured on intact rocks and normalised with regard to surface area and reported as surface distribution coefficients (K_a) (Crawford et al., 2006; Missana et al., 2006).

It is believed that water composition has great importance on RN retention but the high heterogeneity of crystalline rock

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contributes to the variability of sorption parameters (Carbol and Engkvist, 1997). The identification of higher sorbing minerals, through the analysis of the RN distribution on the solid surface can contribute to minimise the contribution of rock heterogeneity to sorption data. Once main sorbing minerals are identified for a chosen RN, a deeper sorption study can be carried out (Missana et al., 2009b; Missana and García-Gutiérrez, 2012).

In this study, the ion beam technique micro-Particle Induced X-ray Emission (μ PIXE) is selected to analyse Se(IV) micro-scale surface distribution onto intact diorite samples coming from the Äspö Hard Rock Underground Research Laboratory (Sweden). The Äspö Laboratory was excavated at a depth of 450 m below the island of Äspö and has been extensively investigated for disposal of nuclear waste in Sweden (Stanfors et al., 1999).

Äspö diorite samples used in this study were extracted, handled and transported under anoxic atmosphere to preserve real DGR conditions (KIT-INE, 2011; Schäfer et al., 2012). Maintaining redox conditions during the whole experiment, from rock extraction to micro-scale distribution analyses, is important to minimise uncertainties in determining sorption parameters for redox sensitive radionuclides, and it had not been done before.

Selenium (^{79}Se), which is formed by nuclear fission and has a half-life of 3×10^5 y, was selected for the study because it is one of the radionuclides with major contribution to the total radiation dose in (DGR). Selenium mobility depends on its speciation under DGR prevailing conditions. Selenium may exist in four oxidation states, and its aqueous speciation is influenced by pH and Eh (Parsons et al., 2013).

Under reducing conditions, the rather insoluble species selenides (Se^{2-}) and elemental selenium Se^0 are dominant. Aqueous selenite (Se(IV) as SeO_3^{2-}), and selenate (Se(VI) as SeO_4^{2-}) oxyanions are predominant mobile forms in mid and strongly oxidising conditions, respectively (Breyneert et al., 2010; Charlet et al., 2012; Kang et al., 2012).

Radionuclides predominantly present as anions or oxyanions are assumed to be non-sorbing or to exhibit weak sorption with low K_d values (Carbol and Engkvist, 1997). Selenium available sorption data indicate weak but non-negligible sorption on crystalline rocks (Elrashidi et al., 1989; Garcia-Gutierrez et al., 1999; Iida et al., 2011; McKinley and Scholtis, 1993; Papelis, 2001), and it is believed that selenite sorption is generally higher than selenate one (Elrashidi et al., 1989). Sorption of anionic species should only occur on positively charged minerals.

The μ PIXE technique was selected to measure selenium(IV) sorption on diorite rocks because it allows quantifying elemental distribution directly on the rock surface at mineral micro-scale. Other technique allowing micro-scale distribution like μ -synchrotron radiation X-ray fluorescence (μ -XRF), which combined with μ -ray absorption spectra (μ -XAS) technique, has the advantage of measuring elemental speciation, but are generally applied on sediments, soils or single minerals (Oram et al., 2008; Strawn et al., 2002). A comparative of PIXE and XRF techniques, applied to multi-elemental investigations in the field of environment, pointed out that both techniques are somehow complementary, with equivalent sensitivity, being XRF suitable for large sample areas (Benydech et al., 1997). Indeed, XRF–XAS are not usually applied onto rocks exhibiting the type of surface mineral heterogeneity of crystalline rock.

The application of μ PIXE to visualise heterogeneous radionuclide retention on granite surface was first proposed in Alonso et al. (2004). Further analytical efforts were done and, it was possible to quantify Au nanoparticle distribution on granite surface (Alonso et al., 2009). First micro-scale analyses on uranium surface retention on Äspö diorite samples were presented in Alonso et al. (2012). No previous quantitative study on Se micro-scale

distribution, carried out, both under oxic and anoxic conditions, on intact crystalline rock is available.

2. Experimental set-up

2.1. Materials

Diorite samples were drilled at the Äspö Hard Rock Underground Research Laboratory, located on the southeast coast of Sweden (Stanfors et al., 1999), and were handled, transported and stored under anoxic conditions (Schäfer et al., 2012).

For μ PIXE analyses, rock sheets of around 2.5 g, 1–2 cm² area and 5–6 mm thick, were cut inside a glove box (N_2 atmosphere and 1% CO_2).

Main mineralogical composition of Äspö diorite samples is presented in Table 1 (Johansson et al., 1998; Widestrand et al., 2001), with major presence of biotite, plagioclase/albite, K-feldspar, quartz and epidote. Presence of accessory phases such as titanite, apatite, magnetite, pyrite, Fe-oxyhydroxides and calcite is also expected (Widestrand et al., 2001).

Diorite density used for PIXE quantitative calculations was 2.47 g/cm³ and an average BET surface area of 0.07 m²/g, measured on the same solid samples, was considered (Missana and García-Gutiérrez, 2012).

