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Two cation exchange models for direct and inverse modelling of solution major cation composition in equilibrium with illite surfaces.

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Christophe Tournassat*, H el ene Gailhanou, Catherine Crouzet, Gilles Braibant, Anne Gautier,
Arnault Lassin, Philippe Blanc, Eric C. Gaucher

BRGM, French Geological Survey, Environment and Process Department, 3 Av. Claude
Guillemin, BP 6009, 45060 Orl eans Cedex 2, France

* Corresponding author: c.tournassat@brgm.fr

BRGM, EPI/DES

3 Av. Claude Guillemin

BP 6009, 45060 Orl eans Cedex 2, France

Tel: +33 2 38 64 47 44

Fax: +33 2 38 64 30 62

Abstract

Na-K, Na-Ca and Na-Mg exchange isotherms were performed on the fine fraction ($< 2 \mu\text{m}$) of Imt-2 illite samples at a total normality of about 0.005 mol/L in anionic chloride medium. The derived selectivity coefficients for Na-K, Na-Ca and Na-Mg were found to vary as a function of the exchanger composition and compared well with the data collected in the literature for similar experimental conditions. Two models were built to reproduce the data: the first was a multi(2)-site model with constant Gaines and Thomas selectivity coefficients; the second was a one-site model taking into account surface species activity coefficients.

The results of the models were in rather good agreement with both our data and literature data. The multi-site model proved to be efficient in predicting the exchanger composition as a function of the Na-Ca-Mg-K concentrations in solution, whereas the one-site model proved to be a better approach to derive the Na-Ca-Mg-K concentrations in solution based on the knowledge of the exchanger composition and the total normality of the solution. The interest of this approach is illustrated by the need for major cation solute concentration predictions in compacted clay for the characterization of nuclear deep disposal host rock repositories.

Introduction

The objective of the present study was to provide an up-to-date cation exchange constant database for Na, K, Ca and Mg on illite surfaces. Cation exchange databases are easily found in chemical reaction databases provided with speciation calculation codes, such as PHREEQC2 (PARKHURST and APPELO, 1999). However, (i) these databases contain no or few references to published results and (ii) the tabulated selectivity coefficients should be considered for montmorillonite only.

Knowledge of reliable cation exchange selectivity coefficients for major cations on illite is of importance in the context of nuclear waste deep disposal studies in order to simulate the porewater solute composition. The exchanger composition provides information about the relative amount of Na^+ , K^+ , Ca^{2+} , Mg^{2+} in solution:



where X^- represents one mole of the exchanger. The exchanger composition, an easily measurable parameter in compacted clayey rocks, is then an “image” of the porewater major cation composition, which cannot be directly characterized by water extraction and concentration measurements due to the low water content of these rocks (BRADBURY and BAEYENS, 1998; PEARSON et al., 2003; GAUCHER et al., Accepted). The following calculation shows how to obtain the Na^+ concentration assuming that (i) the exchanger composition is

known, (ii) the sum of the equivalent concentrations of Na^+ , K^+ , Ca^{2+} , Mg^{2+} is equal to the sum of the equivalent concentrations of Cl^- and SO_4^{2-} (i.e. neglecting H^+ and other minor cation contributions) and (iii) the exchange selectivity coefficients are known.

In the following, the Gaines and Thomas convention is used to express the equilibrium equation with the exchanger phase (e.g. SPOSITO, 1981). According to this convention, the activity of an exchanged species is equal to the equivalent fraction occupied by the cation on the exchanger phase, times an activity coefficient. This activity coefficient is here set equal to 1 for the analysis that follows (Eqs. 1 to 8).

Exchange reaction equilibria then lead to the following equations:

$$K_{ex}^{Na/Mg} = \frac{\{Na^+\}^2}{\{Mg^{2+}\}} \times \frac{E_{MgX_2}}{E_{NaX}^2} \quad \text{Eq. 1}$$

$$K_{ex}^{Na/Ca} = \frac{\{Na^+\}^2}{\{Ca^{2+}\}} \times \frac{E_{CaX_2}}{E_{NaX}^2} \quad \text{Eq. 2}$$

$$K_{ex}^{Na/K} = \frac{\{Na^+\}}{\{K^+\}} \times \frac{E_{KX}}{E_{NaX}} \quad \text{Eq. 3}$$

where values in brackets are representative of species activities and E_i is representative of the equivalent fraction on the exchanger of surface species i . The concentrations of each solution species as a function of the Na^+ concentration are then:

$$[Mg^{2+}] = \frac{\gamma_{Na^+}^2}{\gamma_{Mg^{2+}}} \times \frac{[Na^+]^2}{K_{ex}^{Na/Mg}} \times \frac{E_{MgX_2}}{E_{NaX}^2} \quad \text{Eq. 4}$$

$$[Ca^{2+}] = \frac{\gamma_{Na^+}^2}{\gamma_{Ca^{2+}}} \times \frac{[Na^+]^2}{K_{ex}^{Na/Ca}} \times \frac{E_{CaX_2}}{E_{NaX}^2} \quad \text{Eq. 5}$$

$$[K^+] = \frac{\gamma_{Na^+}}{\gamma_{K^+}} \times \frac{[Na^+]}{K_{ex}^{Na/K}} \times \frac{E_{KX}}{E_{NaX}} \quad \text{Eq. 6}$$

where γ_i is the activity coefficient of the species i in solution. These coefficients can be obtained using Debye-Hückel, Davies or Pitzer equations.

By combining Eqs. 4 to 6 with the electro-neutrality relationship:

$$[Cl^-] + 2 \times [SO_4^{2-}] = 2 \times [Ca^{2+}] + 2 \times [Mg^{2+}] + [Na^+] + [K^+] \quad \text{Eq. 7}$$

where values in square brackets are concentrations, one obtains:

$$\begin{aligned} & \frac{2 \times \gamma_{Na^+}^2}{E_{NaX}^2} \times [Na^+]^2 \times \left(\frac{E_{MgX_2}}{\gamma_{Mg^{2+}} \times K_{ex}^{Na/Mg}} + \frac{E_{CaX_2}}{\gamma_{Ca^{2+}} \times K_{ex}^{Na/Ca}} \right) \\ & + [Na^+] \times \left(1 + \frac{\gamma_{Na^+}}{\gamma_{K^+}} \frac{[Na^+]}{K_{ex}^{Na/K}} \times \frac{E_{KX}}{E_{NaX}} \right) \\ & - [Cl^-] - 2 \times [SO_4^{2-}] \\ & = 0 \end{aligned} \quad \text{Eq. 8}$$

Bicarbonate concentrations are neglected in the electro-neutrality relationship, because they were found to represent a minor fraction ($\sim 2\%$) of the anionic charge in the considered clayey systems (e.g. GAUCHER et al., Accepted, for a Callovian-Oxfordian formation with total normality about 0.05-0.1 mol/L, or PEARSON et al., 2003 for an Opalinus Clay formation). Second order equations similar to Eq. 8 can be derived for K, Ca and Mg. One obtains five second order equations with ten unknown parameters (the five concentrations and the associated activity coefficients). Debye-Hückel, Davies or Pitzer (for concentrated solutions) equations give five other independent equations for the activity coefficients. Hence, the mathematical system is fully constrained (ten unknowns with ten independent equations) and the Na, K, Ca and Mg concentrations can be calculated, based on the exchanger composition and the Cl^- and SO_4^{2-} concentrations (and possibly other anions that contribute significantly to the total anion equivalent concentration). However, a good precision on the selectivity coefficient value is needed to obtain reliable concentration values. The present work aims at obtaining these selectivity coefficients for Na, K, Ca and Mg on illite.

Data collected from the literature is widely used in the following work together with new exchange data obtained in our laboratories. Data from the literature always originated from exchange experiments where both the solution and the exchanger composition were

measured. New exchange data were obtained in the framework of the French Nuclear Waste Management Agency (ANDRA) investigation program on the clayey formation surrounding the French Underground Laboratory (URL) in Bure (Meuse Haute-Marne, France).

Materials and experimental methods

Chemicals. All solutions and suspensions were prepared with Millipore Milli-Q 18 M Ω water. NaCl, KCl, MgCl₂ and CaCl₂ solutions were prepared from analytical grade salts.

Clay material preparation. IMt-2 clay sample material was obtained from the Source Clays Repository (<http://www.clays.org/sourceclays/SourceClaysCCM.html>). After saturating the suspension with NaCl (0.5 mol/L), it was successively treated with a H₂O₂/HNO₃ mixture (pH ~ 2) to remove carbonate and organic matter impurities, then with a mixture of sodium hydrosulphite/HCl (pH 3) to remove iron and manganese oxi(hydroxi)des. Each of the preceding treatments was followed by careful washing with deionised water. The clay was then washed with a mixture of NaCl (1 mol/L) and HCl (10⁻⁴ mol/L). The fine fraction (< 2 μ m) of the sample was then isolated by sedimentation, redispersed in NaCl (1 mol/L) and washed with deionised water until the supernatant exhibited a negative response to the silver nitrate test.

Cation exchange isotherms. Na-K, Na-Ca and Na-Mg exchange isotherms were performed at a total normality of ~ 0.005 mol/L in chloride anionic background. The chloride anionic background was preferred to a perchlorate background since it better represents the natural systems studied in our laboratories. Moreover, the effect of cation-anion pairing is expected to be limited at this concentration in the light of results obtained with

montmorillonite (SPOSITO et al., 1983a; SPOSITO et al., 1983b; FLETCHER and SPOSITO, 1989; TOURNASSAT et al., 2004b; CHARLET and TOURNASSAT, 2005; FERRAGE et al., 2005). The method described in TOURNASSAT et al., 2004b was used to perform exchange isotherms, with the exception of the use of cobalt hexamine instead of ammonium acetate as an extracting agent of exchanged cations (CIESIELSKI and STERCKEMAN, 1997). The pH of the experiment was 5.

Presentation, thermodynamic convention and interpretation of the results.

The cation exchange selectivity coefficient is representative of the relative affinity of the exchanger for two considered cations. In the case of a Na/K or Ca/K exchange, selectivity coefficient values above 1 would denote an affinity for K greater than for Na and Ca, meaning a “preference” of the surface for K. The selectivity coefficient is not a thermodynamic exchange constant, since it varies as a function of the exchanger composition (e.g. JENSEN, 1973).

In the following, two main thermodynamic conventions for cation exchange selectivity coefficients will mainly be used: the Gaines and Thomas convention described above and the Vanselow convention (e.g. SPOSITO, 1981; MCBRIDE, 1994). The Vanselow selectivity coefficient of a monovalent-monovalent exchange (e.g. Na-K) is:

$$K_v^{Na/K} = \frac{N_K \times \{Na^+\}}{N_{Na} \times \{K^+\}} \quad \text{Eq. 9}$$

and the Vanselow selectivity coefficient of a divalent-monovalent exchange (e.g. Ca-K) is:

$$K_v^{Ca/K} = \frac{\{Ca^{2+}\} \times N_K^2}{N_{Ca} \times \{K^+\}^2} \quad \text{Eq. 10}$$

where N_i represents the molar fraction of the cation i on the exchanger and where values in brackets represent the activity of solute species. Knowing the cation exchanger composition

makes it possible to switch easily from one convention to the other: in the case of homovalent exchange, Gaines and Thomas and Vanselow selectivity coefficient values are identical and for monovalent / divalent exchange, the following formula applies:

$$K_{GT}^{Na/Ca} = K_v^{Na/Ca} \times \frac{N_{Na}^2 \times E_{Ca}}{E_{Na}^2 \times N_{Ca}} \quad \text{Eq. 11}$$

On the one hand, the Gaines and Thomas convention is very useful in the calculation approach shown by Eqs. 1 to 8. Moreover, this calculation convention is available in all numerical speciation codes (e.g. CRUNCH, STEEFEL, 2001, GEOCHEMIST WORKBENCH, BETHKE, 1996, PHREEQC2, PARKHURST and APPELO, 1999), as opposed to the Vanselow convention (especially in PHREEQC2). On the other hand, the Vanselow convention is the only one that enables the calculation of exchange species activity coefficients directly as a function of their variation with changes in the exchanger composition (SPOSITO, 1989), an approach that is developed at the end of this paper. The data in the figures are always presented at least in the Vanselow convention in order to enable comparison between the figures. The exchanger composition is expressed in the following in terms of the equivalent exchanged fraction of the cations participating in the exchange process, i.e. E_{Na} , E_K , E_{Ca} and E_{Mg} (SPOSITO, 1981). The activity of solute species was computed using PHREEQC v2.12 and the Llnl.dat database provided with the software (PARKHURST and APPELO, 1999, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/).

Experimental results

The complete set of data obtained in this study and from the literature is given in the table of Electronic Appendix 1. It can be seen from this table that the K_v values calculated for divalent/monovalent cation exchange on the basis of the data reported by Thellier and Sposito

(THELLIER and SPOSITO, 1988; THELLIER and SPOSITO, 1989b) are different from the values reported by these authors by a factor 2, probably due to a misuse of equivalent/kg instead of mole/kg for divalent cations in Thellier's K_v calculation.

