

K–Ca–Mg binary cation exchange in saline soils from the north of Chile

Manuel Gacitúa^A, Mónica Antilén^{A,C}, and Margarita Briceño^B

^APontificia Universidad Católica de Chile, Facultad de Química, Vicuña Mackenna 4860, 6904411, Santiago, Chile.

^BUniversidad Arturo Prat, Av. Arturo Prat 2120 Casilla 121, Iquique, Chile.

^CCorresponding author. Email: mantilen@uc.cl

Abstract. The selectivities of the K–Ca and K–Mg cation exchange reactions were studied in batch experiments carried out with 7 Chilean saline sandy soils with low organic matter (OM) content, and rich in quartz and halite, by using the experimental Gaines and Thomas procedure and the semi-empirical Rothmund–Kornfeld approach.

The soils present high reactivity to the exchange process in terms of CEC and a preference order from the surface for the cation of $K > Ca > Mg$. In addition, the existence of different types of exchange sites was determined; some were specific for determined cations and others presented free competition. The proposed exchange reaction for both equilibria was thermodynamically possible and the studied cations presented a decreasing mobility order $K > Ca > Mg$, which follows the increasing order of hydrated ionic radii.

As for the Rothmund–Kornfeld semi-empirical approach, it can be employed on soils classified as Aridisol due to good fit with the experimental data. On the other hand, the Gaines and Thomas approach is only experimentally applicable since poses some restrictions concerning to salinity and carbonate contents in the studied soils.

Additional keywords: exchange equilibria, saline soils, thermodynamic models.

Introduction

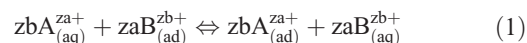
Soils affected by salts located in the north of Chile, which extends from 17°30' to 21°39'S and from 68°25'W to the Pacific Ocean, with dry weather and little rainfall per year, high average temperature, and low plant development, are distinctive (Chong 1988). These soils are classified as Aridisols and are characterised mainly by low parental mineral weathering, high salt content, low organic matter content, slight alkalinity, high limestone content, and sandy texture (Luzio 1986). The study of cationic exchange is important because it enables the selectivity displayed by some soils towards chemical species that are determined as plant nutrients or as soil and water contaminants to be established. Thus, using the determined selectivity coefficient, thermodynamic parameters describing an exchange reaction can be established. Approximations such as Gaines and Thomas (Gaines and Thomas 1953) and Rothmund–Kornfeld (Bond 1995) have been used to gain an insight into the exchange behaviour characteristics, mainly of Andepts and other inorganic fractions of soils in Chile. (Escudey and Galindo 1988; Escudey *et al.* 1997, 2001, 2002; Salazar *et al.* 2002). However, these approximations have been applied on soils with high Na and saline content, which might turn binary equilibria into ternary ones. Salinity in this Chilean region is a feature that hinders agricultural activities and, besides, restrains the extrapolation of our already obtained results to these surfaces. Thus, application of the experimental Gaines and Thomas model and the semi-empirical Rothmund–Kornfeld approach to saline systems will enable the cationic exchange

equilibrium to be described by means of a simplification in the thermodynamic parameter determination.

With the aim of studying and determining thermodynamic behaviour and cationic preference in Chilean soils affected by salts, to obtain more specific data about ion exchange, a study of heterovalent cation exchange equilibria was performed, evaluating the applicability of: (i) the Gaines and Thomas physicochemical approach, which requires a large number of equations and involves a complex experimental design; and (ii) the Rothmund–Kornfeld approach, where the method is potentially more accurate because it avoids some extrapolation of the data required for the thermodynamic approach (Bond 1995).

Theory

The cation exchange equilibrium according to the Gaines and Thomas model (Gaines and Thomas 1953) may be expressed as:



where z represents the ion valence, and (ad) and (aq) refer to the solid phase and solution, respectively.