Two high saline waters were prepared following the chemical composition described in Heck and Schäfer (2011), in agreement with Äspö natural groundwater sampled in the area where diorite samples were extracted (Schäfer et al., 2012). The chemical composition of the two waters, respectively used for sorption experiments carried out under oxic (named Äspö oxic water) or anoxic conditions inside a glove box (named Äspö anoxic water), are presented in Table 2.

A solution of selenite (Se(IV)) with a concentration of 10^{-1} M was prepared dissolving high purity Na_2SeO_3 (SigmaAldrich) in HCl 0.1 M.

Sorption experiments were carried out both inside the glove box (anoxic conditions), and under atmospheric conditions (oxic conditions), for comparison.

2.2. Sorption experiments

Prior to sorption experiments, rock samples were immersed for hydration during 1 day in 8 mL of the corresponding synthetic oxic or anoxic water. Selenium solution was then spiked to a final selenium concentration of 10^{-3} M, to facilitate selenium detection by μ PIXE analyses. This high Se concentration was selected to improve Se detection by PIXE analyses. Since Se sorption under experimental conditions is not high, site saturation is unlikely. Upon selenium addition, pH was acidified and readjusted with NaOH 0.1 M. Final pH and electric conductivity (EC) were pH 7.6 ± 0.2 and EC = 13.2 ± 0.2 mS/cm, for experiments under oxic conditions, and pH 6.8 ± 0.2 and EC = 13.6 ± 0.2 mS/cm under anoxic conditions. Final pH and EC values of synthetic waters are comparable to those reported for Äspö natural waters in the area where diorite samples were drilled (Heck and Schäfer, 2011).

Selenite speciation in both Äspö synthetic waters (Table 2), at the pH fixed for sorption experiments, was checked using the selenium thermodynamic database of CHES code, mainly equivalent to EQ3/6 with the Se species described in Missana et al. (2009b) and a redox potential of 0.5 V. Calculations were carried out with the Chess code (van der Lee and De Windt, 1999). Two oxyanions, $\text{SeO}_3[2-]$ and $\text{HSeO}_3[-]$, were predicted to be the dominant aqueous species in different proportions in both waters, depending on the pH: 82% $\text{SeO}_3[2-]$ and 18% $\text{HSeO}_3[-]$ under oxic conditions, and 46% $\text{SeO}_3[2-]$ and 54% $\text{HSeO}_3[-]$ under anoxic conditions.

Table 1
Mineral occurrence (in weight%) of Åsö diorite samples and structural formula. Values from ⁽¹⁾ (Johansson et al., 1998) and ⁽²⁾ (Widestrand et al., 2001).

Mineral	%	Formula
Plagioclase/albite	45 ⁽¹⁾ –47 ⁽²⁾	NaAlSi ₃ O ₈ –CaAlSi ₂ O ₈
Biotite	15 ⁽¹⁾ –18 ⁽²⁾	K(Mg,Fe) ₃ AlSi ₃ O ₁₀ (OH,F) ₂
K-feldspar	15 ⁽¹⁾ –10 ⁽²⁾	KAlSi ₃ O ₈
Quartz	14 ^{(1)–(2)}	SiO ₂
Epidote	6 ⁽¹⁾ –5 ⁽²⁾	Ca ₂ Fe ³⁺ Al ₂ Si ₃ O ₁₂ (OH)
Chlorite	**	(Mg,Fe,Al) ₁₂ (Si,Al) ₈ O ₂₀ (OH) ₁₆
Muscovite	**	KAl ₃ Si ₃ O ₁₀ (OH,F) ₂
Zircon	**	ZrSiO ₄
Sphene/titanite	**	CaTiSiO ₄ (OH,F)
Accessory minerals (Apatite, magnetite, Pyrite, Fe-oxyhydroxides and calcite)	6 ⁽²⁾	****

Values from ⁽¹⁾ (Johansson et al., 1998) and ⁽²⁾ (Widestrand et al., 2001).

** Trace.

**** No indicated.

Table 2
Chemical composition of aqueous solutions used for Se sorption experiments carried out under oxic and anoxic conditions (Missana and García-Gutiérrez, 2012) (n.d. not determined).

Element	Synthetic Åsö water (oxic experiments)	Synthetic Åsö water (anoxic experiments)
Unit	mg/L	mg/L
Na ⁺	1800	1700
Ca ²⁺	1000	1200
Mg ²⁺	0.09	105
K ⁺	<0.1	0.42
Li ⁺	n.d.	13
Cl ⁻	4600	4700
SO ₄ ²⁻	0.42	400
Br ⁻	n.d.	17
F ⁻	<0.1	1.2
Al	<0.03	<0.03
Fe	<0.03	<0.03
Si	<0.3	n.d.
Alk (meq/L)	<0.1	0.24

n.d.: not determined.

No precipitation was predicted in both anoxic and oxic cases. Sorption experiments lasted 15 days. Before μ PIXE analyses the sample surfaces were cleaned with deionised water to eliminate precipitates that could bias surface analyses.

