Sodium/Calcium Exchange in Montmorillonite and Illite Suspensions

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ABSTRACT

The effect of salt concentration and exchanger composition on Na/Ca exchange in montmorillonite and illite suspensions (0.02 to 0.08 g clay/g water) was studied, where the equivalent fraction of exchangeable Ca, \( E_{Ca} \), ranged from 0.6 to 1. A theoretical evaluation based on double-layer theory for montmorillonite indicates that the formation of tactoids and internal surfaces at the Ca\(^{2+}\) end of the exchange isotherm can cause the Vanselow selectivity coefficient, \( K_{v} \), to depend on exchangeable cation composition and total electrolyte concentration. Whereas for montmorillonite, \( K_{v} \) increased with \( E_{Ca} \) (0.6 < \( E_{Ca} \) < 1), as predicted for internal surfaces, the reverse was true for illite, where external surfaces predominate. Likewise, for a given Na adsorption ratio, dilution of the equilibrium solution for illite (0.5 < \( E_{Na} \) < 1) and for montmorillonite (\( E_{Na} \) ≈ 0.6) decreased \( K_{v} \) as predicted for external surfaces.

The average Gapon selectivity coefficient for the montmorillonite (0.011) and illite clays (0.223) with \( E_{Na} \) < 0.8, suggests that the value for soils (0.0148) reflects their mixed mineralogy.

Additional Index Words: quasicrystals (tactoids), external and internal surfaces, Gapon selectivity coefficient, Vanselow selectivity coefficient, adsorption ratio.


CATION-EXCHANGE EQUATIONS describe the distribution of cations between the exchanger phase and its equilibrium solution. Several approaches have been used in deriving these equations. The formal thermodynamic treatment, based on the mass action principle, gives no direct information about the molecular mechanisms and forces operating in the system. Another approach, based on the diffuse double-layer theory, consists of a molecular description of the Coulombic forces which are operative in the process of exchange. Discrepancies between the experimental results and those predicted by the diffuse double-layer theory facilitate the evaluation of the magnitude of other forces acting in the Na/Ca ionic distribution on clay surfaces. In this study, the effect of the presence of the Ca quasicrystals on the ionic distribution is considered. Also, the equations based on the thermodynamic and the diffuse double-layer approach are compared with the empirical Gapon equation (U. S. Salinity Laboratory Staff, 1954).

Here we report the effect of solution phase composition on that of the exchange phase for Ca/Na equilibrium on Wyoming montmorillonite and Fithian illite in the range of exchangeable Na fraction, \( E_{Na} \), commonly found in agricultural soils (\( E_{Na} \) < 0.40). Since in this range montmorillonite forms quasicrystals or tactoids (Shainberg and Otoh, 1968), we expected that the presence of internal surfaces would affect the selectivity coefficient. The differences in the cation exchange selectivity coefficients between the two clays were analyzed according to the various theories and the application of the findings to the ionic equilibria of saline soils was evaluated.

Theoretical Considerations

For the exchange reaction

\[ 2 \text{Na}^{+} + \text{Ca}^{2+} = \text{CaX}_{2}^{0} + 2 \text{Na}^{+} \]  \[ [1] \]

the thermodynamic exchange equilibrium constant coefficient is represented by

\[ K = \frac{(\text{Na}^{+})^2 (\text{CaX}_2^{0})}{(\text{Na}^{+})^2 (\text{Ca}^{2+})} \]

where X is one equivalent of the anionic part of the exchanger and ( ) refers to the activity of the chemical species. The value of K in Eq. [2] is independent of the convention used in formulating the exchange reaction. Sposito (1979) showed that whereas the adsorbed cations are designated to react in molar quantities (the Vanselow convention) or in equivalents (the Gapon convention), both arbitrary conventions lead to the same value of the thermodynamic equilibrium constant.