The general Rothmund–Kornfeld equation for binary exchange, using the Gaines and Thomas equivalent fractions terms (Bond 1995), is:

$$k_{gt}^{ij} = \frac{N_j^{zi}}{N_i^{zj}} \left[\frac{\gamma_i^{zj} M_i^{zj}}{\gamma_j^{zi} M_j^{zi}} \right]^{n_{gt}^{ij}} \quad (2)$$

where N is the equivalent fraction in the exchanger phase, M is ion concentration in solution, γ is the ion activity coefficient, k_{gt}^{ij} and n_{gt}^{ij} are the Rothmund–Kornfeld empirical constants for the specific pair (i – j) and soil. If Eqn 2 is obeyed, from a plot of $\log[N_j^{zi}/N_i^{zj}]$ v. $\log[\gamma_j^{zi} M_j^{zi}/\gamma_i^{zj} M_i^{zj}]$, $\log(k_{gt}^{ij})$ and n_{gt}^{ij} are obtained from the intercept and the slope, respectively. The equilibrium exchange reaction for each specific pair of ions considered may be written as (Bond and Verburg 1997):

$$\frac{N_{Ca}}{N_K} = k_{gt}^{K-Ca} \left[\frac{\gamma_{Ca} M_{Ca}}{\gamma_K^2 M_K^2} \right]^{n_{gt}^{K-Ca}} \quad (3a)$$

$$\frac{N_{Mg}}{N_K} = k_{gt}^{K-Mg} \left[\frac{\gamma_{Mg} M_{Mg}}{\gamma_K^2 M_K^2} \right]^{n_{gt}^{K-Mg}} \quad (3b)$$

If k_{gt}^{ij} and n_{gt}^{ij} are known, the natural logarithm of the selectivity coefficient (Kc_{ij}) and the equilibrium constant (Ke_{ij}), for each binary equilibrium may be calculated by (Bond 1995):

$$Kc_{ij} = (k_{gt}^{ij})^{\frac{1}{n_{gt}^{ij}}} \left(\frac{N_i^{zj}}{N_j^{zi}} \right)^{\frac{1}{n_{gt}^{ij}} - 1} \quad (4)$$

$$Ke_{ij} = (k_{gt}^{ij})^{\frac{1}{n_{gt}^{ij}}} \exp[(z_i - z_j)/n_{gt}^{ij}] \quad (5)$$

The adsorption isotherms were compared with a non-preference isotherm (Escudey *et al.* 2001).

Material and methods

Soils

Soil samples were selected in relation to longitudinal transect from the altiplano, the Andes slopes, the *Pampa del Tamarugal*,

and the coastal shore of the province of Iquique. All samples were collected at a depth of 0–0.20 m from uncultivated areas La Tirana (LT), Matilla Lama (ML), Alto Hospicio (AH), Pica (P), Canchones (CA), Salar Huasco (SH), and Coposa (CO). The samples were air-dried and sifted through 2-mm sieves. A description and characterisation of all samples is given in Table 1.

Chemical soil characterisation

The pH (1 : 2.5 soil : water or KCl ratio), electrical conductivity (EC), and organic matter (OM) content based on the Walkley–Black method adjusted to Chilean soils (Sadzawka 1991) were determined for all soils. Calcium carbonate (limestone) content was determined by titrimetry with HCl, and total C, S, and N by elemental analysis. Sodium adsorption relation (SAR) and exchangeable sodium percentage (ESP) were assessed by cation exchange (Sadzawka 1991). Particle size distribution was determined using the hydrometer method (Bouyoucos 1962) for all samples.

X-ray diffraction analysis was conducted on a Philips Norelco diffractometer equipped with a Cu–K α radiation source and a Ni filter with pulse high analyser system. The X-ray diffraction analysis was carried out on oriented samples that were saturated with Mg, solvated with glycerol, saturated with K at room temperature, and heated at 550°C.

