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Physico-Chemical Characterisation and Sorption Measurements of Cs, Sr, Ni, Eu, Th, Sn and Se on Opalinus Clay from Mont Terri

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M. Lauber, B. Baeyens, M.H. Bradbury

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

PREFACE

The Waste Management Laboratory at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close cooperation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

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ABSTRACT

Opalinus Clay is currently under investigation as a potential host rock for the disposal of high level and long-lived intermediate radioactive waste.

A throughout physico-chemical characterisation was carried out on a bore core sample from the underground rock laboratory Mont Terri (Canton Jura). The results of these investigations indicate that the major characteristics (mineralogy, cation exchange capacity, cation occupancies, selectivity coefficients, chloride and sulphate inventories) were very similar to a different core sample, previously used for porewater modelling studies. It was concluded that the porewater compositions derived in the earlier studies were reliable and could be used in this work. The organic matter which dissolved from the Opalinus Clay rock was not humic or fulvic acids and the concentration remaining in the liquid phase in the sorption experiments was < 0.5 ppm C. The organic matter is therefore considered to have little or no influence on the sorption behaviour of the studied radionuclides. Redox potential measurements of the Opalinus Clay/synthetic porewater system inside the glove boxes indicated anoxic conditions.

The main focus of the experimental work presented here is on the sorption behaviour of Cs(I), Sr(II), Ni(II), Eu(III), Th(IV), Sn(IV) and Se(IV) on Opalinus Clay equilibrated with synthetic porewaters at pH 6.3 and ~ 8. Sorption isotherms were measured for Cs, Ni, Eu, Th and Se. Single point data were measured for Sr and Sn. For all radionuclides studied the sorption kinetics were measured first. The times required to complete the sorption on the Opalinus Clay varied between one day for Th and one month for Ni and Se. Within the concentration ranges under study the uptake of Cs, Ni, Eu and Se on Opalinus Clay was non-linear, whereas for Th a linear sorption behaviour was observed. For Ni, Eu and Th the sorption increased with increasing pH. For Cs a pH independent sorption behaviour was observed. The concentration dependent uptake of Cs was modelled. The important role of background elements in the sorption experiments is discussed, particularly, in the case of Cs and Ni the lowest equilibrium concentrations were entirely determined by the natural background concentrations.

The results from the investigations presented in this work provided important data sets for the development of a sorption data base required for performance assessment studies of a potential repository in Opalinus Clay. The broad based pool of sorption data generated from this work will provide key data sets for subsequent mechanistic modelling.

ZUSAMMENFASSUNG

Opalinuston wird zurzeit als potentielle Gesteinsformation für die Lagerung hochaktiver und langlebig mittelaktiver Abfälle untersucht.

Ein Bohrkern aus dem Felslabor Mont Terri (Kanton Jura) wurde physikalisch-chemisch charakterisiert. Die Resultate dieser Untersuchungen haben gezeigt, dass die Hauptcharakteristika (Mineralogie, Kationenaustauschkapazität, Kationenbeladung, Selektivitätskoeffizienten, Chlorid- und Sulfat-Gehalte) denjenigen eines anderen Bohrkernes, der früher für die Modellierung des Porenwassers verwendet wurde, sehr ähnlich sind. Aus diesem Grund konnten die berechneten Zusammensetzungen der Porenwässer aus dieser früheren Studie übernommen werden. Die gelösten organischen Substanzen waren weder Humin- noch Fulvinsäuren und die Konzentration in der flüssigen Phase der Sorptionsexperimente war < 0.5 ppm C. Folglich wird angenommen, dass die organischen Substanzen das Sorptionsverhalten der untersuchten Radionuklide nur gering oder nicht beeinflussen. Die gemessenen Redoxpotentiale des Systems Opalinuston/synthetisches Opalinuston-Porenwasser haben gezeigt, dass die Experimente unter anoxischen Bedingungen durchgeführt wurden.

Das Schwergewicht dieser experimentellen Arbeit ist die Untersuchung des Sorptionsverhaltens von Cs(I), Sr(II), Ni(II), Eu(III), Th(IV), Se(IV) und Sn(IV) an konditioniertem Opalinuston bei $\text{pH} = 6.3$ und ~ 8 . Für Cs, Ni, Eu, Th und Se wurden Sorptionsisothermen gemessen. Die Sorption von Sr und Sn wurde lediglich bei einer Nuklidkonzentration bestimmt. Vor diesen Messungen wurde die Sorptionskinetik für jedes Element bestimmt. Die Reaktionszeiten variierten zwischen einem Tag für Th und einem Monat für Eu und Se. Innerhalb der untersuchten Konzentrationsbereiche war die Sorption von Cs, Ni, Eu und Se auf Opalinuston nicht-linear, während für Th ein lineares Sorptionsverhalten beobachtet wurde. Die Sorption von Ni, Eu und Th nahm mit steigendem pH zu. Für Cs war die Sorption pH-unabhängig. Die Sorptionsisotherme wurde für Cs modelliert. Der wichtige Einfluss der natürlich vorhandenen stabilen Elemente im Gestein auf die Sorptionsexperimente wird diskutiert. Insbesondere bei Cs und Ni wurden die tiefsten Gleichgewichtskonzentrationen vollständig durch die natürlich vorhandenen Cs- und Ni-Konzentrationen bestimmt.

Die Resultate der Untersuchungen dienen als Datensatz für die Entwicklung einer Sorptionsdatenbasis für die Sicherheitsanalyse eines möglichen Endlagerstandortes in Opalinuston. Die umfangreiche Menge an gemessenen Sorptionsdaten werden zu einem späteren Zeitpunkt für mechanistische Modellierungsarbeiten verwendet.

RÉSUMÉ

Les Argiles à Opalinus sont actuellement étudiées comme roche d'accueil potentielle pour les déchets de haute activité et de moyenne activité à vie longue.

Les caractéristiques physico-chimiques d'un échantillon de roche obtenu à partir d'un forage du laboratoire souterrain du Mont Terri (canton du Jura) ont été étudiées. Les résultats obtenus ont démontré que les caractéristiques principales de cet échantillon en terme de minéralogie, de capacité d'échange cationique (CEC), d'occupations cationiques, de coefficients de sélectivité et d'inventaires en chlorure et sulfate étaient semblables à celles d'un autre échantillon employé préalablement pour modéliser les eaux interstitielles des Argiles à Opalinus. Pour cette raison, les compositions des eaux interstitielles déduites de ces expériences préalables ont été utilisées dans cette étude. Les substances organiques solubles provenant de la roche ne sont des acides ni humiques ni fulviques. La teneur en matière organique dans la phase liquide des expériences de sorption était inférieure à 0.5 ppm C. Ces substances organiques n'ont donc pas ou peu d'influence sur la sorption des radionucléides étudiés. Les potentiels redox du système Argiles à Opalinus/eaux interstitielles synthétiques mesurés ont montré que les expériences ont été effectuées en milieu anoxique.

Le travail expérimental présenté dans ce rapport a permis d'acquérir des données expérimentales pour la sorption du Cs(I), Sr(II), Ni(II), Eu(III), Th(IV), Se(IV) et du Sn(IV) sur un échantillon d'Argiles à Opalinus conditionné à pH = 6.3 et ~ 8. Pour les éléments Cs, Ni, Eu, Th et Se, les isothermes d'adsorption ont été mesurées. Pour le Sr et le Sn, la sorption n'a été mesurée qu'à une seule concentration en nucléides. Préalablement à ces mesures, les cinétiques d'adsorption de ces différents nucléides ont été déterminées. Les temps de réactions nécessaires pour atteindre "l'équilibre" variaient entre un jour pour le Th et un mois pour l'Eu et le Se. Dans les intervalles de concentration en nucléides étudiés, la sorption du Cs, Ni, Eu et du Se était non-linéaire, tandis que l'adsorption du Th était linéaire. La sorption du Ni, Eu et du Th est plus élevée à pH = 8 qu'à pH = 6.3. La sorption du Cs reste constante dans cet intervalle de pH. L'isotherme d'adsorption du Cs a été modélisée. L'influence des éléments stables naturellement présents dans la roche sur les expériences de sorption est discutée. Par exemple, les plus faibles concentrations en nucléides dans les isothermes d'adsorption du Cs et du Ni ont été entièrement fixées par les concentrations en Cs et Ni naturellement présentes dans le système.

Les résultats obtenus ont permis de développer une base de données de sorption pour les Argiles à Opalinus qui servira aux études d'analyses de sûreté pour un dépôt final de déchets radioactifs. Le vaste ensemble de résultats expérimentaux mesurés dans ce travail sera utilisé ultérieurement pour modéliser les mécanismes de sorption sur cette roche.

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1 INTRODUCTION

An underground rock laboratory situated in a reconnaissance gallery of the Mont Terri motor way tunnel (Canton Jura, Switzerland) is the focus of an international study on the hydrogeological, geochemical and geotechnical characteristics of an Opalinus Clay (OPA) formation (THURY & BOSSART 1999). The site location and the geological profile are depicted in Figure 1. OPA is of interest to the participants because many countries are considering argillaceous sedimentary rocks as potential formations for the disposal of high level radioactive waste e.g. in Switzerland the OPA formation in Benken (Zürcher Weinland). For laboratory based studies such an underground facility is attractive because plentiful amounts of high quality material are available.

The Waste Management Laboratory at the Paul Scherrer Institut (PSI) is carrying out investigations into the physico-chemical characteristics, porewater chemistry and sorption properties of OPA as part of a much wider programme of work co-ordinated by the National Co-operative for the Disposal of Radioactive Waste (Nagra). One of the main aims of the work is to provide data required in performance assessment studies for radioactive waste repositories situated in such formations. Of particular importance in this respect are sorption data bases for which the Radioactive Waste Management Laboratory at PSI is responsible.

This report is divided into two main parts describing the results from physico-chemical investigations on an OPA core sample, and an extensive sorption study of some safety relevant key radionuclides (Cs(I), Sr(II), Ni(II), Eu(III), Th(IV), Se(IV) and Sn(IV)) on the same material.

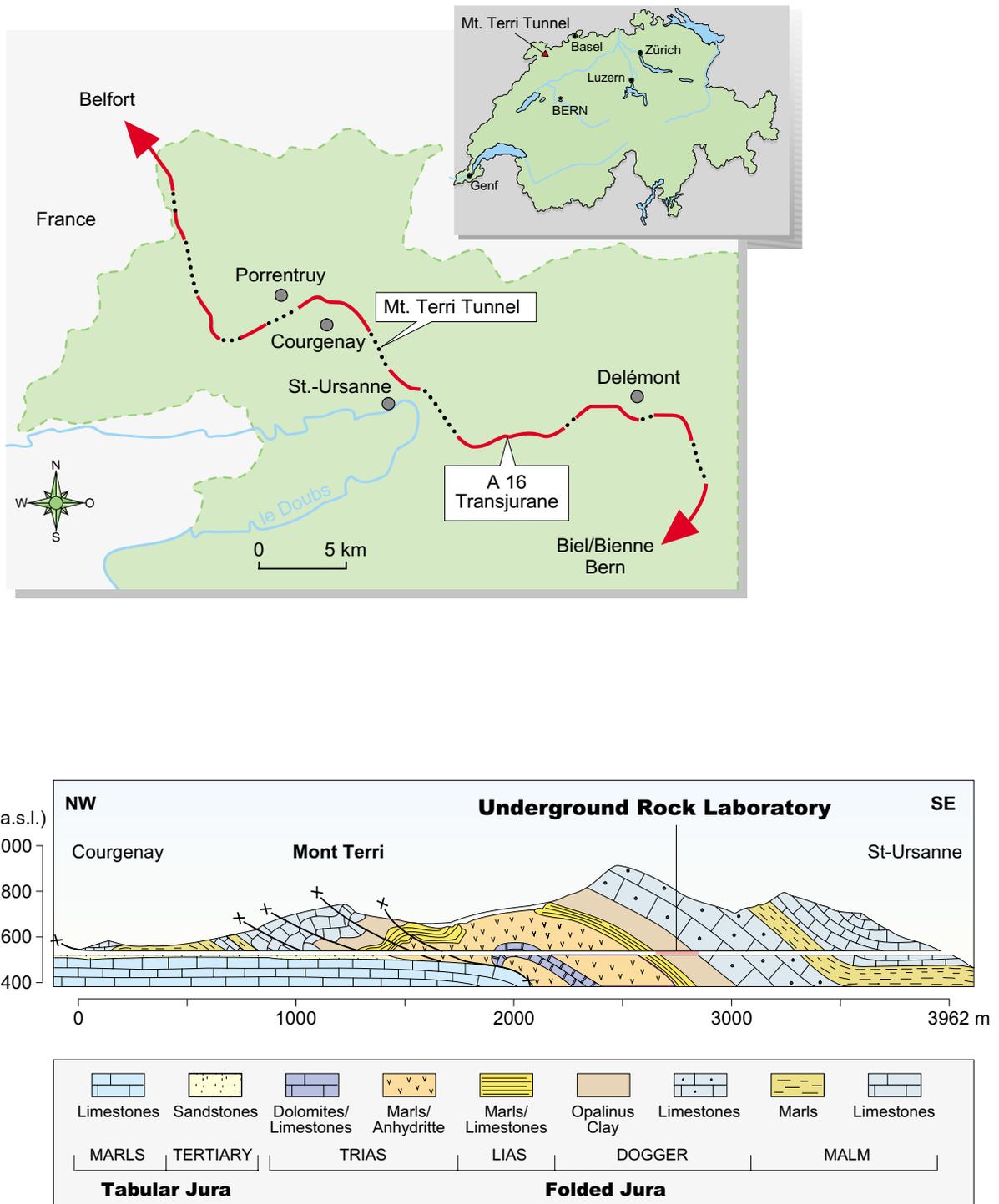


Figure 1: Site location and geological profile.

2 PHYSICO-CHEMICAL CHARACTERISATION OF MONT TERRI OPALINUS CLAY

2.1 General Background

An extensive physico-chemical characterisation study had already been performed on the OPA bore core sample BWS-A1-C12 from Mont Terri (see BRADBURY & BAEYENS 1997a, 1998). However, for the sorption investigations presented in this report insufficient material remained and consequently another core sample from the Mont Terri site was used (BGP-1-C11). In order to check whether both cores had similar physico-chemical characteristics, investigations were carried out on this second core sample and the results obtained compared with those obtained on the BWS-A1-C12 sample.

Briefly, mineralogical analyses, whole rock elemental analyses and N₂-BET surface area measurements were carried out on the BGP-1-C11 sample. In addition, organic matter extractions and redox measurements on the OPA / synthetic porewater system were carried out. Aqueous extractions at different solid-to-liquid (S:L) ratios were performed in order to determine the concentrations of soluble salts present in the rock and to determine the mineral phases which contribute to the composition of the aqueous phase. The nickethylendiamine (Ni-en) cation displacement experiments were carried out to determine the cation occupancies on the clay minerals present in the OPA rock. Acid extraction tests yielded information on the availability of the trace metal content in the OPA. The aqueous, acid and Ni-en extraction tests and the redox measurements were performed in a glove box under N₂-atmosphere (O₂ < 2 ppm) to minimise potential oxidation processes.

In the following an overview of the most important and relevant results of the physico-chemical characteristics of bore core sample BGP-1-C11 are given.

2.2 Reagents and Analytical Methods

All chemicals used in this study were of highest available grade purity and were purchased from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Solutions were prepared with ultrapure deionised water obtained from a Milli-Q® Reagent Grade Water System purchased from Millipore (Molsheim, France).

The cations and sulphur were analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Applied Research Laboratory ARL 3410D ICP-AES). One point calibrations were made for each element. Th was measured by inductively coupled plasma-mass spectroscopy (ICP-MS, VG Elemental Plasma Quad 2).

The anionic species Cl^- , F^- , NO_3^- , SO_4^{2-} and Br^- were analysed by ion chromatography on Dionex DX 500 system using an IonPac AG11 2 mm Guard column and an AS11 2 mm Analytical column and NaOH as eluent (flow rate: 1 ml/min, detection mode: suppressed conductivity).

Inorganic carbon (IC) and dissolved organic carbon (DOC) measurements were performed on a Dohrman 180 D Carbon Analyzer. IC was measured by addition of phosphoric acid. DOC was analysed by catalytic oxidation with peroxodisulfate in phosphoric acid. Four point calibrations were performed with NaHCO_3 and $\text{C}_8\text{H}_5\text{O}_4\text{K}$ for IC and DOC respectively. For the DOC determinations on the liquid phase of the conditioned OPA suspensions which contained high concentrations of chloride, the calibrations were achieved using $\text{C}_8\text{H}_5\text{O}_4\text{K}$ standard reagent diluted in 0.19 M NaCl. It must be pointed out, that measurements of DOC in solutions with high chloride concentrations are difficult to carry out because of the formation of corrosive HCl and Cl_2 that interfere with CO_2 measurements. Preliminary analyses with standard solutions in 0.19 M NaCl were carried out in order to test the feasibility of DOC measurements in such solutions.

pH measurements were carried out on a pH-meter 691 from Metrohm using Inlab (Mettler) and Metrohm combined pH-electrode. Buffer solutions (pH = 4, 7 and 9) were purchased from Merck (Titrisol™ ampoules). For the sorption measurements at pH = 8, which were performed in a 100 % N_2 atmosphere ($\text{CO}_2 < 2$ ppm), two point calibrations were made using buffers which covered the pH range. The sorption measurements at pH = 6.3 were carried out in a 50 % CO_2 / 50 % N_2 atmosphere. Because the pH of the buffer solutions are not stable in such a high CO_2 atmosphere a one point calibration was made with a solution of 1.037×10^{-3} M HNO_3 in 0.3 M NaCl. This solution in equilibrium with a P_{CO_2} of 0.5 bar (50 % CO_2) has a theoretical pH of 3.08.

Redox potential measurements were carried out using combined hemispherical Pt cap, respectively Pt ring electrodes with Ag/AgCl 3 M KCl as reference. The standardisation was performed using a $\text{Fe}(\text{CN})_6^{4-} / \text{Fe}(\text{CN})_6^{3-}$ redox buffer with a potential of 245 ± 5 mV at 25 °C and pH = 7.

2.3 Characterisation of Mont Terri OPA (core sample BGP-1-C11)

2.3.1 Sample Preparation

The OPA used in the experiments was taken from a core obtained from a borehole drilled with water tracered with Na-fluorescence at Mont Terri (Canton Jura) in 1996. The core designation was BGP-1-C11 (15.13 - 15.38 m).

After excavation, the core was carefully cleaned and placed in an aluminium coated plastic bag which was then flushed with N₂ and evacuated before sealing. This bag was put into another plastic bag that was also flushed with N₂ and evacuated before sealing. For transport the double sealed core was placed into a steel cylinder that was flushed with N₂. The cylinder was finally stored in a controlled N₂ atmosphere glove box (O₂ < 2 ppm). The procedure was used in order to minimise the contact of the core with oxygen.

After removing the packaging in the glove box, samples of OPA were taken from the centre of the core after taking away the outer 1 cm using a spade bit. (This procedure was designed to ensure that oxidation effects were minimised and that any contamination from the core drilling was avoided). The whole of the central core samples collected was ground and sieved in order to obtain crushed rock material with sizes ≤ 63 µm. All the experiments described in this report were performed on OPA material, prepared in this manner.

2.3.2 Mineralogy

The mineralogical compositions of the sample BGP-1-C11 (15.13 - 15.38 m) obtained from X-ray diffraction (XRD) and coulometry measurements are given in Table 1. The total amount of organic carbon present in the rock sample is also given in Table 1.

Table 1: Mineralogical composition of Mont Terri OPA, sample BGP-1-C11 (15.13 - 15.38 m) (MAZUREK 1997).

| Mineral | wt % (bore core sample BGP-1-C11) |
|------------------------------|-----------------------------------|
| Calcite | 8 - 10 |
| Dolomite/ankerite | 1.5 - 2.5 |
| Siderite | 3 - 5 |
| Quartz | 10 - 14 |
| K-feldspar | 1.5 - 3 |
| Albite | 0.5 - 2 |
| Pyrite | bdl |
| C (organic) | ≤ 0.4 |
| <u>Clay minerals</u> | |
| Illite | 18 - 26 |
| Illite/smectite mixed layers | 14 - 22 |
| Chlorite | 8 - 12 |
| Kaolinite | 17 - 23 |

bdl = below detection limit.

2.3.3 Surface Area Determination

The N₂-BET surface area measurements were determined from multi-point adsorption isotherms using a Micromeritics Gemini 2360 surface area analyzer. Prior to the measurements the samples were degassed for 2 hours at 200°C. The N₂-BET surface area of the sample BGP-1-C11 as obtained from a triplicate measurement was 33.3 (± 0.8) m² g⁻¹.

2.3.4 Organics

Part of the ~ 0.4 wt. % organic matter (see Table 1) present in OPA rock is soluble. Complexation of metal ions with the dissolved organic matter could potentially influence, i.e. reduce, the sorption of radionuclides in the batch sorption experiments.

The effect of the extractable organic matter from OPA on the sorption behaviour of radionuclides has been previously investigated (LAUBER et al. 1998). In this study ion

exchange experiments with Eu(III) on DOWEX cation exchange resin were carried out at two different pH values, with different aqueous extracts obtained from OPA samples, and with natural groundwater from the Mont Terri test site. Similar experiments were carried out with a reference compound (purified Aldrich Humic Acid) which was known to exhibit strong complexation behaviour with trivalent lanthanides (GLAUS et al. 1997, MAES et al. 1988, 1991). As a result of these experiments the following conclusions were drawn:

- Aqueous and alkaline extractions yielded the same low quantities of organic matter. In the case of humic acids, alkaline extractions would be expected to yield much higher amounts of DOC, due to their higher solubility under alkaline conditions (STEVENSON 1982).
- The DOC extracted from OPA bore core samples and the DOC present in groundwater do not significantly reduce the sorption of Eu(III), Th(IV) and Ni(II) on a DOWEX cation exchange resin. For the extracted DOC, sorption reduction factors were at most one order of magnitude at pH = 8.5. The DOC present in the natural groundwater did not affect sorption at all. At comparable concentrations, the reference humic acid - Aldrich Humic Acid (AHA) - reduced the sorption of Eu(III) on DOWEX by a factor of ~ 1000 at pH = 8.5.
- The measured sorption reductions for Eu(III) at pH 5 and 8.5 with the aqueous extracts showed that the pH had a minor effect on the sorption reduction. The sorption reduction at pH 8.5 was only a factor of 2 to 4 larger than the one at pH 5. In the case of humic acids, an increase of approximately 3 orders of magnitude would have been expected for such a pH change.
- The strongest interaction with humic acids is in general observed for trivalent lanthanides whereas the interaction with other radionuclides such as Cs(I), Sr(II) or Ni(II) is weaker. The interaction with Th(IV) is probably of the same order of magnitude (GLAUS et al. 1997).
- The overall conclusion drawn from this study is that the DOC will not interfere with the sorption measurements carried out with the above mentioned suite of radionuclides on OPA samples from Mont Terri.

Although these results are favourable for sorption experiments on OPA, the DOC concentration remaining in the OPA porewater after the conditioning procedure was checked. In the conditioned porewater at pH = 6.3 the DOC concentration was below the detection limit for solutions containing such high concentrations of NaCl (0.19 M), i.e. < 0.5 ppm C. The DOC concentration in the conditioned porewater at pH = 8 was

not determined because of the high NaCl concentration (0.3 M) in the solution forming corrosive HCl and Cl₂ gases that interfere with CO₂ measurements. Nevertheless there is no reason to believe that higher DOC concentrations are present in the porewater at the higher pH after conditioning.

Considering the low concentrations of DOC measured in the system under investigation and the observations made in the previous study (LAUBER et al. 1998) the DOC is considered to have little or no influence on the sorption experiments.

2.3.5 Redox Measurements

The knowledge of the redox conditions of the OPA system is important since the redox and its buffer capacity can influence the sorption behaviour of the redox-sensitive radionuclides used in this work, i.e. Sn and Se.

Batch sorption experiments were carried out with OPA samples conditioned in synthetic OPA porewaters. Redox potentials of the following suspensions and solutions were measured inside the glove box in 20 ml PE-flasks:

- synthetic OPA porewaters (before and after equilibration with OPA rock) at pH = 6.3 (SOPW1) and 8 (SOPW2).
- supernatant solutions obtained after centrifugation of the OPA suspensions at pH = 6.3 and 8.
- undiluted OPA suspensions at pH = 6.3 and 8 (obtained from the conditioning procedure described in section 3.3).

