

INTERLAYER CATION EFFECTS ON THE HYDRATION STATE OF SMECTITE

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ABSTRACT. BET surface area measurements and XRD and TG analysis were performed on a mixed-layer illite/smectite with 11 percent illite, exchanged with different cations (Li, Na, K, Cs, Mg, Ca, Sr, and Ba), at 30 percent relative humidity. The analyses showed that the exchange cation affects the surface area of clays and so influences the amount of water that can be adsorbed on the clay outer surface. This factor must be taken into account when assessing the actual amount of interlayer water. Most of the exchanged samples studied are homogeneous systems with either one or two water layers in every interlayer. The K-clay, however, is a mixed-layer of one water layer and dehydrated interlayers. D-spacing varies depending on the interlayer cation even when the overall hydration state remains the same. This implies that the density of adsorbed water in a hydrated interlayer depends on the interlayer cation. The study seems to indicate that for Li-, Na-, Mg-, Ca-, Sr-, and Ba-smectite the number of water moles per half formula unit in the interlayer of a fully hydrated smectite (100 percent relative humidity) is approx 4.5.

INTRODUCTION

The thermodynamic nature and stability of layer clays capable of adsorbing considerable amounts of water in their interlayer region has not been satisfactorily determined as yet. This is proven by the fact that many thermodynamic studies of smectites and illite/smectite mixed-layer clays yield inconsistent results. Aagaard and Helgeson (1983) found that mixed-layer illite/smectite can be described as a solid solution of illite and smectite endmembers. Contrary to this, Ransom and Helgeson (1993) concluded that illite and smectite do not form solid solutions corresponding to illite/smectite; Garrels (1984) and Rosenberg, Kittrick, and Sass (1985) found evidence supporting the fact that illite/smectite is composed of two phases rather than one single solid solution phase. Aja, Rosenberg, and Kittrick (1991) and Aja (1991) claimed the existence of four different phases: smectite, illite, and two illite/smectite phases of different composition. On the other hand, May and others (1986) concluded that solubility studies of chemically variable clays developed to determine their thermodynamic status present both conceptual and experimental flaws that invalidate their results.

Many authors have developed thermodynamic models for smectite. These models permit the calculation of thermodynamic parameters for which it is difficult to obtain reliable experimental values. Also, models are helpful in order to have a theoretical understanding of the thermodynamic parameters. Most of these models focus on the TOT unit of smectite (Tardy

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and Garrels, 1974; Nriagu, 1975; Chen, 1975; Stoessel, 1979; Tardy, Duplay, and Fritz, 1987; Varadachari, Kudrat, and Ghosh, 1994; Vieillard, 1994). Some of the models include the stabilization effect of exchange cations (Mattigod and Sposito, 1978; Sposito, 1986) and water (Tardy and Duplay, 1992).

Recently, Ransom and Helgeson (1994) addressed the problem of calculating the free energy of hydration of smectite exchanged with different cations. The question, as they say, is relevant, because it is evident that water plays a role in the thermodynamic stability of these minerals, and it is absolutely necessary to assess this influence. They develop an elegant mathematical elaboration, using data from hydration and dehydration experiments on smectites, to obtain the free energies for hydration reactions. They make some necessary assumptions in order to develop their calculations. Nevertheless, some of these assumptions seem to be presented as real facts rather than reasonable approximations that will permit their mathematical approach. They assume that surface areas of same smectite exchanged with different cations remain constant. Also, they assume that the interlayer molal volume of the smectite occupied by water in a fully hydrated specimen and the water density are constant, regardless of the specific characteristics of the smectite and of the nature and number of the interlayer cations. From this, they conclude that the number of water moles per smectite half formula unit in a fully hydrated smectite is always the same and independent of the smectite and of the interlayer cation. This number is 4.5 water moles per $O_{10}(OH)_2$. This corresponds to two water layers in the smectite interlayer. To represent smectite, they use a solid solution model in which fully hydrated and completely dehydrated thermodynamic components are mixed. The mixture of these components in appropriate rates can account for any hydration state. At the end of their paper they suggest that these thermodynamic components may have a physical meaning and so that partially hydrated smectite is a random mixed-layer of fully hydrated and dehydrated layers.