In Eq. [2], only the activity of the cations in the solution phase is easily computed in terms of molar ion concentration, \( m \), and molar activity coefficient, \( \gamma \). The activity of a species in the adsorbed phase is not as easily computed. If it is assumed that the exchangeable cations are equal to their equivalent fractions, then the Gaines-Thomas selectivity coefficient, \( K_{OT} \), is obtained

\[ K_{OT} = \frac{E_{Ca} \gamma_{Na}^2 \gamma_{Ca}^2}{(E_{Na})^2 \gamma_{Ca} \gamma_{Ca}} \]

where \( E_{Ca} \) and \( E_{Na} \) are the equivalent fractions of the total exchange capacity occupied by the ions specified.

If the activity of an exchangeable cation is equal to its mole fraction, \( N \), Eq. [2] gives the Vanselow selectivity coefficient, \( K_{v} \).

\[ K_{v} = \frac{N_{Na} \gamma_{Na}^2 \gamma_{Ca}^2}{(N_{Na})^2 \gamma_{Ca} \gamma_{Ca}} \]

In a recent paper Sposito and Mattigod (1979) showed that for the exchange reaction of Na with trace metal cations (\( M = \text{Cd}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+} \)) on Camp Berteau montmorillonite, \( K_{OT} \) was constant and independent of the exchanger composition for \( E_{Ca} < 0.7 \). This observation indicated to them that the Vanselow selectivity coefficient was valid; that the cationic mixture on the exchanger phase behaved as an ideal mixture, i.e., the activity of each adsorbed ion was equal to its mole fraction; and that the activity coefficient of each adsorbed ion was equal to one.

van Bladel et al. (1979), studying Na/Ca exchange on Camp Berteau montmorillonite, found an almost constant \( K_{OT} \) at \( E_{Ca} < 0.7 \). However, as they pointed out, "the most striking feature about Na/Ca exchange is the more pronounced selectivity of the clay for Ca\(^{2+}\) ions at the calcium-rich end isotherms." Levy and Hillel (1968) reached the same conclusions for montmorillonite soils. van Bladel et al. (1972) also reported an increased affinity for Ca\(^{2+}\) in terms of the selectivity coefficient as salt concentration decreased at the Ca-rich end isotherm. This range of Ca saturation is typical of agricultural soils and therefore is of high interest.

Does the diffuse double-layer theory provide an explanation for these observations? Babcock (1963) showed that the theory for external planar surfaces predicts an increased affinity for the clay for Ca\(^{2+}\) as the electrolyte concentration increases and decreased affinity for Ca\(^{2+}\) as \( E_{Ca} \) increases. The experimental data do not follow both predictions, as the already noted (Babcock, 1963). However, Shainberg and Otoh (1968) and Bar-On et al. (1970) observed that at \( E_{Ca} > 0.6 \), montmorillonite platelets condense into packets of platelets, consisting of 4 to 8 platelets in a packet with a film of water 0.45-nm thick on each internal surface. The presence of internal surfaces within
the packets may explain the experimental changes in the selectivity coefficients with changes in $E_{ca}$ and electrolyte concentration in the system.

Eriksen (1952) developed an exchange equation for monovalent and divalent ions from the diffuse double-layer theory. Eriksen's equation may be written:

$$\frac{\Gamma_{na}}{\Gamma} = \frac{r}{\Gamma B^{1/4}} \sinh^{-1} \left( \frac{\Gamma B}{4 V_s (m_{oa})^{1/4}} \right)$$

in which

$$r = \frac{m_{oa}}{(m_{oa})^{1/4}}$$

is called the “reduced ratio”. $\Gamma$ is the surface charge density in meq/cm$^2$. $\Gamma_{na}$ is the portion of the surface charge density satisfied by the sodium ions, $m$ represents the molar concentration of the subscript ion, and

$$B = \frac{8,000 \pi T^3}{D R T}$$

where $F$ = 2.89 x 10$^3$ eeu/meq, $D$ is the dielectric constant, $R$ the molar gas content, and $T$ is the absolute temperature. For water systems at 25°C, $B$ = 1.080 x 10$^3$. $V_s$ is defined by

$$V_s = \cosh^{-1} Y_a$$

where $Y_a$ is the dimensionless potential function in the plane midway between the platelets. In most applications of Eq. 13 (Bolt, 1955; Bower, 1959), it was assumed that the platelets are an infinite distance from each other where $Y_a = 0$, and $Y_a$ is equal to 1.0.