The platinum electrodes were dipped into the solutions or suspensions and the flasks covered with parafilm to avoid any evaporation of the solutions within the time of measurement and to reduce contamination from the residual O₂ fraction of the glove box atmosphere. The flasks were gently stirred during the measurements. The OPA porewaters and the supernatant solutions were measured for 24 hours whereas the suspensions were measured for 3 days. Constant potentials, i.e. the potentials did not vary more than ± 10 mV, were reached after 2 to 3 hours and 24 hours for the solutions and suspensions respectively.

Results

The measured redox potentials E (in mV) were transformed to E_h (= potential of the normal hydrogen electrode) using the relation $E_h = E + 230$ mV, since the Ag/AgCl 3 M KCl reference electrode is + 230 (± 1) mV above the normal hydrogen electrode at 25 °C.

The redox potential can be expressed by a non-dimensional value pe , that is the negative logarithm of the equilibrium activity of the electron, using following relation (see for example MOREL 1983):

$$pe = \frac{E_h}{2.3RT/F} = \frac{E_h}{59} \text{ at } 25 \text{ }^\circ\text{C} \quad (1)$$

The measured redox potentials E_h and the pe values of the OPA suspensions, the supernatant solutions and the porewaters are given in Table 2.

Table 2: Overview of the redox potentials E_h (expressed in mV) and pe of the OPA suspensions, the supernatant solutions and the porewaters at pH = 6.3 and 8.

| sample | pH | E_h ¹⁾ (mV) | pe |
|---------------------------------|-----|-----------------------------|--------|
| synthetic OPA porewater (SOPW1) | 6.3 | + 340 | + 5.76 |
| synthetic OPA porewater (SOPW2) | 8 | + 190 | + 3.22 |
| conditioned OPA porewater | 6.3 | + 260 | + 4.41 |
| conditioned OPA porewater | 8 | + 160 | + 2.71 |
| supernatant solution | 6.3 | + 180 | + 3.05 |
| supernatant solution | 8 | + 180 | + 3.05 |
| OPA suspension | 6.3 | + 50 | + 0.85 |
| OPA suspension | 8 | - 130 | - 2.20 |

¹⁾ The uncertainties of the E_h measurements are ± 20 mV.

The redox potentials of the synthetic OPA porewaters are clearly more positive than those of the conditioned OPA porewaters and suspensions. This could be an indication that the redox potential is probably driven by iron species which arises from siderite and pyrite dissolution.

As the batch sorption experiments in this study were performed in suspensions diluted with SOPW1 and SOPW2 at pH = 6.3 and ~ 8 respectively the redox potentials must lie between + 50 and + 340 mV at pH = 6.3 and between - 130 and + 190 mV at pH = 8.

Speciation calculations have been carried out for Sn and Se (both at pH = 6.3 and 8) using the measured redox limits given above. The calculations were performed using the geochemical code MINEQL (WESTALL et al. 1976). All the Se data, i.e. Se(0), Se(IV), Se(VI) and Se(-II), and the Sn(II) data were taken from the thermodynamic data base compilations of PEARSON & BERNER (1991) and PEARSON et al. (1992). The Sn(IV) data and the Sn(II)/Sn(IV) redox equilibrium were taken from AMAYA et al. (1997) and LATIMER (1952) respectively.

Among the redox sensitive elements studied only Se seems to be sensitive to the redox conditions encountered in the sorption experiments. (Sn(IV) remains stable within the given redox ranges both at pH 6.3 and 8.) At the lower redox limits both at pH 6.3 and 8 the calculations yielded a predominance of Se(0), whereas at the higher redox limits Se(IV) is the dominant species. As the experiments were carried in diluted suspensions the real redox conditions probably lie between these limits, i.e. both Se(IV) and Se(0) may be present in the system under study.

2.3.6 Whole Rock Elemental Analysis

Whole elemental analyses were carried out on two samples of OPA rock (core BGP-1-C11) at the Service d'Analyses des Roches et des Minéraux (CNRS), in France. The crushed rock samples were fused with LiBO₂ and dissolved with HNO₃ and then analysed for trace elements by ICP-MS.

The aim was to determine the background impurity metals present in the OPA. The elements which are used in sorption experiments (Cs, Sr, Ni, Eu, Th and Sn) are of particular interest. It must be pointed out that this method yields the total individual element content of the rock which includes quantities present within the lattice of the clay minerals as well as those which are more readily available and could potentially take part in the sorption experiments. The inventories of the elements for which sorption experiments have been carried out are given in Table 3.

Table 3: Metal inventories of the elements used in the sorption experiments of the OPA rock (core BGP-1-C11) as determined by ICP-MS.

| Element | Whole rock inventory (mol kg ⁻¹) |
|---------|---|
| Cs | 4.4 x 10 ⁻⁵ |
| Sr | 2.5 x 10 ⁻³ |
| Ni | 1.2 x 10 ⁻³ |
| Eu | 1.1 x 10 ⁻⁵ |
| Sn | 3.0 x 10 ⁻⁵ |
| Th | 6.4 x 10 ⁻⁵ |

The uncertainty of the metal inventories is $\pm 20\%$.

2.3.7 Acid Extractions

Aqueous extractions at pH ~ 0.5, 3 and 5.5 were carried out on OPA samples with the aim of deducing the quantities of trace cations sorbed. Four extraction tests at constant S:L ratio (0.03 kg L⁻¹) were performed at each pH.

In the first series suspensions of ~ 1 g OPA and 35 ml HNO₃ 1 M were shaken for 24 hours on an end-over-end shaker. The pH of the supernatant solutions was ~ 0.5.

A second series of experiments at pH = 3 were carried out under the same conditions. After 24 hours the pH values of the suspensions were measured and adjusted with HNO₃ 1 M to pH = 3. The suspensions were shaken for another 24 hours and the pH again measured and again adjusted to 3. This procedure was repeated 6 times. After this treatment the pH values of all suspensions were constant. (The pH changed because of the dissolution of calcite present in the OPA.) The suspensions were then shaken for another week.

In the last series (pH = 5.5) suspensions of ~ 1 g of OPA and 35 ml chloroacetate buffer (0.1 M, pH = 3) were equilibrated for 1 week. During this time the pH values of the suspensions were not adjusted, so that the pH changed from 3 to 5.5 (due to calcite dissolution).

For all the extraction tests the centrifugation, sampling and analyses followed the procedures as described in section 2.4.1.

An overview of the concentrations of the major and minor elements extracted from the OPA are listed in Table 4.

Acid extractions lead to the desorption of cations from the clay minerals present in the OPA. In addition, at those low pH values dissolution of calcite, dolomite and partial dissolution of the clay minerals is also observed.

A very pronounced release of Si, Al, Fe, and Mg with decreasing pH is seen in the extraction tests. A less pronounced release is observed for K and Mn. All these elements are structural elements of clay minerals and/or part of minerals such as dolomite, siderite and quartz. The dissolution of clay minerals and minerals is more effective at low pH.

Dissolution of the carbonates (calcite, dolomite and siderite) leads to the release of Ca, Mg and Fe. The iron extracted at the lowest pH represents ~ 2.5 wt. % Fe, which corresponds approximately to 5 wt. % siderite if it is assumed that all of the Fe arises from this mineral. X-ray diffraction measurements yielded 3 to 5 wt. % siderite in the OPA (see Table 1). The complete dissolution of celestite is responsible for the release of Sr.

The increase in concentration for Na, Co, Ni, Zn and Eu with decreasing pH is likely to arise from desorption processes from the clay minerals.

Table 4: Summary of the extracted elements in the acid extraction tests (pH ~ 0.5, 3.3 and 5.5).

| Element | Amount extracted from OPA pH ~ 0.5 (mmol kg ⁻¹) | Amount extracted from OPA pH = 3.3 (mmol kg ⁻¹) | Amount extracted from OPA pH = 5.5 (mmol kg ⁻¹) |
|---------|---|---|---|
| Na | 74.2 (± 0.7) | 66.9 (± 3.2) | nm |
| K | 51.0 (± 0.4) | 36.5 (± 0.5) | 35.5 (± 2.1) |
| Mg | 225.1 (± 3.0) | 156.6 (± 6.5) | 80.3 (± 2.1) |
| Ca | 668.3 (± 8.8) | 587.7 (± 3.3) | 508.9 (± 6.4) |
| Sr | 1.42 (± 0.05) | 1.21 (± 0.05) | 1.20 (± 0.01) |
| Ba | 0.20 (± 0.05) | 0.07 (± 0.05) | 0.08 (± 0.01) |
| Si | 195.2 (± 3.8) | 97.1 (± 2.2) | 36.1 (± 0.8) |
| Al | 285.0 (± 7.9) | 71.5 (± 2.2) | 0.53 (± 0.03) |
| Mn | 6.29 (± 0.09) | 5.10 (± 0.13) | 3.79 (± 0.09) |
| Fe | 450.3 (± 5.7) | 299.1 (± 1.4) | 59.4 (± 2.3) |
| Co | 0.11 (± 0.05) | 0.02 (± 0.05) | bdl |
| Ni | 0.25 (± 0.05) | 0.09 (± 0.05) | 0.01 (± 0.01) |
| Zn | 0.69 (± 0.05) | 0.67 (± 0.17) | 0.06 (± 0.01) |
| Eu | 0.005 (± 0.001) | 0.004 (± 0.001) | bdl |
| S | 34.8 (± 2.5) | 7.05 (± 0.61) | 7.05 (± 0.32) |

All values are the average of 4 sample measurements.

bdl = below detection limit of ICP-OES.

nm = not measured.

Se, Cd, Cs, Cu, Pb, Sn and Th were below the detection limits of ICP-OES.

2.3.8 Iron Extractions

Iron oxides are minor mineral components in (many) natural systems which can influence the sorption behaviour of radionuclides because these exhibit high affinities for such minerals (DZOMBAK & MOREL 1990). The total and the amorphous iron content of the Mont Terri OPA were determined using the dithionite-citrate-bicarbonate extraction method at pH = 7.3 (MEHRA & JACKSON 1960) and the oxalate extraction method at pH = 3 (SCHWERTMANN 1964) respectively. The results are summarised in Table 5.

Table 5: Total iron extracted from Mont Terri OPA using dithionite at pH = 7.3 and iron extracted with oxalate at pH = 3.

| Total iron (present as iron oxides) (mmol kg ⁻¹) | iron extracted with oxalate (mmol kg ⁻¹) |
|---|---|
| 51.08 (± 6.42) | 266.6 (± 16.26) |

All values are the average of two sample measurements.

The high iron concentration extracted with the oxalate procedure does not correspond to the amorphous iron in the OPA because of the dissolution of siderite which is effective at pH = 3. Acid extractions carried out at pH = 3.3 yielded approximately 300 mmol kg⁻¹ Fe which is approximately the Fe concentration extracted using the oxalate procedure (see Table 4). The iron extracted with the dithionite method mainly consists of the total iron oxide of the OPA because the siderite dissolution is much less effective at pH 7.3 than at pH 3. The conditioning procedures of the OPA described in section 3.3 released "only" approximately 0.2 and 0.04 mmol kg⁻¹ Fe at pH = 6.3 and 8 respectively.

2.3.9 Chloride and Sulphate Inventories

Sulphate and chloride data are important for the calculations of in situ pore water compositions (see BAEYENS & BRADBURY 1991, BRADBURY & BAEYENS 1997a). Therefore, aqueous extractions were carried out on OPA samples in de-ionised water at a series of S:L ratios (in the range of 0.05 to 1.5 kg L⁻¹). The suspensions were shaken end-over-end for 1 and 4 weeks in a N₂ glove box (the extractions at the two highest S:L ratios were only shaken for 4 weeks). After the reaction times the

samples were centrifuged (1 hour at 95000 *g* max.) and the supernatants were analysed for SO_4^{2-} and Cl^- .

Figures 2 and 3 summarise the SO_4^{2-} and Cl^- concentrations measured in the aqueous extractions as function of S:L ratio for 1 and 4 weeks equilibration times respectively. Clearly no time effects are seen for both anions. The SO_4^{2-} and Cl^- concentrations are both linearly dependant on the S:L ratio, i.e. dilution occurs. The SO_4^{2-} and Cl^- inventories in the OPA deduced from this data are $1.8 (\pm 0.2) \text{ mmol kg}^{-1}$ and $11.1 (\pm 0.8) \text{ mmol kg}^{-1}$ respectively.

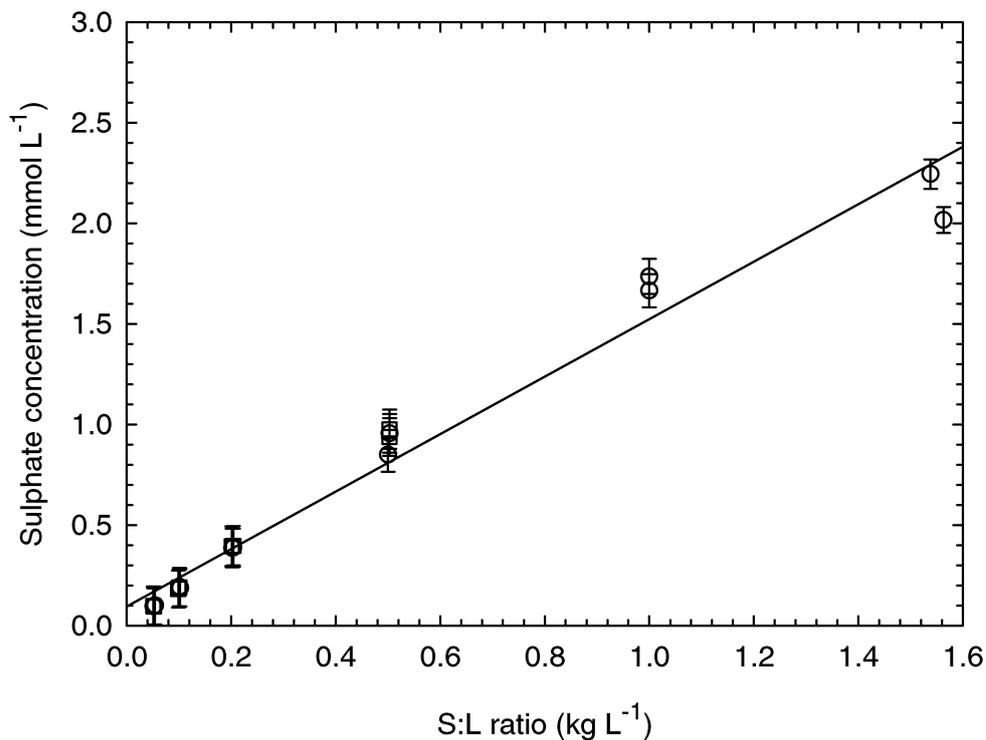


Figure 2: Sulphate concentrations measured in the aqueous extracts as function of S:L ratio. □ = 1 week extractions, ○ = 4 week extractions.

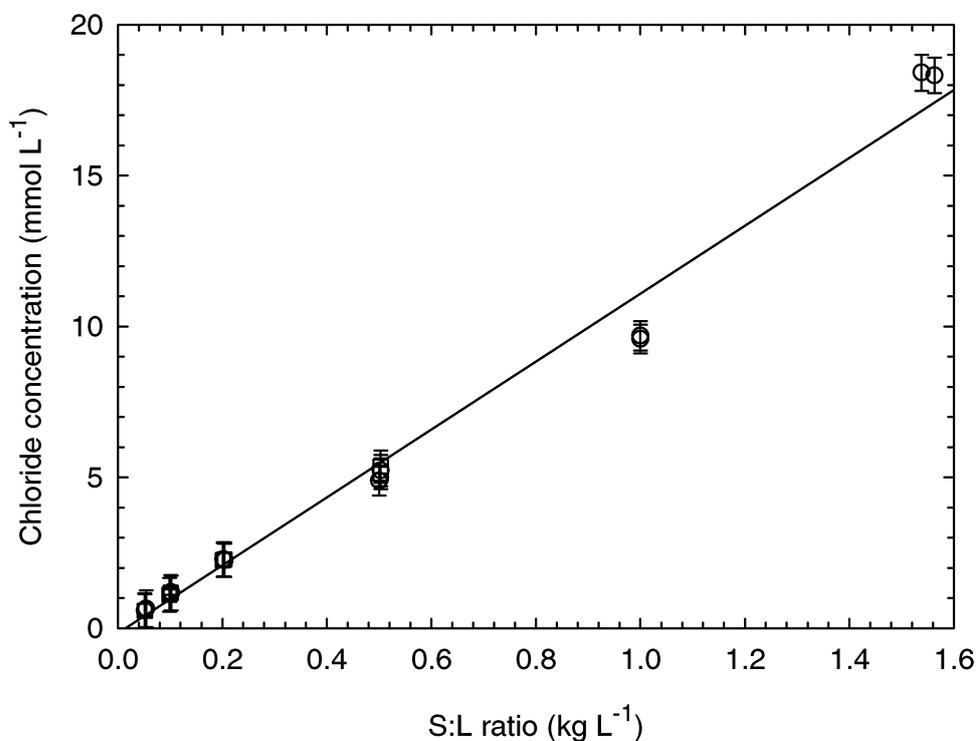


Figure 3: Chloride concentrations measured in the aqueous extracts as function of S:L ratio. □ = 1 week extractions, ○ = 4 week extractions.

2.3.10 Cation Exchange Capacity

Nickelethylendiamine (Ni-en) is a powerful high selective complex which displaces all exchangeable cations from the clay minerals into solution (PEIGNEUR 1976, MAES & CREMERS 1986). Ni-en extraction tests are used to determine the cation exchange capacities of the clay minerals in rocks. Generally, a Ni-en sorption isotherm is determined in order to evaluate the concentrations of Ni-en required for complete displacement of all cations from the clay mineral exchange sites (BAEYENS & BRADBURY 1991). This was not carried out since Ni-en CEC data on OPA were already available (BRADBURY & BAEYENS 1997a, 1998). Nevertheless to check the Ni-en CEC of core BGP-1-C11 Ni-en extraction tests were carried out at four different (high) S:L ratios between 0.25 and 1.5 kg L⁻¹ and total Ni concentrations of around twice the CEC measured on core BWS-A1-C12.

Nickelethylendiamine (Ni-en) solutions were prepared by adding a 3 fold excess of ethylenediamine (en) with respect to Ni. The pH of the solutions was adjusted to ~ 8 with HNO₃ in order to fully coordinate the metal ion with en. The total concentrations of Ni-en were 3.75 x 10⁻² M, 7.50 x 10⁻² M, 1.50 x 10⁻¹ M and 2.27 x 10⁻¹ M. Given quantities of these solutions were added to OPA samples (bore core BGP-1-C11) in order to reach S:L ratios between 0.25 and 1.5 kg L⁻¹. The suspensions were shaken for one week on an end-over-end shaker and centrifuged afterwards for one hour at 95000 g max. The supernatants were analysed for Ni.

Figure 4 shows the sorbed Ni-en on the OPA as function of the Ni equilibrium concentration. The plateau clearly indicates that all exchangeable cations on the rock have been removed. The cation exchange capacity (CEC) obtained from this data was 120.9 (± 3.6) meq kg⁻¹ (average of 7 measurements).

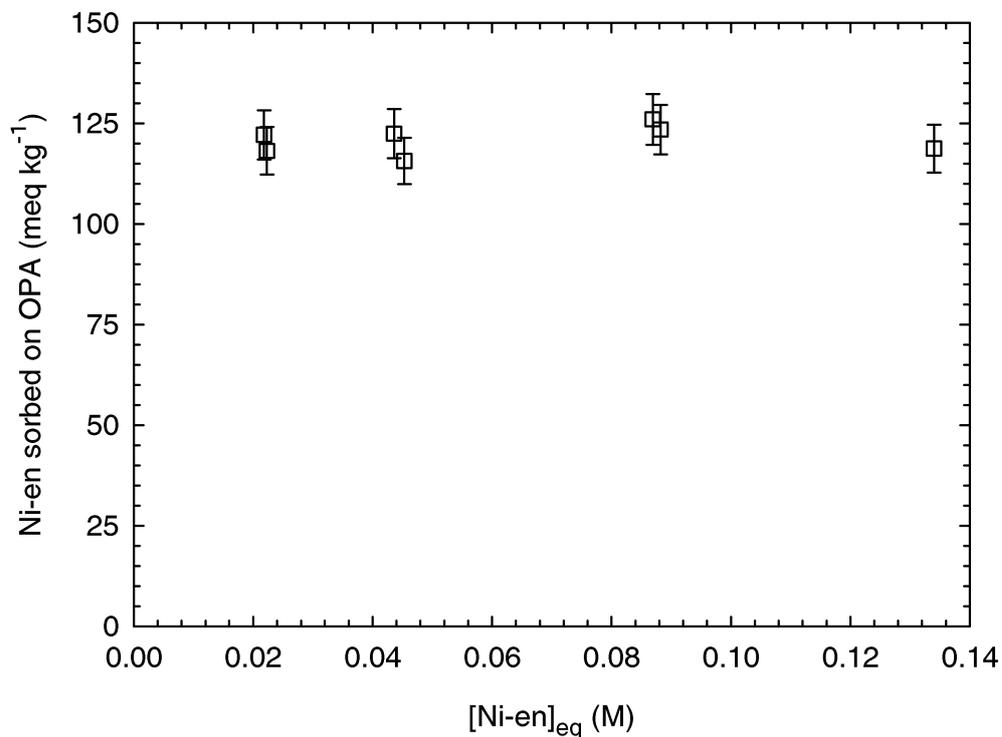


Figure 4: Ni-en sorbed on OPA as function of Ni equilibrium concentration.

2.4 Cation Occupancies on OPA

Two types of ion extraction experiments were performed. The first consisted of aqueous extractions aimed to quantify the amounts of soluble salts present in the rock (particularly chlorides, see section 2.3.9), and to determine which mineral phases contribute significantly to the composition of the aqueous phase. A second series of extractions using nickelethylenediamine (Ni-en) solutions are carried out to determine cation occupancy data for the clay minerals in the OPA. Both types of extractions were carried out at high solid-to-liquid (S:L) ratios of 1 and 1.5 kg L⁻¹. The reason for the choice of these high S:L ratios is that in the Ni-en tests the effect of dissolution processes from sparingly soluble minerals (calcite/dolomite) is minimised. In this way the cations displaced from the clay minerals dominate the solution composition.

Finally, selectivity coefficients for the major cations were deduced from these two extraction data sets. These results were then compared with similar data obtained on the OPA BWS-A1-C12 sample (BRADBURY & BAEYENS 1997a, 1998).

2.4.1 Aqueous Extractions

The aqueous extractions were carried out on OPA samples in de-ionised water at two different S:L ratios (1 and 1.5 kg L⁻¹). The suspensions were shaken end-over-end for 4 weeks inside an inert atmosphere glove box to avoid any complications due to oxidation effects. Previous studies have indicated that this time period is required in order to reach equilibrium with the carbonate minerals (see BRADBURY & BAEYENS 1998). After the reaction times the samples were centrifuged (1 hour at 95000 g max.) and the supernatants were analysed for major and minor ions, DOC and inorganic carbon (C Inorg.). (Detailed analytical results are given in Table 6.)