Results for Na/K exchange selectivity coefficients are shown in Fig. 1. $K_v^{Na/K}$ is shown to vary as a function of the exchanger occupancy. This has already been shown for Na/K exchange on montmorillonite with the same trend of $K_v^{Na/K}$ decreasing as a function of increasing E_K (JENSEN, 1973). One can also note a large scattering of results in the low K occupancy zone ($E_K < 0.2$), the data points obtained in this study for the Na/Ca and Na/Mg experiments having the highest values and showing no clear trend. This behaviour could be due to several experimental reasons. The first is the possible effect of pH (the pH of the present experiment was 5 whereas the pH of the Thellier and Sposito experiment was 7), although Thellier et al. observed little effect of pH on the Na-Ca selectivity coefficient (THELLIER et al., 1992). The nature of the extracting reagent could also have an effect on the K desorption (cobalt hexamine vs. ammonium). Finally, we used the $< 2 \mu\text{m}$ fraction whereas Thellier and Sposito used a $< 115 \mu\text{m}$ fraction. This latter effect is certainly predominant with an increase in the effect of edge sorption sites as the particle size decreases.

Results for Na/Ca exchange selectivity coefficients are shown in Fig. 2. The trend observed on the data as a function of exchanger occupancy is in good agreement with the data taken from Thellier and Sposito (THELLIER and SPOSITO, 1988; THELLIER and SPOSITO, 1989b) under similar ionic strength conditions. Once again, one can observe considerable variability in the selectivity coefficient as a function of the exchanger composition. Note that the Na plus Ca occupancy never reaches 100% because of the presence of K in all of the experiments: the presence of K in solution and on the exchanger cannot be avoided due to its presence in the structural formula of illite and the weathering of the mineral.

In the exchanger occupancy region, where Na or Ca account for almost all the cations present, the experimental points describe a bell-shaped curve. Similar observations are also made for Na/Mg and Ca/Mg exchange (not shown here, see Electronic Appendix 1). In the middle region (both E_{Na} and E_{Ca} values are above 0.2), the exchange can be considered to be ideal with a constant selectivity coefficient value.

These new cation exchange data, together with data taken from the literature, illustrate the need to derive reliable parameters for calculating the exchange selectivity coefficients for illite. Two models are proposed in the following. The first is a multi-site approach and the second is a one-site approach, each of them having their own applicability domains.

Multi-site modelling approach

A multi-site modelling approach for cation exchange processes on illite has been shown to be successful in predicting Cs^+ sorption under various conditions of pH and ionic strength (e.g. BROUWER et al., 1983; POINSSOT et al., 1999; ZACHARA et al., 2002; LIU et al., 2004) or to explain the variation in CEC measurements as a function of ionic strength with the ^{22}Na isotope dilution technique (BAEYENS and BRADBURY, 2004).

A similar approach was therefore adopted here in order to fit both the results of our experiments and the data obtained from literature. Data obtained in this study were first fitted with a two-site model, referred to as $\equiv Illa^-$ and $\equiv Illb^-$, in agreement with the description of illite reactive surfaces with the presence of frayed edge and basal surface sites (e.g. POINSSOT et al., 1999; ZACHARA et al., 2002).

Relative amounts of these two sites and Gaines and Thomas (e.g. SPOSITO, 1981) Na-K, Na-Ca and Na-Mg exchange selectivity coefficients were fitted concomitantly using the freely available parameter minimization PEST software (DOHERTY, 2004) in combination with PHREEQC v2.12 (PARKHURST and APPELO, 1999) and the Llnl.dat chemistry database for solute species. Solute concentrations were used as input data and the difference between

measured and calculated equivalent fractions of Na, Ca, K, and Mg on the exchanger were minimized by varying the fitting parameters given above. A second round of parameter minimization was then performed, where the difference between the measured and calculated natural logarithms of the Vanselow selectivity coefficients were minimized. This second round gave results identical to the first one. This second round of minimization was necessary to enable the comparison of the results of the two-site model with the results of the one-site model that was fitted only with the difference between measured and calculated natural logarithm of the Vanselow selectivity coefficients (see below, one-site model approach section).

Data from the literature were then simulated. The same selectivity coefficients were used, but the relative proportion of the sites was varied (while maintaining a constant total CEC) to capture the change in sorption behaviour as a function of the particle size distribution (or maximum particle size) considered. Only data at total normality (TN) > 0.005 mol/L and with a complete description of the exchanger were used, i.e. excluding data where K occupancy is not available. The results of this fitting approach are given in Table 1 and Fig. 3.

The data of this study are reproduced by the model with quite low standard deviations on the difference between the measured and simulated equivalent fraction of each cation

($\sigma_i = \sqrt{\frac{mean - x_i}{N}}$ where x_i is the observable parameter, *mean* is the mean of this parameter

and N the number of scores): $\sigma_{XNa} = 0.052$, $\sigma_{XK} = 0.037$, $\sigma_{X2Ca} = 0.054$ and $\sigma_{X2Mg} = 0.061$.

Data from the literature are reproduced with the following standard deviations on the difference between the measured and simulated equivalent fraction of each cation: $\sigma_{XNa} = 0.066$, $\sigma_{XK} = 0.020$, $\sigma_{X2Ca} = 0.073$ and $\sigma_{X2Mg} = 0.057$ for data acquired at TN = 0.005 mol/L, $\sigma_{XNa} = 0.166$, $\sigma_{XK} = 0.031$, $\sigma_{X2Ca} = 0.178$ and $\sigma_{X2Mg} = 0.077$ for data acquired at TN < 0.005 mol/L down to 0.001 mol/L (not shown), and $\sigma_{XNa} = 0.114$, $\sigma_{XK} = 0.009$, $\sigma_{X2Ca} = 0.102$ and

$\sigma_{X2Mg} = 0.105$ for data acquired at $TN > 0.005$ up to 0.1 mol/L (most of the data were given without K occupancy measurement, not shown). One notes that the data at $TN < 0.005$ mol/L are poorly reproduced as compared to the other data, especially for Na and Ca. Incidentally, the change in selectivity coefficients for Na-Ca exchange for example is very significant between $TN = 0.002$ mol/L and $TN = 0.005$ mol/L (see Fig. 4, $\sim 1 \log_{10}$ unit difference). Between 0.005 mol/L and 0.0092 mol/L, the change in the selectivity coefficient value is within the uncertainty of the measurement. This behaviour explains why the two-site model selectivity coefficients derived at 0.005 mol/L enable the results at $TN > 0.005$ mol/L to be predicted with good confidence, bearing in mind that most of the data obtained at these total normalities were obtained without K occupancy measurements.

Recently, Liu et al. (LIU et al., 2004) have proposed a two-site model explicitly taking into account the variation in the water activity in order to simulate the changes in Cs-Na and Cs-K exchange selectivity coefficients as a function of ionic strength. However, this method was applied to ionic strengths ranging from 0.01 to 5 mol/L, where the water activity value exhibits large variations. In the present study, water activity is nearly constant between 0.001 mol/L and 0.01 mol/L. Moreover, in their model, one of the “driving forces” of the selectivity coefficient change as a function of ionic strength is also the difference in the number of moles of water per equivalent exchange capacity. This difference is high when a Na^+ ion is replaced by a Cs^+ ion because of the peculiar hydration properties of Cs at phyllosilicate surfaces. On the contrary, the difference when Na^+ is replaced by Ca^{2+} is expected to be small. Hence, no attempt was made to try to reproduce with the Liu et al. model the ionic strength effect that is observed in this study.

The modelling problem concerning data at low ionic strength could not have been fixed with the two-site model approach even by considering activity coefficients in the form of Davies or

(Wateq) Debye-Hückel activity coefficients as proposed by the PHREEQC v2.12 capabilities.

The Wateq Debye-Hückel activity coefficient is of the following form

$$\log_{10} \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + Ba_i^0 \sqrt{I}} + b_i I \quad \text{Eq. 12}$$

where γ_i is the activity of the exchanged species i , A and B are constants dependent only on temperature, a_i^0 and b_i are exchanged species specific parameters, I is the ionic strength and z_i is the number of equivalents of exchanger in the exchange species i , e.g. 1 for NaX and 2 for CaX₂ (PARKHURST and APPELO, 1999, pp 89). In the case of a Na→Ca exchange, one can evaluate the effect of Wateq Debye-Hückel activity coefficients by considering the variations - $\Delta \log_{10} K_{GT}(I)$ - they impose on the Gaines and Thomas selectivity coefficient as a function of the ionic strength:

$$\Delta \log_{10} K_{GT}^{NaCa}(I) = 2A\sqrt{I} \times \left(\frac{1}{1 + Ba_{XNa}^0 \sqrt{I}} - \frac{1}{1 + Ba_{X_2Ca}^0 \sqrt{I}} \right) + (b_{X_2Ca} - 2b_{XNa}) \times I \quad \text{Eq. 13}$$

A judicious choice of parameter b_{X_2Ca} and b_{XNa} could help to fit the difference observed between the selectivity coefficient values obtained at ionic strength values 0.001 and 0.005 mol/L. However, these b_{X_2Ca} and b_{XNa} parameters are related to a linear behaviour as a function of ionic strength. This linear behaviour is not in agreement with the observation that shows a very sharp change between 0.003 and 0.005 mol/L and almost no change below and above 0.005 mol/L. A sensibility test was performed on the influence of a^0 parameters on the $\Delta \log_{10} K_{GT}(I)$ value as a function of ionic strength. Considering two ionic strengths of 0.001 and 0.005 mol/L together with a^0 parameters varying from 0 to 100 for XNa and X₂Ca, one obtains a maximum difference of 0.03 log₁₀ unit in $\Delta \log_{10} K_{GT}(I)$, which is clearly not sufficient to explain the experimental difference, the order of magnitude of which is about one log₁₀ unit.

In Table 1, one notes that only the Na-K exchange selectivity coefficient reaction has different values for the two sites $\equiv\text{Illb}^-$ and $\equiv\text{Illa}^-$. For Na-Ca and Na-Mg exchange, the selectivity coefficient value remains constant and the variation in the selectivity coefficient as a function of the exchanger composition cannot be reproduced. Indeed, the bell-shaped curve observed for example for Na \rightarrow Ca exchange, at a single ionic strength, cannot be reproduced by considering a multi-site model, whatever the number of sites considered in the calculation. Considering a population of sites with decreasing affinity for Ca, one can easily show that these sites will be filled by order of affinity with Ca as a function of Ca occupancy of the exchanger, thereby creating a monotonic decrease in the global Na \rightarrow Ca selectivity coefficient when the equivalent exchanged fraction of Ca increases. Note that it is well known that the use of a constant Gaines and Thomas selectivity coefficient leads to a Vanselow selectivity coefficient that varies slowly with the charge fraction of adsorbed divalent cations. However, this effect is not sufficient to model the sharp part of the curve at high bivalent cation exchanger loading (Fig. 2). Fig. 2 also shows the variation in the selectivity coefficient as a function of the equivalent fraction of exchanged calcium in Na/Ca exchange experiments using various thermodynamic conventions: Vanselow, Gaines and Thomas, Gapon and Rothmund and Kornfeld (see SPOSITO, 1981 and Appelo C. A. J. and Parkhurst D. L. Calculating cation exchange with PHREEQC (Version 2), <http://www.xs4all.nl/~appt/pub/>). None of these representations enables a monotonic decrease in the selectivity coefficient as a function of the exchanger occupancy to be obtained, with the exception of the Rothmund and Kornfeld convention. However, this thermodynamic convention led to a large scattering between experimental points even for the points originating from the same experiment. The increase in the Na \rightarrow Ca (or Na \rightarrow Mg) selectivity coefficient concomitant to the increase in the Ca content on the exchanger signals the presence of a cooperative effect for exchanged Ca. We propose here two possible explanations for this effect. The first one relies on

probabilities of exchange site combinations, given that Ca needs to exchange with two Na sites (Fig. 5).

The probabilities of the occurrence of configurations 1, 2 and 3 are directly linked to the cation exchanger composition. Assuming a pure Na/Ca system, and a random distribution of Na and Ca on the exchanger, one obtains the following probabilities of occurrence for the 3 situations given in Fig. 5:

$$P_1 = \left(\frac{E_{Na}}{E_{Na} + E_{Ca} / 2} \right)^2 \quad \text{Eq. 14}$$

$$P_2 = 2 \times \left(\frac{E_{Na}}{E_{Na} + E_{Ca} / 2} \right) \times \left(\frac{E_{Ca} / 2}{E_{Na} + E_{Ca} / 2} \right) \quad \text{Eq. 15}$$

$$P_3 = \left(\frac{E_{Ca} / 2}{E_{Na} + E_{Ca} / 2} \right)^2 \quad \text{Eq. 16}$$

Now, assuming that configuration 2 is favoured thermodynamically compared to configuration 1, it is expected that the value of the selectivity coefficient of the exchange process is correlated with the probability P_2 . In Fig. 6, it can be seen that the shape of the variation in the P_2 probability value as a function of the Ca equivalent fraction is similar to that observed for the selectivity coefficient in Na/Ca exchange experiments (Fig. 2).