Many studies have been conducted on smectite hydration states, but it is difficult to use them in order to test Ransom and Helgeson's (1994) assumptions and conclusion. As they state, many of these studies do not discriminate between water externally adsorbed and interlayer water. The interference of external water is avoided in those works that look at the smectite d-spacings. These studies show that the basal spacings of smectite exchanged with different cations are different (for instance, Mooney, Keenan, and Wood, 1952; Iwasaki and Watanabe, 1988; Bérend and others, 1995), and also that smectite behavior during dehydration in temperature dynamic conditions depends on the exchange cation (Collins, Fitch, and Catlow, 1992). Nevertheless, these different d-spacings do not rule out Ransom and Helgeson's (1994) assumptions, because they can be caused by different interstratificates of the fully hydrated and dehydrated layers that they assume. On the other hand, some studies both experimental (Glaeser and Méring, 1968; Sato, Watanabe, and Otsuka, 1992) and calculations (Skipper, Sposito, and Chang, 1995) show that the magnitude and location of smectite layer charge do influence

the interlayer hydration complex. In this paper I use X-ray diffraction, BET surface area measurements, and thermogravimetry to assess the effect of the interlayer cation on smectite hydration state.

MATERIALS AND METHODS

The material used for the study is the $<1\ \mu\text{m}$ size fraction of a bentonite from La Serrata deposit in Almería, southeast Spain. The $<20\ \mu\text{m}$ size fraction of the same bentonite has been characterized elsewhere (Cuadros and Linares, 1995). X-ray diffraction (XRD) analysis of oriented, glycolated mounts of the $<20\ \mu\text{m}$ size fraction showed it to be a random mixed-layer illite/smectite (I/S) with 11 percent illite (Cuadros and Linares, 1995). The XRD patterns of the oriented mounts of the $<1\ \mu\text{m}$ size fraction are identical to those of the $<20\ \mu\text{m}$ size fraction. Hence percent illite in I/S and mixed-layer ordering are the same for both fractions. The $<20\ \mu\text{m}$ size contains phases other than I/S. On the one hand, selective chemical analysis for non-crystalline phases detected up to 1.5 percent weight of such phases; on the other hand, XRD of powder specimens detected crystalline phases up to 3 percent, mainly plagioclase. In fact, a minute plagioclase peak could be observed in XRD patterns of the oriented mounts at $3.21\ \text{\AA}$. Nevertheless, this peak completely disappears in the $<1\ \mu\text{m}$ size fraction, which means that the crystalline contaminant phases were substantially or completely removed. Hence, it seems likely that the small amounts of those phases other than I/S cannot alter the experimental results of this study.

Total area of the $<20\ \mu\text{m}$ size fraction was determined by water adsorption at 30 percent relative humidity (NaCl-saturated solution atmosphere at 25°C ; Keeling, 1961). The total area is $632\ \text{m}^2/\text{g}$.

The bentonite $<1\ \mu\text{m}$ size fraction was exchanged with different cations: Li, Na, K, Cs, Mg, Ca, Sr, and Ba. For cation exchange, $0.13\ \text{g}$ of the clay was dispersed in $10\ \text{ml}$ of the corresponding chloride salt solution. The solution concentrations were 0.5 and $1\ \text{M}$ for the divalent and monovalent cations, respectively. After 24 hrs, clay and solution were separated by centrifugation, and the exchange process was repeated under the same conditions. Then, the clay was repeatedly washed by centrifugation using the AgNO_3 test (Moore and Reynolds, 1989a) until no Cl^- was detected.