Cation exchange equilibria

The equivalent of 3 g of dry soil was placed into a 50-mL centrifuge tube, homoionised with 0.5 M KCl, and washed with double-distilled water until no chloride and low-constant electrical conductivity was detected in the supernatant. The samples were then equilibrated with solutions of a given

Table 1. General characterisation of soil samples

n.d., Not detected

Characteristic	Coposa	Salar Huasco	Pica	Matilla Lama	Canchones	La Tirana	Alto Hospicio
Soil order/source	Aridisol	Aridisol	Aridisol	Aridisol	Aridisol	Aridisol	Aridisol
Sampling location							
Latitude	20°38'S	20°18'S	20°28'S	20°31'S	20°25'S	20°21'S	19°35'S
Longitude	68°40'W	68°52'W	69°15'W	69°22'W	69°33'W	69°40'W	70°11'W
Altitude (m)	3730	3700	1100	1020	993	1012	499
EC (dS/m)	0.6 ± 0.1	0.2 ± 0.1	0.5 ± 0.0	0.6 ± 0.1	64.7 ± 0.1	86.5 ± 0.0	12.4 ± 0.0
SAR	46.0	2.0	3.0	6.3	1333.0	520.0	116.0
ESP	5.7	2.9	4.3	8.6	95.2	88.6	63.5
Classification ^A	Normal	Normal	Normal	Normal	Saline-sodium	Saline-sodium	Saline-sodium
Limestone (%)	6.0 ± 0.2	0.5 ± 0.0	2.8 ± 0.2	1.4 ± 0.2	12.0 ± 0.2	4.4 ± 0.2	6.5 ± 0.2
Organic matter (wt%)	0.18 ± 0.02	0.41 ± 0.02	0.07 ± 0.00	0.04 ± 0.00	1.16 ± 0.02	1.05 ± 0.02	0.20 ± 0.02
pH (H ₂ O 1 : 2.5)	7.81 ± 0.11	6.78 ± 0.05	8.53 ± 0.01	8.65 ± 0.06	8.55 ± 0.02	8.39 ± 0.03	8.27 ± 0.03
C–N analysis (%)							
C	0.03	1.99	0.01	0.05	0.98	0.29	0.96
N	0.31	0.43	0	0.29	0.36	0.37	0.30
S	0.51	0.85	0.54	0.00	2.31	0.69	2.98
Mineralogical composition >50%	Sodium anorthite	Quartz	Quartz	Quartz	Halite	Halite	Quartz
Particle size distribution (g/kg)							
Clay	63	10	41	n.d.	50	91	50
Lime	261	45	30	n.d.	50	221	263
Sand	656	945	929	100	900	688	687

^ASoil Taxonomy Classification, USDA.

concentration containing various KCl–CaCl₂ and KCl–MgCl₂ ratios, with K equivalent fraction, X_K , in solution in the range 0–1, with a total of 8 different solutions at constant ionic strength (0.050 ± 0.005 mol/L). The suspension was centrifuged and resuspended 3 times with the same solution to ensure equilibration at the composition of the added solution. The samples were kept in suspension overnight under orbital shaking, and were then centrifuged and weighed to determine the amount of retained solution, after subtraction of tube plus soil weight. Exchangeable plus soluble ions were replaced by 4 washings with 20 mL each of 0.15 M NH₄NO₃. Potassium, Ca, and Mg were determined by atomic absorption spectroscopy and corrected for the entrapped solution in the sample. The mean K+Ca and K+Mg values exchanged over all X_K were estimated as the cation exchange capacity (CEC) at soil equilibrium pH. Solution phase activity coefficients were obtained from the Davies equation (Stumm 1996).

Results and discussion

Chemical characterisation

The general characterisation of the soils is presented in Table 1. These soils can be described as of low OM content, with a mineralogy dominated by highly crystalline compounds such as quartz, halite, or sodium anorthite, with dolomite and calcite also present less significantly.

In general, the pH was alkaline or close to neutrality for all soils, as in SH soil, for example, showing an important development of alkalinity related to erosive factors.