A second explanation is linked to the flocculation behaviour of illite. Thellier and Sposito (THELLIER and SPOSITO, 1989a) have studied the effect of electrolyte concentration and exchangeable cations on the flocculation of Silver Hill Illite. As with montmorillonite (e.g. SCHRAMM and KWAK, 1982), they have shown that bivalent cations favour the flocculation of illite particles as compared to monovalent cations and that turbidity is developed gradually as the equivalent fraction of bivalent cations decreases from the 0.8 value. This effect of the bivalent cation on the flocculation of illite suspension is perfectly in agreement with an increase in the selectivity coefficient for Na→Ca exchange as a function of the increase in the exchanged Ca, when considering the effect of stacking of the illite particles (Fig. 7). As

already depicted by other authors for smectite monolayers (e.g. MCBRIDE, 1994, Fig. 7), the stacking of illite external basal surfaces might favour divalent and multivalent cations as compared to monovalent cations.

This last explanation would also be in agreement with the effect of ionic strength on the Na/Ca and Na/Mg selectivity coefficients. Fig. 8 shows the effect of the ionic strength on the percentage of light transmission through a suspension of Na/Ca exchanged illite (data from THELLIER and SPOSITO, 1989a). The plotted experimental points correspond to conditions where equivalent bivalent cation fractions are ~ 0.5 . Under these conditions, the solution composition is mainly dominated by Na^+ cations ($> 97\%$). The light transmission is related to the flocculation (high percentages) or dispersion (low percentages) of the clay suspension (THELLIER and SPOSITO, 1989a). One can not fail to note the sharp transition at approximately 4 mmol/L, in agreement with the sharp variation observed for the Na/Ca and Na/Mg selectivity coefficient in the same ionic strength range value.

The stacking of illite particles then seems to have a marked effect on the selectivity coefficient for monovalent/bivalent cation exchange, but this cannot be taken into account in the above multi-site approach since the nature and the properties of the sites change as a function of the exchanger composition.

From this modelling result analysis, it appears that, concerning the prediction of the cation exchanger composition, the two-site model with constant Gaines and Thomas selectivity coefficients proposed in Table 1 can be used with good confidence for $\text{TN} > 0.005$ mol/L and for exchanger occupancy as follows: $E_{\text{Na}} \in [0.1; 0.7]$, $E_{\text{K}} \in [0.05; 1]$, $E_{\text{Ca}} \in [0.25; 0.9]$, $E_{\text{Mg}} \in [0.25; 0.9]$. However, the ratio between the two types of site is needed. For natural systems, we think it likely that the values given in Table 1 for the literature data (0.93 and 0.07) should be used in the absence of other information. The values for the present study were obtained on the 2 μm fine fraction instead of the 115 μm fraction for most other studies, a fraction that is

more representative of a natural illite. The proportion of K^+ high affinity sites in the present study (sites $\equiv Illb^- = 7 - 12\%$) can be compared with the proportion of Cs^+ high affinity sites in other literature studies: 0.045% (Hanford sediment, LIU et al., 2004), $0.4 + 3 \sim 3.4\%$ (Illite, COMANS et al., 1991), 1.5% (Illite, POINSSOT et al., 1999). The proportion of K^+ high affinity sites is at least twice as high as the reported proportion of Cs^+ high affinity sites. This proportion can also be compared to the Type II sites and planar sites described by Baeyens and Bradbury (BAEYENS and BRADBURY, 2004) for $Na \rightarrow Ca+Mg$ exchange: 20% and 80% respectively. The $Illb^-$ sites considered in the present model are then rather more similar to type II sites described in the literature than frayed edge sites whose influence is not visible in the Na-Ca-Mg-K exchange experiments, due to their low proportion. A third type of site should then certainly be added to our model. However, the data available in the literature do not enable its properties towards major cations (Na, Ca, Mg, K) to be calculated.

The exchange selectivity constants for $Na \rightarrow Ca$ exchange can also be compared with those given by Baeyens and Bradbury: $\log_{10} K_{GT}(Na \rightarrow Ca) = 0.30$ for planar sites (80% of the sites) and $\log_{10} K_{GT}(Na \rightarrow Ca) = 1.90$ for type II sites (20% of the sites). The values obtained in our study lie in the middle: $\log_{10} K_{GT}(Na \rightarrow Ca) = 0.53$ for both sites. This could be explained by the fact that the values derived in (BAEYENS and BRADBURY, 2004) were not obtained from direct measurements of all the cations present on the exchanger and that K was never considered in their calculation. If K had been considered, their deduced amount of exchanged Ca would have been lowered and then the selectivity coefficient would have been lowered as well. The same type of problem may also have applied in the study carried out by Zachara et al. (ZACHARA et al., 2002). They treated their experiments as binary (e.g., Cs-Ca), when in fact K and even Na were almost certainly present, or in the case of Cs-Na, as binary when K, Mg, and Ca were present. This is a probable explanation for the underprediction of

Cs retardation in column experiments using batch-derived data where no data on other cations (e.g. other than Cs and Na) were available.

Note that for $TN > 0.2$ mol/L in pure anionic chloride medium, the formation of chloride-cation pairs on the illite surface could explain the deviation of the model result towards the high TN data available in Shainberg et al. (SHAINBERG et al., 1980): in these experiments the illite affinity for Ca increased when the TN increased. A Gaines and Thomas selectivity coefficient of $10^{3.5}$ for $Na \rightarrow CaCl^+$ exchange reaction has been derived to fit these nine data points (not shown). This high selectivity coefficient value is in agreement with high selectivity coefficient values derived for chloride-cation pair exchange on montmorillonite surfaces (SPOSITO et al., 1983b; SPOSITO et al., 1983c; TOURNASSAT et al., 2004a; CHARLET and TOURNASSAT, 2005; FERRAGE et al., 2005).

As explained in the introduction, our interest lies primarily in the prediction of the solution composition as a function of the exchanger composition rather than conversely. It is possible to apply the procedure outlined in the introduction with a two-site model instead of a one-site model, provided that the ratio between the two types of site is known.

The prediction capability of the two-site model (inverse modelling) was then tested using the parameters listed in Table 1 for the literature data, keeping the total normality of the solution at the experimental value. All calculations were performed with PHREEQC v2.12 and the Llnl.dat associated database for solute species. When dealing with the literature data at $TN \geq 0.005$ mol/L, the standard deviations on the difference between the experiment concentration values and the modelled concentration values in \log_{10} units are as follows: $\sigma_{[Na^+]} = 0.32$, $\sigma_{[K^+]} = 1.31$, $\sigma_{[Ca^{2+}]} = 0.43$ and $\sigma_{[Mg^{2+}]} = 0.34$. Surprisingly, this standard deviation is higher for K^+ concentration predictions than for the other cations despite the fact that the standard deviation on the difference between the measured and simulated equivalent fraction of the model was the lowest for K exchanger occupancy in the direct modelling. Most of this deviation

originates from a “Ca-Mg” exchange experiment in THELLIER and SPOSITO, 1988, with a low K content. If this experiment is neglected, the standard deviation on the difference between the experimental concentration values and the modelled concentration values in \log_{10} units becomes $\sigma_{[K^+]} = 0.63$. When considering the total dataset from the literature, standard deviations are similar: $\sigma_{[Na^+]} = 0.30$, $\sigma_{[K^+]} = 1.16$ (0.61 without the Ca-Mg experiment cited above), $\sigma_{[Ca^{2+}]} = 0.64$ and $\sigma_{[Mg^{2+}]} = 0.51$.

Hence, based on the experimental cation exchange occupancy and the two-site model presented here, the potassium concentration can be calculated with an accuracy of $\pm \sim 1 \log_{10}$ unit. Other elements are calculated with an accuracy of $\pm \sim 0.3-0.6 \log_{10}$ unit. The concentration prediction capability of the present two-site model is then not very accurate, especially for potassium whose concentration can be underestimated or overestimated by a factor of ten. On the contrary, the direct modelling of cation exchange occupancy leads to rather good results as long as one remains within the range of the site occupancy given previously. One should note that the sites proportion is the key factor governing the success of the model.

One-site modelling approach

The uncertainty on the concentration prediction capability of the two-site model presented above leads us to model the data in a different way: the changes in selectivity coefficient are interpreted here as a continuous change in surface species activity coefficient. The use of a one-site model for cation-exchange on illite represents a departure from the approach used in all recent studies. Although questionable from a theoretical point of view, it will be shown in the following that this approach allows a better concentration prediction capability than a two-site model with constant selectivity coefficients.

Given the multi-site microscopic reality of the exchange process on illite surfaces, it is unlikely that the following proposed one-site method is thermodynamically correct. Instead, it

should be regarded as an empirical method to approach the exchange selectivity coefficients as a function of exchanger composition and ionic strength.

Activity coefficients and exchange equilibrium constants calculation in binary exchanges. The calculation method presented here concerns only monovalent and divalent species. Instead of using a generic term for chemical species, we have chosen to present the calculations with Na, K and Ca as example cases. More generic representations of these calculations can be found in for example Chu and Sposito (CHU and SPOSITO, 1981).

Let us consider the Ca-K divalent-monovalent exchange reaction:



The constant associated with this exchange is:

$$K^{Ca/K} = \frac{\{\text{Ca}^{2+}\} \times \{\text{KX}\}^2}{\{\text{CaX}_2\} \times \{\text{K}^+\}^2} \quad \text{Eq. 17}$$

The surface species activities are given by the following relationship

$$\{\text{KX}\} = N_K \times f_K^{CaK} \quad \text{Eq. 18}$$

where N_K is the molar fraction of the surface species KX (in this particular case

$N_K = \frac{[\text{KX}]}{[\text{KX}] + [\text{CaX}_2]}$), and f_K^{CaK} is the activity coefficient of the surface species KX that

depends on the exchanger composition. By introducing the Vanselow selectivity coefficient (VANSELOW, 1932), one derives

$$K^{Ca/K} = K_v^{Ca/K} \times \frac{f_K^{CaK^2}}{f_{Ca}^{CaK}} \quad \text{Eq. 19}$$

At constant T and P, and considering no variation in the surface water activity, the Gibbs-Duhem equation, applied to the exchanger phase only, gives (SPOSITO, 1989, see Electronic Appendix 2 for more details):

$$2 \times \ln f_K^{CaK} = -E_{Ca} \times \ln K_v^{Ca/K} + \int_0^{E_{Ca}} \ln K_v^{Ca/K} \times dE'_{Ca} \quad \text{Eq. 20}$$

$$\ln f_{Ca}^{CaK} = E_K \times \ln K_v^{Ca/K} - \int_0^{E_K} \ln K_v^{Ca/K} dE'_K \quad \text{Eq. 21}$$

$$\ln K^{Ca/K} = \int_0^1 \ln K_v^{Ca/K} dE'_K = - \int_0^1 \ln K_v^{Ca/K} dE'_{Ca} \quad \text{Eq. 22}$$

Similar equations are obtained in the case of a homovalent exchange (e.g. Na/K or Ca/Mg, See Electronic Appendix 2)

Eqs. 20 to 22 can be evaluated by finding an expression that relates $\ln K_v$ and the exchanger composition (SPOSITO, 1989; AGBENIN and YAKUBU, 2006). The curves obtained in this study for Na/Ca exchange (in the presence of a minor presence of K^+ on the exchanger) are very sharp near to the 0 and 1 values for E_{Ca} or E_{Na} respectively (Fig. 2). For practical reasons, it is then necessary to introduce into the $\ln K_v^{Ca/K}$ equation a term that is easily integrated and that can account for the sharp shapes of the curves. It was found that exponential terms were far more efficient than high order polynomial terms because exponential terms do not introduce oscillations of the fitting curve in the central region of the curve, where E_{Ca} or E_{Na} stand between 0.3 and 0.6

By considering the following equation:

$$\ln K_v^{Ca/K} = {}^0a_{CaK} + {}^1a_{CaK} E_K + {}^2a_{CaK} E_K^2 + {}^3a_{CaK} E_K^3 + B_{CaK} \times e^{-b_{CaK} E_K} + C_{CaK} \times e^{-c_{CaK} (1-E_K)} \quad \text{Eq. 23}$$

and by applying it to other binary exchanges, it should be possible to fit reasonably well even very complicated shaped $\ln K_v$ curves.