2.3. PIXE analyses on specific minerals: surface distribution coefficients (K_a)

Three different diorite samples contacted with selenium, both under oxic or anoxic conditions were selected for μ PIXE measurements.

In each diorite sample, four 2 mm \times 2 mm areas were randomly chosen on each sample for analyses by the nuclear ion beam technique micro-Particle Induced X-ray Emission (μ PIXE) (Johansson et al., 1995). Selected areas usually included some dark mineral, to facilitate area identification. This pre-selection may minimise the effect of the areas of null retention, but it is considered representative enough since significant number of predominant and minority minerals was always detected.

μ PIXE measurements were performed at the nuclear microprobe facility of the Laboratori Nazionali di Legnaro (LNL-INFN, Legnaro – Padova, Italy) (Cristofolini et al., 1998). Samples were irradiated with 2 MeV protons with a beam size of 4 μ m², at perpendicular incidence to the sample. The typical beam currents ranged between 700 pA and 1 nA. These currents allowed attaining

good detection limits (few tens of ppm, dependent on the studied area) in a reasonable time; spatial resolution is limited to 2 μ m. An ORTEC Ge detector with a polymer window of 0.4 μ m thickness and with a 160 eV maximum nominal resolution was used for the X-ray detection. A funny filter 48 μ m thick with a hole in the centre that allows passing 14% of the total signal, was introduced during measurements to reduce the flux of the X-rays emitted by the major (light) elements composing the rock to enhance the sensibility to heavy elements, but still allowing μ PIXE to accurately measure sample composition. The collected charge for each measurement was about 5–6 μ C.

μ PIXE technique includes a scanning system that allows mapping of the studied area and recording the characteristic X-rays emitted the sample by each point. Elemental distribution maps are obtained during the acquisition, by recording the signal of the main characteristic X-ray line ($K\alpha$ or $L\alpha$). In these maps the elemental heterogeneous distribution can be visualised but, the intensity is not corrected and may include other contributions, mainly coming from superposition of characteristics X-ray lines of other elements or background noise.

To get quantitative information analysis of the individual PIXE spectra is necessary.

In the spectra, the element X-ray lines ($K\alpha$, $K\beta$, $L\alpha$, $L\beta$, ...) emitted by the elements composing the area are recorded. Under the experimental conditions, elements with atomic number higher than Na can be detected.

With the GUPIX code the spectra are simulated, the peak area of the main emitted X-ray line is converted to elemental concentration (in ppm), and the presence of a certain mineral is verified.

In this study, the μ PIXE images (2 mm \times 2 mm) were processed with the Mappix code (Ceccato, 2009), which allows selecting specific regions (corresponding to different minerals), to get the individual PIXE spectrum. In this way, in each diorite sample (cm²), the main minerals are identified and processed. The PIXE spectrum and the surface area (S_A in m²) of these selected regions were recorded for quantitative analyses.

PIXE spectra were deconvoluted with the GUPIX code (Maxwell et al., 1995) that allows to fit PIXE spectra by extracting the characteristic X-ray peak intensities and converting them to relative elemental concentrations (Johansson et al., 1995; Maxwell et al., 1995). Fitting was carried out assuming that all elements were in oxide form, that samples are thick and that the concentration sum was 100%.

Both the mineral composition and the selenium concentration retained (Se_{RETAINED}) on each selected region can be obtained. The Se concentration was obtained from the intensity of the correspondent $K\alpha$ X-ray peak (at $E = 11.22$ keV). Selenium limit of detection under experimental conditions was around 40 ppm.

To calculate selenium distribution coefficients (K_a , in m), the following equations was applied:

$$K_a \text{ (m)} = \left(\frac{Se_{\text{RETAINED}}/S_A}{(Se_{\text{INI}} - Se_{\text{RETAINED}})/V_{\text{LIQ}}} \right) \quad (1)$$

where Se_{INI} is the initial selenium (in grams), S_A is the area of the analysed mineral (in m²), the sample depth analysed is 10⁻⁶ m and V is the solution volume (in m³). Since the aim of the study was to evaluate the effect of surface heterogeneity on the variability of selenium sorption values, the Se_{RETAINED} (in grams) values considered were: (1) The average value of the Se obtained on the whole 2 mm \times 2 mm analysed diorite areas and (2) Se_{RETAINED} measured on selected single minerals, considering the average value of at least three regions identified as same mineral. The uncertainties considered for the K_a were the average standard deviation. Since Se limit of detection is about 40 ppm, a $K_a < 1 \times 10^{-6}$ m is below detection limit.

3. Results and discussion

Figs. 1–4 show representative examples of the elemental distribution maps obtained by μ PIXE measurements on 2 mm \times 2 mm Åspö diorite areas immersed in selenite solution, respectively under anoxic (Figs. 1 and 2) and oxic conditions (Figs. 3 and 4).

In all figures it appears that the elemental distribution is heterogeneous. By combining information from different major elements, like Al, Si, K, Ca, Fe or Ti, the main minerals present in each area can be identified (Table 1). Minerals generally identified were quartz, plagioclase, K-feldspar, muscovite and Fe-minerals like biotite or epidote (with Ca content). Minor presence of zircon, chlorite or sphene/titanite was also detected. The minerals identified in each area are indicated in the figure legends.