The surface areas of all cation exchanged samples were measured by nitrogen gas adsorption using a volumetric vacuum apparatus (Micromeritics ASAP 2400). Approx $0.1\ \text{g}$ of the sample was used for the measurements. They were performed at the boiling point of liquid nitrogen ($77\ \text{K}$) using a molecular cross-section area of $0.162\ \text{nm}$. Prior to the nitrogen adsorption, the samples were out-gassed at 110°C under vacuum until no gas evolution could be detected with a pressure gauge. Surface areas were calculated by the BET method, using a series of nine data points over the P/P_0 range of 0.05 to 0.25 on the nitrogen adsorption isotherm. These areas were corrected for the micropore area detected by means of the Harkins and Jura (t-plot) method.

The cation-exchanged samples were prepared as oriented aggregates by dispersing them in water ($52\ \text{mg}/\text{ml}$) and placing some drops of the suspension on glass slides to dry. The mounts were X-rayed using a Siemens D500,

at 30 kV and 30 mA, with a step size of $0.05^\circ 2\theta$ and a count time of 1 sec. The experimental patterns were compared to simulations calculated using the NEWMOD program (Robert C. Reynolds, Dartmouth College, Hanover, New Hampshire). MEWMOD calculates $00l$ reflection intensities of phyllosilicates for a variety of mixed-layering, interlayer cation composition and interlayer adsorption complexes. Moore and Reynolds (1989b) contains a description of the program as well as many examples of its use.

The variables used in the NEWMOD program calculations were: The 11 percent illite present in the random I/S was simulated as dioctahedral mica with 0.8 atoms of K per half formula unit and a d-spacing of 9.98 \AA . The results analyzed later to assess smectite hydration state (table 1) correspond only to smectite interlayers. The number of Fe atoms per half formula unit was 0.17, taken from the sample chemical analysis (Cuadros and Linares, 1995). The low and high number of layers in the crystallites were 3 and 8 respectively. The smectite d-spacings, which include cation size and the number of water layers, were determined by matching with the experimental patterns. The interlayer cations were the corresponding ones for the experimental pattern if they were available in the NEWMOD program. Li, Cs, and Ba were not available, and they were simulated using the most similar cation available, in the way suggested in the NEWMOD program manual. The cation simulation consisted of changing the number of cations in the interlayer (by varying cation exchange capacity) so as to place the correct number of electrons in the interlayer, that is, the number of electrons that would be present in the actual cation-exchanged clay. This procedure corrects for the most important effect, the X-ray scattering factor. Correction for the cation size was included in the determination of the d-spacing by comparison with the experimental patterns.

The samples were also studied by means of thermogravimetric analysis (TGA) in a Perkin-Elmer Thermal System VII. The sample weight ranged

TABLE 1

Characterization of the clay-water system for the different exchange cations, using different techniques. The number of water moles per smectite half formula unit in the XRD column is calculated assuming 4.5 water moles/ $\text{O}_{10}(\text{OH})_2$ in a fully hydrated interlayer. The corresponding values in the TGA column are calculated after correction for water adsorbed in the clay external surface

| | XRD | | | | TGA | |
|----|-------------------------------|-----------------|--|---|--------|--|
| | d-Spacing (\AA) | Water layers | Water moles/ $\text{O}_{10}(\text{OH})_2$ | Surf. area (m^2/g) | % Loss | Water moles/ $\text{O}_{10}(\text{OH})_2$ |
| Li | 12.5 | 1 | 2.25 | 69 | 11.4 | 2.68 |
| Na | 12.47 | 1 | 2.25 | 61 | 9.6 | 2.28 |
| K | 12.8 | 0.42 | 0.95 | 32 | 6.3 | 1.54 |
| Cs | 12 | — | — | 67 | 7.1 | 1.80 |
| Mg | 14.5 | 2 | 4.5 | 46 | 14.5 | 3.74 |
| Ca | 15 | 2 | 4.5 | 55 | 14.2 | 3.65 |
| Sr | 14.9 | 2 | 4.5 | 23 | 13.9 | 3.94 |
| Ba | 12.5 | 1 | 2.25 | 49 | 9.9 | 2.69 |