One can then obtain:

$$\ln K^{Ca/K} = {}^0a_{CaK} + \frac{{}^1a_{CaK}}{2} + \frac{{}^2a_{CaK}}{3} + \frac{{}^3a_{CaK}}{4} + \frac{B_{CaK}}{b_{CaK}} \times (1 - e^{-b_{CaK}}) + \frac{C_{CaK}}{c_{CaK}} \times (1 - e^{-c_{CaK}})$$

Eq. 24

$$\begin{aligned} \ln f_{Ca}^{CaK} &= \\ &= \frac{{}^1a_{CaK} E_K^2}{2} + 2 \times \frac{{}^2a_{CaK} E_K^3}{3} + 3 \times \frac{{}^3a_{CaK} E_K^4}{4} \\ &\quad + e^{-b_{CaK} E_K} \times \left(E_K \times B_{CaK} + \frac{B_{CaK}}{b_{CaK}} \right) + e^{-c_{CaK} (1-E_K)} \times \left(E_K \times C_{CaK} - \frac{C_{CaK}}{c_{CaK}} \right) - \frac{B_{CaK}}{b_{CaK}} + \frac{C_{CaK} \times e^{-c_{CaK}}}{c_{CaK}} \end{aligned}$$

Eq. 25

$$\begin{aligned} \ln f_K^{CaK} &= \\ &\left(\frac{1}{4} E_{Ca}^2 \times ({}^1a_{CaK} + 2 \times {}^2a_{CaK} + 3 \times {}^3a_{CaK}) - \frac{1}{6} E_{Ca}^3 \times (2 \times {}^2a_{CaK} + 6 \times {}^3a_{CaK}) + \frac{1}{8} E_{Ca}^4 \times 3 \times {}^3a_{CaK} \right) \\ &\quad + \frac{1}{2} \times \left(\frac{B_{CaK}}{b_{CaK}} \times (-e^{-b_{CaK}}) + e^{-b_{CaK} (1-E_{Ca})} \times B_{CaK} \times \left((1-E_{Ca}) + \frac{(1-b_{CaK})}{b_{CaK}} \right) \right) \\ &\quad + \frac{1}{2} \times \left(\frac{C_{CaK}}{c_{CaK}} + e^{-c_{CaK} (E_{Ca})} \times C_{CaK} \times \left((1-E_{Ca}) - \frac{(1+c_{CaK})}{c_{CaK}} \right) \right) \end{aligned}$$

Eq. 26

The same type of equations are obtained for $\ln K^{Na/K}$, $\ln f_{Na}$ and $\ln f_K$ (see Electronic Appendix 2 for more details).

Given the above formula, the activity coefficient of surface species should be calculated on the basis of the K_v data given as a function of the exchanger composition only. However, based on literature data, we have shown that the ionic strength has an influence on the selectivity constant value. This information partially invalidates the above approach. The effect of ionic strength is likely to originate in changes in the electrostatic field near to the surface, creating conditions favourable or not to the aggregation of particles (see discussion in the multi-site modelling approach section). Considering the role of ionic strength, Eq. 19 must be rewritten:

$$K^{Ca/K} = K_v^{Ca/K} \times \frac{g_K^2}{g_{Ca}} \quad \text{Eq. 27}$$

with g a function depending on the exchanger composition and the ionic strength. This means that all of the polynomial and exponential coefficients given in Eqs. 24 to 26 are a function of ionic strength. It is not now conceivable to define such a function for all of the necessary parameters. However, as a simplification, one can assume that: $g = f \times h$ where h is a function of ionic strength (I) only. Defining the reference state at $I = 0$, the h function should converge to 1 when I converges to 0. By analyzing data from Thellier and Sposito (THELLIER and SPOSITO, 1989b), one should also note that the logarithm of h function ratios converge to one other limit at $I \sim 0.004-0.005$, then describing a sigmoid curve, in correlation with the flocculation behaviour of illite suspension (THELLIER and SPOSITO, 1989a). They have also shown that this flocculation behaviour is a function of the bivalent cation exchanged fraction. However, no attempt was made to calculate explicitly all h functions as a function of their relative cations. The logarithm of h function ratios were approached with a complementary error function (*erfc*) with the form of:

$$\ln h_K^{NaK} - \ln h_{Na}^{NaK} = \alpha_{NaK} \times \text{erfc}\left(\beta_{NaK} - \frac{I}{\gamma_{NaK}}\right), \quad \text{Eq. 28}$$

for monovalent / monovalent interactions or

$$2 \times \ln h_K^{CaK} - \ln h_{Ca}^{CaK} = \alpha_{CaK} \times \text{erfc}\left(\beta_{CaK} - \frac{I}{\gamma_{CaK}}\right). \quad \text{Eq. 29}$$

for monovalent / divalent interactions.

These functions must be considered as a very convenient way of trapping the ionic strength effect. The Na-K, Ca-Na, and Mg-Na systems were described with such functions leading to nine new fitting parameters and allowing other systems (Ca-Mg, Ca-K and Mg-K) to be described by combinations of the former ones.

Activity coefficient and exchange equilibrium constant calculations in multicomponent exchanges. Chu and Sposito (CHU and SPOSITO, 1981) have demonstrated that ternary exchange thermodynamic parameters cannot be deduced from binary parameters only. However, we decided voluntary to oversimplify our system given (i) that it already contains a lot of fitting parameters and (ii) that a one-site true thermodynamic description is certainly not possible due to the multi-site nature of the exchange process.

We assume here firstly that the activity coefficients for Na, K, Ca and Mg exchanged species in a multicomponent exchange can be approximated from the individual binary contributions without crossing terms, i.e.:

$$\ln f_{Ca}^{NaKMgCa} = \ln f_{Ca}^{CaK} + \ln f_{Ca}^{CaNa} + \ln f_{Ca}^{CaMg} \quad \text{Eq. 30}$$

However, in a Ca-Mg exchange experiment in the presence of Na and K, one can note that the $\ln K_v^{Ca/K}$ value depends only on E_{Na} and E_K , not on the ratio between E_{Mg} and E_{Ca} (Fig. 9). This means that Ca and Mg have a joint similar effect on the Ca-K exchange selectivity coefficient. This effect is taken into account by considering the following combination:

$$\ln f_K^{CaMgNaK} = \ln f_K^{NaK} + \ln f_K^{CaMgK} \quad \text{Eq. 31}$$

where $\ln f_K^{CaMgK}$ is the weighted mean of $\ln f_K^{CaNa}$ and $\ln f_K^{CaMg}$ (see Electronic Appendix 2 for the full formula).

With this approach we then obtained four mathematical expressions for the activity coefficients of exchanged Na, K, Ca and Mg:

$$\ln f_K^{CaMgNaK} = \ln f_K^{NaK} + \ln f_K^{CaMgK} \quad \text{Eq. 32}$$

$$\ln f_{Na}^{CaMgKNa} = \ln f_{Na}^{NaK} + \ln f_{Na}^{CaMgNa} \quad \text{Eq. 33}$$

$$\ln f_{Ca}^{MgKNaCa} = \ln f_{Ca}^{CaK} + \ln f_{Ca}^{CaNa} + \ln f_{Ca}^{CaMg} \quad \text{Eq. 34}$$

$$\ln f_{Mg}^{CaKNaMg} = \ln f_{Mg}^{MgK} + \ln f_{Mg}^{MgNa} + \ln f_{Mg}^{CaMg} \quad \text{Eq. 35}$$

The efficiency of the model to capture the variations in the selectivity coefficients as a function of exchanger composition and ionic strength was then tested.

Modelling of experimental and literature results

Equilibrium constants and activity coefficients were obtained from the polynomial and exponential coefficients as described above. The fitting approach also takes into consideration one additional constraint concerning the exchange equilibrium constants consistency, which is the constant additivity, i.e. for a Ca/Na/K system:

$$\ln K^{Ca/Na} + 2 \times \ln K^{Na/K} = \ln K^{Ca/K} \quad \text{Eq. 36}$$

The least square fitting approach of these parameters was broken down into several steps:

- Firstly, only data at TN = 0.005 mol/L were considered and the a , B , b , C and c parameters were fitted for Na, K and Ca, considering that the parameters for Mg were identical to Ca.
- Secondly, the Mg parameters were fitted together with the former parameters obtained for Na, K and Ca.
- Finally, the α , β and γ parameters, concerning ionic strength effects, were fitted for the system Ca-Na, Na-K and Mg-Na separately before a last fitting round concerning all of the parameters.

This approach was reiterated until the fit was found to be satisfactory. Note that the fitted systems are always multi-component (most of them are quaternary systems) and thereby highly non-linear. Reiteration of the fitting procedure was then necessary. The parameters obtained from this regression analysis are given in Tables 2 and 3. Of course, we are aware

that these coefficients are not definitive and certainly not the best solutions, given the high number of fitting parameters. Complementary experiments are needed to better constrain them, especially Ca-K and Mg-K binary exchanges at different ionic strengths and with data at high K surface coverage. The result of the fit is presented in Figs. 10 and 11 together with standard deviation of the simulation as compared to the experimental data.

The concentration prediction capability of the model was then tested using the same procedure as that used for the two-site model: the TN was kept at the experimental TN and the selectivity coefficients were calculated as a function of the normality and the exchanger composition. A Gaines and Thomas convention was used because the calculations were performed with PHREEQC v2.12. Gaines and Thomas selectivity coefficients were recalculated according to Eq. 11.

Results are shown in Fig. 12 together with the standard deviation of the simulation as compared to the experimental data. Note that the K concentrations in the Na-Ca and Na-Mg exchange experiment of the present study have been discarded, as for the presentation of the two-site model result. On the contrary, results concerning Na, Ca and Mg concentrations of the present study are also presented.

Significant deviations are observed mainly for Mg concentrations, but the precision of the concentration prediction is far better than the precision obtained with the two-site model. For the two-site model we obtained the following standard deviations on the difference between the experiment concentration values and the modelled concentration values in \log_{10} units $\sigma_{[\text{Na}^+]} = 0.30$, $\sigma_{[\text{K}^+]} = 1.16$, $\sigma_{[\text{Ca}^{2+}]} = 0.64$ and $\sigma_{[\text{Mg}^{2+}]} = 0.51$. With the present one-site model, one obtains: $\sigma_{[\text{Na}^+]} = 0.13$, $\sigma_{[\text{K}^+]} = 0.10$, $\sigma_{[\text{Ca}^{2+}]} = 0.30$ and $\sigma_{[\text{Mg}^{2+}]} = 0.45$, highlighting the improvement of the fit, especially for the potassium concentration prediction. Even points that lack data measurement for K^+ in solution and on the exchanger are well predicted (data from SHAINBERG et al., 1980; SPOSITO and LEVESQUE, 1985). The proposed one-site model thereby

makes it possible to recover the concentrations of the major cations in a solution in contact with an illite whose exchanger composition is known.

Application to natural and engineered systems

Natural systems with a clay fraction constituted only by illite are not common. Here we consider the example of illite rich layers in the Callovian-Oxfordian formation for the calculation of exchanger selectivity coefficients towards Na, Ca, Mg and K. Data on exchanger composition and ionic strength were obtained from Gaucher et al. (GAUCHER et al., 2004) and are given in Table 4. Selectivity coefficients in the Vanselow convention were calculated using the model described in this paper (Table 4). Associated concentrations in porewater can then be calculated, provided the total normality is known and the sulphate and chloride anion proportions are known. In agreement with Gaucher et al. (GAUCHER et al., Accepted), we considered a solute S(+6)/Cl(-1) equivalent ratio of 2 as an approximation. The results of the calculation (Table 4) shows that the porewater composition is likely to be constituted mainly of Na cations (~ 54% of the cation equivalent concentration) then Ca cations (~ 30%), Mg cations (~ 14%), K cations representing less than 2% of the cation equivalent charge with concentrations ranging from 1.4 to 2 mmol/L. Future porewater extraction results from the Bure underground research laboratory will help to verify the accuracy of the model.

Conclusions

We have shown that our one-site model considering the ionic strength effect and variations in the surface species activity coefficients is efficient for the determination of water major cation

composition for a wide range of exchanger compositions. For natural systems, this model still needs to be refined in order to consider the presence of smectite and illite/smectite rather than pure illite. Moreover, the compaction effect deserves further study as a similar effect of compaction is expected as compared to that of ionic strength. It is obvious that this model will be the most efficient for illite exhibiting the same shape parameters, provided the proportions of the different types of sites are controlled by the morphology of the particles. As a matter of interest, the data fitted here concern only Silver Hill Illite (Imt-1 and 2, Montana) and Fithian Illite (Illinois).

For the prediction of the exchanger composition as a function of the solution cation concentrations, a multi-site model as presented in the first part of this paper is certainly more appropriate, even if some features of the exchange isotherm, e.g. the “bell-shaped” aspect of the curve, cannot be predicted. Ideally, we believe that the two approaches should be combined in order to take into account the peculiar behaviour of Cs or K cations on high affinity sites such as frayed edge sites.