Table 6: Aqueous extraction data at high S:L ratios. Equilibration time is 28 days.

| S:L Ratio (kg L ⁻¹) | 1 | 1.5 |
|----------------------------------|-------------------|-------------------|
| pH | 8.1 | 7.8 |
| <u>concentrations (M)</u> | | |
| Na | 1.89 (± 0.04) E-2 | 2.66 (± 0.09) E-2 |
| K | 9.04 (± 0.95) E-4 | 1.54 (± 0.10) E-3 |
| Mg | 3.63 (± 0.46) E-4 | 9.40 (± 0.70) E-4 |
| Ca | 4.12 (± 0.28) E-4 | 9.19 (± 0.63) E-4 |
| Sr | 5.00 (± 0.30) E-6 | 9.25 (± 0.36) E-6 |
| F ⁻ | 1.31 (± 0.09) E-4 | 8.40 (± 0.71) E-5 |
| Cl ⁻ | 9.64 (± 0.07) E-3 | 1.84 (± 0.02) E-2 |
| SO ₄ ²⁻ | 1.70 (± 0.05) E-3 | 2.13 (± 0.16) E-3 |
| C Inorg. (M) | 5.67 (± 0.22) E-3 | 6.77 (± 0.12) E-3 |
| Σ Cations (Eq. L ⁻¹) | 2.14 (± 0.02) E-2 | 3.19 (± 0.05) E-2 |
| Σ Anions (Eq. L ⁻¹) | 1.89 (± 0.04) E-2 | 2.95 (± 0.03) E-2 |
| Si (M) | 3.74 (± 0.35) E-4 | 5.82 (± 1.32) E-4 |
| S (M) | 1.73 (± 0.03) E-3 | 2.19 (± 0.10) E-3 |
| C Org. (M) | 3.95 (± 0.30) E-4 | 2.54 (± 0.91) E-4 |

The results in Table 6 indicate that the charge balance of the aqueous extractions are good and generally better than ± 5%. Within experimental uncertainty, the SO₄²⁻ and S determination are in good agreement and therefore all the sulphur appears to be present as sulphate. In addition, the SO₄²⁻ extraction results given in section 2.3.9 indicated that there was no increase in SO₄²⁻ or total S at a given S:L ratio between 1 and 4 week reaction times. This is taken to indicate that pyrite is not oxidising during the course of the experiments.

2.4.2 Niclethylenediamine Extraction Tests

Ni-en extraction tests at S:L ratios of 1 and 1.5 kg L⁻¹ were performed under the same experimental conditions as described above for the aqueous extraction tests except that samples were only shaken for 7 days. Ni-en concentrations of 1.5 x 10⁻¹ M and 2.27 x 10⁻¹ M were used and which are equivalent to approximately twice the exchange capacity to ensure the complete displacement of all exchangeable cations. The cation concentrations measured in the Ni-en extraction solutions are expressed in meq kg⁻¹ in Table 7. There are no significant trends in the data and the individual measurements generally agree to better than 5%.

Table 7: Extracted cations and Ni-en sorbed on OPA (bore core BGP-1-C11). All data are expressed in meq kg⁻¹.

| | S:L ratio 1.0 kg L ⁻¹ | S:L ratio 1.5 kg L ⁻¹ | average |
|--------------|----------------------------------|----------------------------------|---------------|
| Na | 53.2 (± 1.4) | 50.4 (± 0.6) | 51.8 (± 0.8) |
| K | 11.0 (± 0.05) | 9.2 (± 0.4) | 10.1 (± 0.2) |
| Mg | 21.5 (± 0.1) | 19.3 (± 0.2) | 20.4 (± 0.1) |
| Ca | 34.5 (± 0.7) | 33.3 (± 1.8) | 33.9 (± 1.0) |
| Sr | 0.9 (± 0.02) | 0.9 (± 0.02) | 0.9 (± 0.01) |
| Σ cations | 121.1 (± 1.6) | 113.1 (± 2.0) | 117.1 (± 1.3) |
| Ni-en sorbed | 124.7 (± 1.8) | 118.7 (± 2.3) | 121.7 (± 2.3) |

2.4.3 Cation Occupancies

In order to calculate selectivity coefficients, the in situ fractional cation occupancies of Na, K, Mg and Ca on the clay minerals need to be determined. These cation occupancies can be derived from the Ni-en extraction data together with information from the aqueous extraction tests. In the latter, mean inventories for Cl⁻ and SO₄²⁻ of 11.1 and 3.6 meq kg⁻¹ respectively were measured. These quantities are also released in the Ni-en extraction tests together with their associated cations and a correction needs to be made for this. The procedure followed is the same as described in BRADBURY & BAEYENS (1997a, 1998). Here it is assumed that the Cl⁻ and SO₄²⁻ inventories are associated with the Na and Ca quantities in the Ni-en extracts respectively (Case I).

Na occupancy

From the Ni-en extraction results (Table 7), the average Na in the OPA sample was $51.8 (\pm 0.8)$ meq kg⁻¹. This quantity is made up of the Na displaced from the exchange sites of the clay minerals and the Na present in the porewater associated with the Cl⁻ inventory of $11.1 (\pm 0.8)$ meq kg⁻¹. Hence the Na occupancy on the clay minerals is taken to be the difference between these two values i.e. $40.7 (\pm 1.1)$ meq kg⁻¹.

K occupancy

The K inventory obtained at high S:L ratios is considered to be the best approximation to the loading on the clay minerals (see BRADBURY & BAEYENS 1997a, 1998) i.e. the K occupancy is taken to be $10.1 (\pm 0.2)$ meq kg⁻¹.

Mg occupancy

The Mg extracted in meq kg⁻¹ at the two different S:L ratios remains essentially constant with an average value of $20.4 (\pm 0.1)$ meq kg⁻¹ (Table 7), which is taken to represent the Mg loading on the clays.

Ca occupancy

The situation for Ca is slightly more complex than for Mg because of the presence of sulphate. As discussed in BRADBURY & BAEYENS (1998) there are two possibilities treating the sulphate question. Here it is assumed to a first approximation that all of the sulphate is associated with Ca (corresponding to Case I in the study of BRADBURY & BAEYENS (1997a, 1998)). As in the case of Mg, there is no trend in the displaced Ca inventory as a function of S:L ratio. The Ca loading on the clay is therefore the difference between the averaged quantity of displaced Ca, $33.9 (\pm 1.0)$ meq kg⁻¹ (Table 7), and the SO₄²⁻ inventory of $3.6 (\pm 0.4)$ meq kg⁻¹. The in situ Ca occupancy is thus taken to be $30.3 (\pm 1.1)$ meq kg⁻¹.

Sr occupancy

At this stage the data does not allow to evaluate the in situ Sr occupancy because part of the Sr is displaced from the clay minerals but Sr is also released through celestite dissolution. Both processes cannot be disentangled from the experimental data (see also section 3.6).

The cation occupancies deduced for OPA in the undisturbed in situ state are summarised in Table 8. The cation exchange capacity is taken as the sum of the individual occupancies and yields a mean value of $101.5 (\pm 1.6)$ meq kg⁻¹. This value is ~ 16 % less than the Ni-en CEC (see Table 7). This discrepancy was also observed in the work of BRADBURY & BAEYENS (1998).

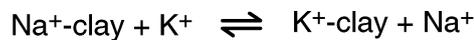
Table 8: In situ cation occupancies on the clay minerals in OPA (BGP-1-C11).

| Cation | Cation occupancies (meq kg ⁻¹) |
|-----------|--|
| Na | 40.7 (± 1.1) |
| K | 10.1 (± 0.2) |
| Mg | 20.4 (± 0.1) |
| Ca | 30.3 (± 1.1) |
| Σ cations | 101.5 (± 1.6) |

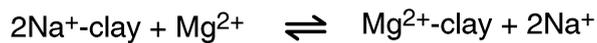
2.5 Derivation of Selectivity Coefficients

Selectivity coefficients, K_c , of K, Mg, and Ca are calculated with respect to Na for the OPA system. Na was chosen as the reference cation since it is the most abundant cation present. (Because of the very low levels of Sr measured no reliable selectivity coefficient could be evaluated from the experimental data.)

The exchange reactions and the associated mass action equations defining the selectivity coefficients are given below:



$${}_{\text{Na}}^{\text{K}}K_c = \frac{N_{\text{K}}}{N_{\text{Na}}} \cdot \frac{a_{\text{Na}}}{a_{\text{K}}} \quad (2)$$



$${}_{\text{Na}}^{\text{Mg}}K_c = \frac{N_{\text{Mg}}}{N_{\text{Na}}^2} \cdot \frac{a_{\text{Na}}^2}{a_{\text{Mg}}} \quad (3)$$



$${}_{\text{Na}}^{\text{Ca}}K_c = \frac{N_{\text{Ca}}}{N_{\text{Na}}^2} \cdot \frac{a_{\text{Na}}^2}{a_{\text{Ca}}} \quad (4)$$

where "a" represents solution activities and N_{Na} , N_{K} , N_{Mg} and N_{Ca} are equivalent fractional cation occupancies defined as,

$$N_B = \frac{\text{Quantity of cation B on the permanent charge sites of the clay minerals (meq kg}^{-1}\text{)}}{\text{CEC (meq kg}^{-1}\text{)}} \quad (5)$$

where B = Na⁺, K⁺, Mg²⁺ or Ca²⁺.

As can be seen from the above mass action relations the quantities required to calculate the selectivity coefficients are the same in each case i.e. the appropriate aqueous cationic activities and fractional cation occupancies on the solid. The important data here are the results from the aqueous extraction tests, see Table 6, and the in situ cation occupancies given in Table 8 which will be used to derive K_c values for this OPA sample.

When de-ionised water is contacted with the OPA samples mineral dissolution and exchange reactions occur modifying the original cation occupancies on the clay minerals given in Table 8. For Na and K it is relatively straightforward to calculate the new occupancies, but for Ca and Mg the presence of dissolving minerals which contain these elements have to be taken into consideration.

Na occupancies on OPA

The Na in the aqueous extract originates from two sources; the exchangeable Na on the clay and the NaCl in the porewater. The measured Na concentration in the 1:1 S:L ratio aqueous extract is 1.89×10^{-2} M (Table 6), which corresponds to $18.9 (\pm 0.4)$ meq kg^{-1} (the Na concentration at S:L = 1.5 kg L^{-1} is 2.66×10^{-2} M, corresponding to $17.7 (\pm 0.6)$ meq kg^{-1}). The quantity of Na present as NaCl is $11.1 (\pm 0.8)$ meq kg^{-1} (see above) and thus only $7.8 (\pm 0.9)$ meq kg^{-1} is displaced from the clay ($6.6 (\pm 0.7)$ meq kg^{-1} at S:L = 1.5 kg L^{-1}). Since the original Na occupancy was $40.7 (\pm 1.1)$ meq kg^{-1} (Table 8), the new occupancy in equilibrium with the aqueous extract must be $32.9 (\pm 1.4)$ meq kg^{-1} or $N_{\text{Na}} = 0.32 (\pm 0.02)$ (the new occupancy at S:L = 1.5 kg L^{-1} is $34.1 (\pm 1.3)$ meq kg^{-1} and N_{Na} is equal to $0.34 (\pm 0.02)$ for the extraction data at 1.5 kg L^{-1} .)

K occupancies on OPA

The exchangeable K on the clay minerals was assumed to be the only source of this element and therefore the quantity remaining on the solid in the aqueous extraction experiment is simply determined from the mass balance. The measured K concentration in the aqueous extract at S:L = 1 kg L^{-1} is 9.04×10^{-4} M which corresponds to $0.9 (\pm 0.1)$ meq kg^{-1} (at S:L = 1.5 kg L^{-1} the K concentration is 1.54×10^{-3} M, corresponding to $1.0 (\pm 0.1)$ meq kg^{-1}). The K occupancy in the aqueous extract is thus $9.2 (\pm 0.2)$ meq kg^{-1} or $N_{\text{K}} = 0.09 (\pm 0.01)$ (The K occupancy at S:L = 1.5 kg L^{-1} is $9.1 (\pm 0.2)$ meq kg^{-1} and N_{K} also equal to $0.09 (\pm 0.01)$).

Mg and Ca occupancies on OPA

The calculation for bivalent cations occupancies cannot be done in the same manner since solid phases containing these elements are dissolving. Instead it is noted that the relation

$$N_{\text{Na}} + N_{\text{K}} + N_{\text{Mg}} + N_{\text{Ca}} = 1 \quad (6)$$

must be valid.

Hence, since the Na and K occupancies in the aqueous extracts have been calculated (see above), the sum of the fractional occupancies of Mg and Ca can be found as $N_{\text{Mg}} + N_{\text{Ca}} = 0.59 (\pm 0.02)$ at S:L = 1 kg L⁻¹ ($0.57 (\pm 0.02)$ at S:L = 1.5 kg L⁻¹).

A similar approach can be applied here as used in the study of BRADBURY & BAEYENS (1997a, 1998) where for a system in equilibrium with calcite and dolomite the Ca²⁺/Mg²⁺ activity ratio is 1.35. On the other hand, the Ca²⁺/Mg²⁺ occupancy ratio on the in situ OPA is $1.49 (\pm 0.05)$ (see Table 8). These two results can only be compatible if the selectivity of Ca²⁺ with respect to Mg²⁺ is greater than unity. Substituting the above values into the following mass action equation

$$K_c^{\text{Ca/Mg}} = \frac{N_{\text{Ca}}}{N_{\text{Mg}}} \cdot \frac{a_{\text{Mg}}}{a_{\text{Ca}}} \quad (7)$$

yields a $K_c^{\text{Ca/Mg}}$ value of $1.1 (\pm 0.04)$.

This selectivity coefficient is in good agreement with literature values for illite $K_c^{\text{Ca/Mg}} \sim 1$ (SPOSITO & LEVESQUE 1985, THELLIER & SPOSITO 1988).

The Ca-Mg selectivity coefficient of 1.1 can be used together with the Ca²⁺/Mg²⁺ cationic activity ratio in the aqueous extracts and the relation $N_{\text{Mg}} + N_{\text{Ca}} = 0.59 (\pm 0.02)$ at S:L = 1 kg L⁻¹ ($0.57 (\pm 0.02)$ at S:L = 1.5 kg L⁻¹) to calculate the Mg and Ca equivalent fractional occupancies in the aqueous extract experiment from equation (6). These values are $0.26 (\pm 0.02)$ and $0.32 (\pm 0.03)$ for Mg and Ca respectively at S:L = 1 kg L⁻¹. (N_{Mg} and N_{Ca} are equal to $0.28 (\pm 0.02)$ and $0.30 (\pm 0.02)$ for Mg and Ca respectively for the extraction data at 1.5 kg L⁻¹.)

Calculation of the selectivity coefficients

The fractional cation occupancies calculated for the two S:L ratio data sets can be used together with the concentrations of Na, K, Mg, and Ca measured in the corresponding aqueous extract experiment (Table 6) expressed in terms of cation activities to calculate selectivity coefficients from equations (2) to (4). The values for $K_c^{\text{K/Na}}$, $K_c^{\text{Mg/Na}}$ and $K_c^{\text{Ca/Na}}$ are summarised in Table 9. The selectivity coefficients obtained

here are not significantly different from the ones obtained on the BWS-A1-C12 sample (see Table 13) and are in generally good agreement with literature values on illite and Boom clay ${}_{\text{Na}}^{\text{K}}K_{\text{c}} = 5 - 10$; ${}_{\text{Na}}^{\text{Mg}}K_{\text{c}} = 3.8$; ${}_{\text{Na}}^{\text{Ca}}K_{\text{c}} = 2 - 7$ (BRUGGENWERT & KAMPHORST 1982; BAEYENS 1982; BROUWER et al. 1983).

Table 9: Selectivity coefficients for K-Na, Mg-Na and Ca-Na exchange equilibria on OPA for Case I.

| Selectivity coefficients (I=0) | derived from data at S:L = 1 kg L ⁻¹ | derived from data at S:L = 1.5 kg L ⁻¹ | average |
|--|---|---|-------------|
| ${}_{\text{Na}}^{\text{K}}K_{\text{c}}$ | 5.9 (± 0.7) | 4.6 (± 0.4) | 5.3 (± 0.4) |
| ${}_{\text{Na}}^{\text{Mg}}K_{\text{c}}$ | 3.8 (± 0.8) | 3.0 (± 0.5) | 3.4 (± 0.5) |
| ${}_{\text{Na}}^{\text{Ca}}K_{\text{c}}$ | 4.1 (± 0.6) | 3.3 (± 0.5) | 3.7 (± 0.4) |

2.6 Comparison

The porewater composition of OPA was previously derived from physico-chemical data of core sample BWS-A1-C12 (BRADBURY & BAEYENS 1997a, 1998). As the sorption experiments were carried out on a different core sample (BGP-1-C11) a series of key physico-chemical investigations were performed in order to check whether the core sample BGP-1-C11 had similar characteristics.

The mineralogies, the chloride and sulphate inventories, the CEC and the selectivity coefficients of both core samples are summarised in Tables 10 to 13.

Table 10: Comparison of the mineralogical composition of Mont Terri OPA, sample BGP-1-C11 (15.13 - 15.38 m) and BWS-A1-C12 (13.82 - 14.02 m) (MAZUREK 1997).

| Mineral | wt % (bore core sample BGP-1-C11, this work) | wt % (bore core sample BWS-A1-C12) |
|------------------------------|--|------------------------------------|
| Calcite | 8 - 10 | 11 |
| Dolomite/ankerite | 1.5 - 2.5 | < 2 |
| Siderite | 3 - 5 | 4 |
| Quartz | 10 - 14 | 14 |
| K-feldspar | 1.5 - 3 | 2 |
| Albite | 0.5 - 2 | 2 |
| Pyrite | bdl | 1.7 |
| C (organic) | ≤ 0.4 | ≤ 0.7 |
| <u>Clay minerals</u> | | |
| Illite | 18 - 26 | 16 - 22 |
| Illite/smectite mixed layers | 14 - 22 | 6 - 12 |
| Chlorite | 8 - 12 | 5 - 9 |
| Kaolinite | 17 - 23 | 26 - 32 |

bdl = below detection limit.

The main clay minerals in both OPA core samples are the 2:1 type illite and the illite/smectite mixed layer and the 1:1 type kaolinite. In bore core sample BWS-A1-C12 both types are present in approximately the same proportions, whereas in bore core sample BGP-1-C11 (used in this work) the 2:1 type is present at approximately twice the 1:1 type. The other minerals are present in both bore core sample in comparable proportions.

Table 11: Comparison of the sulphate and chloride inventories of sample BGP-1-C11 and BWS-A1-C12.

| bore core sample | SO ₄ ²⁻ inventory (mmol kg ⁻¹) | Cl ⁻ inventory (mmol kg ⁻¹) |
|-----------------------|--|--|
| BGP-1-C11 (This work) | 1.8 (± 0.2) | 11.1 (± 0.8) |
| BWS-A1-C12 | 1.9 (± 0.2) | 12.3 (± 1.6) |

The SO₄²⁻ and Cl⁻ inventories determined in both OPA core samples are approximately equal (the differences of the SO₄²⁻ and Cl⁻ inventories are ~5 % and ~10 % respectively).

Table 12: Comparison of the CEC of sample BGP-1-C11 and BWS-A1-C12.

| bore core sample | CEC (meq kg ⁻¹) |
|-----------------------|-----------------------------|
| BGP-1-C11 (This work) | 120.9 (± 3.6) |
| BWS-A1-C12 | 125.3 (± 6.5) |

The difference of the Ni-en CEC determined on both bore core samples is less than 5 %.

Table 13: Comparison of the selectivity coefficients for K-Na, Mg-Na and Ca-Na exchange equilibria on OPA derived from data obtained from core sample BGP-1-C11 and BWS-A1-C12.

| Selectivity coefficients (I=0) | core sample BGP-1-C11 (This work) | core sample BWS-A1-C12 (Case I) |
|--------------------------------|--------------------------------------|------------------------------------|
| $K_{Na} K_c$ | 5.3 (± 0.4) | 5.0 (± 0.7) |
| $Mg_{Na} K_c$ | 3.4 (± 0.5) | 3.9 (± 1.5) |
| $Ca_{Na} K_c$ | 3.7 (± 0.4) | 4.7 (± 1.8) |

The selectivity coefficients for K-Na, Mg-Na and Ca-Na exchange equilibria derived from aqueous and Ni-en extraction data of the 2 bore cores are, within experimental error, comparable.

From the above it is clear that the mineralogies, the sulphate and chloride inventories, the CEC and the K-Na, Mg-Na and Ca-Na selectivity coefficients of both core samples are very similar. Consequently the sorption experiments could be carried out in water chemistries derived from the data obtained from core sample BWS-A1-C12 (BRADBURY & BAEYENS 1998).

3 **SORPTION MEASUREMENTS ON MONT TERRI OPALINUS CLAY**

3.1 **Introduction**

One of the main reasons for carrying out the following extensive sorption programme on OPA was to provide critical input data for the development of sorption data bases. Such data bases are required in performance assessment studies for high level radioactive waste repositories sited in OPA rock formations.

Further, there are mechanistic sorption studies on illite and kaolinite running in parallel to the OPA sorption work. (Illite and kaolinite are the main clay mineral components of OPA.) The sorption data measured on the natural system provide important base data sets against which predictions from sorption models can be tested.

Batch sorption experiments were carried out using the radionuclides $^{134}\text{Cs(I)}$, $^{85}\text{Sr(II)}$, $^{63}\text{Ni(II)}$, $^{152}\text{Eu(III)}$, $^{228}\text{Th(IV)}$, $^{75}\text{Se(IV)}$ and $^{113}\text{Sn(IV)}$. The first five radionuclides were chosen as representatives of nuclides in important chemical groups in the periodic table: alkaline, alkaline earth and transition metals, trivalent lanthanides and actinides and tetravalent actinides respectively. Tin was chosen because it is an important fission product (fission yield $\sim 0.06\%$; half life $\sim 10^5$ years) and because there is very little reliable sorption data for this metal existing in the open literature. Selenium was chosen for similar reasons and to include the sorption behaviour of an anionic species on the OPA system. Selenite is expected to be the stable form of this element under the experimental conditions used in this work.

The sorption measurements were carried out in controlled atmosphere glove boxes. One part of the experiments (pH = 8) was done under N_2 atmosphere with a gas purity of 99.995%. Another part of the work (pH = 6.3) was carried out in a CO_2/N_2 (50 % CO_2 / 50 % N_2) atmosphere. This gas mixture was obtained from Sauerstoff Lenzburg AG. The purity of the CO_2 and N_2 gases were 99.995 % and 99.999 % respectively. Porewater calculations for OPA at different pH values are presented in Figure 1 in BRADBURY et al. (1998) and shows the dependency of the partial pressure of CO_2 on pH. The equilibrium P_{CO_2} at pH = 6.3 required a partial pressure of $10^{-0.3}$ bar which was obtained in a 50 % CO_2 / 50 % N_2 atmosphere. The high P_{CO_2} together with the carbonate minerals buffers the OPA system under these conditions. At pH = 8 a much lower partial pressure of P_{CO_2} is required (ca. 10^{-4} bar) and for this reason the sorption experiments were carried out in a 100 % N_2 atmosphere. In order to ensure stable pH conditions the OPA system was buffered with tris-hydroxymethyl-aminomethane (TRIS).

3.2 Water Chemistry

A thoroughly physico-chemical characterisation study on Mont Terri OPA (core sample BWS-A1-C12) and the accompanying porewater modelling studies were already available (BRADBURY & BAEYENS 1997a, 1998) before completion of the physico-chemical characterisation of sample BGP-1-C11 which is used in this work. Two porewater compositions were calculated at pH = 6.3 and 8 using the existent model and associated parameters. (A pH of 8 was chosen because this value seems to be the most likely in situ pH in the OPA formation (PEARSON et al. 1999). The second pH value of 6.3 was selected to determine the effect of pH on sorption.) It should be noted that the calculated porewater compositions are considered to be valid because both OPA samples have very similar physico-chemical characteristics (see section 2.6).

The calculated water compositions at pH = 6.3 ($P_{CO_2} = 0.5$ bar, $I = 0.3$ M) and pH = 8 ($I = 0.39$ M) are given in Table 14.