from 4 to 21 mg. The heating rate was 10°C/min. The study was carried out from room temperature to 450°C in a flowing air atmosphere. The upper temperature limit selected was to be as high as possible without reaching dehydroxylation, because it is known that smectites retain hydration water at very high temperatures (Fripiat, Chaussidon, and Tonillaux, 1960; Cuadros and others, 1994). Previous TGA runs up to 1000°C permitted us to localize the dehydroxylation temperature range so it could be avoided in the dehydration experiments. XRD and TGA analyses were conducted at 30 percent relative humidity, which corresponded to the room relative humidity. Humidity was constantly checked during the experiments. It remained always in the range 30 to 34 percent. For TGA analyses, the air flow was connected only after the experiment had begun, to avoid weight loss during the set up.

RESULTS

Surface area.—BET surface areas of the cation exchanged clays are within the expected values. Nevertheless, the Harkins and Jura method detected the presence of micropores. Micropores are those pores with a diam <20 Å. The existence of these micropores hinders BET area calculations because nitrogen accumulates within them, violating the assumption that every nitrogen layer starts to build up only when the previous one is completed. Micropores in phyllosilicates are assumed to correspond mainly to interlayer space (Davis and Kent, 1990). BET surface areas and the estimated micropore areas, both in m²/g, for the cation exchanged specimens are: Li 73, 4; Na 83, 22; K 32, 0; Cs 76, 9; Mg 54, 8; Ca 63, 8; Sr 23, 0; Ba 49, 0. Subtraction of the estimated micropore area from BET area approximately eliminates interlayer space from surface area measurements and yields the actual values for the specimen external areas. The results after this correction are shown in table 1. This is a minor correction for all specimens except for the Na exchanged one. The reason why the Na specimen presents such a high micropore area is not clear. Interlayer spacing of dehydrated smectite depends on the different interlayer cation size. Larger cations produce larger d-spacings, which should facilitate nitrogen entrance during BET experiments (Knudson and MacAtee, 1973, 1974; Bérend and others, 1995). Micropore area estimations in this work do not follow a trend linked to cation size, suggesting that other factors may be involved. Cation size, its location in the interlayer, and the resulting d-spacing might cause a complex effect ranging from blocking nitrogen entrance in the interlayer to creating voids and channels that favor nitrogen entrance and condensation.

Surface area values in table 1 show an important variation. The fact that surface area of smectites depends on the exchange cation is widely recognized (Greene-Kelly, 1964; Knudson and McAtee, 1974; Bérend and others, 1995). The reason for this dependence is not quite solved, although the most important facts involved are known. The interlayer cation modifies the stacking order of layers in smectite crystallites (Gaultier and Mamy, 1979; Besson, Glaeser, and Tchoubar, 1983) which may have an effect on particle external aggregation and surface. Other factors affecting surface area could