The dimensionless potential function in the plane midway between the platelets within a tactoid is a function of the salt concentration and can be calculated from the diffuse double-layer theory (van Olphen, 1977). We realize that the accuracy of the diffuse double-layer calculations for the small distance between the platelets (0.9 nm) within a tactoid is limited. The theory involves the assumption of uniformly charged surfaces, ions as point charged, ideal ionic solutions, etc. (van Olphen, 1977). These assumptions are not valid at small distance from the clay surface. However, the trend superimposed on the cation exchange equations as a result of tactoid formation should be evident. In the following calculations it is assumed that the internal surfaces are Ca-saturated, the surface charge density is 1.3 x 10$^{-7}$ meq cm$^{-2}$ (van Olphen, 1977), and the activity coefficients of the ions in the solution and exchange phase are 1. The calculated value for $V_s$ are presented in Table 1 together with the values for the Vanolsew selectivity coefficient on both the external and internal surfaces.

On external surfaces the affinity of the clay for Ca$^{2+}$ decreases with increasing sodium saturation or decreasing $E_{na}$ and the internal surface selectivity coefficient decreases from 0.80 at $E_{na}$ = 0.58 to 0.24 at $E_{na}$ = 0.04 for the 0.001M NaCl solutions and a similar trend exists for the higher concentrations. This effect is readily explained in terms of the electrostatic forces. The preference of the cation exchanger for Ca$^{2+}$ increases with an increase in the negative electric potential in the diffuse double layer. The negative electric potential in the diffuse double-layer is reduced with an increase in the fraction of adsorbed Ca ions. Thus, the affinity of the clay for the divalent cation (competing with the monovalent ions) also diminishes. Also, the affinity of the clay for Ca$^{2+}$ increases with increasing electrolyte concentration. Compressing the ions in the diffuse double layer leads to stronger interaction between the divalent cation and the negative surface, and more Ca$^{2+}$ is adsorbed.

The affinity of the internal surfaces for Ca$^{2+}$ is between 2 to 15 times (depending on the exchange composition and the electrolyte concentration—see Table 1), that of the external surfaces. This effect is readily explained by the electrostatic forces. With the overlapping of the diffuse double layers, the negative electric potential also increases and the divalent ion is strongly attracted into the internal space. For internal surfaces, the affinity of the clay for Ca$^{2+}$ decreases with an increase in salt concentration. With an increasing salt concentration, $Y_a$ decreases, and the divalent Ca ion is more affected by the changes in the electrical potential than the monovalent Na ion. Also, the affinity of the clay for Ca$^{2+}$ increases with increasing Ca saturation in agreement with the experimental results reported by van Bladel et al. (1972) and Levy and Hilled (1968). However, it should be pointed out that the diffuse double-layer calculation (Table 1) may be misleading. In these calculations it was assumed that $E_{na}$ for a given salt concentration, was constant and independent of $E_{ca}$. It is probable that this potential also diminishes with increasing $E_{ca}$ and therefore the affinity of the internal surfaces for Ca$^{2+}$ does not increase with $E_{ca}$ as much as the calculation shows.

It is evident that the effects of salt concentration and degree of saturation on $K_{ca}$ depend on the type of the surface (external vs. internal). In illitic and kaolinitic soils, where external surfaces predominate, an increase in Ca saturation, at a given concentration, will decrease $K_{ca}$. Conversely, in montmorillonitic soils for an $E_{ca}$ range where tactoids are formed ($E_{ca} > 0.7$), an increase in $E_{ca}$ should increase $K_{ca}$. Similarly, the effect of concentration, at constant Na adsorption ratio, $R_{na}$, should vary depending on the clay. In soils of mixed mineralogy, it is possible that the net effect will be that both the solution composition and the solution concentration have no effect on the selectivity coefficient.