Table 14: Composition of the calculated OPA porewater at pH = 6.3 (synthetic OPA porewater SOPW1, $P_{CO_2} = 0.5$ bar, $I = 0.3$ M) and pH = 8 (synthetic OPA porewater SOPW2, $I = 0.39$ M).

| Element | Total concentration (M) | |
|--------------------|-------------------------|----------|
| | SOPW1 | SOPW2 |
| | pH = 6.3 | pH = 8 |
| Na | 1.90 E-1 | 2.46 E-1 |
| K | 4.24 E-3 | 5.60 E-3 |
| Mg | 1.41 E-2 | 2.23 E-2 |
| Ca | 1.84 E-2 | 2.91 E-2 |
| Sr | 2.18 E-4 | 2.60 E-4 |
| C _{inorg} | 1.73 E-2 | 1.78 E-4 |
| SO ₄ | 2.81 E-2 | 2.75 E-2 |
| Cl | 1.86 E-1 | 3.00 E-1 |
| F | 1.37 E-4 | 1.21 E-4 |
| Si | 2.80 E-4 | 3.19 E-4 |

3.3 Conditioning of Mont Terri OPA (core sample BGP-1-C11)

Prior to the sorption measurements the crushed core sample was conditioned to the OPA porewater (see Table 14). The aim of this procedure was to produce an OPA suspension in well defined porewater composition that is in equilibrium with the calculated porewater. The procedure was as follows:

Dialysis bags were washed with de-ionised water before filling with 25 g of crushed OPA and 60 ml synthetic OPA porewater (SOPW1 at pH = 6.3 or SOPW2 at pH = 8) (see section 3.2). The bags were sealed so that an air pocket was trapped inside which promoted a good mixing during end-over-end shaking. Four such dialysis bags were placed in a 2 L polyethylene flask filled with synthetic OPA porewater and then shaken for 24 hours. After this time, the equilibrated solutions in the flasks were replaced by fresh synthetic OPA porewater and the bottles were again shaken for 24 hours. This procedure was repeated four times. Finally the OPA suspensions inside the dialysis bags were emptied into a quantity of the last equilibrated synthetic OPA porewater in order to give a suspension having a sorbent concentration of $\sim 100 \text{ g L}^{-1}$. The exact clay content was determined by heating 5 ml of the suspension overnight at $105 \text{ }^\circ\text{C}$ and weighing the residue. The dry weight of 20 ml synthetic OPA porewater was determined in the same manner in order to make salt corrections.

Three batches were necessary for the sorption experiments at pH = 6.3 (batch 1 to 3) and one batch at pH = 8 (batch 4).

3.3.1 Major Constituents

The major elements in the synthetic OPA porewaters SOPW1 and SOPW2, and in the conditioned OPA porewaters were analysed by ICP-OES. The results are given in Tables 15 and 16.

Table 15: Major elements in synthetic and in conditioned OPA porewater at pH = 6.3 (batch 1 to 3).

| Element | OPA porewater (SOPW1) | Conditioned OPA (batch 1) | Conditioned OPA (batch 2) | Conditioned OPA (batch 3) |
|--------------------|------------------------|---------------------------|---------------------------|---------------------------|
| Concentrations (M) | | | | |
| Na | 1.87 (\pm 0.02) E-1 | 1.87 (\pm 0.06) E-1 | 1.86 (\pm 0.02) E-1 | 1.89 (\pm 0.03) E-1 |
| K | 4.63 (\pm 0.26) E-3 | 3.74 (\pm 0.05) E-3 | 4.29 (\pm 0.05) E-3 | 4.28 (\pm 0.05) E-3 |
| Mg | 1.46 (\pm 0.02) E-2 | 1.47 (\pm 0.02) E-2 | 1.37 (\pm 0.02) E-2 | 1.41 (\pm 0.02) E-2 |
| Ca | 1.84 (\pm 0.03) E-2 | 1.89 (\pm 0.02) E-2 | 1.79 (\pm 0.05) E-2 | 1.87 (\pm 0.02) E-2 |
| Sr | 2.21 (\pm 0.05) E-4 | 2.09 (\pm 0.06) E-4 | 2.22 (\pm 0.05) E-4 | 2.20 (\pm 0.06) E-4 |
| Al | 1.78 (\pm 0.58) E-6 | 1.06 (\pm 1.08) E-6 | 4.79 (\pm 1.40) E-6 | 1.89 (\pm 1.26) E-6 |
| Si | 2.87 (\pm 0.05) E-4 | 3.90 (\pm 0.05) E-4 | 4.02 (\pm 0.36) E-4 | 3.30 (\pm 0.09) E-4 |
| Fe | 1.52 (\pm 0.63) E-7 | 2.44 (\pm 0.04) E-5 | 2.63 (\pm 1.00) E-5 | 1.49 (\pm 0.09) E-5 |
| S | 2.80 (\pm 0.09) E-2 | 2.81 (\pm 0.06) E-2 | 3.02 (\pm 0.02) E-2 | 2.79 (\pm 0.08) E-2 |

The results are the average of two sample measurements.

Table 16: Major elements in synthetic OPA porewater and conditioned OPA porewater at pH = 8 (batch 4).

| Element | OPA porewater (SOPW2) | Conditioned OPA (batch 4) |
|--------------------|------------------------|---------------------------|
| Concentrations (M) | | |
| Na | 2.56 (\pm 0.02) E-1 | 2.48 (\pm 0.02) E-1 |
| K | 5.83 (\pm 0.03) E-3 | 5.79 (\pm 0.02) E-3 |
| Mg | 2.10 (\pm 0.02) E-2 | 2.14 (\pm 0.04) E-2 |
| Ca | 2.80 (\pm 0.02) E-2 | 2.85 (\pm 0.05) E-2 |
| Sr | 2.76 (\pm 0.04) E-4 | 2.63 (\pm 0.02) E-4 |
| Al | 2.59 (\pm 0.40) E-7 | 6.41 (\pm 1.52) E-6 |
| Si | 3.34 (\pm 0.09) E-4 | 2.91 (\pm 0.03) E-4 |
| Fe | 1.43 (\pm 0.72) E-7 | 3.94 (\pm 1.43) E-6 |
| S | 2.76 (\pm 0.07) E-2 | 2.80 (\pm 0.02) E-2 |

The results are the average of two sample measurements.

The concentrations of the major elements Na, K, Mg, Ca, Sr, Si and S (SO_4^{2-}) in the liquid phases of the conditioned OPA batches remained essentially constant during the conditioning procedures and are very similar to the synthetic porewaters.

In the porewater modelling studies (BRADBURY & BAEYENS 1997a, 1998) the presence of Al and Fe was not included, and were not taken into account in the calculation of synthetic porewater compositions (see Table 14). They were also not included in the preparation of the synthetic porewaters. The measured Fe and Al concentrations in SOPW1 and SOPW2 arise from impurities in the chemicals used in the preparation of the synthetic porewaters. The increase in Al and Fe in the conditioned OPA suspensions are due to dissolution processes. The presence of

siderite (FeCO_3) is responsible for the high Fe concentrations. However, solubility calculations indicated that for both pH = 6.3 and 8 siderite remained undersaturated.

3.3.2 Background Concentrations

As shown in Table 3, section 2.3.5, some of the elements used in the sorption experiments (Cs, Ni, Eu, Th and Sn) are naturally present at trace levels in the OPA rock. These elements are also present at trace concentrations in the liquid phase of the OPA suspensions used for the sorption experiments. These background elements can play an important role in the sorption experiments performed at low (trace) concentrations, particularly in sorption experiments where the background concentrations are equal or greater than the added inactive and active concentrations. For this reason the concentrations of the elements above were determined in the synthetic OPA porewater SOPW1 and in the conditioned OPA porewater batch 1 at pH = 6.3. The porewaters were freeze dried and the salts were analysed by ICP-MS at the CNRS, Service d'Analyses des Roches et des Minéraux, in France. (Similar analyses were not repeated on the SOPW2 and the conditioned porewater at pH = 8, because of the high chloride contents in these waters which lead to problems in the ICP-MS measurements.)

The results are listed in Table 17.

Table 17: Background concentrations of the elements used in the sorption investigations in synthetic OPA porewater (SOPW1) and in conditioned OPA porewater (batch 1) at pH = 6.3.

| Element ¹⁾ | OPA porewater (SOPW1) | Conditioned OPA (batch 1) |
|-----------------------|-----------------------|---------------------------|
| Concentrations (M) | | |
| Cs | 4.8 E-8 | 2.3 E-8 |
| Sr | 2.0 E-4 | 2.0 E-4 |
| Ni | 3.8 E-7 | 1.9 E-8 |
| Eu | 4.9 E-10 | 9.7 E-11 |
| Th | < 1.0 E-11 | < 1.0 E-11 |
| Sn | 4.5 E-8 | 3.8 E-8 |

¹⁾ The measurements were performed by ICP-MS at the CNRS, Service d'Analyses des Roches et des Minéraux, in France. The uncertainties of all concentrations are $\pm 20\%$.

The background concentrations of Cs, Eu, Ni and Sn in synthetic and conditioned OPA porewater at pH = 6.3 are not negligible and have to be taken into account in the evaluation of the sorption isotherms. The Th background concentrations are below the detection limit and must not be considered in the evaluation of the sorption experiments. The Sr background concentrations in the porewaters are determined by the solubility limit of celestite i.e. the sorption is determined by the system itself.

3.4 Experimental Procedures for Sorption Experiments

In the following, general procedures used in the batch sorption experiments are described. Details specific to the individual experiments e.g. nuclide concentrations, S:L ratios, equilibration times and any deviation from the normal procedures are given in the appropriate sections.

3.4.1 Standard Solutions

Sorption isotherms were measured in synthetic OPA waters at pH 6.3 and 8. Standard solutions having a range of nuclide concentrations were prepared by successively diluting an original synthetic OPA water containing a high concentration of the nuclide in question. The standard solutions were labelled by adding known quantities of radioisotope. These labelled standard solutions were allowed to stabilise for at least one day in their polyethylene containers before use in the sorption tests in order to allow wall sorption to proceed to completion. A number of samples of these standard solutions (reference activities) were always counted simultaneously with the sample solutions from the batch sorption tests.

The radioisotopes ^{63}Ni , ^{134}Cs , ^{85}Sr , ^{152}Eu and ^{75}Se were obtained from Amersham International Ltd. (Buckinghamshire, GB). ^{228}Th and ^{113}Sn were purchased from Isotope Products Laboratories (California, USA).

Radiochemical assays of ^{63}Ni were carried out on a Canberra Packard TRI-CARB 2250CA or TRI-CARB 2750 TR/LL liquid scintillation analyzer. The radioisotopes ^{134}Cs , ^{85}Sr , ^{152}Eu , ^{228}Th and ^{75}Se were radio assayed on a Canberra Packard COBRA QUANTUM γ -Counter. ^{113}Sn was measured with both counters.

3.4.2 Stability Tests

Solubility calculations for Cs, Ni, Se, Eu and Th in the synthetic OPA porewaters at pH = 6.3 and 8 have been carried out, using the geochemical code MINEQL (WESTALL et al. 1976) and the thermodynamic data base compilations (PEARSON & BERNER 1991, and PEARSON et al. 1992), to estimate the experimental conditions for which each nuclide should be stable. Since the thermodynamic data cannot always be relied upon, the stabilities of the above nuclides were experimentally checked prior to performing the sorption experiments. The procedure was as follows: Series of salt solutions of the nuclide above at given concentrations were prepared in the respective synthetic OPA porewaters (SOPW1 and SOPW2) and were kept for a time period of 3 days to one week. The solutions were then analysed by ICP-OES before and after centrifugation (1 hour at 95000 g max.) and if their concentrations remained constant it was concluded that they were stable.

Table 18 presents the highest (stable) starting concentrations used for each element for which isotherms were measured in the two different synthetic OPA porewaters.

Table 18: Highest stable starting concentrations of Cs, Ni, Eu, Th and Se used in the isotherm sorption measurements in the synthetic OPA porewaters at pH = 6.3 and 8.

| Element | SOPW1 (pH = 6.3) (M) | SOPW2 (pH = 8) (M) |
|---------|-------------------------|-----------------------|
| Cs | 1.0 E-3 | 1.0 E-3 |
| Ni | 1.0 E-3 | 1.0 E-4 |
| Eu | 1.0 E-6 | 9.0 E-7 |
| Th | 8.0 E-7 | 8.0 E-7 |
| Se | 1.0 E-3 | 1.0 E-3 |

Solubility studies of Sn(IV) in NaClO₄ 0.1 M have been carried out by AMAYA et al. (1997) and indicated very low solubilities of $\sim 3 \times 10^{-8}$ M and $\sim 10^{-7}$ M at pH ~ 7 and 8 respectively. For this reason only single point sorption measurements with Sn(IV) were performed at the lowest possible initial concentration ($\sim 8 \times 10^{-9}$ M) which allowed still good counting statistics after sorption.

For Sr only single point sorption measurements were carried out at the concentrations in the OPA porewaters SOPW1 and SOPW2 which were fixed via the saturation with respect to celestite (SrSO₄) (see Table 14).

3.4.3 Sorption Kinetics

Prior to beginning the sorption isotherm experiments, sorption kinetic tests were performed with all of the radionuclides at trace concentrations (see the individual results for details). In the case of Cs and Ni kinetic experiments were also carried out at higher concentrations. The aim of these kinetic tests was to determine the times required to reach "equilibrium" (steady-state) for sorption on the OPA. Kinetic tests were only carried out at pH = 6.3 and it was assumed that the results were valid for pH = 8.

General experimental procedure for Cs, Ni, Eu, Th and Se(IV):

2 ml aliquots of OPA suspensions and 30 ml of the appropriately labelled standard solutions were transferred into 40 ml centrifuge tubes and shaken end-over-end for between 4 hours and ~ 8 months (~ 2 months for Se). For each of the radionuclides listed above two series of 16 centrifuge tubes were prepared. (The first series was carried out at trace concentration and the second one at the highest initial radionuclide concentration used in the sorption isotherm experiments). After the selected time period two samples were centrifuged (1 hour at 95,000g max.) and two 5 ml aliquots of the supernatant solutions were taken for radio assay together with standard samples. The counting times were chosen to give ≤ 0.7 sigma errors. For the Ni measurements 15 ml scintillation liquid (Instagel™ or Ultimagold™) was added before counting. After sampling the pH in the supernatant was measured.

General procedure for Sn(IV):

The technique used to measure the sorption kinetics for Sn(IV) was different because of the low solubility of Sn in the OPA porewater and the expectedly high sorption on OPA. For these reasons tests were carried out at trace concentrations and a very low S:L ratio in 250 ml centrifuge bottles.

1 ml aliquots of OPA suspensions and 240 ml of synthetic OPA porewater were transferred into 250 ml centrifuge bottles. Each bottle was labelled with a known quantity of ^{113}Sn before shaking end-over-end for times between 1 and 60 days at pH = 6.3 (28 days at pH = 8). At the beginning of these kinetic tests 6 standard solutions were prepared by adding a given quantity of ^{113}Sn to 10 ml aliquots of synthetic OPA water (reference activities). The bottles were then centrifuged (1 hour at 47,500 g max.) and two 10 ml aliquots of the supernatant solutions were sampled for

radio assay. The samples and the standard solutions were left at least for 24 hours after sampling before counting, i.e. after the secular equilibrium ^{113}Sn - $^{113\text{m}}\text{In}$ was reached. 10 ml Ultimagold™ scintillation liquid was added before β -counting. ^{113}Sn was then measured by γ -counting for comparison. The results obtained from γ - and β -counting were essentially the same. After sampling the pH was measured.

3.4.4 Wall Sorption

Wall sorption is unavoidable in batch tests and their effects on sorption must be evaluated. The measuring of wall sorption in blank tests in the absence of the solid phase is not valid since competitive sorption effects between the solid phase and the wall are ignored.

In the studies of Ni and Zn sorption on Na-montmorillonite (BAEYENS & BRADBURY 1995) an acid leaching procedure was used on the test tubes after completion of the sorption experiments. These acid leaching tests showed that in the presence Na-montmorillonite the extend of wall sorption was dependent on pH, magnitude of sorption and on the S:L ratio. Generally the effects were very low and introduced a maximum uncertainty in the $\log R_d$ values of ~ 0.05 log units.

In this study the effect of wall sorption in the case of Eu, Th and Sn was tested in a different way. Because of the low solubilities and high sorption the tests were carried at low S:L ratios (0.4 g L^{-1}). For each of the elements above the amount of radionuclide sorbed on the wall of the bottles was determined using the following procedure: 5 ml (Eu and Th) or 10 ml (Sn) homogeneous aliquots of suspension were sampled from each bottle after a given time interval before centrifugation. The activity of these suspensions were then compared with the initial activity of the standard solutions (the activity measurements were solely carried out by γ -counting). In all cases no differences between the initial activity and the activity in the suspensions after equilibration were measured indicating that even in the presence of small amounts of OPA no wall sorption occurred.

3.4.5 Isotherms

Sorption isotherms, i.e. the uptake of radionuclides as function of the radionuclide equilibrium concentration at constant pH in synthetic OPA porewater were performed for Cs, Ni, Eu, Th and Se. For Sr only single point measurements were made at total concentrations of 2.2×10^{-4} M (pH = 6.3) and 2.6×10^{-4} M (pH = 7.7), since this represents the inactive Sr background concentration in the OPA water fixed by the saturation of celestite. Sn sorption experiments were only performed at trace concentrations because of its low solubility at both pH 6.3 and 8 (see section 3.4.2).

Two "types" of isotherm experiments were conducted. In the first case the total concentration of radionuclide was varied at constant S:L ratio whereas in the second case the total concentration of radionuclide was kept constant and the S:L ratio varied. Changing the S:L ratio allowed the radionuclide equilibrium concentrations to be varied up to near the maximum stable level (see section 3.4.2). For Cs, Ni and Se the first "type" of experiment was used. For Eu and Th both procedures were used because of their low solubilities in the OPA porewaters.

General procedure for "type 1" experiments:

2 ml aliquots of OPA suspensions (5 ml in the case of the Ni sorption experiments) and 30 ml of labelled standard solutions at a range of nuclide concentrations were transferred into 40 ml centrifuge tubes and shaken end-over-end for 1 month (2 weeks in the case of Eu and Th). The times were chosen to be sure that the uptake of nuclide by the solid was complete. The centrifugation, sampling, counting procedures and pH measurements were as described in section 3.4.3.

General procedure for "type 2" experiments:

240 ml aliquots of inactive stock solutions of Eu or Th and variable amount of OPA suspensions (between 1 and 14 ml) were transferred into 250 ml centrifuge bottles. Each bottle was then labelled with a constant volume of radioisotope stock solution before being shaken end-over-end for 2 weeks (The kinetic tests showed that this time was sufficient for sorption to be completed). The centrifugation, sampling, counting procedures, pH measurements and wall sorption measurements followed as described in section 3.4.3.

3.4.6 Presentation of the Data

The sorption results in this work are presented either as distribution ratios R_d ($L\ kg^{-1}$) against equilibrium concentrations, or as adsorption isotherms (sorbed radionuclide concentrations vs. equilibrium concentrations). The equilibrium aqueous concentration of the radionuclide is calculated from the measured activity of the supernatant solution and the known activity of the initial solution. The distribution ratio R_d and the sorbed radionuclide $[C]_{\text{sorbed}}$ are defined as:

$$R_d = \frac{C_{\text{in}} - C_{\text{eq}}}{C_{\text{eq}}} \cdot \frac{L}{S} \quad (8)$$

$$[C]_{\text{sorbed}} = (C_{\text{in}} - C_{\text{eq}}) \cdot \frac{L}{S} \quad (9)$$

where:

- C_{in} = initial nuclide concentration (M)
- C_{eq} = equilibrium nuclide concentration (M)
- L = volume of the liquid phase (L)
- S = mass of the solid phase (kg)

The Freundlich isotherm can be expressed as follows:

$$[C]_{\text{sorbed}} = a \cdot (C_{\text{eq}})^b \quad (10)$$

or in logarithmic form as:

$$\log [C]_{\text{sorbed}} = \log a + b \cdot \log (C_{\text{eq}}) \quad (11)$$

where "a" and "b" are positive empirical parameters, with $0 < b < 1$. The parameters "a" and "b" are obtained from the linear regression of a plot of $\log [C]_{\text{sorbed}}$ versus $\log C_{\text{eq}}$; "b" is the gradient and "a" the intercept. It should be realised that equation (10) is strictly an empirical expression and is regarded as an equation without chemical significance other than its often remarkable ability to correlate sorption data measured as a function of the nuclide concentration under constant conditions (SPOSITO 1980).

3.4.7 Uncertainties

Estimates of the maximum error in each operation in similar batch sorption tests to those performed in this work have been done by BAEYENS & BRADBURY (1995) and yielded an uncertainty in $\log R_d$ of ~ 0.15 log units. When sorption experiments were repeated the R_d values varied within ± 0.2 log units. This uncertainty was taken to be realistic and all R_d values in this work are given with this error. This error estimate includes possible sources of errors (e.g. weighing, volumetric and counting errors).

The uncertainty on pH consists of the pH uncertainty of the Titrisol™ buffer solutions (± 0.02 pH for the buffer solutions pH = 4, 7 and 9), of the HNO₃ standard solution (± 0.02 pH, i.e. 5% in [H⁺]) and of the pH sample measurement (± 0.02 pH). The calibration of the pH-meter was either performed with 2 buffer solutions (experiments at pH = 8) or with the HNO₃ standard solution (experiments at pH = 6.3). The statistical uncertainties on pH measurement are therefore ~ 0.04 pH for the pH calibrations with 2 buffer solutions and ~ 0.03 pH for the calibration with the HNO₃ standard solution. However repeated pH measurements for a series of tests indicate that an uncertainty of ± 0.05 pH is considered to be realistic.

In the sorption isotherm experiments performed at high pH the measured pH values varied between pH = 7.7 (Sr) and 8.1 (Sn and Se). These variations were not due to the uncertainty of pH measurements but more likely to the low buffer capacity of the OPA system. (The concentration of the TRIS buffer used to adjust the pH to 8 was low (2×10^{-3} M) in order to minimise competitive effects with OPA.) The most important deviation was observed with Sr (~ 0.3 pH units) because the sorption experiments were performed with unconditioned OPA (see section 3.6). The TRIS buffer concentration was too low to keep the pH at 8 during the equilibration time.

In the experiments at pH = 6.3 no significant pH deviations were observed, because the system was strongly enough buffered by the carbonate minerals in the high PCO₂ atmosphere.

3.5 Cs Sorption Data

3.5.1 Background Cs

The Cs inventory on the OPA rock material as determined from ICP-MS analysis (see Table 3) was $\sim 4.4 \times 10^{-5} \text{ mol kg}^{-1}$. The Cs background concentration in the conditioned OPA porewater system (batch 1, pH = 6.3) was $\sim 2.3 \times 10^{-8} \text{ M}$ (see Table 17). The quantity of Cs sorbed on the OPA rock through the conditioning of OPA with the synthetic porewater (SOPW1) has also to be taken into account. In the conditioning procedure a total volume of 9.0 L SOPW1 was equilibrated with 0.1 kg rock (see section 3.3). Using equation (8) together with the data for Cs given in Table 17, the quantity of Cs sorbed during the conditioning is $\sim 2.3 \times 10^{-6} \text{ mol kg}^{-1}$. With these data it is possible to estimate a Cs distribution coefficient from the following:

$$\begin{aligned} \log R_d &= \log [\text{Cs}]_{\text{solid phase}} - \log [\text{Cs}]_{\text{eq}} = \log (4.6 \times 10^{-5}) - \log (2.3 \times 10^{-8}) \\ &= \sim 3.3 \text{ L kg}^{-1}. \end{aligned} \quad (12)$$

The experimentally measured $\log R_d$ value at the lowest Cs equilibrium concentration in the conditioned OPA at pH = 6.3 is very closely to this value, indicating that probably the total Cs inventory on OPA is available for sorption.

The equilibrium Cs concentration given in the plots below refers to the total Cs in solution. In batch tests this quantity cannot be determined simply from the amounts of Cs added and changes in radiocesium activity levels when inactive Cs is intrinsically present in the system. In such cases equilibrium concentrations should be determined from a mass balance equation which takes into account the Cs inventory on OPA. (The assumption is that Cs sorption is fully reversible.)

$$V \cdot [\text{Cs}]_{\text{added}} + m \cdot I_{\text{Cs}} = m \cdot R_d \cdot [\text{Cs}]_{\text{eq}} + V \cdot [\text{Cs}]_{\text{eq}} \quad (13)$$

$$[\text{Cs}]_{\text{eq}} = \frac{(V \cdot [\text{Cs}]_{\text{added}} + m \cdot I_{\text{Cs}})}{(m \cdot R_d + V)} \quad (14)$$

where:

$$\begin{aligned} R_d &= \text{distribution coefficient (L kg}^{-1}\text{)} \\ [\text{Cs}]_{\text{solid phase}} &= \text{concentration of Cs sorbed on the OPA (mol kg}^{-1}\text{)} \\ [\text{Cs}]_{\text{eq}} &= \text{equilibrium concentration of Cs (M)} \end{aligned}$$

| | | |
|----------------|---|---|
| $[Cs]_{added}$ | = | total concentration of Cs added, i.e. inactive Cs plus ^{134}Cs (M) |
| m | = | mass of OPA (kg) |
| V | = | volume (L) |
| I_{Cs} | = | intrinsic Cs inventory ($mol\ kg^{-1}$) |

The intrinsic Cs inventory is unimportant at high Cs concentrations where $V \cdot [Cs]_{added} \gg m \cdot I_{Cs}$, but becomes increasingly important as the concentration decreases. At the lowest Cs concentrations added in the experiments the term $m \cdot I_{Cs}$ became dominant and the Cs equilibrium concentration was consequently defined by the Cs background concentration of the OPA system.