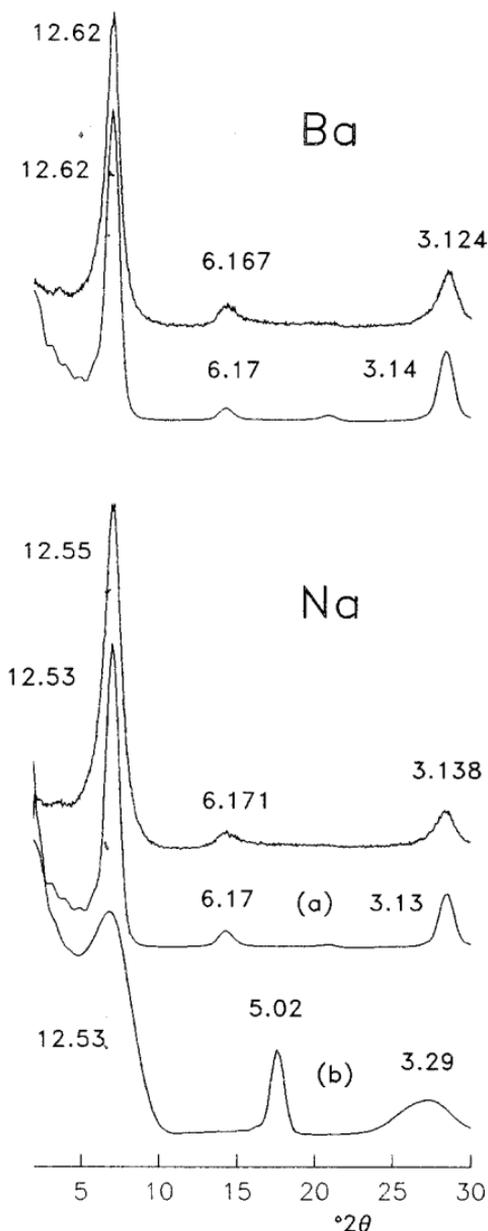


Fig. 1. Experimental XRD patterns and simulations of some of the cation exchanged species. Spacing labels are in \AA . For the Na-clay there are two simulations: (A) where all interlayers have one water sheet.

be crystallite thickness and/or the size of particle aggregates. Different interlayer cations induce clay dispersion in water in a different extent. The more extensive the dispersion the thinner the crystallites or the smaller the clay aggregates. It is possible that after the smectite drying process subsequent to cation exchange, crystallite thickness and/or aggregate size are

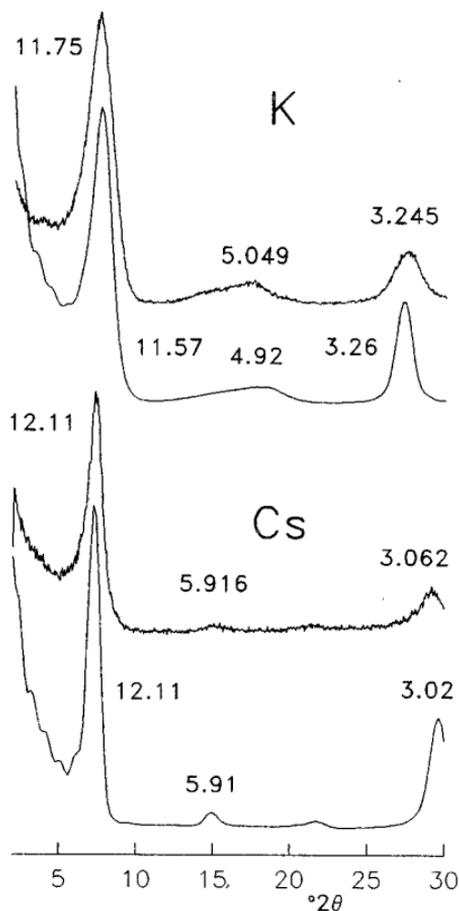


Fig. 1(B) where the clay is a mixed-layer of fully hydrated (2 water sheet) and dehydrated interlayers.

proportional to their corresponding values in water dispersion. Surface areas of the exchanged clays would be different for each exchange cation.

X-Ray patterns.—Some of the experimental XRD patterns and their NEWMOD simulations are presented in figure 1. The patterns depend on the exchange cation, as it is well known. The simulations were calculated in order to assess the number and disposition of the water molecules in the smectite interlayer. Those calculations that are not shown simulated the corresponding experimental patterns with similar success as the ones in figure 1.

The d-spacings of the hydrated layers and the number of water layers resulting from the calculations are shown in table 1. For all cations except for K the calculations show a homogeneous distribution of water in all smectite interlayers. For K, they show an interstratification of layers with one water sheet in the interlayer space and d-spacing of 12.8 Å (42 percent of the layers) and completely dehydrated layers with d-spacing 9.98 Å. That is, the value 0.42 in table 1 does not indicate the existence of 0.42 water layers in every

interlayer, but one water layer in 42 percent of the layers. For the Cs exchanged smectite, the simulation shows that all layers have the same hydration state. Reasons discussed in the next section indicate that there are not enough water molecules to form a complete sheet in the interlayer space. Water molecules are separated from each other. In this situation, the exact amount of water present cannot be determined using XRD data. These results are in agreement with previous data showing that Cs smectite d-spacing remains almost unaltered around 12 Å in the whole range of relative water vapor pressure (Newman, 1987). This indicates that at low relative humidity there are some water molecules in the interlayer causing it to expand at a definite value. Higher vapor pressure causes more water molecules to accommodate in the void interlayer space but does not affect d-spacing.