### MATERIALS AND METHODS

Clay-size fractions of Wyoming montmorillonite (API 25) and Fithian illite (API 35) were separated from larger size fractions by sedimentation. Na- and Ca-montmorillonite were prepared by equilibration with 1M solutions of NaCl and CaCl$_2$. Then, the clay was washed with distilled water by centrifugation until an AgNO$_3$ test indicated that the equilibrium solution was free of chloride. The salt-free gel was freeze-dried and stored in a desiccator. The illite was equilibrated and freeze-dried in the manner described for the montmorillonite clays. This procedure was followed to remove the CaCO$_3$ that contaminated the reference clay. Na/Ca clay suspensions with exchangeable Na fractions ($E_{na}$) of 0.10, 0.20, and 0.40 were prepared by adding the appropriate amounts of homoionic dry clays to Na/Ca salt solutions of equal $R_{na}$. Two concentrations of clay suspensions were studied: 2.0 and 4.0% clay (wt/vol) for montmorillonite clay and 4.0 and 8.0% clay for illite suspensions. The salt solution concentrations were 0.01, 0.10, 0.50, 1.0, and 2.0 M Na$^+$, respectively. The clay gels were shaken for 1 hour and thereafter centrifuged. The ion composition of the supernatant was analyzed according to standard methods. The exchangeable ions were extracted from the clay fraction using solutions of 1.0N MgOAc at pH 6. The ion concentrations of the extract were analyzed and soluble Na and Ca ions were calculated from the chloride concentration and the known composition of the equilibrium solutions.

### RESULTS AND DISCUSSION

The composition of the equilibrium solution and of the exchangeable ions are presented in Table 2. Two Na adsorption ratios are given, based on total $R_{na} = m_{na}/m_{ca}$, where the ion concentrations are expressed in mmol liter$^{-1}$.

### Table 1—Na/Ca selectivity coefficient ($K_{ca}$) as predicted by the diffuse double-layer theory for external and internal surfaces.

<table>
<thead>
<tr>
<th>$R_{na}$</th>
<th>Total chloride concentration</th>
<th>$E_{na}$</th>
<th>$K_{ca}$</th>
<th>$E_{ca}$</th>
<th>$K_{ca}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.010</td>
<td>0.24</td>
<td>0.41</td>
<td>0.66</td>
<td>0.60</td>
</tr>
<tr>
<td>0.001</td>
<td>0.100</td>
<td>0.22</td>
<td>0.48</td>
<td>0.09</td>
<td>0.28</td>
</tr>
<tr>
<td>0.001</td>
<td>0.200</td>
<td>0.16</td>
<td>0.90</td>
<td>2.00</td>
<td>0.92</td>
</tr>
<tr>
<td>0.001</td>
<td>0.300</td>
<td>0.39</td>
<td>0.55</td>
<td>0.18</td>
<td>2.96</td>
</tr>
<tr>
<td>0.001</td>
<td>0.400</td>
<td>0.37</td>
<td>0.60</td>
<td>4.20</td>
<td>2.84</td>
</tr>
<tr>
<td>0.001</td>
<td>0.500</td>
<td>0.31</td>
<td>0.92</td>
<td>2.00</td>
<td>2.29</td>
</tr>
<tr>
<td>0.001</td>
<td>0.600</td>
<td>0.58</td>
<td>0.80</td>
<td>6.50</td>
<td>0.40</td>
</tr>
<tr>
<td>0.001</td>
<td>0.700</td>
<td>0.57</td>
<td>0.83</td>
<td>4.20</td>
<td>2.08</td>
</tr>
</tbody>
</table>

† $E_{ca}$ = 0.100.