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References

- Agbenin J. O. and Yakubu S. (2006) Potassium-calcium and potassium-magnesium exchange equilibria in an acid savanna soil from northern Nigeria. *Geoderma* **In Press**, **Corrected Proof**.
- Baeyens B. and Bradbury M. (2004) Cation exchange capacity measurements on illite using the sodium and cesium isotope dilution technique: effects of the index cation, electrolyte concentration and competition: modeling. *Clays and Clay Minerals* **52**, 421-431.
- Bethke C. M. (1996) *Geochemical reaction modeling*. Oxford University Press.
- Bradbury M. H. and Baeyens B. (1998) A Physicochemical characterisation and geochemical modelling approach for determining porewater chemistries in argillaceous rocks. *Geochimica et Cosmochimica Acta* **62**, 783-795.
- Brouwer E., Baeyens B., Maes A., and Cremers A. (1983) Cesium and Rubidium ion equilibria in illite clay. *Journal of Physical Chemistry* **87**, 1213-1219.
- Charlet L. and Tournassat C. (2005) Fe(II)-Na(I)-Ca(II) cation exchange on montmorillonite in chloride medium; evidence for preferential clay adsorption of chloride – metal ion pairs in seawater. *Aquatic Geochemistry* **11**, 115-137.
- Chu S. Y. and Sposito G. (1981) The thermodynamics of ternary cation exchange systems and the subregular model. *Soil Science Society of America Journal* **45**, 1084-1089.
- Ciesielski H. and Sterckeman T. (1997) Determination of cation exchange capacity and exchangeable cations in soils by means of cobalt hexamine trichloride. Effects of experimental conditions. *Agronomie* **17**, 1-7.
- Comans R. N. J., Haller M., and De Preter P. (1991) Sorption of cesium on illite: Non-equilibrium behaviour and reversibility. *Geochimica et Cosmochimica Acta* **55**, 433-440.
- Doherty J. (2004) PEST Model-independent parameter estimation (ed. W. N. Computing).
- Ferrage E., Tournassat C., Rinnert E., Charlet L., and Lanson B. (2005) Evidence for calcium-chloride ion pairs in the interlayer of montmorillonite and implications on hydration state. A XRD profile modelling approach. *Clays and Clay Minerals* **53**, 348-361.
- Fletcher P. and Sposito G. (1989) The chemical modeling of clay/electrolyte interactions for montmorillonite. *Clay Minerals* **24**, 375-391.
- Gaucher E., Robelin C., Matray J. M., Negrel G., Gros Y., Heitz J. F., Vinsot A., Rebours H., Cassabagnere A., and Bouchet A. (2004) ANDRA underground research laboratory: Interpretation of the mineralogical and geochemical data acquired in the Callovian-Oxfordian Formation by investigative drilling. *Physics and chemistry of the earth* **29**, 55-77.
- Gaucher E. C., Altmann S., Blanc P., Bardot F., Jacquot E., Lassin A., Negrel G., Braibant G., Breeze D., Crouzet C., and Gautier A. (Accepted) Porewater chemistry simulation of the Callovian-Oxfordian Formation. *Compte-Rendu Geosciences*.
- Jensen H. E. (1973) Potassium - calcium exchange equilibria on a montmorillonite and a kaolinite clay. *Agrochimica* **17**, 181-190.
- Liu C., Zachara J. M., and Smith S. C. (2004) A cation exchange model to describe Cs⁺ sorption at high ionic strength in subsurface sediments at Hanford site, USA. *Journal of Contaminant Hydrology* **68**, 217-238.
- McBride M. B. (1994) *Environmental Chemistry of Soils*. Oxford University Press.

- Parkhurst D. L. and Appelo C. A. J. (1999) User's guide to phreeqc - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, Report No. 99-4259.
- Pearson F. J., Arcos D., Boisson J.-Y., Fernandez A. M., Gäbler H.-E., Gaucher E., Gautschi A., Griffault L., Hernan P., and Waber H. N. (2003) Mont Terri project - Geochemistry of water in the Opalinus clay formation at the Mont Terri Rock Laboratory. In *Geology Series*, Vol. 5 (ed. F.O.W.G.).
- Poinsot C., Baeyens B., and Bradbury M. H. (1999) Experimental and modelling studies of caesium sorption on illite. *Geochimica et Cosmochimica Acta* **63**, 3217-3227.
- Schramm L. L. and Kwak J. C. T. (1982) Influence of exchangeable cation composition on the size and shape of montmorillonite particles in dilute suspension. *Clays and Clay Minerals* **30**, 40-48.
- Shainberg I., Oster J. D., and Wood J. D. (1980) Sodium/calcium exchange in montmorillonite and Illite suspension. *Soil Science Society of America Journal* **44**, 960-964.
- Sposito G. (1981) *The thermodynamics of soil solution*. Oxford University Press.
- Sposito G. (1989) *The chemistry of soils*. Oxford University Press.
- Sposito G., Holtzclaw K. M., Charlet L., Jouany C., and Page A. L. (1983a) Sodium-calcium and sodium-magnesium exchange on Wyoming bentonite in perchlorate and chloride background ionic media. *Soil Science Society of America Journal* **47**, 51-56.
- Sposito G., Holtzclaw K. M., Jouany C., and Charlet L. (1983b) Cation selectivity in sodium-calcium, sodium-magnesium, and calcium-magnesium exchange on Wyoming bentonite at 298 K. *Soil Science Society of America Journal* **47**, 917-921.
- Sposito G., Jouany C., Holtzclaw K. M., and LeVesque C. S. (1983c) Calcium-Magnesium exchange on Wyoming bentonite in the presence of adsorbed sodium. *Soil Science Society of America Journal* **47**, 1081-1085.
- Sposito G. and LeVesque C. S. (1985) Sodium-calcium-magnesium exchange on Silver Hill Illite. *Soil Science Society of America Journal* **49**, 1153-1159.
- Steeffel C. I. (2001) GIMRT, version 1.2: Software for modeling multicomponent, multidimensional reactive transport. User's Guide, Report No. UCRL-MA-143182.
- Thellier C. and Sposito G. (1988) Quaternary cation exchange on Silver Hill illite. *Soil Science Society of America Journal* **52**, 979-985.
- Thellier C. and Sposito G. (1989a) Influence of electrolyte concentration and exchangeable cations on the flocculation of Silver Hill illite. *Soil Science Society of America Journal* **53**, 711-715.
- Thellier C. and Sposito G. (1989b) Influence of electrolyte concentration on quaternary exchange by Silver Hill illite. *Soil Science Society of America Journal* **53**, 705-711.
- Thellier C., Sposito G., and Holtzclaw K. M. (1992) Proton effects on quaternary cation exchange and flocculation of Silver Hill illite. *Soil Science Society of America Journal* **56**, 427-433.
- Tournassat C., Ferrage E., Poinsignon C., and Charlet L. (2004a) The titration of clay minerals. Part II. Structural-based model and implications for clay reactivity. *Journal of Colloid and Interface Science* **273**, 234-246.
- Tournassat C., Greneche J. M., Tisserand D., and Charlet L. (2004b) The titration of clay minerals. Part I. Discontinuous backtitration technique combined to CEC measurements. *Journal of Colloid and Interface Science* **273**, 224-233.
- Vanselow A. P. (1932) Equilibria of the base-exchange reaction of bentonites, permutites, Soil colloids and zeolites. *Soil Science* **33**, 95-113.

Zachara J. M., Smith S. C., Liu C., McKinley J. P., Serne R. J., and Gassman P. L. (2002)
Sorption of Cs⁺ to micaceous subsurface sediments from the Hanford site, USA.
Geochimica et Cosmochimica Acta **66**, 193-211.

Tables

Table 1. Two-site model parameters for the modelling of Na-K-Ca-Mg exchange experiments. Data from the literature are taken from: SHAINBERG et al., 1980; SPOSITO and LEVESQUE, 1985; THELLIER and SPOSITO, 1988; THELLIER and SPOSITO, 1989b; THELLIER et al., 1992.

	$\equiv\text{IIIa}^-$		$\equiv\text{IIIb}^-$	
	This study	Literature data	This study	Literature data
Site proportions				
	0.88	0.93	0.12	0.07
Exchange selectivity coefficients				
Na-K	0.52		6.7	
Na-Ca	0.53		0.53	
Na-Mg	0.55		0.55	

Table 2. Ionic strength coefficients (Eqs. 28 and 29).

	Na/K	Ca/Na	Mg/Na
α	0.43	-0.8	-1.1
β	17.58	17.58	17.58
χ	1.915×10^{-4}	1.915×10^{-4}	1.915×10^{-4}

Table 3. Polynomial and exponential coefficients obtained for Ca/K, Ca/Na, Na/K, Mg/Ca, Mg/Na and Mg/K exchange reactions, together with calculated thermodynamic exchange reaction equilibrium constants.

Ca/K exchange				
Polynomial coefficients		Exponential coefficients		$\ln K^{CaK}$
$^0 a_{CaK}$	1.43	B_{CaK}	7.39	6.13
$^1 a_{CaK}$	0.293	b_{CaK}	1.055	
$^2 a_{CaK}$	0.162	C_{CaK}	-0.837	
$^3 a_{CaK}$	0.222	c_{CaK}	7.078	
Ca/Na exchange				
Polynomial coefficients		Exponential coefficients		$\ln K^{CaNa}$
$^0 a_{CaNa}$	1.34	B_{CaNa}	254	6.08
$^1 a_{CaNa}$	-0.342	b_{CaNa}	58.77	
$^2 a_{CaNa}$	-0.816	C_{CaNa}	-0.026	
$^3 a_{CaNa}$	3.542	c_{CaNa}	0.010	
Na/K exchange				
Polynomial coefficients		Exponential coefficients		$\ln K^{NaK}$
$^0 a_{CaK}$	-0.83	B_{CaK}	3.478	0.025
$^1 a_{CaK}$	-1.964	b_{CaK}	2.520	
$^2 a_{CaK}$	10.08	C_{CaK}	-211.4	
$^3 a_{CaK}$	-3.57	c_{CaK}	111.6	
Mg/Ca exchange				
Polynomial coefficients		Exponential coefficients		$\ln K^{MgCa}$
$^0 a_{NaK}$	0.40	B_{NaK}	0.575	0.593
$^1 a_{NaK}$	0.000	b_{NaK}	0.546	
$^2 a_{NaK}$	0.000	C_{NaK}	-23.98	
$^3 a_{NaK}$	0.000	c_{NaK}	97.20	
Mg/Na exchange				
Polynomial coefficients		Exponential coefficients		$\ln K^{MgNa}$
$^0 a_{MgNa}$	3.98	B_{MgNa}	257.14	6.68
$^1 a_{MgNa}$	-9.05	b_{MgNa}	55.11	
$^2 a_{MgNa}$	6.506	C_{MgNa}	-0.329	
$^3 a_{MgNa}$	2.850	c_{MgNa}	0.009	
Mg/K exchange				
Polynomial coefficients		Exponential coefficients		$\ln K^{MgK}$
$^0 a_{MgK}$	2.17	B_{MgK}	7.65	6.72
$^1 a_{MgK}$	0.287	b_{MgK}	1.234	
$^2 a_{MgK}$	0.160	C_{MgK}	-0.636	
$^3 a_{MgK}$	0.220	c_{MgK}	7.044	

Table 4. Cation exchange composition and associated total normality (TN) of selected illitic samples (GAUCHER et al., 2004).

Litho-facies	Sample name	Core levels (m)		Cation exchange occupancy (eq/kg)				TN (mmol/L)
				Ca	Mg	K	Na	
C2b1	EST05703	493.47	493.67	0.065	0.033	0.012	0.024	85
	EST05712	495.50	495.70	0.061	0.032	0.012	0.024	93
	EST05724	498.47	498.67	0.066	0.034	0.013	0.027	80
	EST05738	501.50	501.70	0.066	0.034	0.012	0.025	101
	EST05748	503.93	504.13	0.064	0.033	0.013	0.025	136

Table 5. Decimal logarithm of cation exchange selectivity coefficients for selected samples (Table 4) in Gaines and Thomas convention associated with calculated concentrations of Na, K, Ca and Mg in the porewater of the samples.

Litho-facies	Sample name	TN (mmol/L)	Gaines and Thomas exchange selectivity coefficients (log ₁₀ scale)			Calculated concentrations (mmol/L)			
			Na/Ca	Na/Mg	Na/K	Na	K	Ca	Mg
			C2b1	EST05703	85	0.67	0.78	1.23	45.7
	EST05712	93	0.67	0.78	1.23	49.9	1.5	14.1	6.7
	EST05724	80	0.68	0.79	1.22	46.5	1.4	10.9	5.1
	EST05738	101	0.67	0.78	1.23	51.8	1.5	16.2	7.6
	EST05748	136	0.67	0.78	1.23	63.4	2.0	24	11.3

Figure captions

Fig. 1. Vanselow selectivity coefficient of Na/K exchange as a function of the relative exchanger occupancy by K. Open circles: this study, TN (total normality) = 0.005 mol/L, Na/K exchange experiment. Black circles: this study, TN = 0.005 mol/L, Na/Ca exchange experiment. Grey circles: this study, TN = 0.005 mol/L, Na/Mg exchange experiment. Open triangles: THELLIER and SPOSITO, 1988, TN = 0.005 mol/L. Open squares: THELLIER and SPOSITO, 1989b TN = 0.005 mol/L.