Figure 1 also shows the calculated patterns for the Na exchanged clay (b) where it is assumed that smectite is a mixed-layer of a two water layer hydrate and the completely dehydrated specimen. The calculation is unable to simulate correctly the experimental patterns. Neither peak positions nor peak shapes are fitting. Analogous results were obtained for the other alkali ions.

Thermogravimetric analysis.—The TGA study was included in order to have a second means of assessing the amount of water present in the interlayer of the exchanged species. This technique presents the difficulty that both water adsorbed in the outer surface and interlayer water are included in the results. Nevertheless, the surface area values allow the correction of the results for the presence of externally adsorbed water, at least in an approximate way. The amount of external water was assessed and subtracted as follows. The total area of the clay (interlayer plus surface), measured on the <20 µm size fraction without cation exchange, is 632 m²/g. The external surface area of the same size fraction measured by the BET technique is 60 m²/g (Lasaga and Cama, personal communication). This value was not corrected for micropore area. The samples from the <20 µm size fraction contained the original interlayer cations: Ca, Mg, Na, and K, in the same equivalent proportion (Cuadros and Linares, 1995). The averaged value of the BET surface areas measured in this work (<1 µm) corresponding to these cations and not corrected for micropore surface is 58 m²/g. This value is very similar to the one determined for the <20 µm size fraction of 60 m²/g. If surface areas of both size fractions are the same, it is likely that their total areas (surface plus interlayer) are also the same. Hence, the value 632 m²/g for total area can be used in this study.

Because the total area is much higher than the external surface area we can consider that the former remains constant, unaffected by the variations of the latter produced by the different exchange cations. It is then possible to subtract the amount of water proportional to the corresponding surface area from the total loss in the TGA experiments. As an example, consider the Li exchanged specimen. Its external surface area is 69 m²/g, which is 11 percent of the total area. Hence, 11 percent of the total water loss is subtracted. The values of total weight loss and the corrected ones are shown in table 1. The latter are expressed as moles of water per half formula unit of the dry

smectite. This procedure assumes that water adsorbs uniformly in the interlayer and the external surface. This is not an unlikely assumption because the conditions in both regions are similar: there is the same surface formed by basal oxygens of the tetrahedral sheet and the same exchange cations balancing for the excess of lattice negative charge. In any case, because the total area is one order of magnitude higher than the surface area, the error introduced in such approximation should not be critical. The TGA traces are shown in figure 2.

DISCUSSION

This study shows (table 1) that the differences between surface area values due to the exchange cation can be very important. There is some uncertainty about the exact surface area values due to microporosity. Nevertheless, surface areas are different also for exchanged specimens in which microporosity was not detected. Surface area variation should be considered to assess the real amount of water adsorbed in the interlayer for a series of homoionic smectite.

The XRD analysis in this study shows that all exchanged clays except K have a homogeneous distribution of water in all their layers. The number of water layers in that distribution is displayed in table 1. Some cation exchanged specimens present one water sheet in all interlayers, and the others two water sheets in all interlayers. The K exchanged clay presents a heterogeneous distribution of water, consisting of partially hydrated interlayers (42 percent of the interlayers) and completely dehydrated ones.

The different behavior of Cs and K exchanged clays is interesting because we would expect them to behave similarly. The latter develops a heterogeneous distribution of water, perhaps in response to an also heterogeneous layer charge distribution in the clay. Nevertheless, Cs induces a homogeneous water distribution in which water molecules do not form a complete sheet but are separated from each other. This is the necessary conclusion if we compare the number of water moles per half formula unit calculated using TGA for K and Cs (table 1). They are very similar. XRD shows that 58 percent of the layers in the K-smectite are dehydrated. Cs accommodates a similar number of water molecules in the totality of the interlayers, which necessarily implies that there is no development of a full water sheet in the interlayers.