Selenium was detected in diorite samples immersed in selenium solution, while no Se was detected in the untreated Åspö samples – not contacted with selenium, so that Se background of the sample is below detection limit. Se distribution was also heterogeneous, their concentration being higher in certain regions and, at first sight, large differences between Se retention behaviour under oxic or anoxic are not easily observed.

In Figs. 1–4, red squares numbered in the elemental maps are the different regions/minerals selected to analyse Se_{RETAINED} on single minerals. The same procedure was applied in all other studied diorite areas. Despite the fact that the areas studied are unique and different, we believe that the selection of figures is representative of the general Se distribution.

In the maps, the elemental concentrations are normalised to a colour scale, from black (null) to white (100). In general, higher Se concentration is perceived on Fe-bearing minerals, but non-null selenite concentration is also detected in most Åspö diorite minerals, especially under oxic conditions (Figs. 3 and 4), and in some cases Se seems to be retained on areas not specifically linked to a composing mineral.

The elemental visualisation is certainly useful because it allows identifying the main retentive regions. However, as mentioned before, in order to be sure that an element is present in an area and to determine its concentration, further quantification is required. To do so, in all these selected regions, the individual PIXE

spectrum is obtained for quantitative analyses. As example, Fig. 5 presents the PIXE spectra obtained on the Åspö diorite sample immersed in Se(IV) solution under anoxic conditions that corresponds to regions indicated in Fig. 4. Fig. 5A is the average PIXE spectrum of the whole 2 mm \times 2 mm area. Fig. 5B is the spectrum obtained on the biotite region (region (3) in Fig. 4). Fig. 5C is the spectrum obtained on K-feldspar (region (4) in Figs. 4) and 5D presents the spectrum obtained in the sphene/titanite (region (2) in Fig. 4).

The fit of individual PIXE spectra are shown in Fig. 5. In each area of the region analysed (S_A in m^2), the elemental concentration is obtained and compared to theoretical average mineral compositions. The Se concentration retained (Se_{RETAINED}) is also determined and distribution coefficients are calculated with Eq. (1).

Table 3 presents the average selenium surface distribution coefficients (K_a in m) measured on 2 mm \times 2 mm diorite areas and the individual values measured on selected minerals, both under oxic and anoxic conditions. Obtained distribution coefficients are in agreement with the qualitative information obtained in the μ PIXE elemental maps.

On average, higher selenite surface distribution coefficients are measured under anoxic conditions (average K_a of $(9 \pm 1) \times 10^{-5}$ m) compared to $K_a = (4 \pm 1) \times 10^{-5}$ m measured under oxic conditions.

The same applies to K_a values measured on individual minerals, which K_a were sometimes one order of magnitude higher under anoxic conditions, except for titanite (Table 3).

Under reducing conditions, higher K_a values were measured on biotite minerals (region (5) in Fig. 1 and region (2) in Fig. 2), or chlorites (region (4) in Fig. 1 and (3) in Fig. 2) with Fe^{2+} presence. Appreciable values were also measured in other Fe-bearing minerals like epidote (region (3) in Fig. 1). At the experimental conditions (pH 6.8) most minerals are negatively charged, but these minerals exhibit points of zero charge close to experimental conditions (biotite at pH 6–7 (Alonso et al., 2009), and pH 5.5 for chlorite or epidote (Fornasiero and Ralston, 2005)), so that positively charged sites can retain Se anion species.

Both under anoxic or oxic conditions, little Se was detected on major minerals composing diorite, like quartz (regions (1) in Figs. 1 and 2), K-feldspar (region (4) in Fig. 2) or plagioclase (region (2) in