Fig. 2. Selectivity coefficient of Na/Ca exchange as a function of the relative exchanger occupancy by Na, in various thermodynamic conventions for cation exchange. Open circles: this study, TN = 0.005 mol/L, Na/Ca exchange experiment in presence of K (Mg concentration was below the detection limit). Open squares: THELLIER and SPOSITO, 1989b TN = 0.005 mol/L, Na/Ca exchange experiment in presence of K and Mg.

Fig. 3. Comparison of measured exchanger occupancies and calculated occupancies with the two-site model on illite samples at TN = 0.005 mol/L. Empty circles: this study; Open squares: THELLIER and SPOSITO, 1989b; Closed diamonds: THELLIER and SPOSITO, 1989b; Open up-triangles: THELLIER and SPOSITO, 1988; Closed up-triangles: THELLIER and SPOSITO, 1988; Open down-triangles: THELLIER and SPOSITO, 1988; Closed down-triangles: THELLIER and SPOSITO, 1988; Open diamonds: THELLIER and SPOSITO, 1988. Some symbols may be hidden by others. Two different symbols for the same literature reference denote two different experiments in the cited reference. Full lines indicate the 1:1 relationship. See Electronic Appendix 1 for more details on the original data.

Fig. 4. Effect of ionic strength on the Na → Ca selectivity coefficient for illite. Empty circles: THELLIER and SPOSITO, 1988, TN = 0.005 mol/L; Closed circles: this study, TN = 0.005 mol/L; Open squares: THELLIER and SPOSITO, 1989b, TN = 0.002 mol/L; Closed squares: THELLIER and SPOSITO, 1989b, TN = 0.0092 mol/L.

Fig. 5. Schematic representation of Na/Ca exchange mechanism in different site configurations.

Fig. 6. Occurrence probabilities of site configurations for Na/Ca cation exchange. Configuration numbers refer to those given in Fig. 5.

Fig. 7. Schematic diagram of Na⁺ and Ca²⁺ exchange cations retained on illite surface in a dispersed suspension (A) and in a flocculated suspension (B). Modified after MCBRIDE, 1994

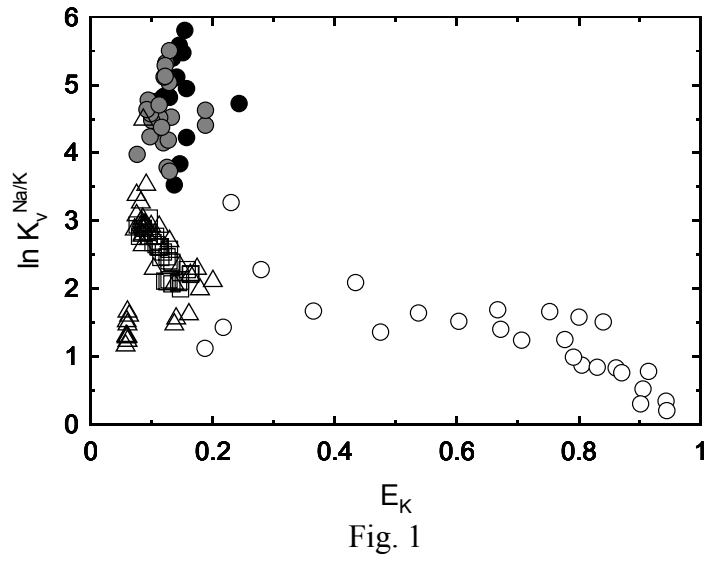
Fig. 8. Percentage light transmission of an illite suspension as a function of ionic strength in a Na + Ca or Mg perchlorate solute background, exchanged Ca or Mg equivalent charge representing approximately half of the exchanger composition. Circles = Ca; Triangles = Mg. See THELLIER and SPOSITO, 1989a for more experimental details.

Fig. 9. $\ln K_v^{Ca/K}$ values as a function of E_{Ca} in a Ca-Mg exchange experiment. Circles and squares: THELLIER and SPOSITO, 1988, 0.005 M perchlorate. Up-pointing triangle and down-pointing triangle: THELLIER and SPOSITO, 1989b, 0.001 M and 0.005 M perchlorate respectively. Full lines indicate the mean of the $\ln K_v^{Ca/K}$ series values.

Fig. 10. Comparison of measured and calculated $\ln K_v$ values for Na/K, Na/Ca, Na/Mg, Ca/Mg, K/Ca and K/Mg exchange reactions at $TN \geq 0.005$ mol/L. Circles and crosses: THELLIER and SPOSITO, 1989b, $TN = 0.0092$ mol/L. Squares and stars: THELLIER and SPOSITO, 1989b, $TN = 0.005$ mol/L. Up-pointing triangles, "plus" signs and down-pointing triangles: THELLIER and SPOSITO, 1988, $TN = 0.005$ mol/L. Diamonds: this study, $TN = 0.005$ mol/L. Some symbols hide each other. Dotted lines indicate the 1:1 relationship and one natural logarithm unit below and above.

Fig. 11. Comparison of measured and calculated $\ln K_v$ values for Na/K, Na/Ca, Na/Mg, Ca/Mg, K/Ca and K/Mg exchange reactions at $TN < 0.005$ mol/L. Circles and crosses: THELLIER and SPOSITO, 1989b, $TN = 0.0036$ mol/L. Squares and stars: THELLIER and SPOSITO, 1989b, $TN = 0.002$ mol/L. Up-pointing triangles and "plus" signs: THELLIER and SPOSITO, 1988, $TN = 0.001$ mol/L. Some symbols hide each other. Dotted lines indicate the 1:1 relationship and one natural logarithm unit below and above.

Fig. 12. Comparison of measured and calculated Na, Ca, Mg and K concentrations using the one-site model. Data from this study, SHAINBERG et al., 1980; SPOSITO and LEVESQUE, 1985; THELLIER and SPOSITO, 1988; THELLIER and SPOSITO, 1989b; THELLIER et al., 1992. Symbols hide each other and therefore are not explained here in relation to the data source. Full lines represent the 1:1 relationship.