We now examine cation influence on water density in the interlayer, that is, the number of water molecules that can be found in a given volume. Mooney, Keenan, and Wood (1952) find that the amount of water adsorbed by Ca-, Ba-, and Na-Wyoming bentonite at high relative water vapor pressure (0.8-1) is similar, but the amount adsorbed on the Cs bentonite is much lower. Although these data are not corrected for water externally adsorbed, they suggest that the exchange cation does influence the amount of water accommodated in the interlayer space in fully or near-to-fully hydrated smectites. The present study was conducted at 30 percent relative humidity, and so samples were not fully hydrated, but it is possible to look at cation effect on the hydration state of smectite. Cation hydration energy depends on

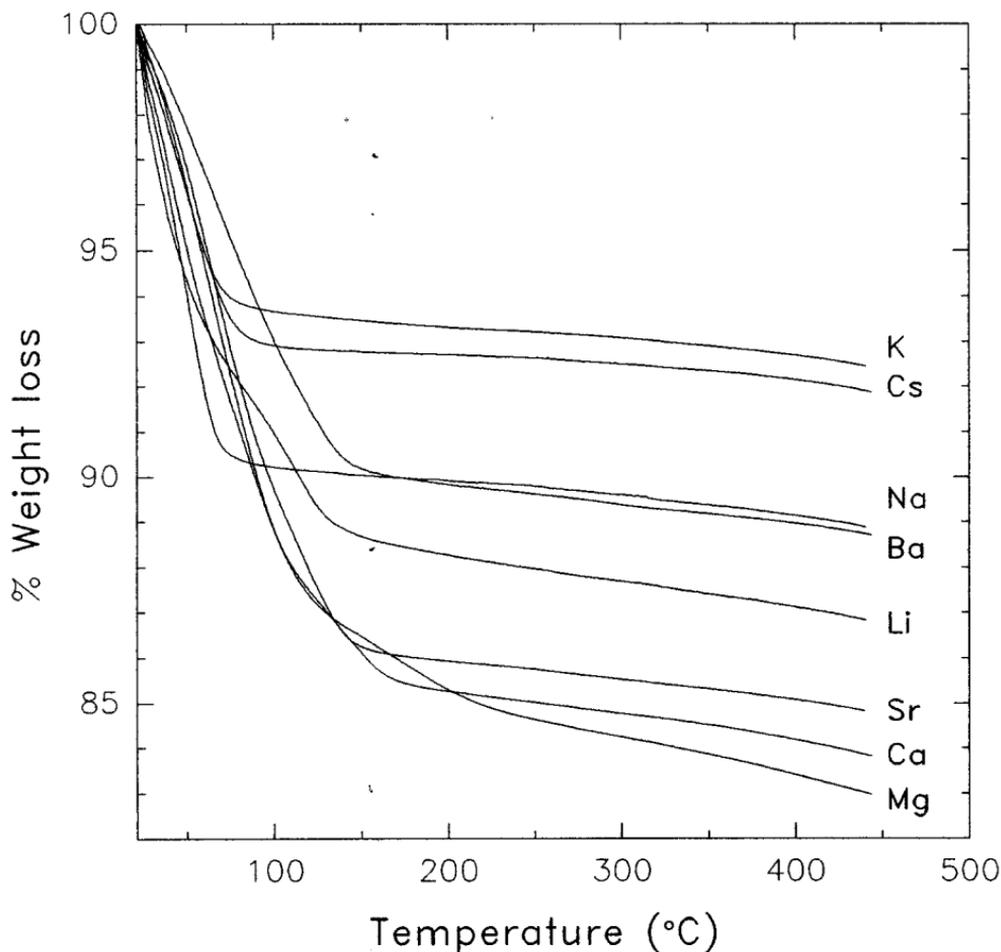


Fig. 2. Weight loss in the TGA analyses.

its charge:radius ratio. The higher this ratio the more water molecules will surround it in the closest coordination sphere and/or the more strongly they will be held. Hence, different cations are likely to favor different arrangements of water molecules in the interlayer.