With respect to the salinity of the soils, the SAR and ESP values show the high degree of sodium salinity of the soils from LT, AH, and CA. This agrees with the EC values of the medium. Furthermore, besides being soils classified as Aridisols, it is possible to classify the samples according to their salinity, where ML, P, SH, and CO soils having normal salinity, while LT, AH, and CA soils are classified as sodium-saline. As to the limestone content, it agrees with the capacity for developing an alkaline pH, with the presence of cations such as Ca²⁺ or Mg²⁺, forming insoluble carbonates and decreasing the pH to values close to 8.2; these soils are called calcareous, and all the soils studied, except those from SH, fall into this category.

With respect to particle size distribution, all the soils have low clay content, not greater than 10%. All of the soils are composed of at least 65% sandy fraction, which confirms their origin and slight weathering. This information is of particular significance for the chemical and physicochemical studies carried out, because even though the existence of cation exchange has been shown to exist between the solution and the sandy soil fraction (Barticevic *et al.* 1975), it is the clay fraction that is mainly responsible for the occurrence of the cation exchange processes, together with the organic matter content (Salazar *et al.* 2002).

The CEC values obtained (Table 2) contrast with the values expected from the slight reactivity of soils with low clay content in cation exchange processes, illustrating the total number of cation exchange sites present in the soil surface. Moreover, the CEC obtained was constant, fulfilling one of the most important restrictions of the Gaines and Thomas thermodynamic model. Therefore, and considering the low presence of OM in the soils,

Table 2. Cation exchange capacity (CEC, cmol(+)/kg) and pH at equilibrium

Soil	K–Ca		K–Mg	
	CEC	pH	CEC	pH
CO	8.2 ± 1.1	7.00 ± 0.16	9.7 ± 0.5	6.77 ± 0.12
SH	3.3 ± 0.5	6.13 ± 0.15	2.7 ± 0.4	5.82 ± 0.10
P	11.6 ± 0.4	8.21 ± 0.50	4.6 ± 0.2	8.72 ± 0.10
ML	6.6 ± 0.5	7.44 ± 0.39	4.9 ± 0.6	8.24 ± 0.21
CA	15.6 ± 0.4	8.21 ± 0.39	9.9 ± 0.4	8.49 ± 0.23
LT	21.3 ± 0.8	8.55 ± 0.31	11.9 ± 1.0	8.89 ± 0.23
AH	89.4 ± 2.3	8.45 ± 0.11	2.7 ± 0.3	8.24 ± 0.14

this would not be a factor of primary importance in the CEC of these kinds of soils.

The pH values were constant (Table 2), with a maximum average fluctuation of ± 0.50 units, and together with the low probability of the existence of variable surface charge because of the origin of the soils, pH would not be a factor in the variation of the CEC due to modification of the surface (Galindo *et al.* 1992). Therefore, since there are no important differences in the pH of the soils, the CEC can be compared, and it was found that their average values for the K–Ca equilibria were in general higher than those for K–Mg. That difference indicates that the exchange process is more important in the presence of Ca²⁺ than of Mg²⁺, and that is evidence of a selectivity of the system for Ca²⁺ over Mg²⁺.

The CEC of the AH soil is higher than that of the other soils, and it is related to the supply of Ca²⁺ and K⁺, with values of 88.0 and 1.3 cmol(+)/kg, respectively, which for Ca²⁺ exceeds the amount of cation offered by the equilibrating solutions used. An explanation of this behaviour is that it is due to the high natural Ca²⁺ content of the soil, as carbonates and other salts, which would not be totally removed either by the homoionisation processes or by the washing before the exchange. Therefore, these findings lead us to assert that the limestone content of some samples would be influencing the CEC results for cationic-exchange equilibria, which can be minimised by removal of carbonates before making the exchange equilibria. Furthermore, due to SAR high values, Na⁺ cation was determined in the displacement stage with average values of 2.3 ± 0.1 and 7.3 ± 0.4 cmol(+)/kg in the K–Ca and K–Mg equilibria, taking into account all soils. These results would reveal that Na in soils is mainly exchanged by the combination of K–Ca cations rather than by K–Mg cations, which would be associated with the exchanger preferences.