3.5.2 Cs Kinetics and Isotherm Results

Two series of sorption kinetic tests were performed with Cs at pH = 6.3 at $3.2 \cdot 10^{-7}$ M and $9.3 \cdot 10^{-4}$ M. The sorption isotherm experiments were performed both at pH = 6.3 and 7.9 between these two concentrations. The experimental conditions are listed in Table 19 and the measured data are given in Figures 5 to 7.

Table 19: Experimental conditions for the Cs sorption kinetic and sorption isotherm measurements on conditioned OPA batch 1 (pH = 6.3, $I = 0.3$ M) and sorption isotherm measurements on conditioned OPA batch 4 (pH = 7.9, $I = 0.39$ M).

| Experimental Conditions | Figure 5 (kinetic) | Figure 6 (isotherm) | Figure 7 (isotherm) |
|--|---|--|--|
| Initial Cs concentration (M) ¹⁾ | $3.2 \cdot 10^{-7}$ and $9.3 \cdot 10^{-4}$ | $3.2 \cdot 10^{-7}$ to $9.3 \cdot 10^{-4}$ | $3.4 \cdot 10^{-7}$ to $9.4 \cdot 10^{-4}$ |
| Equilibration time (days) | 1 - 220 | 28 | 28 |
| S:L ratio ($g\ L^{-1}$) | 5.97 | 5.97 | 6.24 |
| pH | 6.3 | 6.3 | 7.9 |
| Nr. of measurements | 32 | 34 | 34 |

¹⁾ The Cs background concentration is taken into account.

Figure 5 clearly shows that the uptake of Cs at trace and high concentrations were essentially completed after ~ 3 days equilibration time.

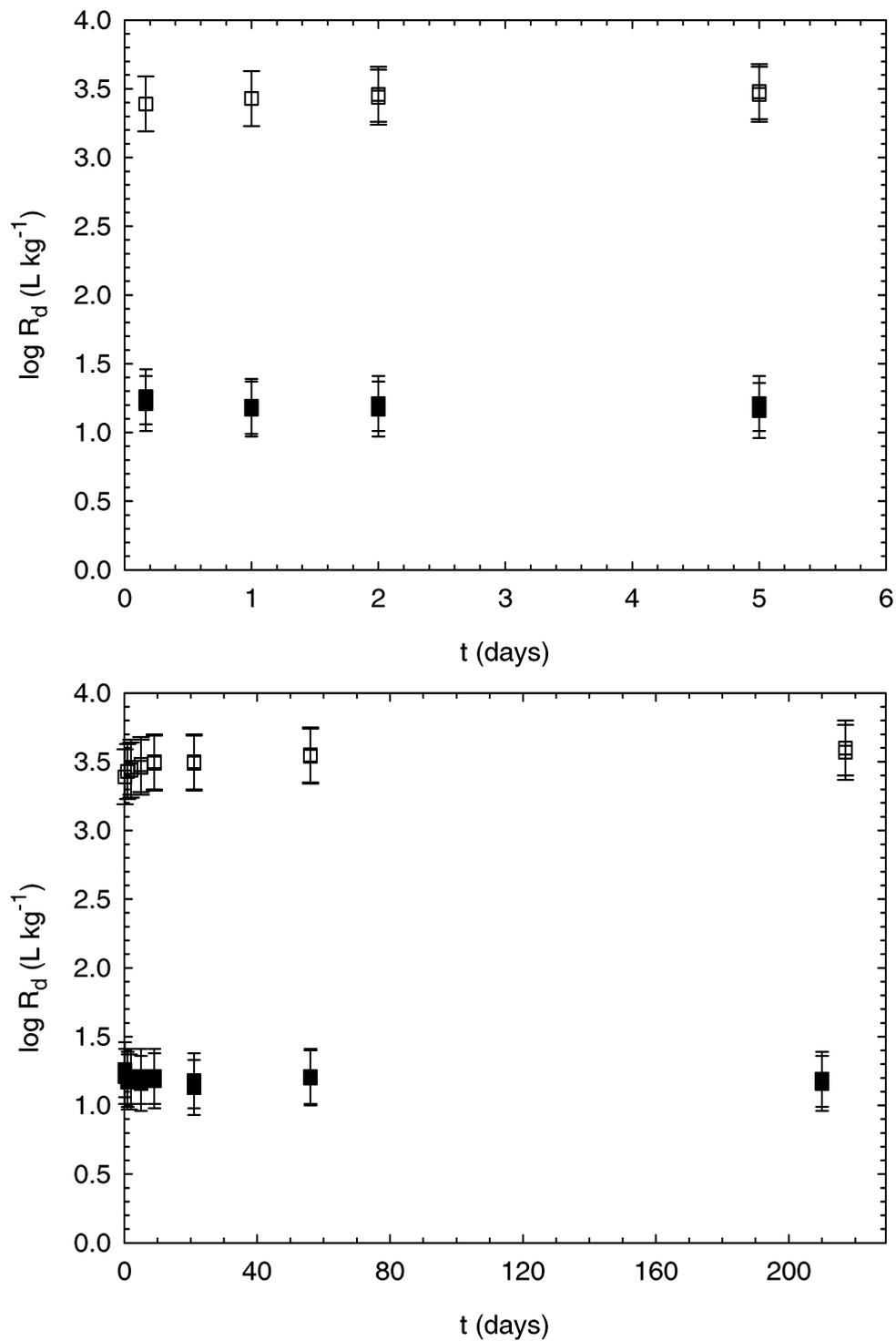


Figure 5: Cs sorption kinetic data on conditioned OPA at pH = 6.3 and $[Cs]_{tot} = 3.2 \times 10^{-7} \text{ M}$ (\square) and $[Cs]_{tot} = 9.3 \times 10^{-4} \text{ M}$ (\blacksquare). Short and long-term kinetics.

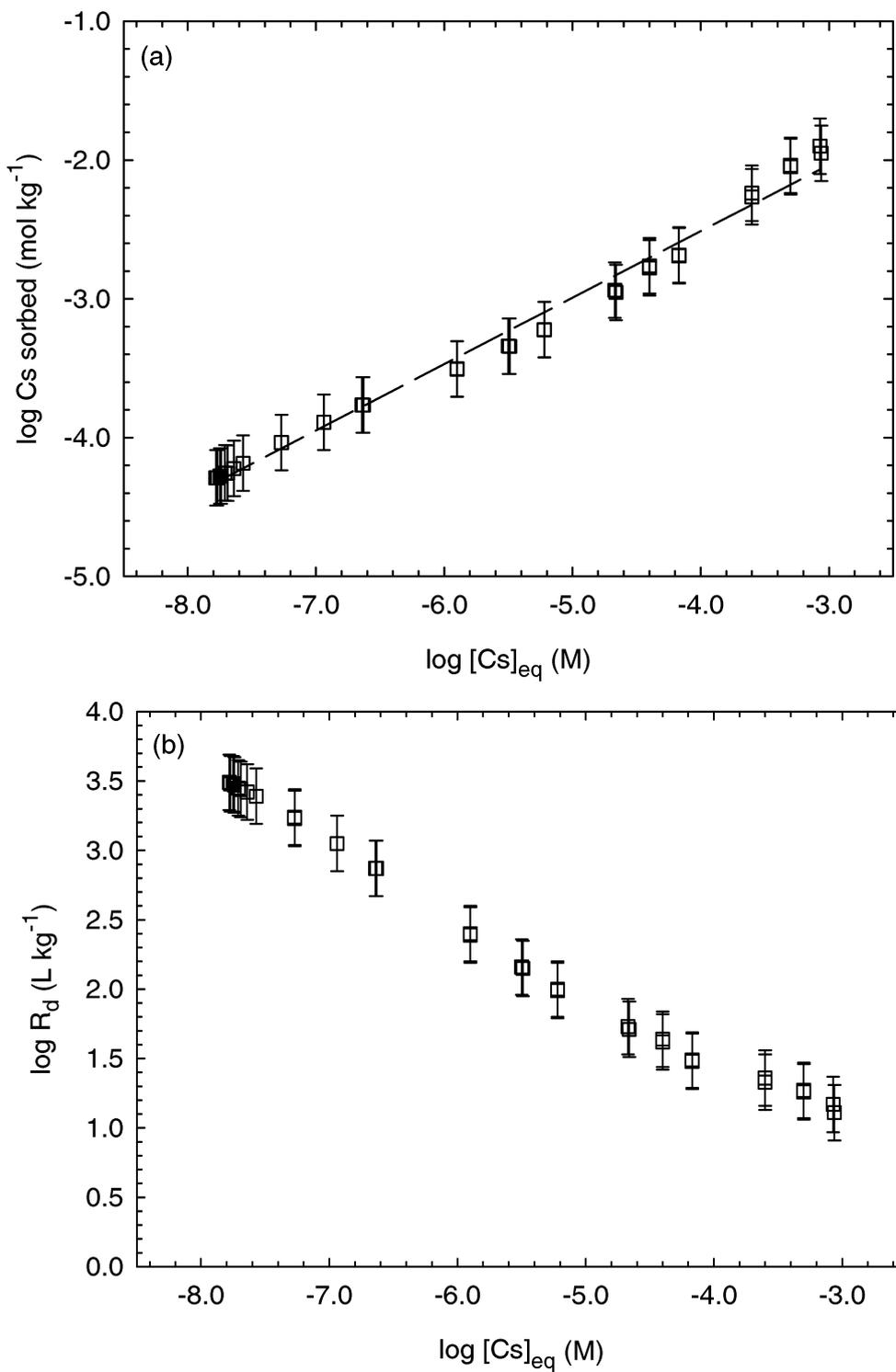


Figure 6: Cs sorption isotherm data on conditioned OPA at pH = 6.3.

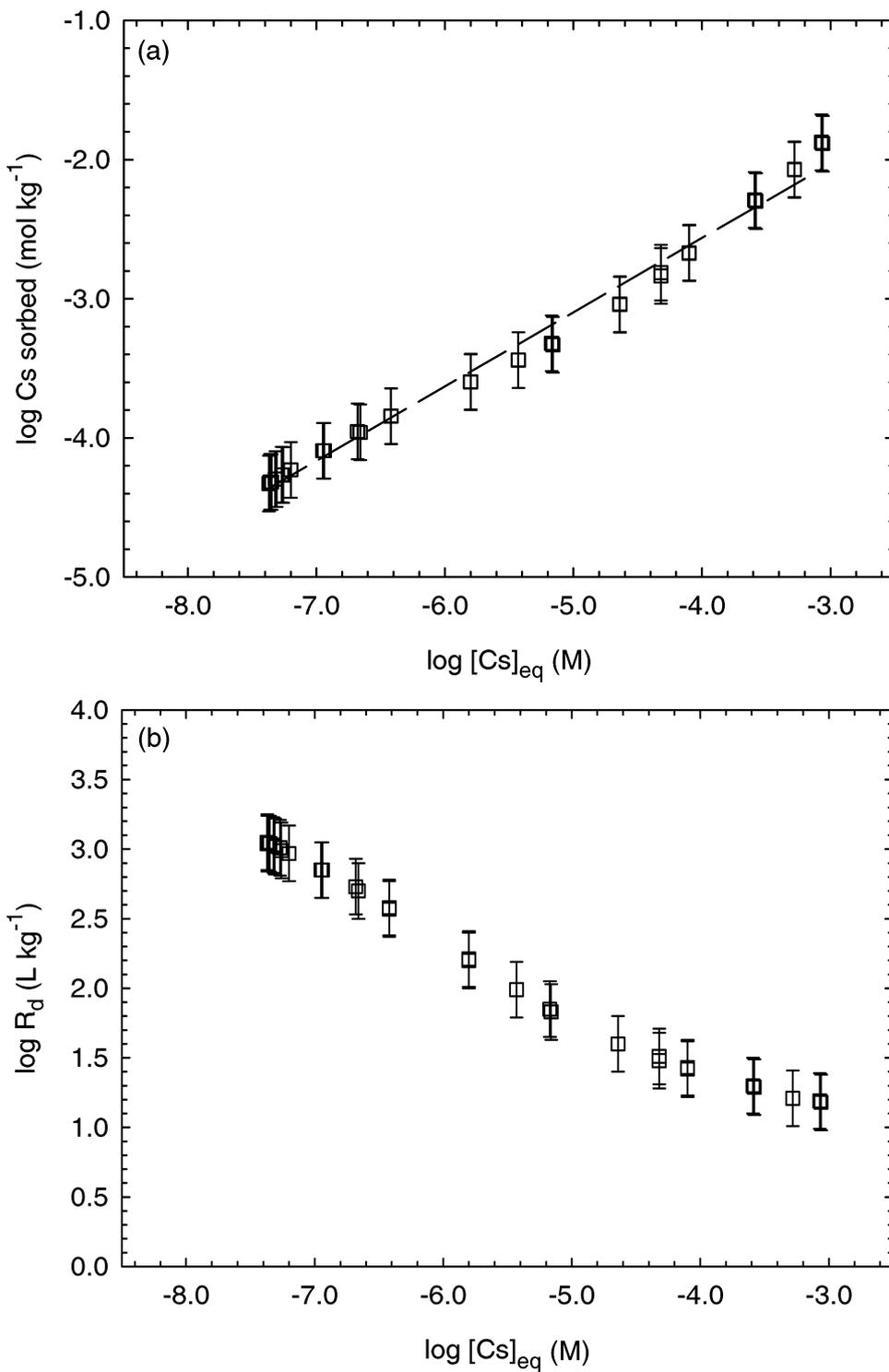


Figure 7: Cs sorption isotherm data on conditioned OPA at pH = 7.9.

Figures 6a and 7a present the sorption of Cs on OPA at the two different pH values in the form of an isotherm (quantity of Cs sorbed versus Cs equilibrium concentration).

Within the equilibrium concentration ranges studied (between $1.6 \cdot 10^{-8}$ and $7.9 \cdot 10^{-4}$ M at pH = 6.3, between $4.0 \cdot 10^{-8}$ and $7.9 \cdot 10^{-4}$ M at pH = 7.9) the sorption of Cs on OPA both at pH 6.3 and 7.9 is dependent on concentration, i.e. a non-linear sorption is observed.

Table 20 summarises the Freundlich parameters (see section 3.4.6) obtained from the linear regressions of the plots of $\log [Cs]_{\text{sorbed}}$ versus $\log [Cs]_{\text{eq}}$. The fitted isotherms are presented as dashed lines in Figures 6a and 7a.

Table 20: Freundlich parameters of Cs at pH = 6.3 and 7.9.

| pH | Concentration range $\log [Cs]_{\text{eq}}$ (M) | $\log a$ | b | r^2 |
|-----|--|---------------------|--------------------|-------|
| 6.3 | -7.8 to -3.1 | -0.60 (\pm 0.05) | 0.48 (\pm 0.01) | 0.990 |
| 7.9 | -7.4 to -3.1 | -0.43 (\pm 0.06) | 0.53 (\pm 0.01) | 0.989 |

The parameter "b" is both at pH = 6.3 and 7.9 clearly below 1, indicating that the sorption is non-linear within the concentration ranges under investigation.

Figures 6 b and 7 b show the sorption data in the form of $\log R_d$ versus equilibrium Cs concentration plots.

The sorption isotherms are more or less pH independent. This is an indication for a cation exchange mechanism. The sorption is slightly lower at pH = 7.9 than at pH = 6.3 at low Cs equilibrium concentrations. This effect could be related to the higher K concentration of $\sim 5.8 \cdot 10^{-3}$ M in the system at pH = 7.9 compared to $\sim 4.6 \cdot 10^{-3}$ M at pH = 6.3. K is known to be competitive to Cs in sorption (SAWHNEY 1970).

A generalised Cs sorption model for the concentration dependent uptake of Cs on argillaceous rocks has recently been developed (BRADBURY & BAEYENS 2000). This relatively simple three site cation exchange sorption model is based on selectivity coefficient and site capacity data derived from literature data on illite. The sorption is calculated first on a reference illite which has fixed site capacities for each of the three sites considered, and the result is then scaled to the illite content present in the natural

rock. Figure 8 presents the calculated Cs sorption isotherms for the two OPA isotherms measured in this work at pH 6.3 and 7.9 in the corresponding porewater compositions (see Tables 15 and 16). The curves are calculated by taking an average illite content of 22 wt. % (see Table 1). It must be pointed out that illite/smectite mixed layers are also present in the OPA rock in approximately equal proportions than illite. DE PRETER (1990) has postulated that there may be sites on illite/smectite mixed layer clay minerals on which Cs (at trace concentrations) could be adsorbed as effectively as on the FES on illite. This could explain that in the lower Cs concentration range the model predicts lower sorption than the measured values.

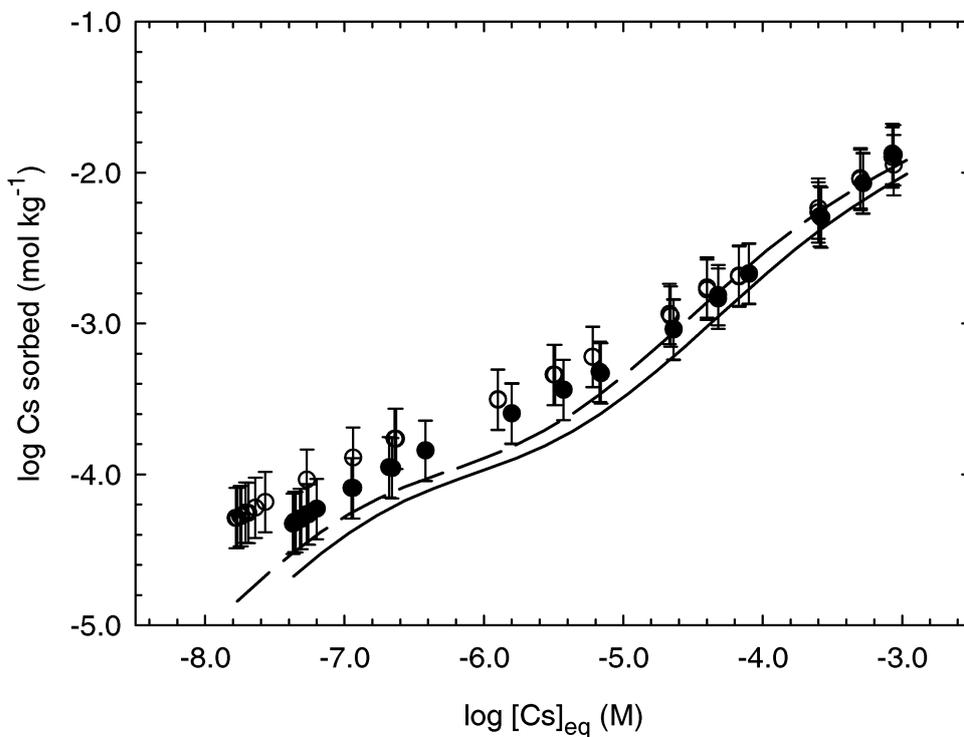


Figure 8: Cs sorption isotherms on OPA at pH = 6.3 and 7.9. ○ and ● = measured data at pH 6.3 and 7.9 respectively. --- and — = model calculations at pH = 6.3 and 7.9 respectively.

3.6 Sr Sorption Data

As the concentration of Sr in the OPA porewaters is fixed by the solubility of celestite, no isotherm measurements can be determined. It was only possible to measure single R_d values for Sr for a given porewater chemistry.

Initial kinetic sorption measurements at pH = 6.3 carried out at a relatively low S:L ratio of $\sim 6 \text{ g L}^{-1}$ showed that the sorption of Sr at celestite saturation ($\sim 2 \times 10^{-4} \text{ M}$) on OPA was too low to be measurable. In order to obtain reliable data, the sorption measurements were carried out at high S:L ratios. Suspensions of $\sim 6 \text{ g}$ unconditioned OPA and 25 ml conditioned OPA porewater, which was labelled with ^{85}Sr tracer, were shaken end-over-end for equilibration times of one week and one month at pH = 6.3. Two series of tests with equilibration times of three and six weeks were performed at pH = 7.7.

The experimental conditions are listed in Table 21 and the results are given in Table 22.

Table 21: Experimental conditions for the sorption of Sr on OPA .

| Experimental Conditions | SOPW1 | SOPW2 |
|----------------------------------|---------|---------|
| Sr equilibrium Concentration (M) | 2.2 E-4 | 2.6 E-4 |
| Time (days) | 7 + 28 | 21 + 42 |
| S:L ratio (g L^{-1}) | 241 | 240.9 |
| pH | 6.3 | 7.7 |
| Nr. of measurements | 6 | 6 |

The conditioning of OPA (see section 3.3) showed that the Sr concentrations after the first equilibration time were the same in the conditioned OPA suspension and the synthetic OPA porewaters (SOPW1 and SOPW2). Further conditioning did not change the Sr concentrations indicating that saturation with celestite was maintained.

Table 22: Sorption data of Sr on OPA at pH = 6.3 and pH = 7.7.

| pH | Equilibration time (weeks) | R_d (L kg ⁻¹) |
|-----|-------------------------------|--------------------------------|
| 6.3 | 1 | 1.68 |
| 6.3 | 1 | 1.67 |
| 6.3 | 1 | 1.66 |
| 6.3 | 4 | 1.60 |
| 6.3 | 4 | 1.55 |
| 6.3 | 4 | 1.61 |
| 7.7 | 3 | 1.26 |
| 7.7 | 3 | 1.31 |
| 7.7 | 3 | 1.31 |
| 7.7 | 6 | 1.28 |
| 7.7 | 6 | 1.31 |
| 7.7 | 6 | 1.24 |

The physico-chemical characteristics of this OPA sample have been determined in Chapter 2 and the specific data for cation exchange capacities and selectivity coefficients (K_c values) are available and are given in Tables 8 and 9.

From the physico-chemical analysis it was not possible to determine the selectivity coefficient for Sr-Na exchange independently because the Sr concentrations were too low. However, the cation exchange behaviour of Ca and Sr are very similar and the same value can be taken for their selectivity coefficients (see for example BRUGGENWERT & KAMPHORST 1982). Note also in this context that BAEYENS (1982) measured a Ca-Sr selectivity coefficient of unity on Boom clay.

Using the selectivity coefficient data (Table 9) an R_d value of 0.65 and 0.41 L kg⁻¹ for Sr was calculated for the OPA system at pH = 6.3 and 7.7 respectively. The calculated values are small and are lower by a factor 2 to 3 compared to the experimental data. A possible hypothesis for this behaviour is that in the Sr sorption measurements, in addition to the cation exchange, the active Sr has isotopically exchanged with celestite resulting in higher R_d values.

3.7 Ni Sorption Data

3.7.1 Background Ni

Acid extractions were carried out on the OPA at pH 5.5, 3.3 and 0.5 (see section 2.3.7). In addition a total rock inventory was determined from ICP-MS measurements (see section 2.3.5). The extracted quantities of Ni from the above tests were 10^{-5} mol kg^{-1} (pH = 5.5), 9×10^{-5} mol kg^{-1} (pH = 3.3), 2.5×10^{-4} mol kg^{-1} (pH ~ 0.5) and 1.2×10^{-3} mol kg^{-1} (whole rock inventory). The acid extraction data for Ni show a clear trend in that at decreasing pH an increased quantity of Ni is obtained. From the above data it is however not possible to associate the Ni inventory which is available for sorption. At pH = 5.5 probably not all of the Ni has desorbed from the OPA. The Ni extracted at pH ~ 0.5 or the whole rock inventory is likely to come from sorbed Ni but also from Ni containing solid phases which have been dissolved. In the evaluation of the isotherms below, it is assumed that the Ni extracted at pH = 3.3 is available for sorption.