The Cs and K specimens in this study show a very different water distribution, indicating a strong influence of the exchange cation. The same conclusion can be drawn from the other samples. Li, Na, and Ba exchanged clays all have one water layer in their interlayer space. The d-spacing for the Li species is slightly larger than the one for the Na-smectite, even though the Li cation is smaller than Na. This indicates that the Li interlayer accommodates more water molecules, because of its higher hydration energy, and/or water molecules adopt a different spatial conformation. The number of water

molecules per half formula unit calculated by means of TGA (table 1) indicates that the former is true. In any case, the cation is affecting water density in the interlayer. On the other hand, Ba and Li have similar charge:radius ratios, and their d-spacings are the same. Calculations of water moles per half formula unit using TGA show also the same values.

The cations promoting two water layer hydrates are Mg, Ca, and Sr. Ca and Sr radii are very similar (see cation radii compilation in Liebau, 1985) and so are their d-spacings and number of water moles calculated from TGA results. Mg is appreciably smaller and so is its d-spacing, although the number of water moles per half formula unit remains similar to those of Ca and Ba. It seems that for Mg the same number of water molecules are confined in a smaller volume due to its higher charge:radius ratio.

Ransom and Helgeson (1994) calculate a value of 4.5 for the number of water moles per half formula unit in a fully hydrated smectite, which corresponds to two planes of interlayer water. Using this number and the number of water layers shown by the XRD simulations (second column of table 1) it is possible to obtain the number of water moles per half formula unit that would be present in each of the samples of this study, *if the water layers* (column 2) *are completely developed*. This number is displayed in the third column. These calculations cannot be applied to the Cs specimen, because as previously discussed, there is no development of a complete water sheet.

The values of water moles per half formula unit from the TGA experiments, corrected for water externally adsorbed, in the last column of table 1 can be compared with the corresponding ones in the third column. The values are similar for the case of Li, Na, and Ba, considering the uncertainty created by the external water adsorption. In these three cases, there is a one water layer complex in the interlayer. For the K specimen the agreement is not as good. For the case of two water layer complexes (Mg, Ca, and Sr) the TGA values are consistently lower than the values calculated for a fully hydrated interlayer after Ransom and Helgeson (1994). The reason for these lower values might be the fact that Mg-, Ca-, and Sr-smectite have already developed a two water layer complex at 30 percent relative humidity, but it is not completely occupied. Iwasaki and Watanabe (1988) show that Ca-smectite forms its two water layer complex at 20 percent relative humidity, and, after that, increasing humidity makes the d-spacing of the smectite increase only slightly, indicating that the water complex remains basically the same. Also, Mooney, Keenan, and Wood (1952) show that their Ca-bentonite continues adsorbing water steadily in the region 20 to 90 percent relative humidity. This is likely mainly due to water adsorption on the external surface, but it is also possible that in this range of increasing relative humidity more water molecules are incorporated to fill the water structure already existent in the interlayer. If this is true, the maximum number of water moles per half formula unit in a full two water layer complex of Mg-, Ca-, and Sr-smectite could be approx 4.5, as Ransom and Helgeson (1994) claim. This could be true also for Li-, Na-, and Ba-smectite, because their one water layer complex seems to have about half the number of water moles. K and Cs specimens seem to depart from this behavior.

CONCLUSIONS

The amount of water adsorbed by smectites is a function of the interlayer cation(s). The interlayer cation modifies the surface area of the smectite and creates water complexes in the interlayer which differ in number of molecules and/or their spatial disposition. The smectite layer charge and its distribution (homogeneous versus heterogeneous) also influences the formation of water complexes, as the K exchanged clay shows. Nevertheless, in the case of full hydration, some of the cations seem to develop interlayer water complexes containing approximately the same number of moles per half smectite formula unit.

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