In relation to the ionic strength variation of solutions and its effect on cation selectivity and the CEC (Pizarro 1994), it is only possible in the presence of surfaces with variable charge. However, preliminary measurements of isoelectric points from these soils would indicate the nonexistence of these kinds of surfaces (M. Antilén, unpublished data). With respect to the rest of the samples, LT and CA have the highest CEC values, in agreement with their higher percentage of the clay fraction, indicating that this factor is important to justify the existing differences.

Exchange isotherms

The selectivity curves belonging to the K–Ca equilibrium, presented in Fig. 1, show that there is a group of soils

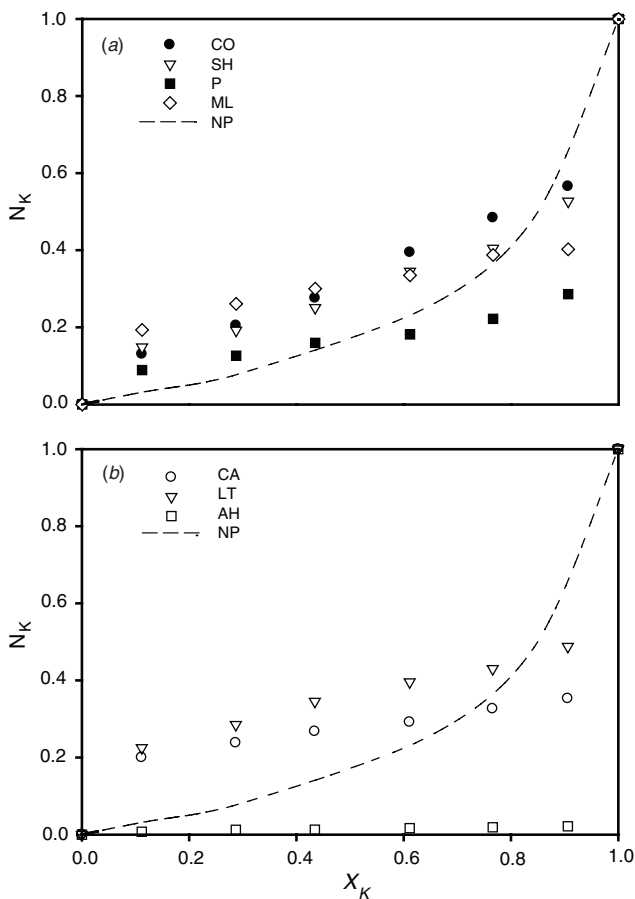


Fig. 1. K–Ca exchange isotherms and no preference (NP) isotherm at: (a) Coposa (CO), Salar Huasco (SH), Pica (P), Matilla Lama (ML); (b) Canchones (CA), La Tirana (LT), and Alto Hospicio (AH) soils.

(LT, ML, SH, CO, and CA) that have preference for K over a wide range of X_K going from approximately 0 to 0.8. However, this preference for K^+ is not as important in relation to Ca^{2+} because the curves are close to the no preference curve. On the other hand, soil P has a slight preference for K^+ , with a change in preference for Ca^{2+} after X_K reaches values close to 0.5, a behaviour that indicates a similar preference for each of the cations offered. For the AH soil it is seen that there is no preference for K^+ over the whole range of values of X_K , indicating preference for the Ca^{2+} .