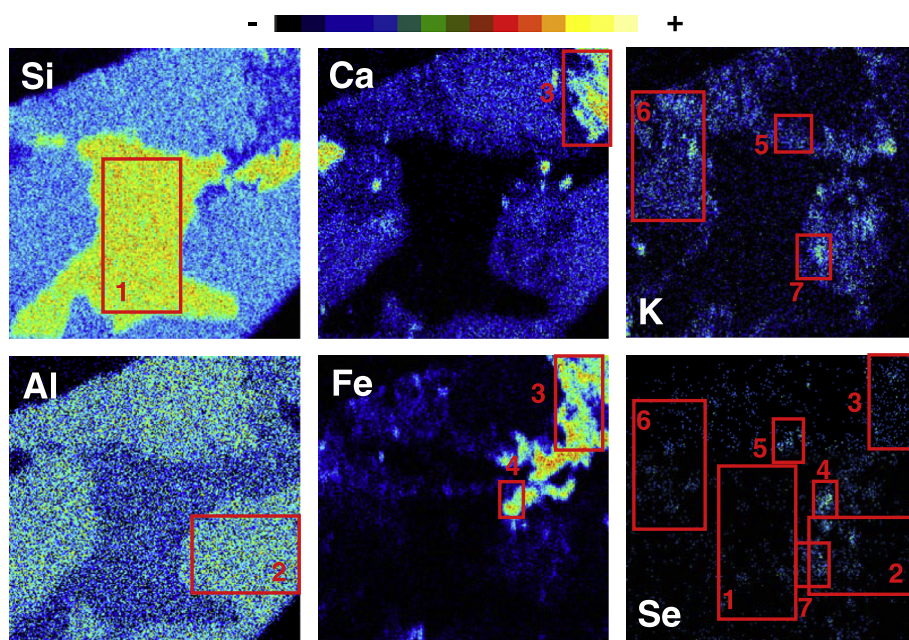


Fig. 1. Elemental maps obtained by μ PIXE on a 2 mm \times 2 mm area of Åspö diorite immersed in Se solution under anoxic conditions. Red squares are the regions selected for individual PIXE analyses: (1) Quartz, (2) Plagioclase, (3) Epidote, (4) Chlorite, (5) Biotite and (6 and 7) Se accumulated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

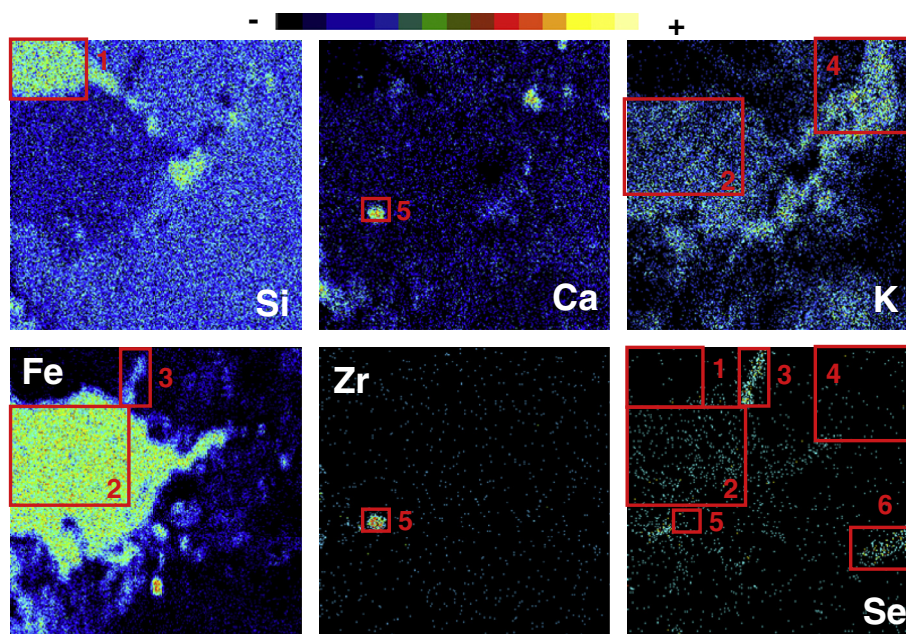


Fig. 2. Elemental maps obtained by μ PIXE on a $2\text{ mm} \times 2\text{ mm}$ area of Åspö diorite immersed in Se solution under anoxic conditions. Red squares are regions selected for individual PIXE analyses: (1) Quartz, (2) Biotite, (3) Chlorite, (4) K-feldspar, (5) Zircon and (6) Se accumulated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