‡ Ion activity coefficients in the solution and exchanger phases were assumed to equal 1.
cation concentration, \( R'_{Na} \), and on ion activities, \( R_{Na} \). The ion activity coefficients in the solution were calculated from the extended form of the Debye-Hückel equation, which includes individual ion size parameters. Although the initial composition of the solutions, \( R_{Na} \), were 10, 20, and 40, and that of the exchange phase, \( E_{Na} \), were 0.10, 0.20, and 0.40, respectively, the equilibrium \( R'_{Na} \) and \( E_{Na} \) values of the solutions were lower for both clays and the changes were more pronounced in the diluted solutions. A similar change in the solution composition also took place. For both clays, \( E_{Na} \), decreased with a decrease in the solution concentration. However, it should be noted that whereas in illite clay, the exchange phase is enriched with exchangeable Na during equilibra-
tions, the reverse was true for montmorillonite. The illite data are easily understood. Calcium ions that have been released from the exchange phase induced the change in the \( R'_{Na} \) of the equilibrium solution. However, this explanation does not hold for the montmorillonite systems, where both the solution and exchange phases were enriched with Ca\(^{2+}\). It seems that in montmorillonite systems, dissolution and hydrolysis of Ca-releasing primary minerals (Rhoades et al., 1968) is enough to enrich both phases with calcium ions. This conclusion is further supported by measured cation exchange capacity (CEC) of the clay as a function of adsorbed cation compositions. The CEC of Ca- and Na-illite was 17.11 and 14.56 meq/100 g, respectively, and for Ca- and Na-montmorillonite it was 105.7 and 79.5 meq/100 g, respectively. The CEC of the two clays as a function of their composition is also presented in Table 2. It is evident that the CEC, as measured in this study, is a function of the exchangeable cation. It seems to us that in the process of preparing homoionic Na clay free of electrolytes, some of the adsorbed Na cations have hydrolyzed (Shainberg, 1973). However, the amount of exchange-
able Na was not affected by the desalting treatment mainly because the Ca ions from the Ca-releasing primary minerals {Rhoades et al., 1968} replace adsorbed Ca that was hydrolyzed. The release of Ca\(^{2+}\) from the primary minerals enhances the hydrolysis of exchange-
able Na.

The effect of salt concentration of \( E_{Ca} \) on the affinity of the two clays for Ca\(^{2+}\), expressed in terms of \( K_v \), is given in Fig. 1. Whereas in illite clay the affinity of the clay for Ca\(^{2+}\) decreased with an increase in the fraction of exchangeable Ca, \( E_{Ca} \), the reverse was true for montmorillonite clay. The decrease in affinity of the illite clay for Ca\(^{2+}\) with increasing \( E_{Ca} \) can be explained by two mechanisms. The first mechanism is derived from the diffuse double-layer theory and assumes uniform exchange sites. According to this ex-
planation, the electrical potential in the diffuse double layer decreases as \( E_{Ca} \) increases, thus the preferen-
tial affinity of the clay for Ca\(^{2+}\) over Na\(^{+}\) also decreases. The other explanation assumes that there are various exchange sites on the clay with various affinities for Ca\(^{2+}\). With increasing \( E_{Ca} \), the sites with the low affinity for Ca\(^{2+}\) are last to be occupied by the Ca ions. Thus the affinity for Ca\(^{2+}\) decreases with an increase in \( E_{Ca} \). These two mechanisms should apply also to montmorillonite systems. However, in montmorillonite clay, the formation of quasicrystals and the presence of internal surfaces (Table 1) domi-
nates and causes the affinity of the clay for Ca\(^{2+}\) to increase with increasing \( E_{Ca} \).

The Vanselow selectivity coefficients for montmoril-
onite clay were almost unaffected by the total elec-
trolyte concentration at concentrations above 30 meq/
liter. These values were 0.7, 0.5, and 1.95 for \( E_{Ca} \), 0.9, 0.8, and 0.6, respectively (Fig. 1). The values for \( E_{Ca} \) = 0.6 agreed with the values predicted by the diffuse double-layer equation (Table 1). At this \( E_{Ca} \) value, the quasicrystals are not stable (Shainberg and Otoh, 1968), and their effect on \( K_v \) is small, and the