The selectivity curves for the K–Mg equilibrium, presented in Fig. 2, show that all the soils have a marked preference for K^+ over Mg^{2+} at all the equivalent fraction values of the equilibrating solution used, X_K . Therefore, from the behaviour seen for both heterovalent cationic equilibria, the following preference sequence of the exchanger can be established: $K^+ > Ca^{2+} > Mg^{2+}$, which coincides with the sequence of increasing hydrated ionic radius, with a range 3.8–5.3 Å for K^+ , 9.6 Å for Ca^{2+} , and 10.8 Å for Mg^{2+} (Mitchell 1993). Therefore, this sequence, coincident with the hydrated ionic radius, shows that this variable is above the magnitude of the charge on the studied species.

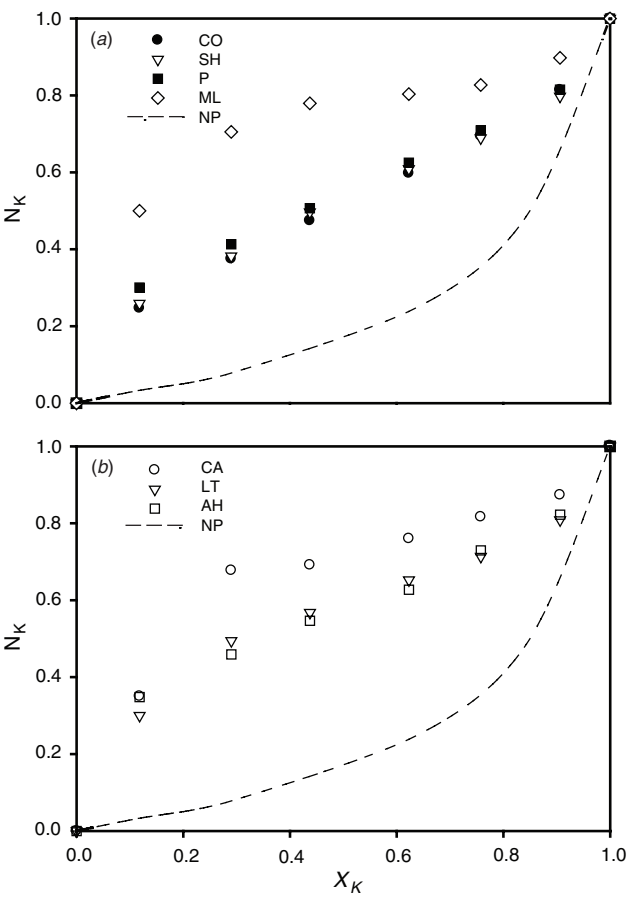


Fig. 2. K–Mg exchange isotherms and no preference (NP) isotherm at: (a) Coposa (CO), Salar Huasco (SH), Pica (P), Matilla Lama (ML); (b) Canchones (CA), La Tirana (LT), and Alto Hospicio (AH) soils.

Thermodynamic equilibrium constants

Thermodynamic constant for K–Ca and K–Mg exchange equilibria of all samples was determined employing the Rothmund–Kornfeld approximation. Empiric parameters k_{gt}^{ij} and n_{gt}^{ij} (Table 3) were obtained. From these parameters, N_i and N_j values can be determined. The values showed a very good fit for K–Ca ($n = 42$, $R^2 = 0.994$) and K–Mg ($n = 42$, $R^2 = 0.991$) compared with those experimentally obtained by the Gaines and Thomas approach. This good fit to the formulation allows the deduction that all exchange sites have been occupied solely by the cations considered in the experiment.

Table 3. Empirical parameters k_{gt}^{ij} , n_{gt}^{ij} and equilibrium thermodynamic constants obtained by Rothmund–Kornfeld approach

Soil	K–Ca			K–Mg		
	k_{gt}^{K-Ca}	n_{gt}^{K-Ca}	$\ln K_{R-K}$	k_{gt}^{K-Mg}	n_{gt}^{K-Mg}	$\ln K_{R-K}$
CO	1.450	0.558	−1.13	0.356	0.568	−3.58
SH	2.251	0.470	−0.40	0.377	0.535	−3.69
P	10.57	0.372	3.66	0.351	0.503	−4.08
ML	3.497	0.267	0.94	0.166	0.309	−9.05
CA	5.426	0.203	3.41	0.212	0.278	−9.16
LT	2.275	0.293	−0.61	0.377	0.364	−5.42
AH	2074	0.305	21.73	0.336	0.452	−4.62