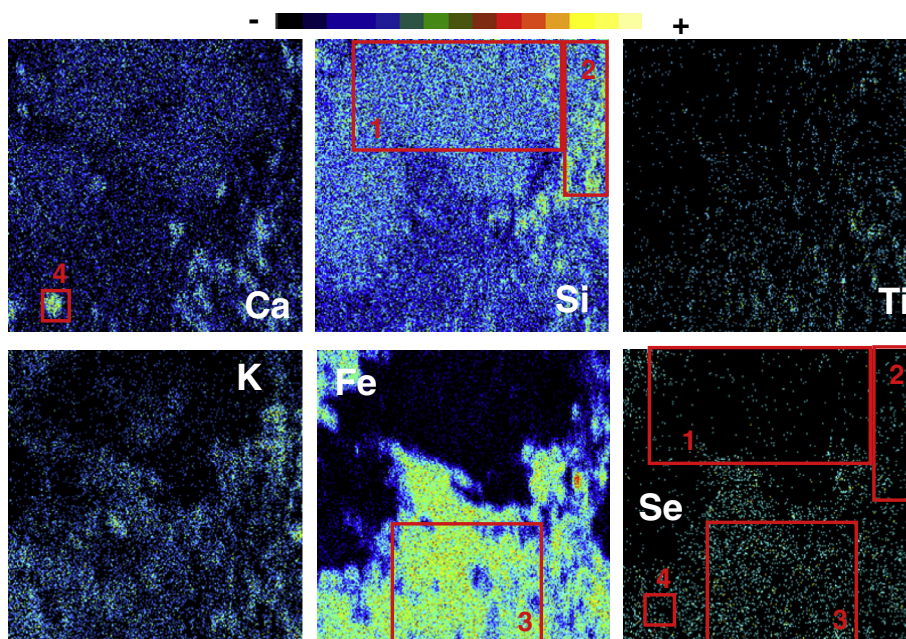


Fig. 3. Elemental maps obtained by μ PIXE on a $2\text{ mm} \times 2\text{ mm}$ area of Åspö diorite immersed in Se solution under oxic conditions. Red squares are regions selected for individual PIXE analyses: (1) Plagioclase, (2) K-feldspar, (3) Biotite and (4) Ca - area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 1. These major minerals are negatively charged under studied conditions (Alonso et al., 2009), so that sorption of Se oxyanions was unlikely. Anyhow, it is noteworthy that not-zero selenium K_a values were measured on those minerals (K_a (anoxic) from 3×10^{-5} to 7×10^{-5} m; K_a (oxic) from 0 to 7×10^{-5} m).

In some areas Se was retained, with presence of Fe, Ca or other elements but not specifically linked to any composing major or minority mineral (Table 1), which deserves special mention.

It should be noted that μ PIXE technique gives information of elemental composition, but not on elemental speciation, so that discussion on possible Se retention mechanisms is supported by available literature.

Se retention seems to be sometimes distributed along grain boundaries of major composing minerals (i.e. region (7) in Fig. 1). Porosity studies carried out on Åspö diorite samples indicated that mineral grain boundaries were not the main migration paths, but

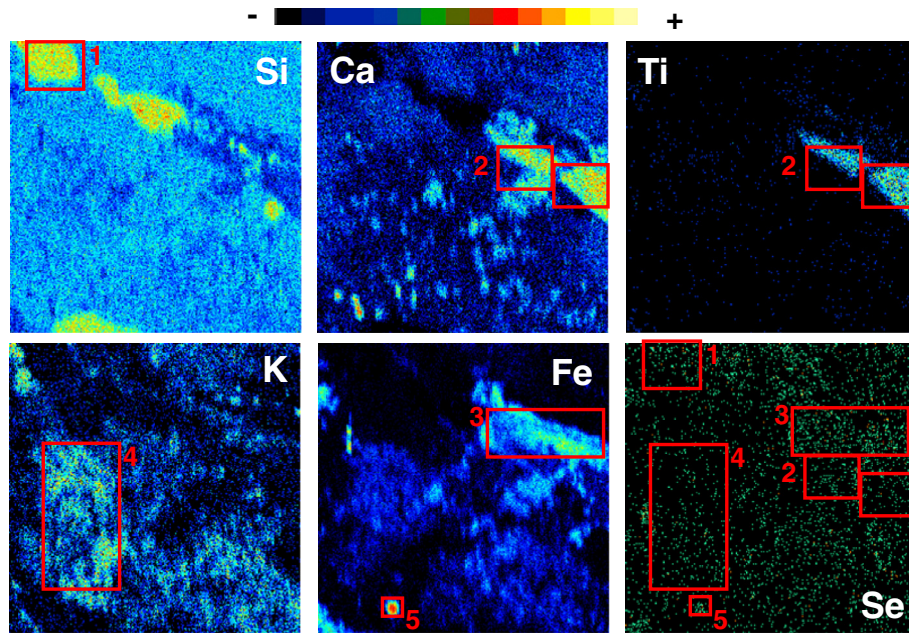


Fig. 4. Elemental maps obtained by μ PIXE on a 2 mm \times 2 mm area of Äspö diorite immersed in Se solution under oxic conditions. Red squares are regions selected for individual PIXE analyses: (1) Quartz, (2) Sphene/titanite, (3) Biotite, (4) K-feldspar and (5) Fe oxide. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

