

Evolution of Ca-K Exchange in Clays with Temperature: The Role of Hydration Processes

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Despite it being widely accepted that hydration processes have an important influence on the stability of clay minerals (Garrels & Tardy, 1982), this kind of phenomenon is rarely taken into account when modelling, mainly due to the complexity involved. Indeed, the hydration of clays depends on a combination of numerous parameters, including the structure and composition of the crystalline layers, the nature of the exchangeable cation, plus environmental parameters, such as temperature, pressure and activity of water. In addition, cation exchange processes may also depend on the state of hydration of clays; the aim of this study is to demonstrate the importance of taking into account the hydration of clay minerals in such a case.

The evolution of the Ca-K exchange constant K_{ex} of a smectite with temperature and pressure is calculated, whilst firstly neglecting and then considering the effects of hydration processes. When hydration is neglected, the reaction of exchange is written as follows: Ca-smectite + K^+ = K-smectite + $1/2 Ca^{2+}$. When hydration processes are taken into account, the reaction becomes: Ca-smectite + $n H_2O$ + K^+ = K-smectite + $1/2 Ca^{2+}$ + $n H_2O$, where n is the number of mole of hydration water per mole of mineral. The temperature and pressure conditions selected varied from 298.15 K, 0.1 MPa at the surface to 423.15 K, 30 MPa at depth, simulating a very simplified system.

The data required are (1) the Ca-K cation exchange constant for hydrated layer silicates at 298.15 K, 0.1 MPa, (2) the evolution of the state of hydration of both Ca-saturated and K-saturated smectites, and (3) the evolution of the energy of hydration as functions of temperature and pressure. The evolution of the state of hydration of the smectites with temperature and pressure is established from previous works, as follows. For each state, the energy of hydration is calculated by integrating the dehydration isotherm as deduced from Tardy & Touret (1987). Assuming that one value of the energy corresponds to a given state of hydration (Lassin et al., 2000), the activity of water dependence can be converted to temperature

or pressure dependence. The method requires the knowledge of the thermodynamic properties of the hydration water, i.e. its standard molar entropy, heat capacity, and volume. These data are taken from Ransom & Helgeson (1994).

The result of the above considerations is that, as expected, a rise in pressure favours hydration while increasing temperatures favour dehydration. In the present case, the dehydrating effect of increasing temperature (with depth) is delayed by the action of increasing pressure (Wang et al., 1996). The Ca-smectite is very hydrated and thus very sensitive to dehydrating conditions. Conversely, the K-smectite is naturally poorly hydrated and thus its state of hydration is less sensitive to varying temperatures and pressures.

Finally, it appears that the cation exchange constant $K_{ex} = [Ca^{2+}]^{1/2}/[K^+]$ decreases at depth when hydration is neglected, but increases when hydration is considered. The evolution of the exchange constant K_{ex} then favours the Ca-smectite at depth whilst hydration is neglected, but favours the K-smectite whilst considering hydration: uptake of K^+ from the solution and release of hydrated Ca^{2+} decrease at depth when hydration is neglected, but are favoured when hydration is considered. The present study illustrates the importance of hydration processes. *These should be considered as a mechanism to be taken into account during modelling the stability of clay minerals.*

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