For the K–Ca equilibrium, the values of $\ln K_{R-K}$ show a relative preference for K^+ over Ca^{2+} in the CO, SH, and LT soils, with negative values. The ML, P, CA, and AH soils have positive values, i.e. they show an overall selectivity of these soils for Ca^{2+} . The values of $\ln K_{R-K}$ for the K–Mg equilibrium indicate that all the soils show preference for K^+ over Mg^{2+} . This is consistent with the analysis of the selectivity curves for K–Mg equilibrium.

Selectivity coefficients, K_c

Selectivity coefficients were worked out using Rothmund–Kornfeld approximation. From Fig. 3, a quantitative indication of the changes in selectivity during the exchange reaction can be observed. Curves shapes suggest the existence of exchange sites with different affinities. For N_K values <0.2 , all soils but AH showed a high K^+ selectivity. This has been ascribed to the existence of few ions; consequently, sites having high interaction with them are occupied. However, as N_K increases, the K^+ selectivity starts decreasing, earlier for P soil, because the amount of K^+ placed in specific sites decreases. Then, a change in the selectivity of

K^+ over Ca^{2+} is observed, which together with the behaviour attained at lower values of N_K would indicate the existence of sites having preference for K^+ . These specific sites would be occupied first, then allowing Ca^{2+} to enter owing to its characteristics in terms of hydrated ionic radius and charge. This possibility is justified by considering that in K–Mg equilibria, Mg^{2+} does not enter these specific sites, probably due to its greater hydrated ionic radius (Escudéy *et al.* 1997).

For the K–Mg equilibrium, all the soils exhibited a marked preference for K^+ over Mg^{2+} on a wide N_K range (from 0 to 0.8–0.9) (Fig. 4). This behaviour supports the assumption about the existence of a large preference of the system for K^+ , whereas for N_K values between 0 and 0.2–0.4 a preference only for K^+ exists, indicating the availability of exclusive sites for this cation. There is also an intermediate range (from 0.2–0.4 to 0.8–0.9) for all the soils in which selectivity for K^+ decreases, indicating the existence of competition for the cations to be adsorbed by vacant sites. However, K^+ is always preferred over Mg^{2+} , probably due to its lower hydrated ionic radius, and therefore greater mobility.