Similar as in the case for Cs, see section 3.5.1, the conditioning procedure has increased the sorbed Ni on the OPA rock. Using the data for Ni as given in Table 17, and a S:L ratio of 0.011 kg L^{-1} (0.1 kg rock was equilibrated with 9.0 L SOPW1), the quantity of Ni sorbed can be calculated from equation (8) and is equal to 3.3×10^{-5} mol kg^{-1} . In the calculation of the isotherms a similar mass balance equation is used as in the case for Cs, see equation (13), with I_{Ni} equal to 1.23×10^{-4} mol kg^{-1} .

3.7.2 Ni Kinetics and Isotherm Results

Two sets of sorption kinetic tests were performed at pH = 6.3 at initial Ni concentrations of 3.7×10^{-7} and 9.2×10^{-4} M. The sorption isotherm experiments were carried out approximately between these two concentration limits (upper limit of 8.7×10^{-5} M at pH = 7.8). The experimental conditions are listed in Table 23 and the measured data are given in Figures 9 to 11.

Table 23: Experimental conditions for the Ni sorption kinetic and sorption isotherm measurements on conditioned OPA batch 1 (pH = 6.3, I = 0.3 M) and sorption isotherm measurements on conditioned OPA batch 4 (pH = 7.8, I = 0.39 M).

| Experimental Conditions | Figure 9 (kinetic measurements) | Figure 10 (isotherm measurements) | Figure 11 (isotherm measurements) |
|--|---------------------------------|-----------------------------------|-----------------------------------|
| Initial Ni concentration (M) ¹⁾ | 3.7 E-7 and 9.2 E-4 | 3.4 E-7 to 8.6 E-4 | 3.4 E-7 to 8.7 E-5 |
| Equilibration time (days) | 7 - 220 | 28 | 28 |
| S:L ratio (g L ⁻¹) | 5.97 | 13.64 | 14.27 |
| pH | 6.3 | 6.3 | 7.8 |
| Nr. of measurements | 32 | 34 | 28 |

1) The Ni background concentration is taken into account.

The uptake of Ni at pH = 6.3 and trace concentrations was complete after ~ 1 week whereas at high concentrations (~ 10⁻³ M) the sorption increased slightly within the observation time of 6 months. Nevertheless the equilibration times for sorption isotherm experiments both at trace and high Ni concentrations were fixed at one month. The same equilibration time was taken for sorption isotherm experiments at pH = 7.8.

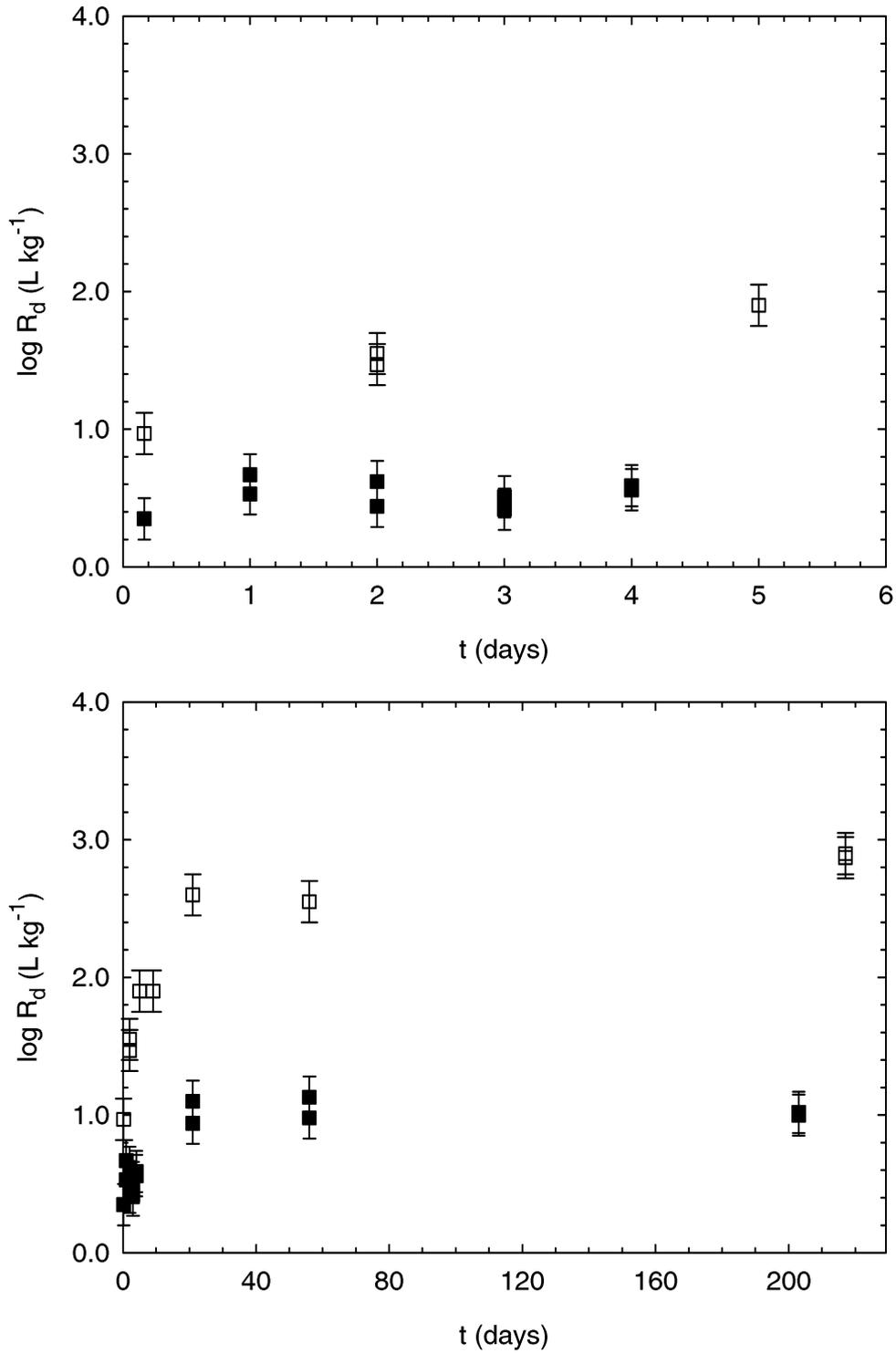


Figure 9: Ni sorption kinetic data on conditioned OPA at pH = 6.3 and $[\text{Ni}]_{\text{tot}} = 3.7 \times 10^{-7} \text{ M}$ (\square) and $[\text{Ni}]_{\text{tot}} = 9.2 \times 10^{-4} \text{ M}$ (\blacksquare). Short and long term-kinetics.

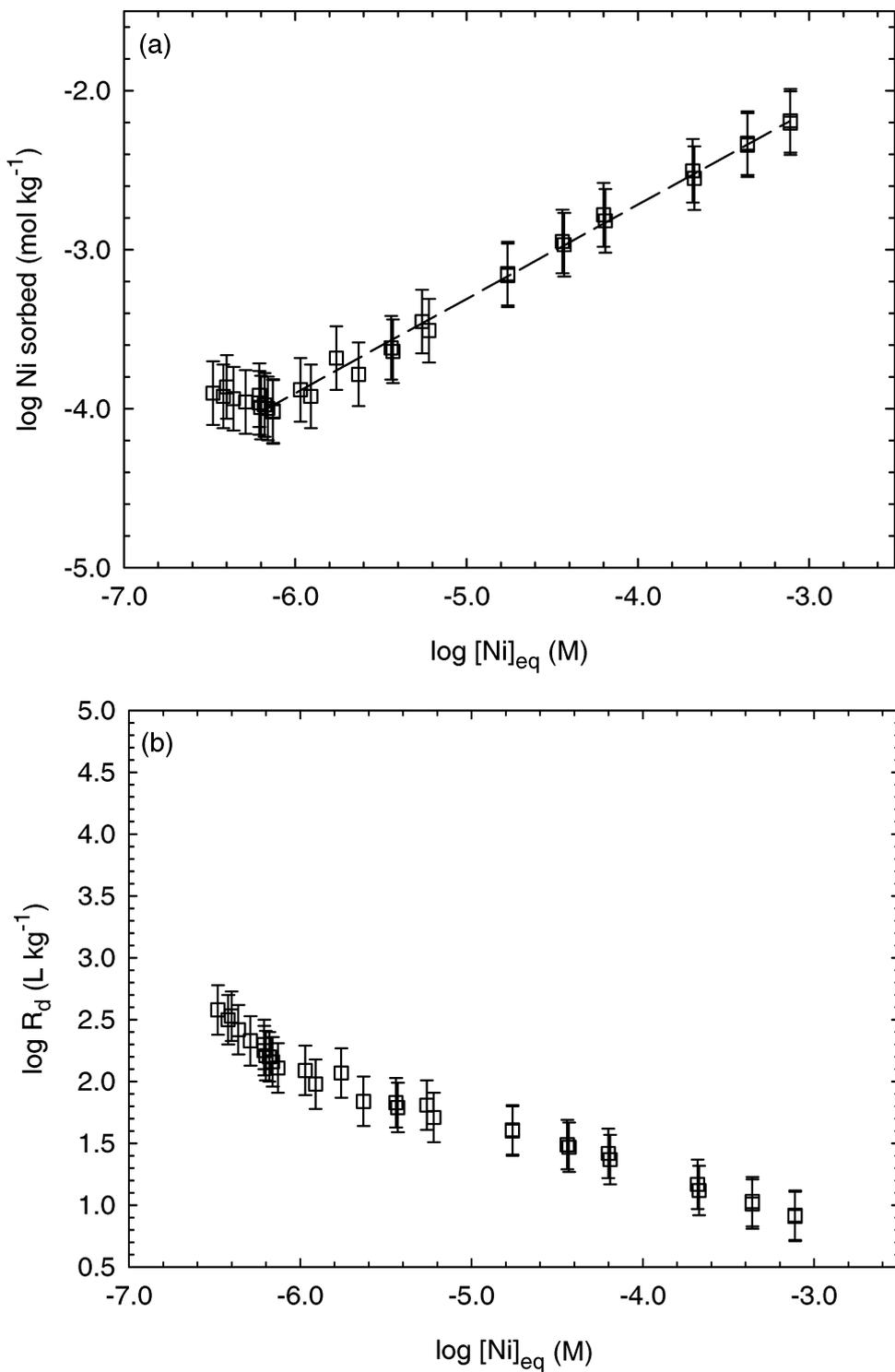


Figure 10: Ni sorption isotherm data on conditioned OPA at pH = 6.3.

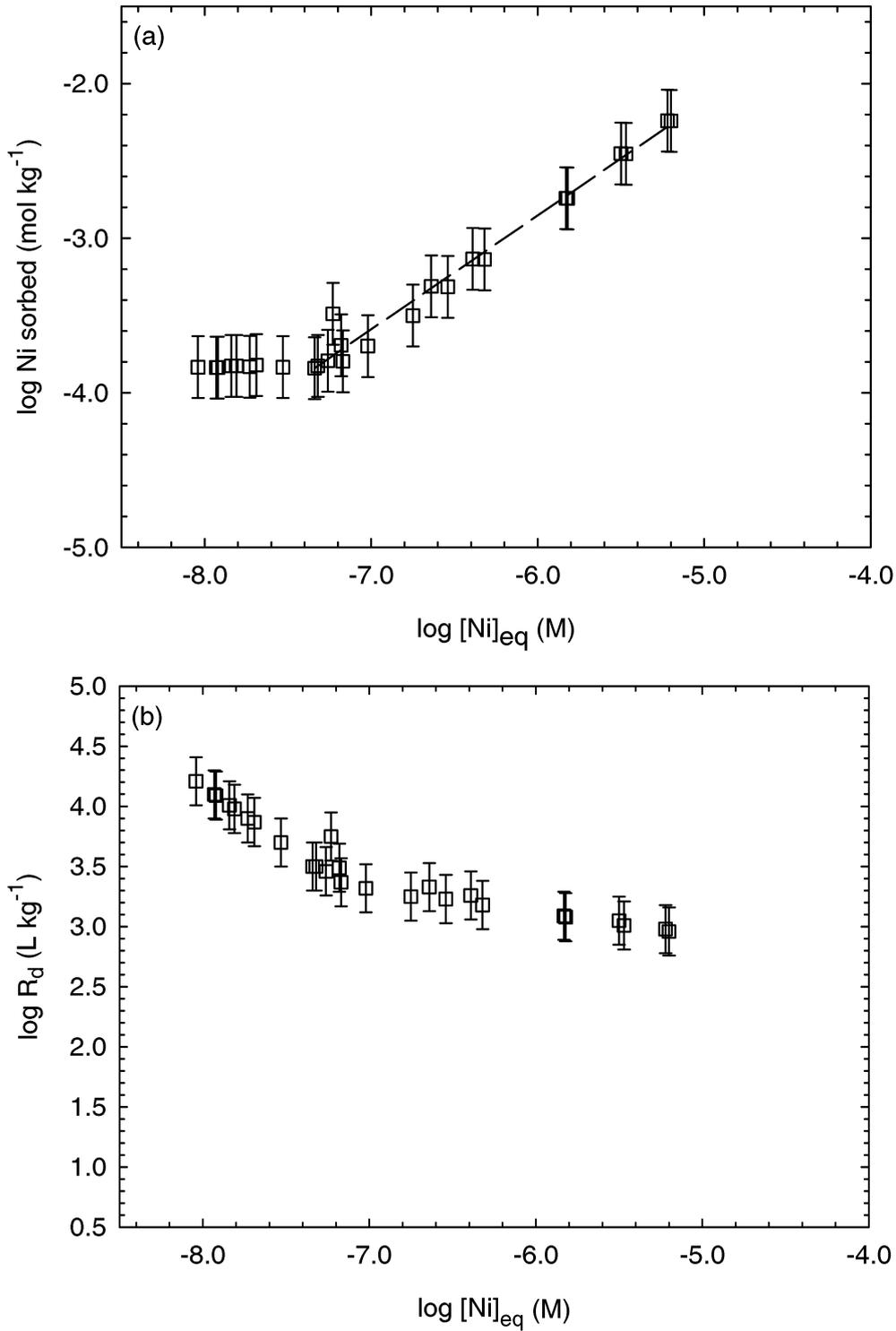


Figure 11: Ni sorption isotherm data on conditioned OPA at pH = 7.8.

The Ni sorption isotherms at pH = 6.3 and 7.8 show a behaviour which is very reminiscent to the sorption isotherms of Zn on Na-montmorillonite (see Figures 9 and 10 in BRADBURY & BAEYENS 1997b) and on Ca-montmorillonite (see Figures 2 and 3 in BRADBURY & BAEYENS 1999).

The isotherms of Ni on OPA show clearly 2 regions. In the Ni equilibrium concentration range of $\sim 10^{-6.4}$ to $10^{-6.2}$ M (Figure 10) and $\sim 10^{-8.0}$ to $10^{-7.5}$ M (Figure 11) the quantities of Ni sorbed on OPA remain essentially constant. This lead to a highly non-linear sorption region for these concentration ranges. This is well illustrated in the log R_d versus Ni equilibrium concentration plots (Figures 10b and 11b).

The explanation put forward in BRADBURY & BAEYENS (1999) for this behaviour is that the sorption is taking place on strong and weak sites. The Ni inventory present on the OPA has already saturated the strong sites and up to the concentration of $10^{-6.0}$ M at pH = 6.3 (Figure 10) and $10^{-7.3}$ M at pH = 7.8 (Figure 11) an inverse concentration dependency of R_d is observed. At higher concentrations sorption of Ni start taking place on lower affinity sites resulting in a much less non-linear Freundlich type isotherm. For this part of the isotherm, the Freundlich parameters are calculated in Table 24 and are shown by dashed lines in Figures 10a and 11a.

Table 24: Freundlich parameters of Ni at pH = 6.3 and 7.8.

| pH | range of evaluation log $[Ni]_{eq}$ (M) | log a | b | r^2 |
|-----|--|---------------------|--------------------|-------|
| 6.3 | -6.2 to -3.1 | -0.35 (\pm 0.05) | 0.59 (\pm 0.01) | 0.994 |
| 7.8 | -7.3 to -5.2 | 1.57 (\pm 0.17) | 0.74 (\pm 0.03) | 0.980 |

Both at pH = 6.3 and 7.8 the parameter "b" is clearly < 1 which is an indication that sorption is non-linear.

A final comment to make regarding the Ni isotherms on OPA is that both sets of data indicate a pH dependent sorption behaviour. The sorption increases at increasing pH which is a strong indicator that a surface complexation mechanisms is present for the Ni uptake on OPA.

3.8 Eu Sorption Data

3.8.1 Background Eu

The total Eu inventory determined on the whole OPA rock material was $\sim 1.1 \times 10^{-5} \text{ mol kg}^{-1}$ (see Table 3). As in the case of Ni, most of this Eu inventory is likely not available for sorption. Acid extractions at pH = 0.5 and 3.3 yielded Eu contents in OPA of 5×10^{-6} and $4 \times 10^{-6} \text{ mol kg}^{-1}$, respectively (see Table 4). As in the case of Ni, the Eu content from the acid extraction at pH = 3.3 is considered in the evaluation of the isotherms presented below. The conditioning procedure has not significantly increased the quantity of Eu sorbed on OPA ($\sim 3.6 \times 10^{-8} \text{ mol kg}^{-1}$). The Eu equilibrium concentrations in the sorption measurements were therefore calculated using the mass balance equation (13) with $I_{\text{Eu}} = 4 \times 10^{-6} \text{ mol kg}^{-1}$.

3.8.2 Eu Kinetics and Isotherm Results

Sorption kinetic tests were performed at pH = 6.3 at an initial concentration of $4.7 \times 10^{-9} \text{ M}$. The sorption isotherm experiments were performed at both pH = 6.3 and 8 in the concentration range of $\sim 5 \times 10^{-9}$ and $\sim 10^{-6} \text{ M}$. Another series of experiments were carried out at constant initial Eu concentration of $\sim 10^{-6} \text{ M}$ with variable S:L ratios to increase the range of measurements to higher equilibrium concentrations (see section 3.4.5). Inactive sorption measurements were also performed in the latter experiments at a S:L ratio of 0.42 g L^{-1} . The initial and the equilibration Eu concentrations were measured by ICP-OES. The distribution coefficients R_d obtained from the inactive tests and from the active experiments are compared in Figures 13 and 14.

The experimental conditions of all experiments are listed in Table 25 and the measured data are given in Figures 12 to 14. The Freundlich parameters, calculated from the isotherms, are listed in Table 26.

Table 25: Experimental conditions for the Eu sorption kinetic and sorption isotherm measurements on conditioned OPA batch 1 and 2 (pH = 6.3, I = 0.3 M) and sorption isotherm measurements on conditioned OPA batch 4 (pH = 8, I = 0.39 M).

| Experimental Conditions | Figure 12 (kinetics) | Figure 13 (isotherm) | Figure 13 (isotherm) variable S:L ratio |
|--|----------------------|----------------------|---|
| Initial Eu concentration and concentration range (M) ¹⁾ | 4.7 E-9 | 9.8 E-9 to 7.1 E-7 | ~ 1.0 E-6 |
| Equilibration Time (days) | 7 - 210 | 28 | 14 |
| S:L ratio (g L ⁻¹) | 5.97 | 5.97 | 0.42 - 5.54 |
| pH | 6.3 | 6.3 | 6.3 |
| Nr. of measurements | 16 | 16 | 16 active + 2 inactive |

1) The Eu background concentration is taken into account.

| Experimental Conditions | Figure 14 (isotherm) | Figure 14 (isotherm) variable S:L ratio |
|--|----------------------|---|
| Initial Eu concentration and concentration range (M) ¹⁾ | 7.8 E-9 to 8.2 E-7 | ~ 9.0 E-7 |
| Equilibration Time (days) | 14 | 14 |
| S:L ratio (g L ⁻¹) | 3.22 | 0.42 - 5.54 |
| pH | 8.0 | 8.0 |
| Nr. of measurements | 16 | 16 active + 2 inactive |

1) The Eu background concentration is taken into account.

Table 26: Freundlich parameters of Eu at pH = 6.3 and 8.

| pH | range of evaluation log [Eu] _{eq} (M) | log a | b | r ² |
|-----|---|---------------|---------------|----------------|
| 6.3 | -9.2 to -6.2 | 1.93 (± 0.10) | 0.78 (± 0.01) | 0.991 |
| 8.0 | -10.1 to -6.9 | 2.71 (± 0.10) | 0.78 (± 0.01) | 0.993 |

The uptake of Eu at pH = 6.3 at trace concentration was complete after ~ 2 weeks equilibration time.

At pH = 6.3 and 8, within the concentration ranges under investigation (between 6.0×10^{-10} and 6.0×10^{-7} M at pH = 6.3, between 7.6×10^{-11} and 1.2×10^{-7} M at pH = 8), the sorption of Eu on OPA is non-linear. (The parameter "b" in Table 26 is below 1 for both pH values). The sorption of Eu on OPA is higher at pH = 8 than at pH = 6.3 which is an indication that surface complexation is the dominating sorption mechanism.

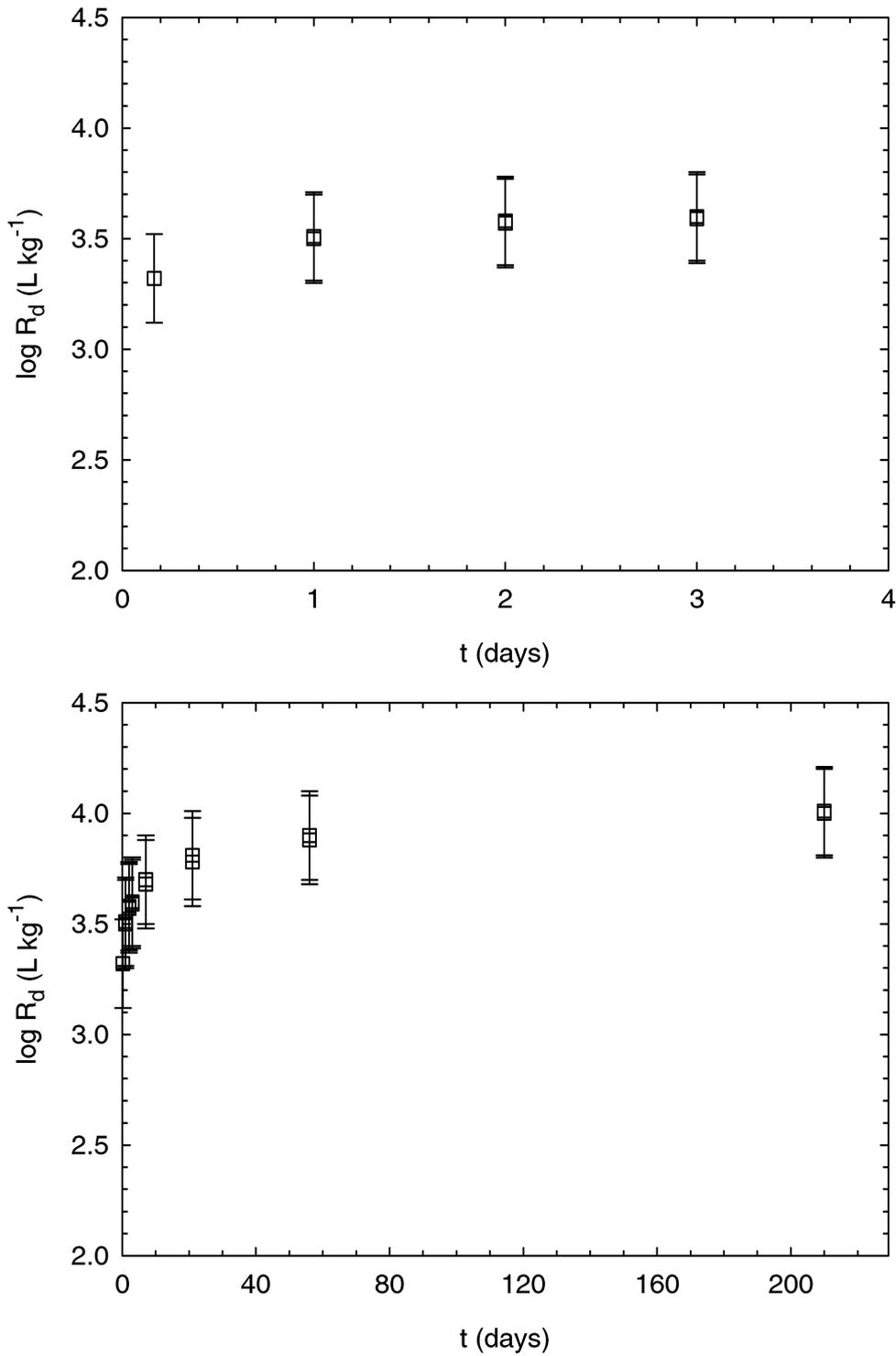


Figure 12: Eu sorption kinetic data on conditioned OPA at pH = 6.3 and $[\text{Eu}]_{\text{tot}} = 4.7 \times 10^{-9} \text{ M}$. Short and long-term kinetics.