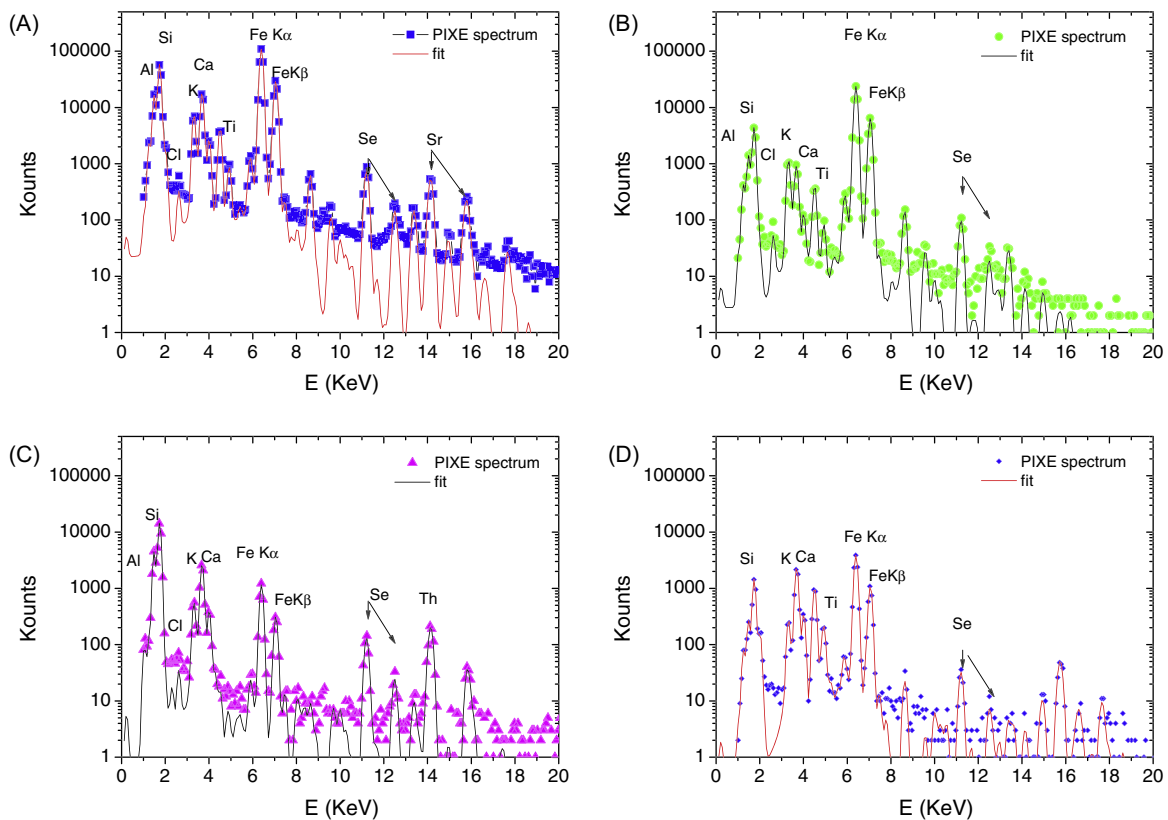


Fig. 5. Individual PIXE spectra obtained on the Äspö diorite sample immersed in Se(IV) solution under anoxic conditions on same regions indicated in Fig. 4. (A) Whole 2 mm \times 2 mm area, (B) Biotite, (C) K-feldspar and (D) Sphene/titanite. The main element X-ray emitted lines are indicated and the spectra fits are included.

other pathways with relatively high porosity were identified, forming a connected network mixture of minerals dominated by biotite, plagioclase and chlorite. The highest porosities were observed in the network were 1.5–3%, found near large quartz and feldspar

mineral crystals (Johansson et al., 1998), as observed in this case around a quartz mineral (region (1) in Fig. 1).

Selenium is sometimes linked to areas with high Fe content but with no detectable presence of other elements (i.e. region (6) in

Table 3

Average distribution coefficients (K_a in m) measured on 2 mm × 2 mm diorite areas and individual distribution coefficients (K_a) measured on identified minerals. The K_d values (m^3/kg) estimated considering a BET surface of $0.07 \text{ m}^2/\text{g}$ (Missana and García-Gutiérrez, 2012) are also presented.

Mineral	K_a (m) anoxic	Estimated K_d (m^3/kg) anoxic	K_a (m) oxic	Estimated K_d (m^3/kg) oxic
Average (2 × 2 mm ²)	$(9 \pm 1) \times 10^{-5}$	$(6.3 \pm 0.7) \times 10^{-3}$	$(4 \pm 1) \times 10^{-5}$	$(3.2 \pm 1) \times 10^{-3}$
Quartz	3.0×10^{-5}	2.1×10^{-3}	$0-3.2 \times 10^{-6}$	$0-2.2 \times 10^{-4}$
Plagioclase	7.4×10^{-5}	5.2×10^{-3}	7.2×10^{-5}	5.0×10^{-3}
K-feldspar	7.0×10^{-5}	4.9×10^{-3}	3.4×10^{-6}	2.4×10^{-4}
Fe-biotite	1.8×10^{-3}	1.3×10^{-1}	$7 \times 10^{-4}-1 \times 10^{-3}$	$(4.9-7) \times 10^{-2}$
Fe-epidote	4.0×10^{-4}	2.8×10^{-2}	5×10^{-5}	3.5×10^{-3}
Chlorite	2.4×10^{-3}	1.7×10^{-1}	****	***
Titanite	1.4×10^{-4}	1.1×10^{-2}	3.7×10^{-4}	2.6×10^{-2}
Zircon	6.6×10^{-5}	4.6×10^{-3}	****	****
Se accumulated areas	1.5×10^{-3}	1.1×10^{-1}	2.5×10^{-4}	1.8×10^{-2}

Fig. 2; or region (5) in Fig. 4). Presence of Fe-oxide micro-precipitates like hematite, with a point of zero charge around pH 7.5, have been proposed to increase selenium retention (Crawford, 2010). Selenium sorption to magnetite, pyrite or Fe-oxyhydroxides can be also expected, since they are present as accessory minerals (Widestrand et al., 2001), but cannot be distinguished by PIXE analyses. For example, Se anions are considered to have a strong affinity with sulphides and to interact with pyrite (Curti et al., 2013) as well as with magnetite (Missana et al., 2009b) or clays (Missana et al., 2009a).