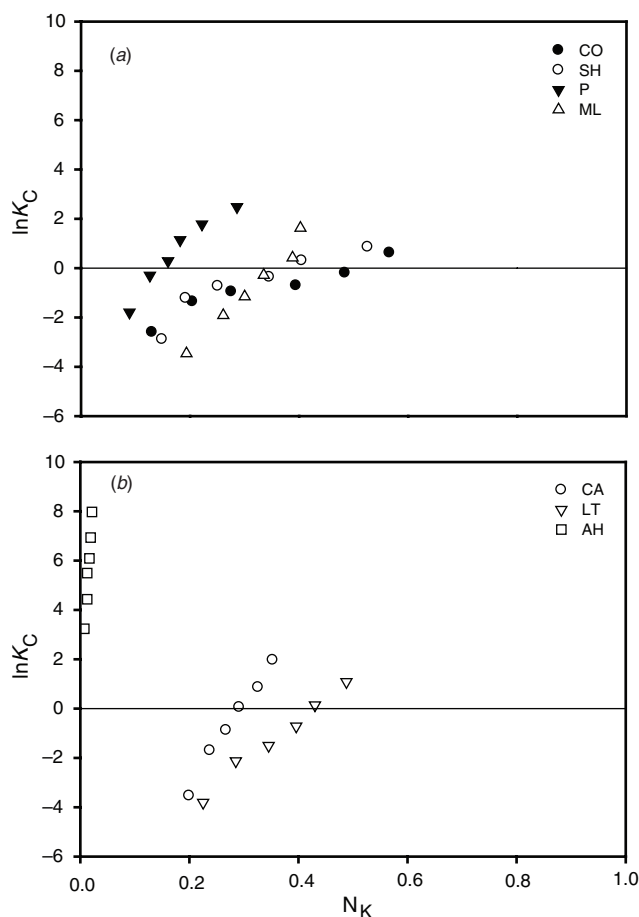


Fig. 3. Selectivity coefficients for K–Ca exchange in saline soils as $\ln K_c$ v. fractional K^+ saturation: (a) Coposa (CO), Salar Huasco (SH), Pica (P), Matilla Lama (ML); (b) Canchones (CA), La Tirana (LT), and Alto Hospicio (AH) soils.

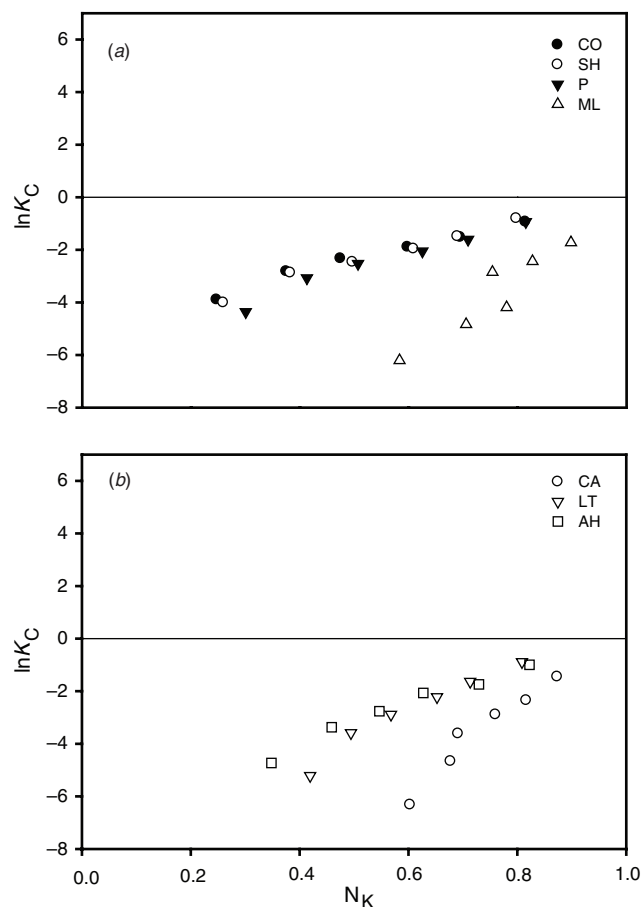


Fig. 4. Selectivity coefficients for K–Mg exchange in saline soils as $\ln K_c$ v. fractional K^+ saturation: (a) Coposa (CO), Salar Huasco (SH), Pica (P), Matilla Lama (ML); (b) Canchones (CA), La Tirana (LT), and Alto Hospicio (AH) soils.

Conclusions

The soils were classified as Aridisols and calcareous, with low organic matter and clay content, a mineralogy dominated mainly by quartz and halite, and the presence of variable amounts of carbonate and a high general salinity.

From the cationic K–Ca and K–Mg exchange equilibria, the preference sequence $K^+ > Ca^{2+} > Mg^{2+}$ is established, which depends on the hydrated ionic radii as well as on the CEC values and the observed cation mobility. In general, the preference shown by the Aridisols is supported by thermodynamic parameters obtained from the Rothmund–Kornfeld model.

The existence of different kinds of exchange sites was established: selective sites for K^+ (detected at low fractional K^+ saturation), and sites in which there is free competition for the K–Ca or K–Mg cations.

Finally, the Gaines and Thomas experimental model is applicable to soils classified as Aridisols, while the Rothmund–Kornfeld approach is suitable for the determination of thermodynamic parameters.

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