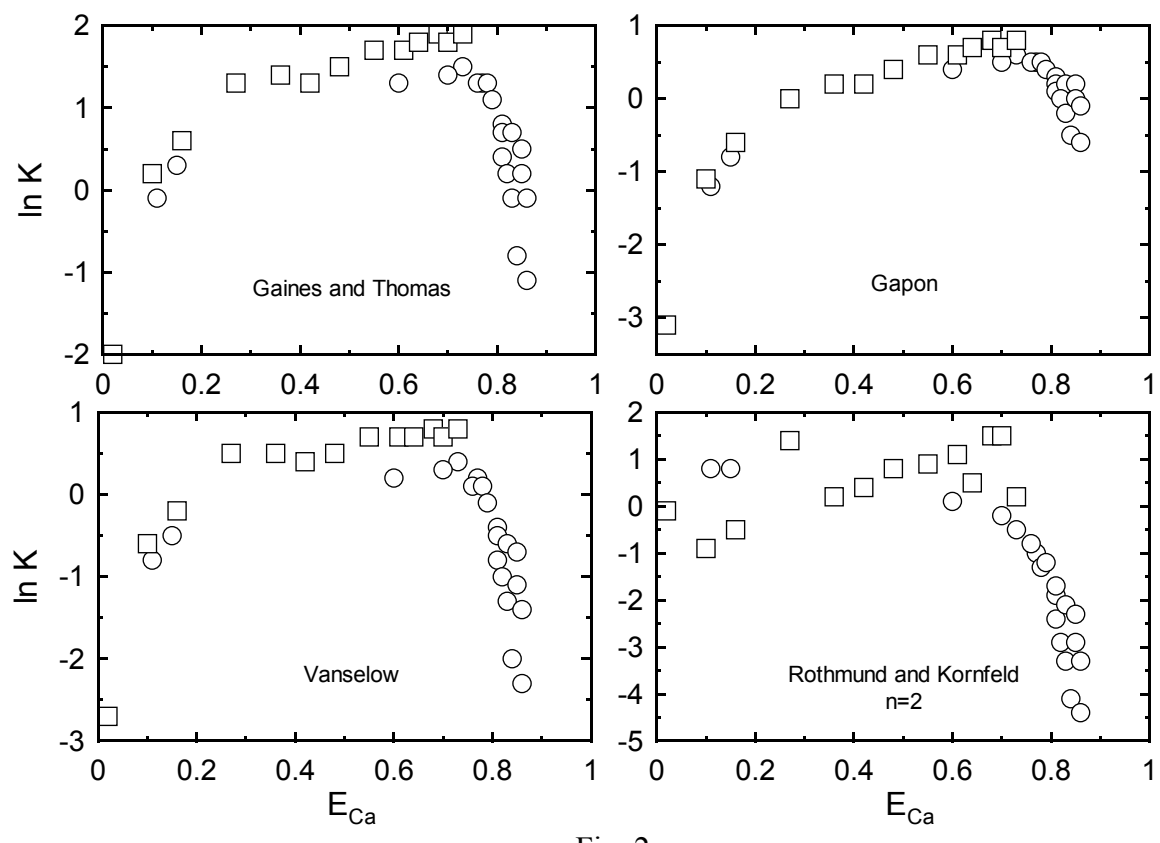


Fig. 2

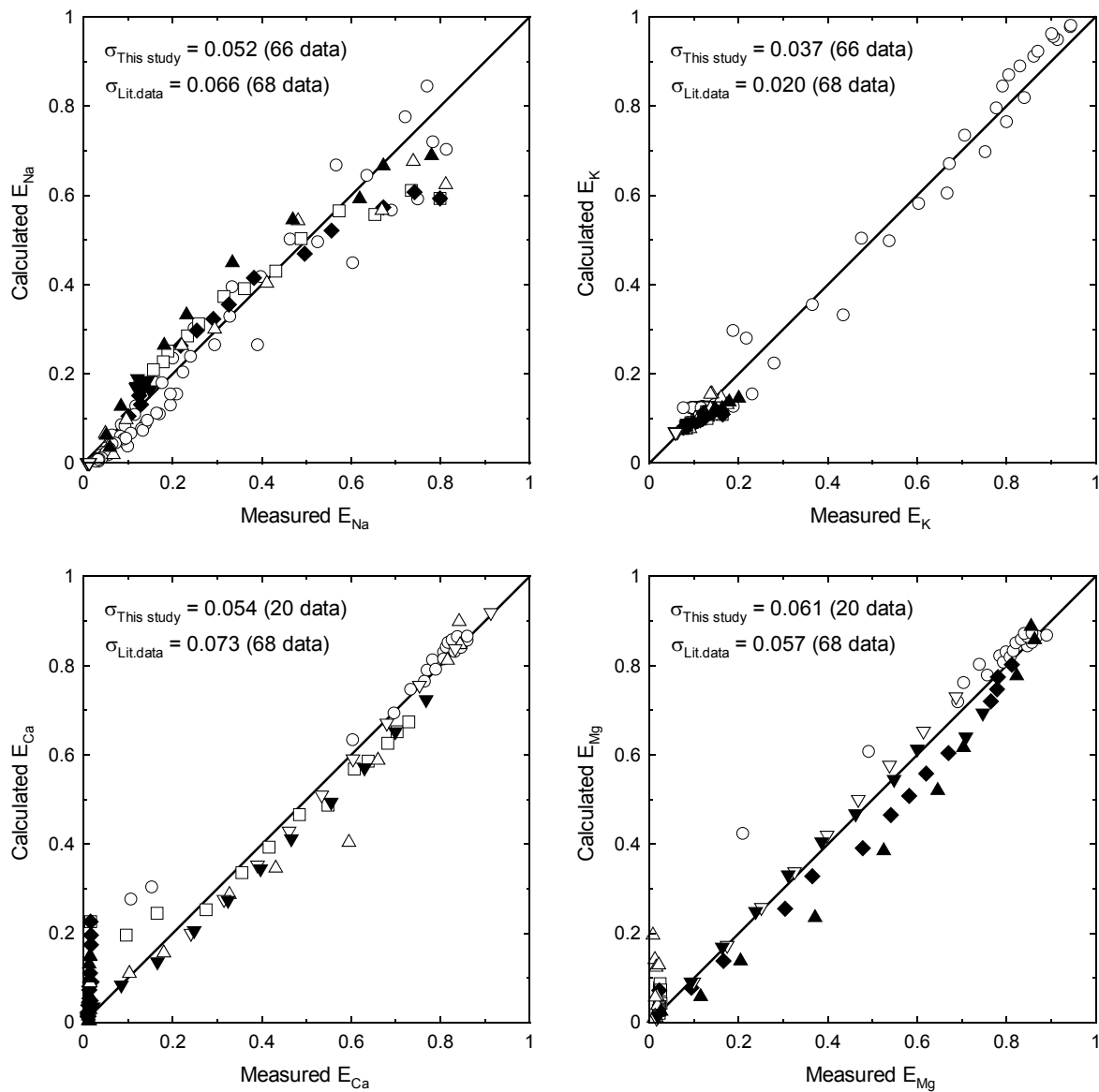


Fig. 3

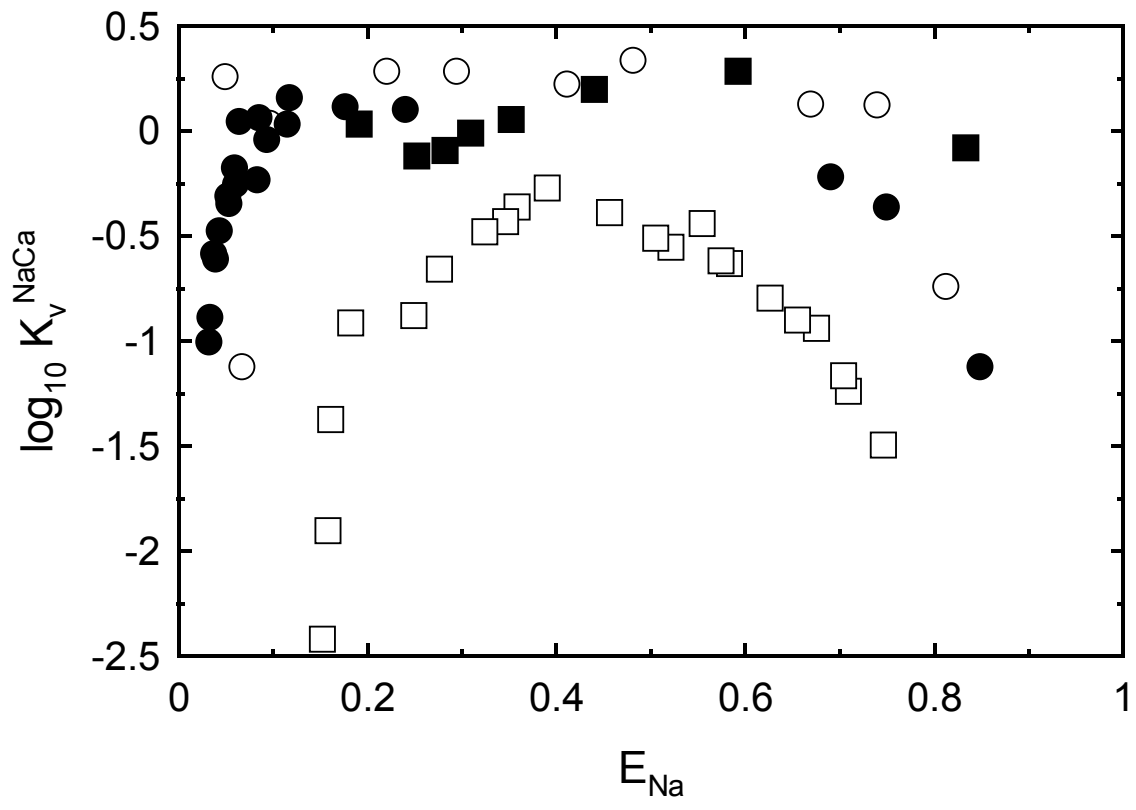
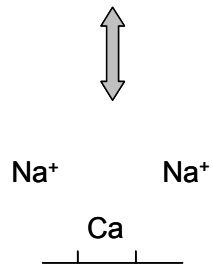
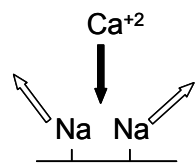
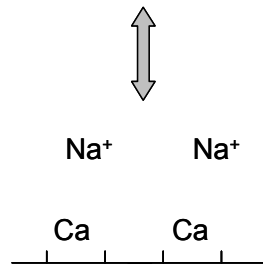
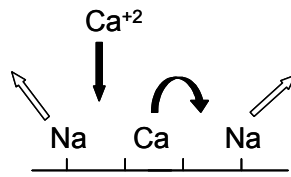