On Ca areas not associated to other elements (i.e. region (4) in Fig. 3), Se retention could be attributed to local precipitation of Ca–Se species ($\text{CaSeO}_3 \cdot 2\text{H}_2\text{O}$ or CaSeO_4), despite geochemical speciation did not predict their formation. Under experimental conditions C is not detected by μPIXE analyses, so that presence of carbonates cannot be discarded. However, carbonate is not expected to sorb significantly in the rock matrix or to influence the distribution of complex Se forms (Crawford, 2010). Selenium incorporation into calcite structure, in the form of oxyanions, by replacing the carbonate group has also been proposed (Renard et al., 2013).

The contribution of these high retentive regions, not linked to specific minerals, can be more relevant in the real case, where rock heterogeneity is expected to be higher.

To facilitate comparison of obtained surface distribution coefficients (K_a in m) with available selenium sorption data, mainly reported as K_d (in m^3/kg), distribution coefficients (K_d) were calculated considering a BET surface area for bulk Äspö diorite of $0.07 \text{ m}^2/\text{g}$ (Missana and García-Gutiérrez, 2012). These estimated K_d values (m^3/kg) are also presented in Table 3 for both oxic and anoxic conditions. The average values were $(6.3 \pm 0.7) \times 10^{-3} \text{ m}^3/\text{kg}$ under anoxic conditions and $(3.2 \pm 1) \times 10^{-3} \text{ m}^3/\text{kg}$ under oxic conditions.

Carbol Engkvist (1997 and references therein) found a Se K_d value of $0.004 \text{ m}^3/\text{kg}$, under oxidising conditions and considering that the dominant aqueous specie is $\text{HSeO}_3[-]$ around pH 7, while $\text{SeO}_3[2-]$ dominates in the pH range of 8–9. They reported higher Se sorption under reducing conditions ($0.04 \text{ m}^3/\text{kg}$) but the final recommended K_d value for Se (–II, IV and VI), without distinction on redox conditions, was $1 \times 10^{-3} \text{ m}^3/\text{kg}$ with an uncertainty interval from 5×10^{-4} to $5 \times 10^{-3} \text{ m}^3/\text{kg}$ (Carbol and Engkvist, 1997).

McKinley and Scholtis (1993) reported a value between $4 \times 10^{-4} \text{ m}^3/\text{kg}$ and $5 \times 10^{-3} \text{ m}^3/\text{kg}$ (maximum $2 \times 10^{-2} \text{ m}^3/\text{kg}$) for Se sorption on granite from different locations, and similar reducing or oxidising conditions (McKinley and Scholtis, 1993).

In Spanish granites, experimental Se sorption K_d obtained on crushed granite, in oxic conditions, ranged between $6 \times 10^{-2} \text{ m}^3/\text{kg}$ and $2 \times 10^{-3} \text{ m}^3/\text{kg}$ (García-Gutiérrez et al., 1999). Sorption values reported for Se(–II), under reducing conditions, on granodiorites ranged from 2.2×10^{-4} to $4 \times 10^{-3} \text{ m}^3/\text{kg}$ (Iida et al., 2011).

K_d values measured here for Se(IV) on diorite Äspö samples are in line with those proposed by other authors on equivalent crystalline rocks.

The main advantage of the present study is that the surface distribution coefficients (K_a) are directly measured on the intact rocks, allowing correlating the rock heterogeneity and selenium sorption, thus restricting the range of sorption values and weighing the contribution of high sorbing minerals or other local in-homogeneities.

4. Conclusions

Selenite average surface distribution coefficients (K_a) were determined on diorite samples, at mineral micro-scale, both under oxic and anoxic conditions. Anoxic conditions were preserved the whole experiment, from rock extraction to sorption experiments.

Se surface retention was higher under anoxic conditions, but the observed sorption behaviour was equivalent under both conditions. Average surface distribution coefficients (K_a) obtained by μPIXE measurements range from $K_a = (9 \pm 1) \times 10^{-5} \text{ m}$ under anoxic to $K_a = (4 \pm 1) \times 10^{-5} \text{ m}$ under oxic conditions. These K_a distribution coefficients were translated to bulk K_d coefficients determined by batch experiments, considering an average BET surface area (S_a) of $0.07 \text{ m}^2/\text{g}$, determined on same solid samples. The K_d values estimated were $(6.3 \pm 0.7) \times 10^{-3} \text{ m}^3/\text{kg}$ in anoxic conditions and $(3.2 \pm 1) \times 10^{-3} \text{ m}^3/\text{kg}$ in oxic conditions, were in line with those reported for selenite oxyanions on equivalent crystalline rock.

The proposed methodology allows restricting the range of sorption values, by measuring distribution coefficients on single minerals and on intact rocks. In this way, the contribution of high sorbing minerals or other local heterogeneities of radionuclide retention is taken into account, and the distribution coefficient variability may be reduced.

Acknowledgments

This study received funding from EU Seventh Framework Programme (FP7/2007–2011) under the grant agreements N° 269658 (CROCK, Crystalline Rock Retention processes) and N° 2620109 (ENSAR, European Nuclear Science and Applications Research).

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