### Table 2—The composition of the equilibrium solutions and the exchange phase.

<table>
<thead>
<tr>
<th>Initial Chloride concentration, ( R'<em>{Na} ) and ( E</em>{Na} \times 100 )</th>
<th>Chloride concentration, ( R'_{Na} )</th>
<th>( R_{Na} )</th>
<th>NaX</th>
<th>CaX</th>
<th>CEC (avg)</th>
<th>( E_{Na} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol liter(^{-1}) (mmol liter(^{-1}))</td>
<td>meq/100 g</td>
<td>meq/100 g</td>
<td>meq/100 g</td>
<td>meq/100 g</td>
<td>meq/100 g</td>
<td>meq/100 g</td>
</tr>
<tr>
<td><strong>Illite</strong></td>
<td><strong>Montmorillonite</strong></td>
<td><strong>Illite</strong></td>
<td><strong>Montmorillonite</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.003</td>
<td>5.9</td>
<td>6.2</td>
<td>1.89</td>
<td>16.2</td>
<td>18.0</td>
</tr>
<tr>
<td>0.030</td>
<td>8.3</td>
<td>9.3</td>
<td>8.4</td>
<td>20.0</td>
<td>17.4</td>
<td>0.185</td>
</tr>
<tr>
<td>0.060</td>
<td>8.7</td>
<td>10.1</td>
<td>3.28</td>
<td>14.7</td>
<td>17.9</td>
<td>0.183</td>
</tr>
<tr>
<td>0.090</td>
<td>9.1</td>
<td>10.9</td>
<td>3.28</td>
<td>14.2</td>
<td>17.5</td>
<td>0.187</td>
</tr>
<tr>
<td>0.120</td>
<td>9.2</td>
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<td>3.10</td>
<td>13.4</td>
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<td>3.19</td>
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<td>0.247</td>
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<td>11.1</td>
<td>17.4</td>
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<td>0.399</td>
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<td>7.00</td>
<td>9.3</td>
<td>16.3</td>
<td>0.429</td>
</tr>
<tr>
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<td>44.2</td>
<td>7.24</td>
<td>9.1</td>
<td>16.3</td>
<td>0.443</td>
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</table>

**Fig. 1**—The Vanselow exchange constant, \( K_v \), for montmoril-
onite and illite as a function of concentration at different equivalent fractions of exchangeable Ca \( E_{Ca} \).
agreement between predicted (assuming Yd = 0) and experimental values for KY is reasonable. Also, at this ENC, the KY values for illite were similar to those of montmorillonite, suggesting again that in both clays the VE Cat K values for illite were similar to those of montmorillonite, and that the diffuse double-layer prediction for the exchange phase is not reasonable. Also, at this ENC, experimental values for kK0 are 0.2. However, kK0 for montmorillonite clay with ENC > 0.2 are larger than those for soils and are only slightly affected by the total salt concentration with a trend for the affinity for Na+ to increase with increase in the salt concentration. Since the theoretical Gapon selectivity coefficients for external surfaces follow similar trends, the Gapon selectivity coefficients for montmorillonite clay may be evaluated from the diffuse double-layer theory only when we recognize that most of the exchange takes place on the external surfaces.

b) The experimental Gapon selectivity coefficients for illite clay are higher than the average kK0 for soils and seem to be independent of the salt concentration.

c) The theoretical Gapon selectivity coefficients for external surfaces are higher than those observed for soils and for clays. In order to obtain a good agreement between the diffuse double-layer exchange equation and the experimental values, Bolt (1955) and Bower (1959) multiplied the surface charge density of the clays with a correction factor larger than 1.0. Increase in surface charge density of the clay leads to higher affinity of the clay for Ca2+ and lower kK0 values because of the increase in the negative electric potential at the clay surface.

Based on the above observations we may conclude that the Gapon selectivity coefficient is not expected to be constant. It is related to the Vanselow selectivity coefficient by the following equation:

\[ k_{G} = \frac{E_{Na} - 0.5 E_{Ca}}{2,000 K_{V} E_{Ca}} \]  

which indicates that kK depends also on the composition of the exchange phase. It is also evident that kK0 value obtained for many soils is a weighted average of the mineralogy of the soils. It seems that for an “average” soil, which contains montmorillonite, illite, and kaolinite, a value for kK0 of 0.015 is obtained. However, “average” soil will deviate, depending on the mineralogy of the soil and the composition of the solution and exchange phases.

ACKNOWLEDGMENT

We want to thank Dr. Kenneth Babcock and Dr. Garrison Sposito for their help in the preparation of this paper.

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