Fig. 4

Configuration 1



Configuration 2



Configuration 3

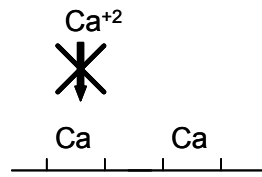


Fig. 5

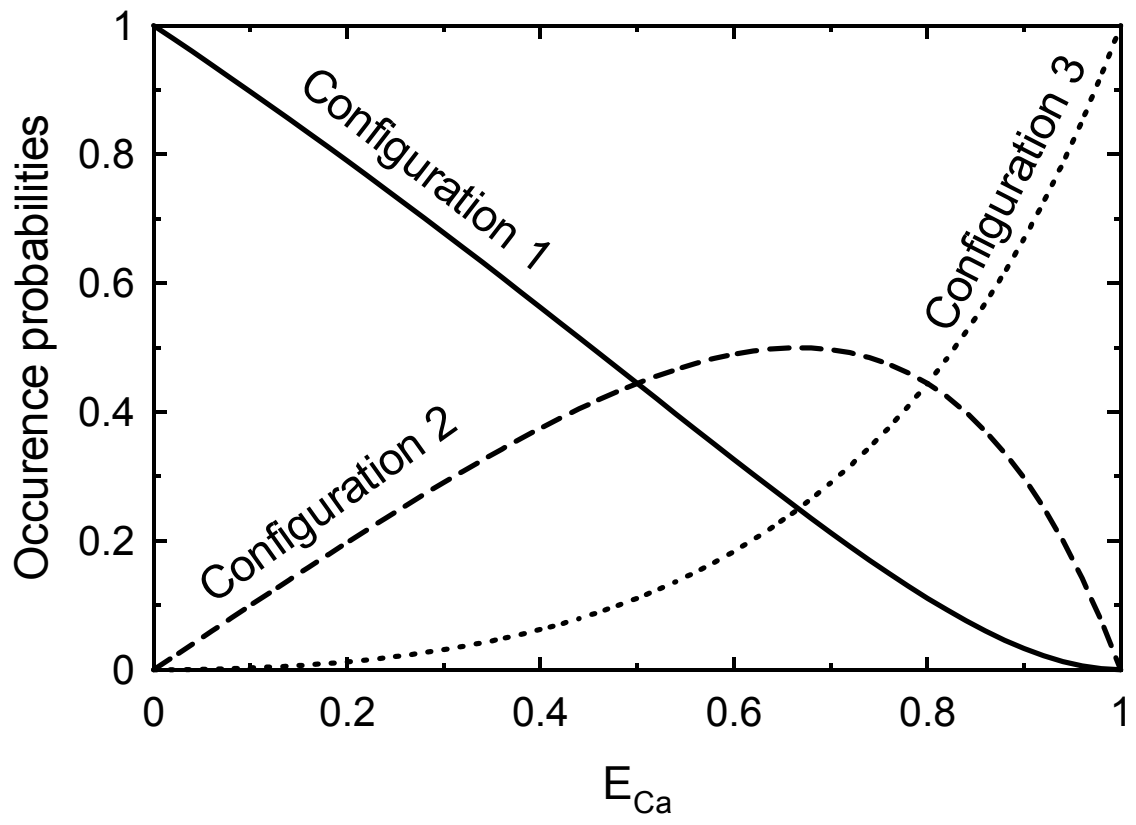


Fig. 6

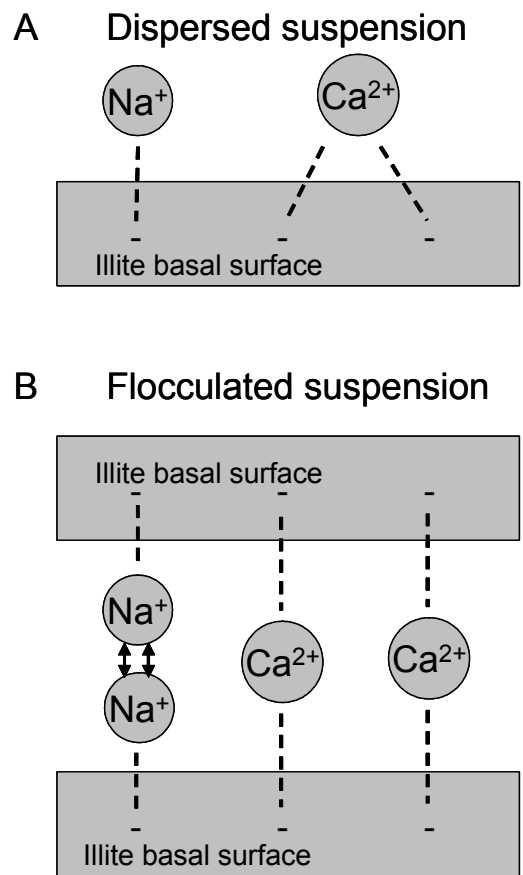


Fig. 7

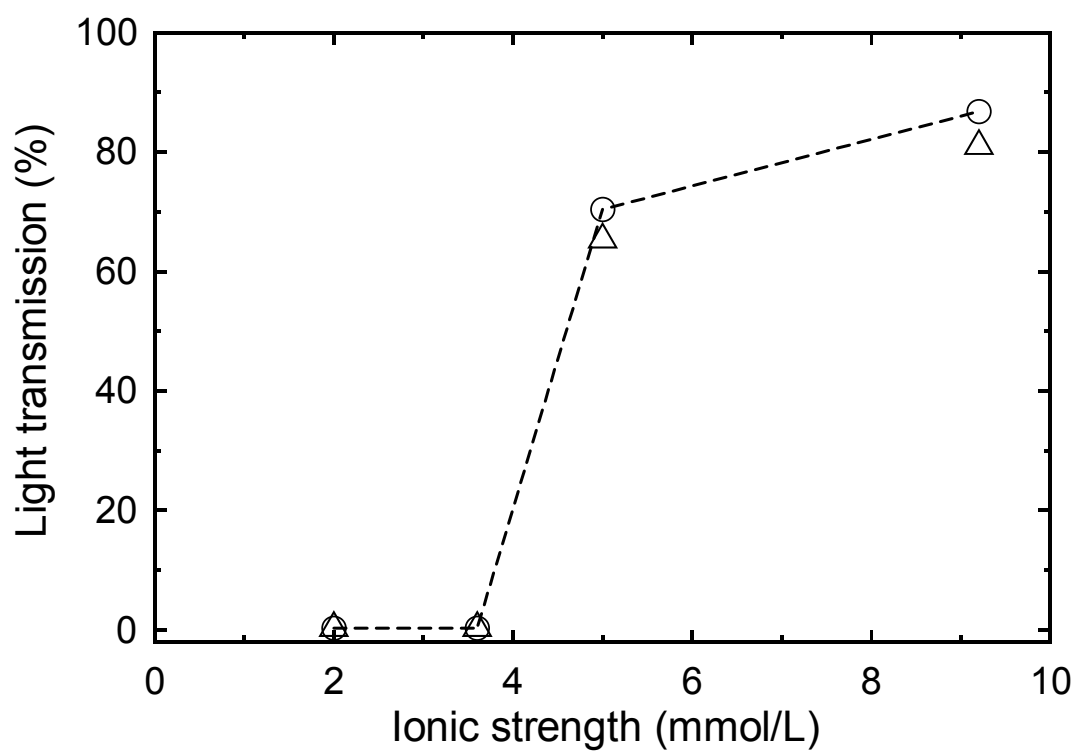


Fig. 8

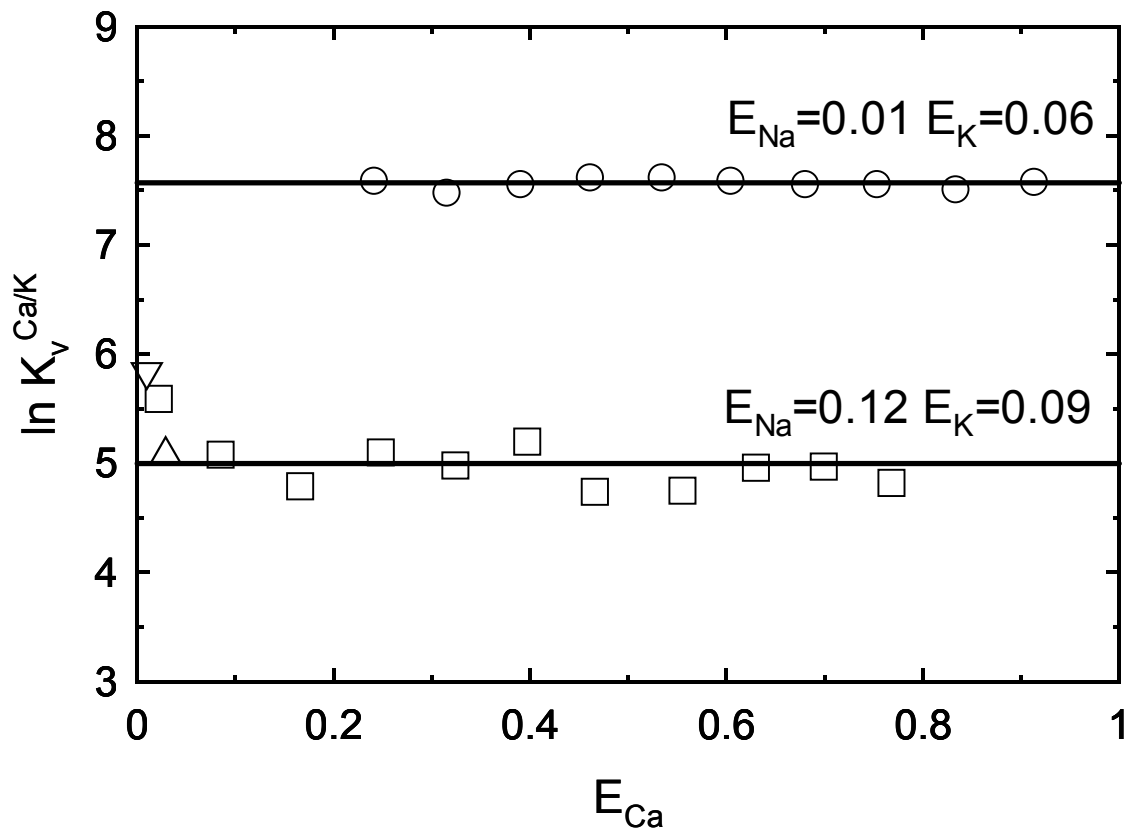


Fig. 9

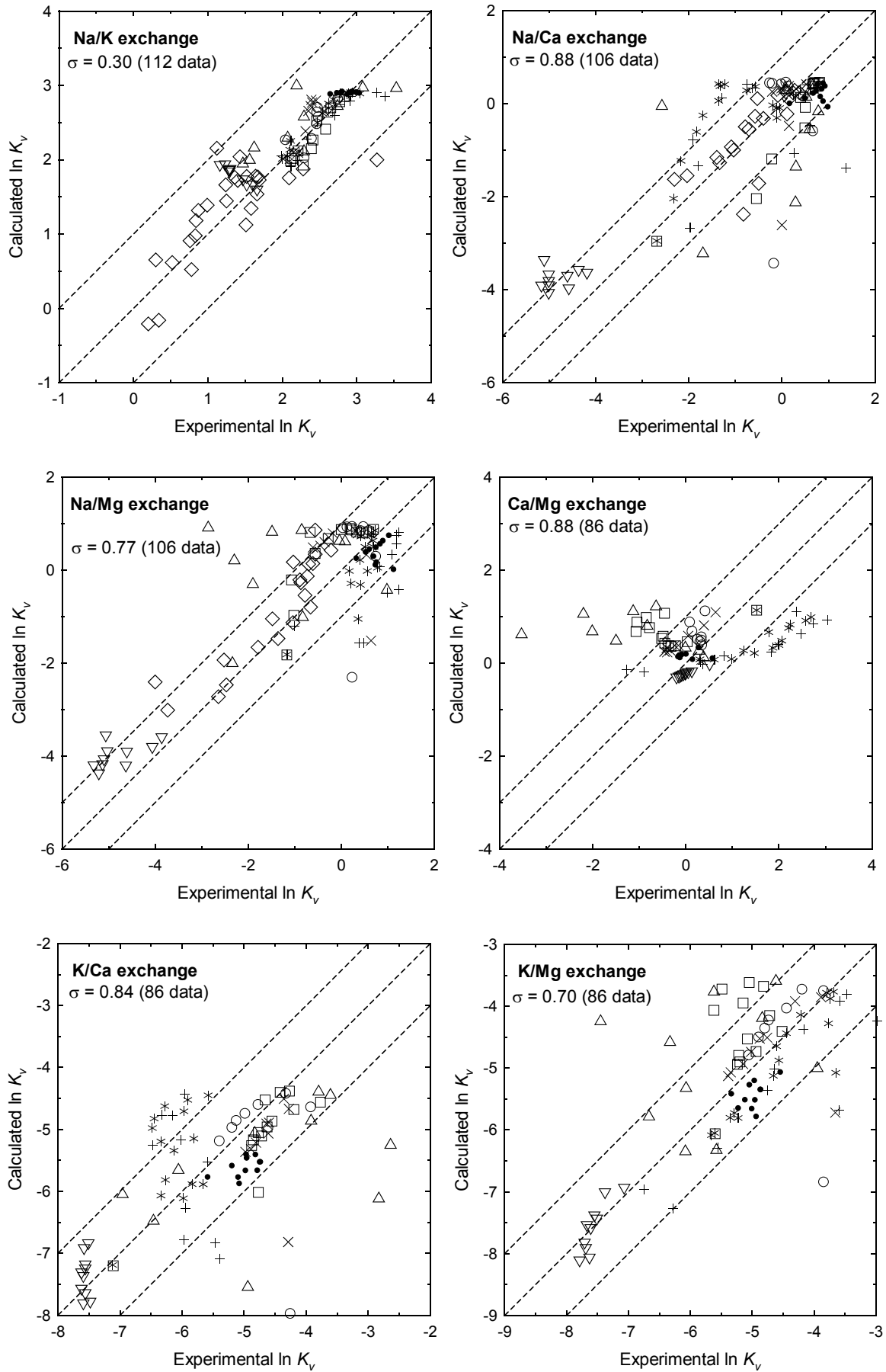


Fig. 10

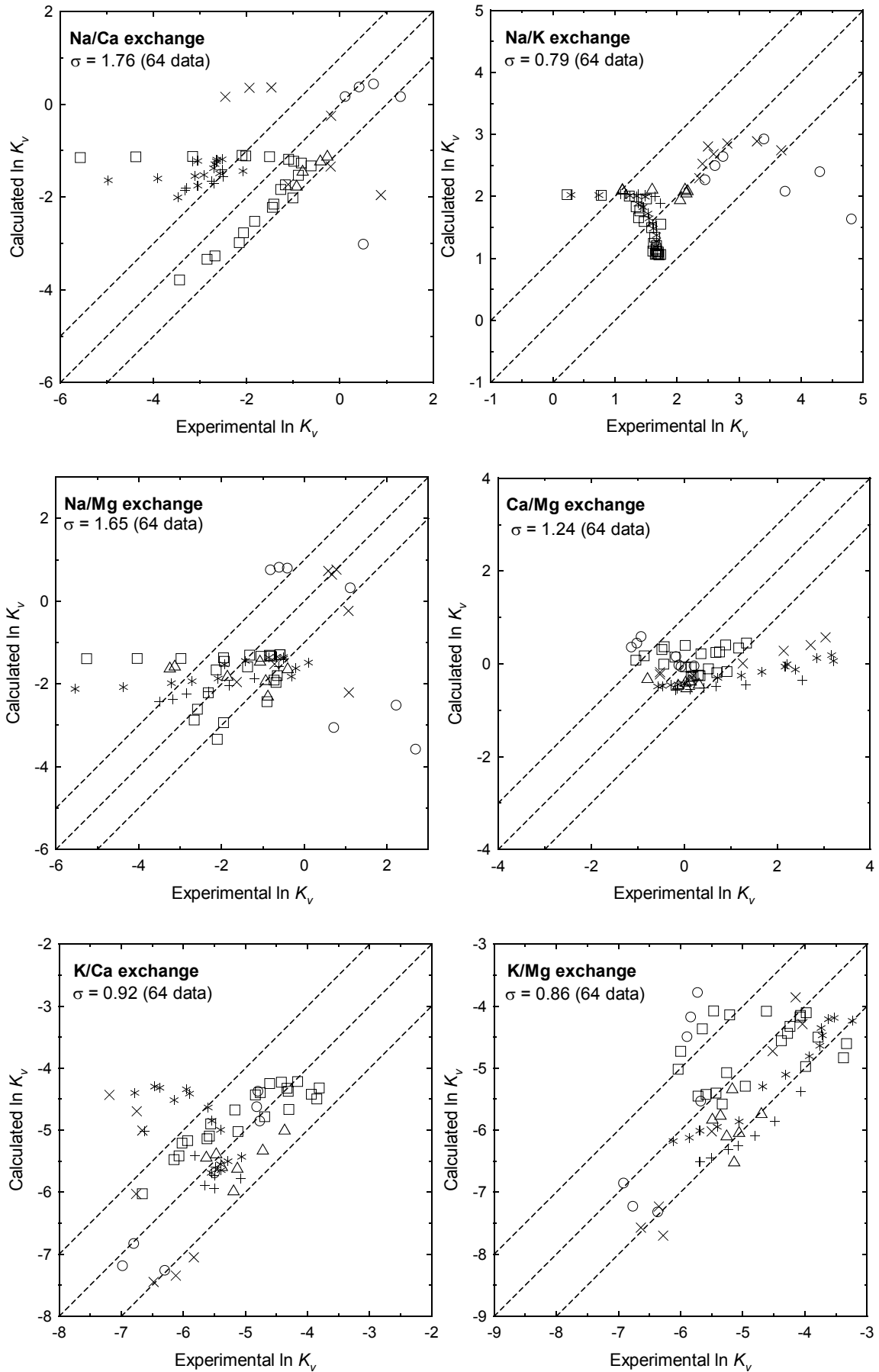


Fig. 11

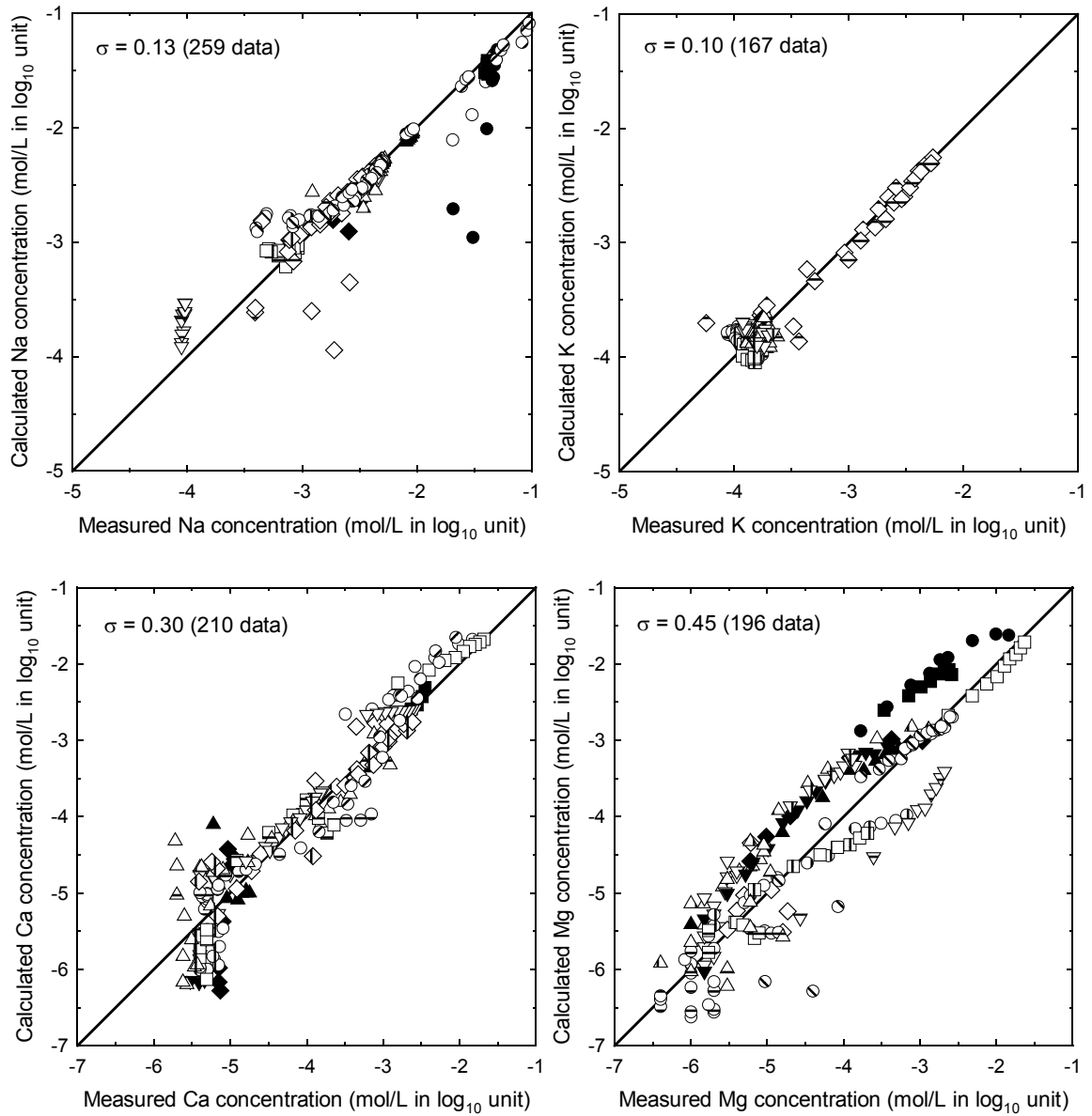


Fig. 12