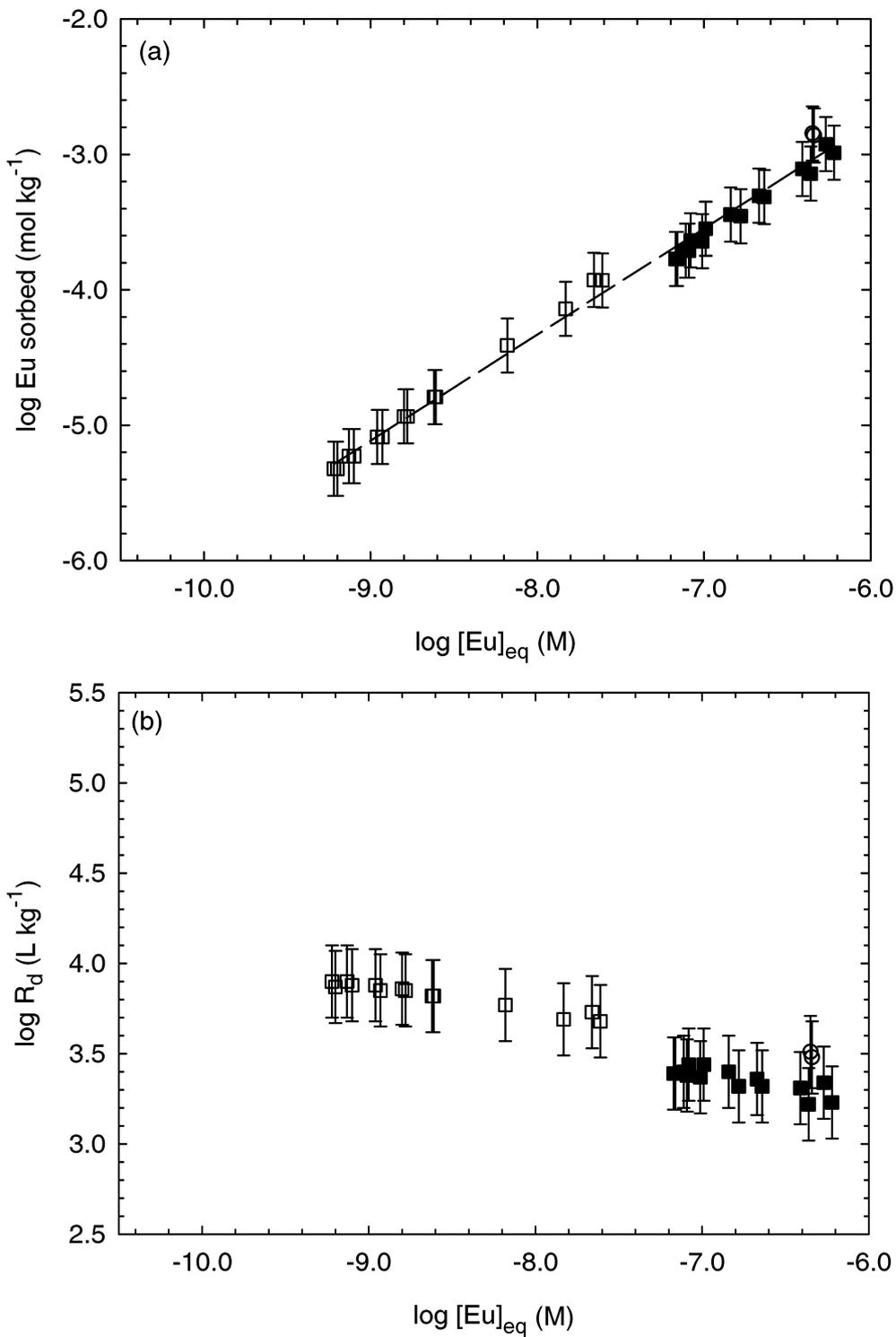


Figure 13: Eu sorption isotherm data on conditioned OPA at pH = 6.3. □ = data measured by Eu concentration variation. ■ = data measured by variation of the S:L ratio. ○ = inactive measurements.

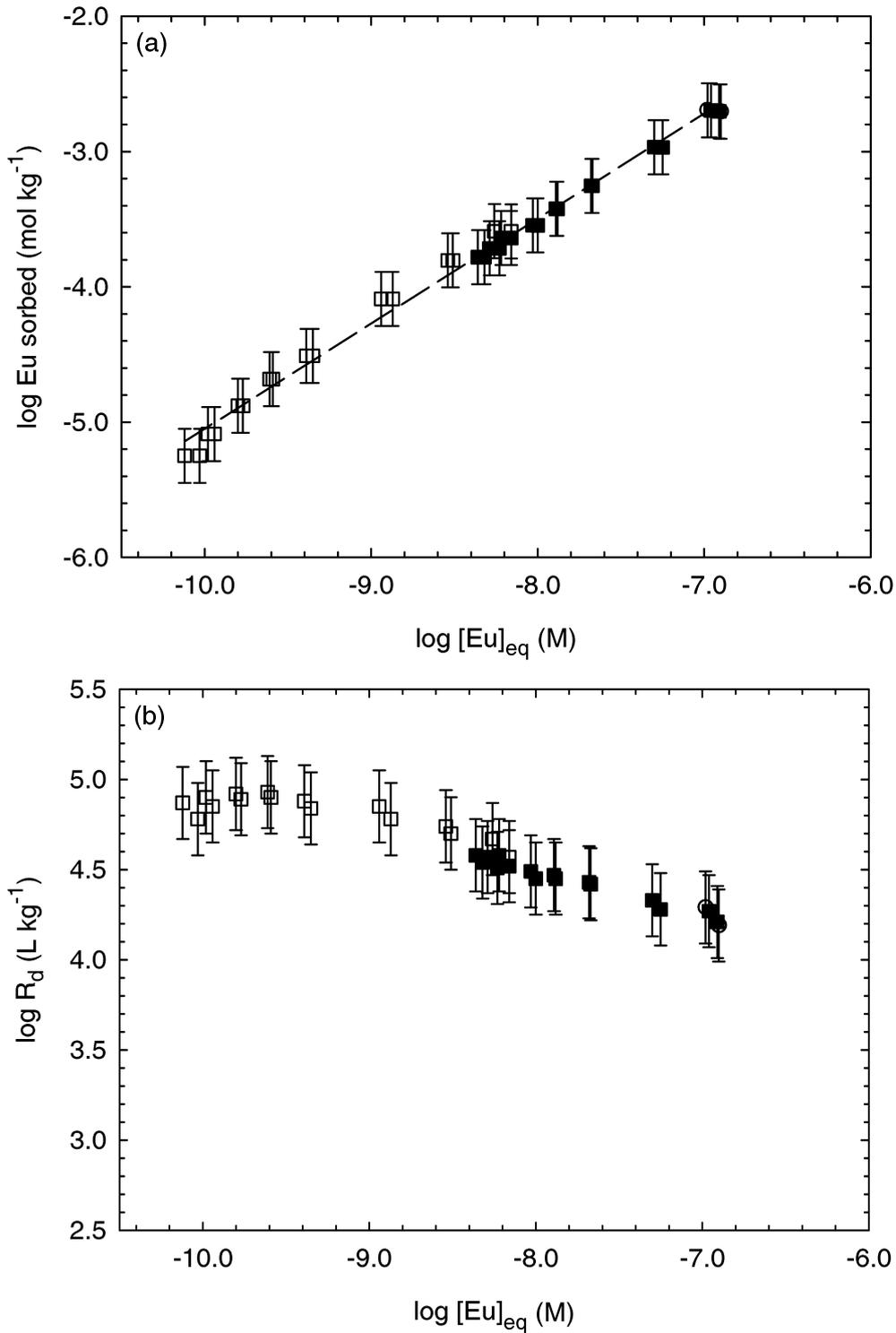


Figure 14: Eu sorption isotherm data on conditioned OPA at pH = 8.0. \square = data measured by Eu concentration variation. \blacksquare = data measured by variation of the S:L ratio. \circ = inactive measurements.

3.9 Th Sorption Data

3.9.1 Background Th

The Th background concentration measured in the conditioned OPA porewater (batch 1, pH = 6.3) was below the reliable detection limit of ICP-MS ($< 10^{-11}$ M, see Table 17). The acid extractions down to pH ~ 0.5 also did not yield any measurable Th. (It should however be noted that these analyses were carried out with ICP-OES where the Th detection limits are higher ($\sim 5 \times 10^{-8}$ M). Consequently no estimate of the Th inventory can be made and the Th equilibrium concentrations in the sorption isotherm measurements were calculated using equation (8) (see section 3.4.6).

3.9.2 Th Kinetics and Isotherm Results

The sorption kinetic tests and the sorption isotherm experiments were similar to those performed for Eu.

The experimental conditions are listed in Table 27 and the measured data are given in Figures 15 to 17. The Freundlich parameters, calculated from the isotherms, are listed in Table 28.

The uptake of Th at pH = 6.3 at an initial Th concentration of 6.7×10^{-11} M was rapid and complete after ~ 24 hours equilibration time.

Table 27: Experimental conditions for the Th sorption kinetic and sorption isotherm measurements on conditioned OPA batch 2 (pH = 6.3, I = 0.3 M) and sorption isotherm measurements on conditioned OPA batch 4 (pH = 8, I = 0.39 M).

| Experimental Conditions | Figure 15 (kinetics) | Figure 16 (isotherm) | Figure 16 (isotherm) variable S:L ratio |
|--|----------------------|----------------------|---|
| Initial Th concentration and concentration range (M) | 6.7 E-11 | 3.8 E-11 to 7.6 E-7 | ~ 8.0 E-7 |
| Equilibration Time (days) | 7 - 210 | 14 | 14 |
| S:L ratio | 5.97 | 6.28 | 0.42 - 5.54 |
| pH | 6.3 | 6.3 | 6.3 |
| Nr. of measurements | 14 | 16 | 16 active + 2 inactive |

| Experimental Conditions | Figure 17 (isotherm) | Figure 17 (isotherm) variable S:L ratio |
|--|----------------------|---|
| Initial Th concentration and concentration range (M) | 3.9 E-11 to 3.0 E-7 | ~ 8.0 E-7 |
| Equilibration Time (days) | 14 | 14 |
| S:L ratio (g L ⁻¹) | 3.22 | 0.42 - 5.54 |
| pH | 8.0 | 8.0 |
| Nr. of measurements | 28 | 16 active + 2 inactive |

Table 28: Freundlich parameters of Th at pH = 6.3 and 8.

| pH | range of evaluation log [Th] _{eq} (M) | log a | b | r ² |
|-----|---|---------------|---------------|----------------|
| 6.3 | -12.6 to -6.9 | 4.00 (± 0.06) | 0.96 (± 0.01) | 0.999 |
| 8.0 | -12.7 to -7.6 | 4.67 (± 0.08) | 0.99 (± 0.01) | 0.998 |

The active and inactive Th sorption tests at both pH = 6.3 and 8 were in good agreement.

At pH = 6.3 and 8, within the concentration ranges under investigation (between 2.5×10^{-13} and 1.3×10^{-7} M at pH = 6.3, between 1.8×10^{-13} and 2.8×10^{-8} M at pH = 8), the sorption of Th on OPA is linear, as the Freundlich parameter "b" of the isotherm is near to unity. The sorption of Th on OPA is generally high and pH dependent which is an indication that surface complexation is the dominating sorption mechanism.

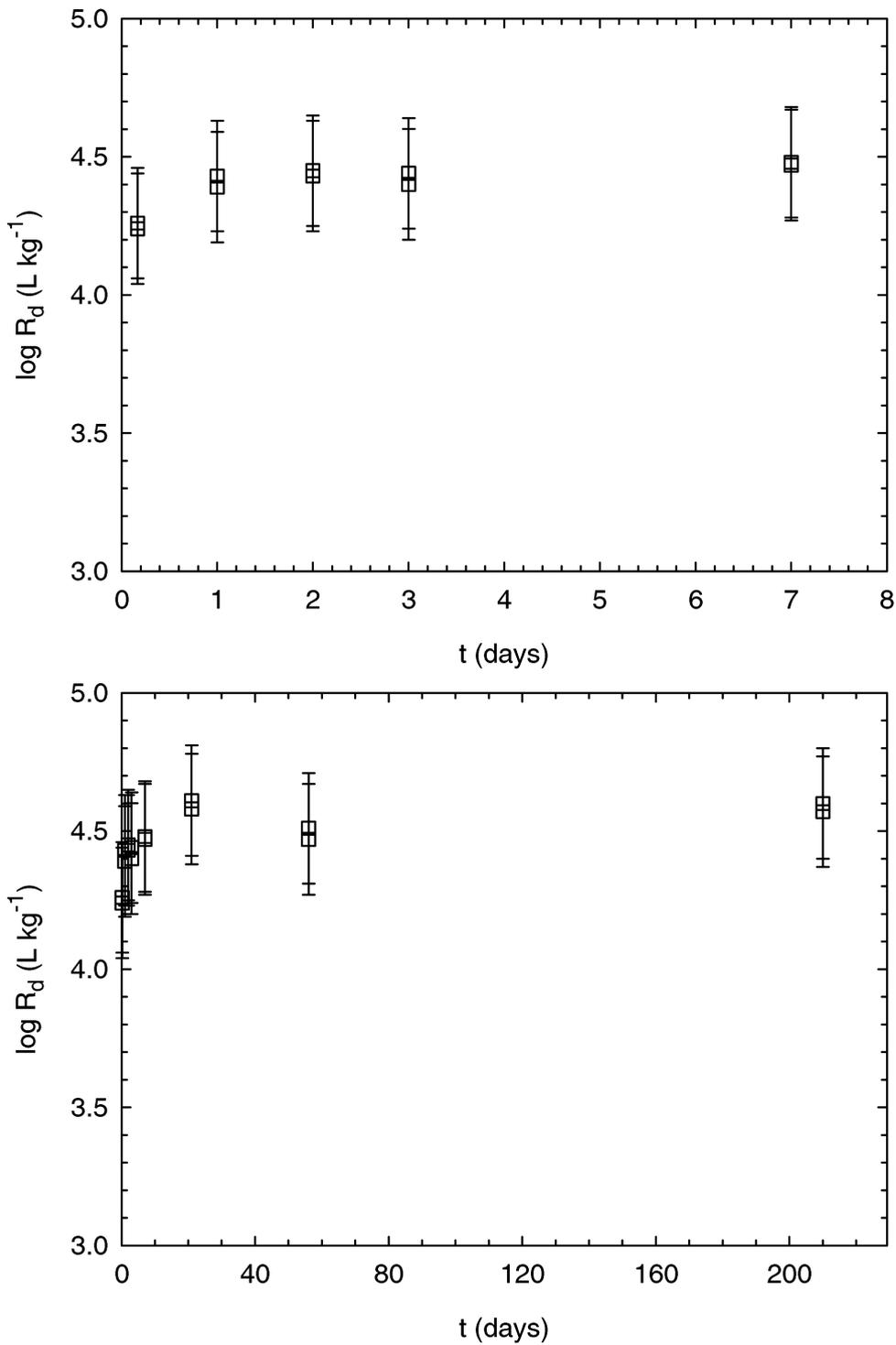


Figure 15: Th sorption kinetic data on conditioned OPA at pH = 6.3 and $[\text{Th}]_{\text{tot}} = 6.7 \times 10^{-11} \text{ M}$. Short and long-term kinetics.

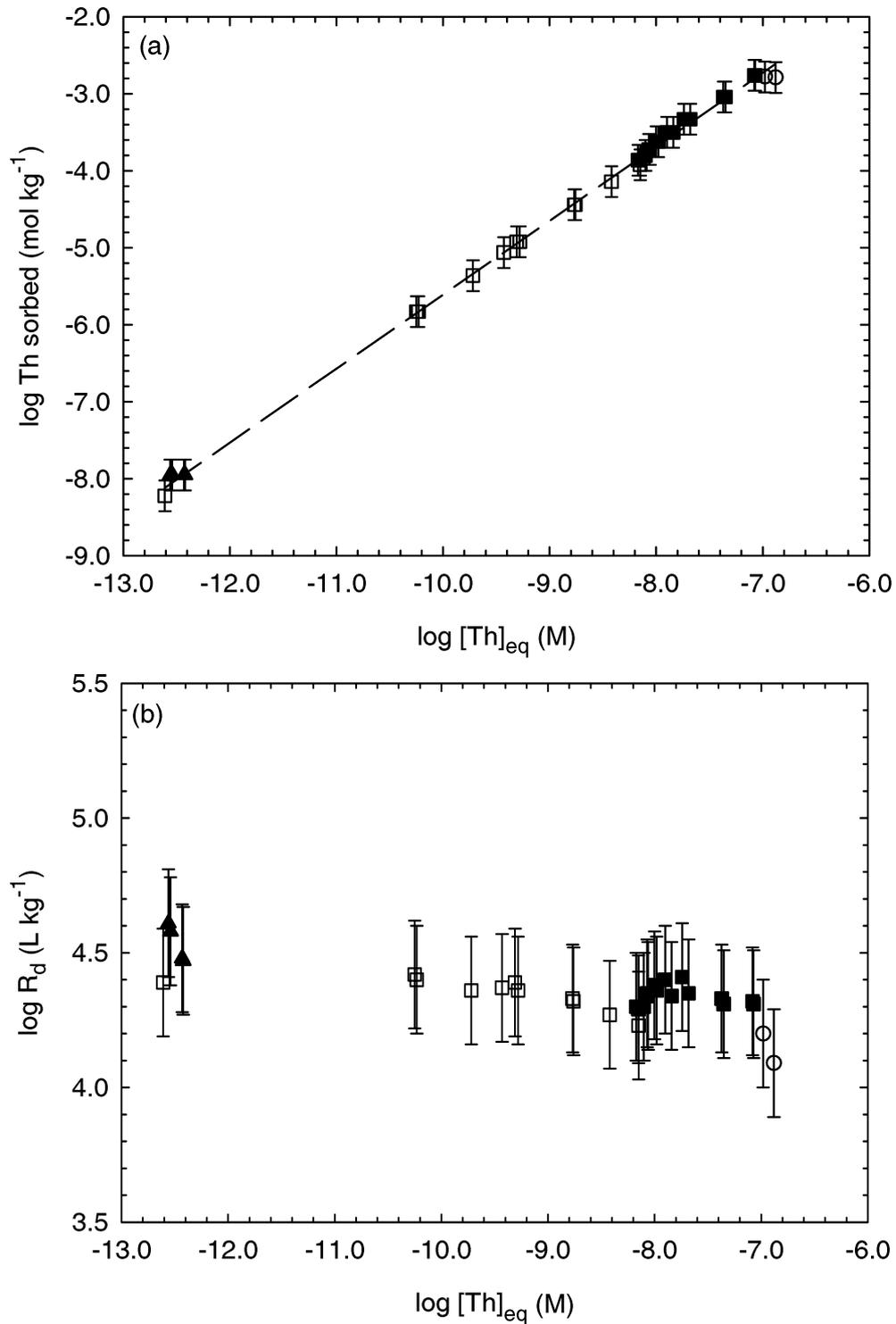


Figure 16: Th sorption isotherm data on conditioned OPA at pH = 6.3.
 □ = data measured by variation of the Th concentration. ■ = data measured by variation of the S:L ratio. ○ = inactive measurements.
 ▲ = data from kinetic measurements (one month equilibration time).

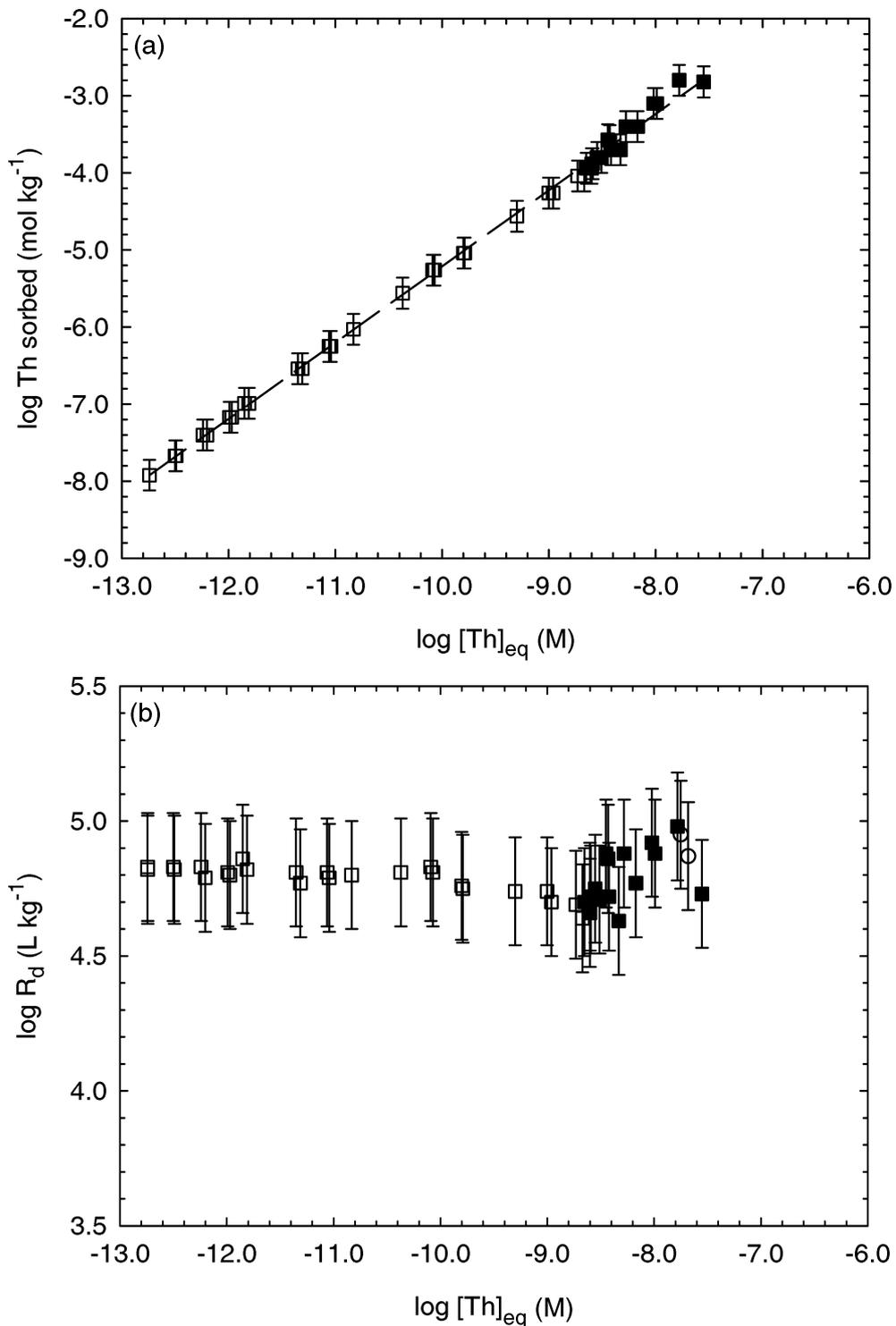


Figure 17: Th sorption isotherm data on conditioned OPA at pH = 8.0. \square = data measured by variation of the Th concentration. \blacksquare = data measured by variation of the S:L ratio. \circ = inactive measurements (pH = 8.7).

3.10 Sn(IV) Sorption Data

3.10.1 Background Sn

The stable Sn concentration in the conditioned OPA porewater (batch 1, pH = 6.3) is $\sim 3.8 \times 10^{-8}$ M (see Table 17). Solubility studies of Sn(IV) by AMAYA et al. (1997) show that the Sn solubility is in the range of ~ 3 to 6×10^{-8} M at pH = 6.3. The measured Sn concentration in the conditioned OPA porewater is well within the range of the solubility of Sn(IV). It is further anticipated that the conditioning procedure did not affect the Sn background concentration since the Sn concentration in the synthetic OPA porewater was $\sim 4.5 \times 10^{-8}$ M (Table 17). If the concentration of Sn in the OPA porewater is determined by the solubility of Sn(IV) oxide, no isotherm measurements can be made. Only single point R_d values can be determined for Sn on OPA. The concentration of the added active Sn tracer in the tests was $\sim 8 \times 10^{-9}$ M. This concentration was required in order to be able to measure the activities in the equilibrium solutions after sorption (see also section 3.4.2).

3.10.2 Sn(IV) Kinetics Results

Sorption kinetic tests were performed at pH = 6.3 at an initial Sn concentration of 5.3×10^{-8} M. Another series of sorption experiments was carried out at pH = 8.1 at similar concentration and for an equilibration time of 4 weeks. The experimental conditions are listed in Table 29 and the measured data are given in Figure 18 and Table 30.

Table 29: Experimental conditions for the Sn sorption kinetic measurements on conditioned OPA batch 3 (pH = 6.3, I = 0.3 M) and sorption measurements on conditioned OPA batch 4 (pH = 8.1, I = 0.39 M).

| Experimental Conditions | Figure 18 (kinetics) | measurements at pH = 8.1 |
|--------------------------------|----------------------|--------------------------|
| Sn initial concentration (M) | 5.3 E-8 | 5.3 E-8 |
| Equilibration time (days) | 7 - 49 | 28 |
| S:L ratio (g L ⁻¹) | 0.36 | 0.36 |
| pH | 6.3 | 8.1 |
| Nr. of measurements | 20 | 6 |

The uptake of Sn at pH = 6.3 at trace concentration was complete after ~ 1 week equilibration time.

At both pH = 6.3 and 8.1 the sorption of Sn on OPA (at trace concentration) is high. The distribution coefficients R_d at pH = 6.3 and 8.1 are approximately equal, i.e. $\log R_d \sim 5.0 (\pm 0.1)$ and $\sim 5.2 (\pm 0.1)$ L kg⁻¹ at pH = 6.3 and 8.1 respectively.

Table 30: Sorption data of Sn on OPA at pH = 8.1 (I = 0.39 M, $[\text{Sn}]_{\text{tot}} = 5.3 \times 10^{-8}$ M).

| pH | Equilibration time (days) | $\log R_d$ (L kg ⁻¹) |
|-----|---------------------------|-------------------------------------|
| 8.1 | 28 | 5.27 (± 0.04) |
| 8.1 | 28 | 4.97 (± 0.03) |
| 8.1 | 28 | 5.21 (± 0.04) |
| 8.1 | 28 | 5.27 (± 0.04) |
| 8.1 | 28 | 5.13 (± 0.04) |
| 8.1 | 28 | 5.13 (± 0.04) |

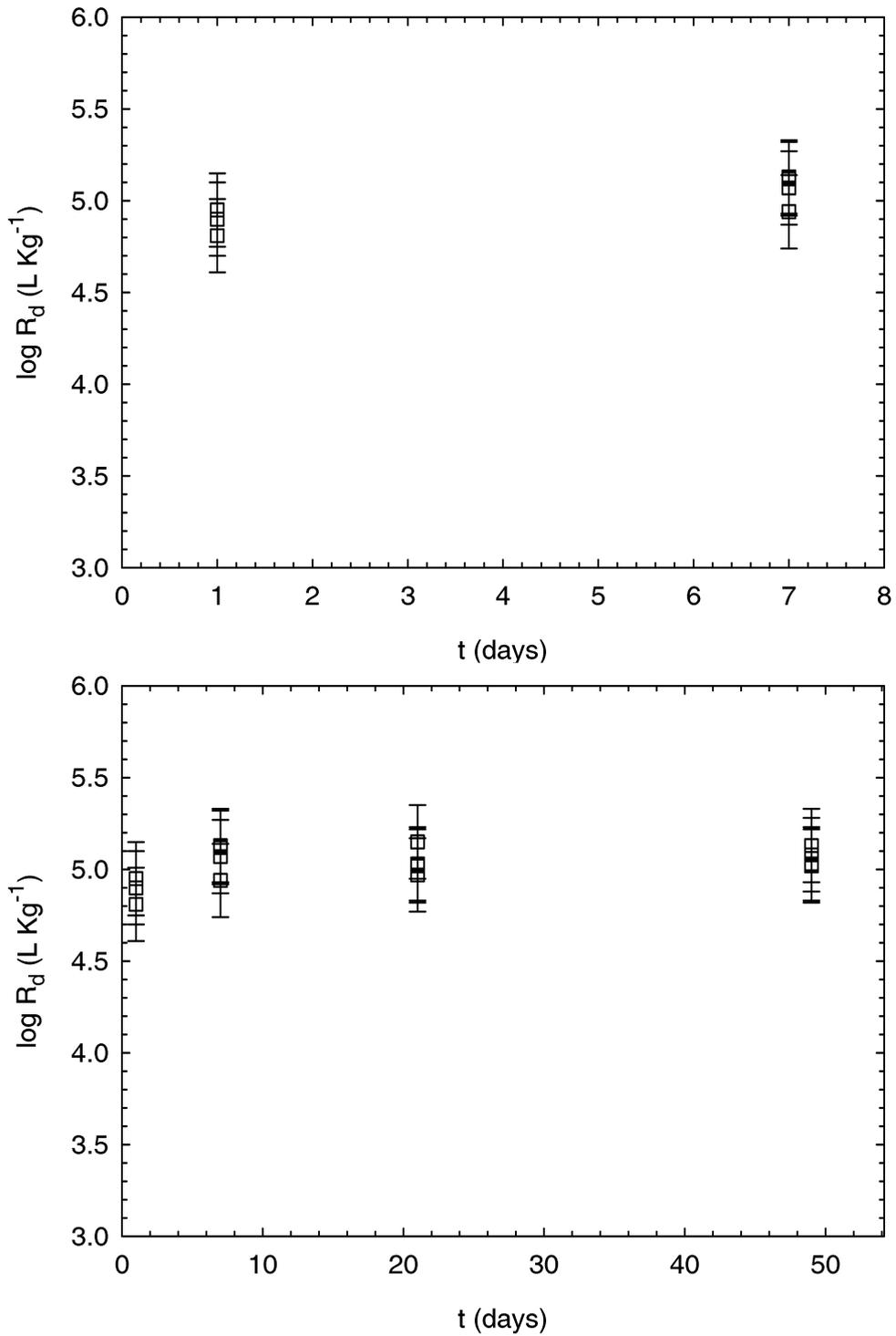


Figure 18: Sn sorption kinetic data on conditioned OPA at $\text{pH} = 6.3$ and $[\text{Sn}]_{\text{tot}} = 5.3 \times 10^{-8} \text{ M}$. Short and long-term kinetics.

3.11 Se(IV) Sorption Data

No background concentrations and no inventory data for the OPA were available. The Se equilibrium concentrations were therefore calculated using equation (8).

3.11.1 Se(IV) Kinetics and Isotherm Results

Sorption kinetic experiments were performed at pH = 6.3 at an initial concentration of 5.4×10^{-9} M. The sorption isotherm experiments were performed at both pH = 6.3 and 7.8 between $\sim 6 \times 10^{-9}$ M and $\sim 10^{-3}$ M. The experimental conditions are listed in Table 31 and the measured data are given in Figures 19 to 21. The Freundlich parameters, calculated from the isotherms are listed in Table 32.

Table 31: Experimental conditions for the Se sorption kinetic and sorption isotherm measurements on conditioned OPA batch 3 (pH = 6.3, I = 0.3 M) and sorption isotherm measurements on conditioned OPA batch 4 (pH = 7.8, I = 0.39 M).

| Experimental Conditions | Figure 19 (kinetic measurements) | Figure 20 (isotherm) | Figure 21 (isotherm) |
|--|----------------------------------|----------------------|----------------------|
| Initial Se concentration and concentration range (M) | 5.4 E-9 | 6.3 E-9 to 9.0 E-4 | 5.7 E-9 to 8.3 E-4 |
| Equilibration time (days) | 7 - 56 | 28 | 28 |
| S:L ratio (g L ⁻¹) | 6.28 | 12.15 | 14.27 + 21.02 |
| pH | 6.3 | 6.3 | 7.8 |
| Nr. of measurements | 14 | 34 | 34 |

Table 32: Freundlich parameters of Se at pH = 6.3 and 7.8.

| pH | range of evaluation log [Se] _{eq} (M) | log a | b | r ² |
|-----|---|----------------|---------------|----------------|
| 6.3 | -8.5 to -7.4 | 1.71 (± 0.51) | 0.97 (± 0.06) | 0.966 |
| | -6.9 to -3.1 | -0.53 (± 0.04) | 0.64 (± 0.01) | 0.996 |
| 7.8 | -9.1 to -6.6 | 3.18 (± 0.09) | 1.09 (± 0.01) | 0.998 |
| | -6.2 to -3.1 | -1.52 (± 0.06) | 0.32 (± 0.01) | 0.979 |

The uptake of Se at pH = 6.3 and 7.8 at trace concentration were complete after ~ 1 month equilibration time.

Within the concentration ranges under investigation (between 2.9×10^{-9} and 8.7×10^{-4} M at pH = 6.3, between 8.5×10^{-10} and 7.9×10^{-4} M at pH = 7.8) the sorption of Se(IV) on OPA at pH = 6.3 and 7.8 is non-linear. Below $\sim 4.0 \times 10^{-8}$ M at pH = 6.3 and below $\sim 2.5 \times 10^{-7}$ M at pH = 7.8 the sorption shows a linear behaviour. (It must be pointed out that no background concentrations and no inventory in OPA were available for Se, so that the linear sorption behaviour at low Se concentrations could be an artefact.)

The sorption of Se(IV) on pure minerals such as hydrous ferric oxides (DZOMBAK & MOREL 1990) is well understood and interpreted via a ligand exchange mechanism. According to such a mechanism the sorption of Se(IV) is pH dependent and increases at decreasing pH. The sorption of Se(IV) on OPA is slightly higher at pH = 7.8 than at 6.3. The redox measurements of OPA suspensions and porewaters (see section 2.3.5) have shown that under the sorption conditions at pH = 6.3 and 7.8 both Se(IV) (HSeO_3^- and SeO_3^{2-}) and Se(0) could be present in the system. This could explain the observed peculiar pH dependency.

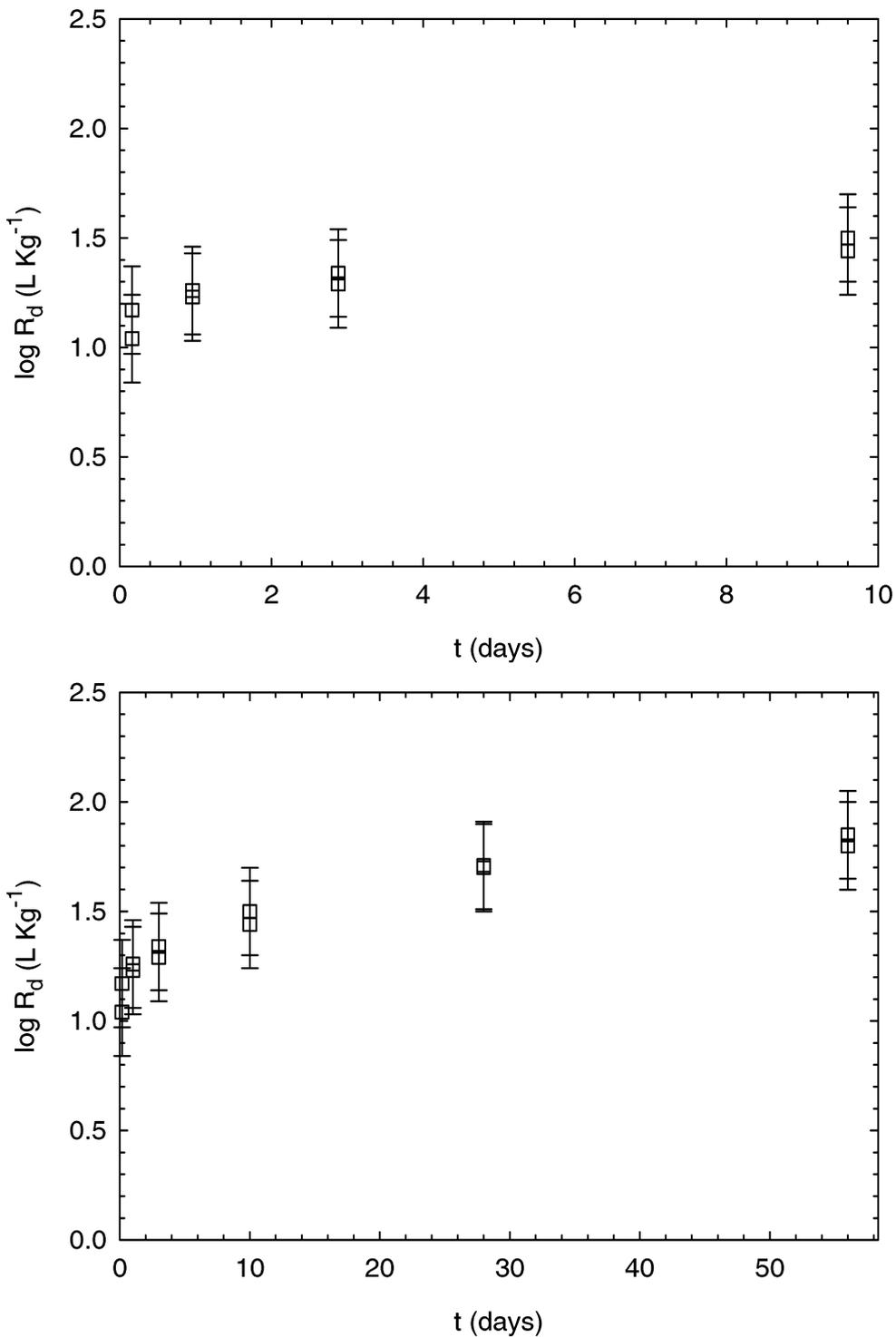


Figure 19: Se sorption kinetic data on conditioned OPA at pH = 6.3 and $[\text{Se}]_{\text{tot}} = 5.4 \times 10^{-9} \text{ M}$. Short and long-term kinetics.

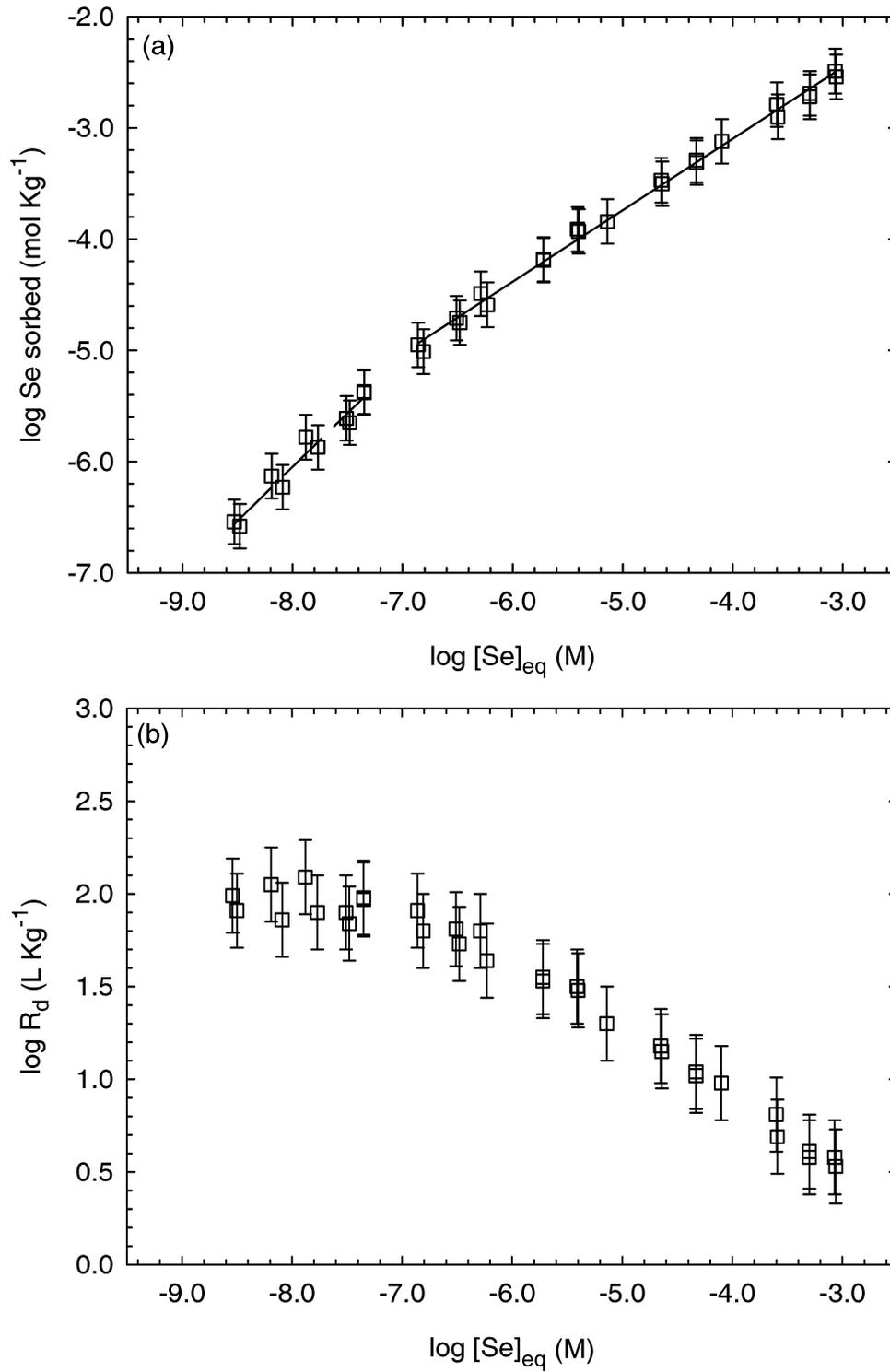


Figure 20: Se sorption isotherm data on conditioned OPA at pH = 6.3.

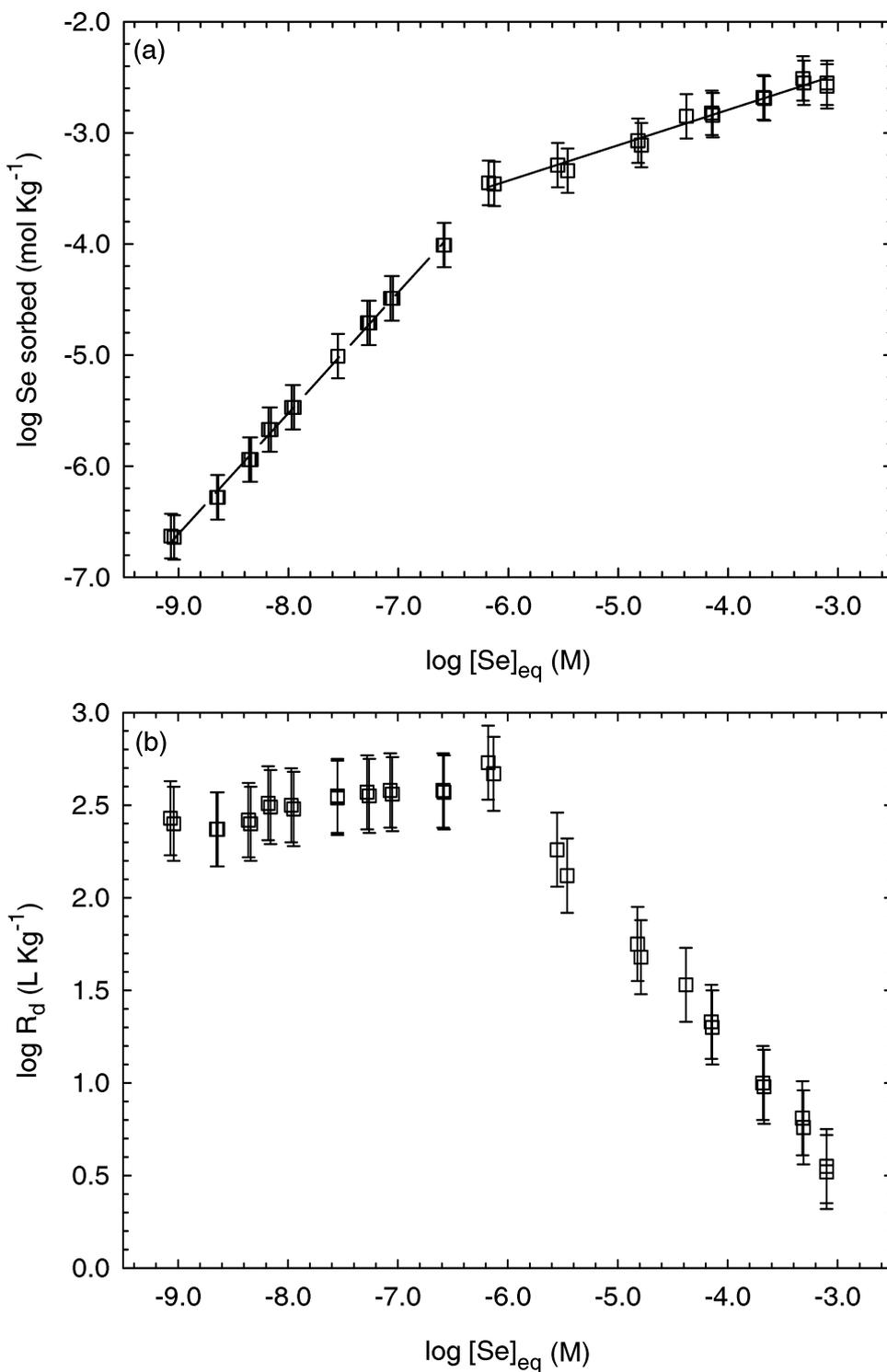


Figure 21: Se sorption isotherm data on conditioned OPA at pH = 7.8.

4 SUMMARY AND CONCLUSIONS

The main focus of this work was to perform sorption studies of key radionuclides on Opalinus Clay (OPA). The data obtained from these studies are required in performance assessment studies for radioactive waste disposal sites situated in such a formation.

In the first part of this work the physico-chemical characteristics of the OPA core sample used in this work (BGP-1-C11) were studied. The aim was to check whether this core sample had similar physico-chemical characteristics to another one (BWS-A1-C12) which was previously used to derive OPA porewater compositions. A comparison of the physico-chemical characteristics of both bore core samples revealed that the mineralogy, the sulphate and chloride inventories and the CEC are very similar. The selectivity coefficients (used to calculate the porewater compositions) for K-Na, Mg-Na and Ca-Na exchange equilibria derived from aqueous and Ni-en extraction data are comparable.

From these results it was concluded that the porewater compositions derived in the earlier studies on Mont Terri OPA samples are reliable. However, in this studies siderite was not taken into account. During the conditioning procedure of core sample BGP-1-C11 Fe was released into solution through the dissolution of siderite. In future sorption studies on OPA this mineral should be considered.

In the second part of this work batch sorption experiments of seven relevant radionuclides (Cs, Sr, Ni, Eu, Th, Se and Sn) were carried out on conditioned OPA at pH values of 6.3 and ~ 8. (These nuclides are representative for alkaline, alkaline earth and transition metals, trivalent lanthanides and actinides, and tetravalent actinides respectively. Se and Sn were chosen because they are important fission products.)

The batch sorption measurements were carried out as a function of time (pH = 6.3) and nuclide concentration (pH = 6.3 and ~ 8). The role of background elements in the sorption experiments performed at low concentrations has been shown. Particularly for Cs and Ni the lowest equilibrium concentration in the isotherm experiments was entirely fixed by the natural background concentration. In sorption experiments carried out on natural systems it is important to determine the inventory of the elements (used in the sorption experiments) present at trace levels in the rock and to determine their concentration in the liquid phase.

The primary goal of the sorption isotherms measurements was to elaborate a sorption data base for Opalinus Clay. In addition the data measured in this study are regarded as key data sets which will be used later as a basis for testing the prediction of the mechanistic sorption models in a natural system.

5 ACKNOWLEDGEMENTS

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