ence between the Mössbauer behaviour of Fe(III) on vermiculite and on montmorillonite (Helsen *et al.*, 1970) may suggest a new approach to the distinction between surfaces of di- or trioctahedral phyllosilicates.

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POSITION OF EXCHANGEABLE CATIONS IN MONTMORILLONITES

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IT IS WELL known that the surface of montmorillonites with two or less layers of adsorbed water molecules exhibits strong Brønsted acidity. In our work on the determination of the acid strength of montmorillonites from Camp Bertau, Morocco, a remarkable difference in acidity was observed depending on the cation occupying the exchange site (Helsen, 1971). The acid strength was calculated from the degree of transformation of triphenylmethanol (Ph_3COH) into its carbonium ion (Ph_3C^+) on the clay surface. The amount of Ph_3C^+ that could be formed by the montmorillonites with different cations is tabulated in Table 1. This acidity is due to the enhanced dissociation of residual water molecules.

The origin of the enhanced dissociation is commonly attributed to the polarizing power of the cations occupying the exchange sites. If this is so, the total amounts of carbonium ions formed should strongly depend on the cation. A glance at Table 1, shows this to be the case for alkali ions but not in the way we would have expected. Indeed, there is no smooth decrease as a function of atomic number, ionic radius, charge density etc. This suggests that several effects are operative simultaneously.

Since the first publication of the results, more data has become available which confirm our results and allow the following hypothesis to be formulated. The polarizing action on the water molecules depends on the charge density of the cation and more generally on the electric field conditions in the interlamellar space (Mamy, 1968; p. 197). Considering, however, the geometry of the surface to which they are attached, the position of the cation with respect to both the surface with the hexagonal cavities and the water molecules of the hydration sphere apparently can modify the influence of the charge density. When a cation of the right radius (≠ as small as possible) is more or

Table 1

Montmorillonite	Radius in Å (*)	Ph_3C^+ max. am. μmol/g	H_2O %	001-spac. Å
Li	0·68	24·7	7·0	12·20
Na	0·97	6·5	4·2	11·65
K	1·33	4·2	1·4	11·55
Rb	1·47	23·6		—
Cs	1·67	22·6		—
Be	0·35	35·7		—
Mg	0·66	39·8	13·5	14·15
Ca	0·99	28·1	11·0	14·15
Sr	1·12	22·7		—
Ba	1·34	18·7		—

* *Handbook of Chemistry and Physics*, Chemical Rubber Cy., 46th Edition, p.F. 117.

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Table 2. Stability constants of alkali cryptates

Cation	Ionic radius in Å		Stability constant Kryptofix		
			222	221	211
	*	* *	Cavity radius in Å		
			1,4	1,15	0,8
Li	0·68	0·86	<2	2·5	4·3
Na	0·97	1·12	3·9	5·3	2·8
K	1·33	1·44	5·3	3·9	<2
Rb	1·47	1·58	4·3	2·5	<2
Cs	1·67	1·84	<2	<2	<2

* *Handbook of Chemistry and Physics*, The Chemical Rubber Company, 46th Edition, p.F. 117: Crystal Ionic Radii.

** Ladd, 1968: *Ionic Radii of Spherical Ions.*

less trapped in the hexagonal cavity, the neighbouring water molecules are partially stripped off and consequently, its polarizing action is counteracted by its geometric or crystallographic, position. In this way we can easily understand why it is not necessarily the smallest ions (e.g. Li^+) which will be trapped preferentially because mass, affinity to the water molecules, ionic radius and so on all together determine their position. Looking at the maximum amounts of Ph_3C^+ formed as a function of the metal ion in Table 1, potassium and sodium should be trapped preferentially. Their ionic radii fit approximately the hexagonal cavity which has a diameter of about 2·6 Å, Rb^+ and Cs^+ have radii far too large to be withdrawn from their hydration sphere into the hexagonal cavity. This hypothesis suits perfectly the conclusions of Calvet (1973, p. 144) who calculated the relative positions of the alkali ions in montmorillonites with respect to a plane passing through the centre of the surface oxygens. When hydrated to the monolayer level, the position was found to be 1·2 Å for Li^+, 1·0 for Na^+, 0·95 for K^+, 1·07 for Rb^+ and 1·43 for Cs^+.

The asymmetrical distribution of alkali ions as proposed by Pézerat and Méring (1958) and Mamy (1968) explains qualitatively the relative acidities of alkali montmorillonites. The same distribution does not hold for alkaline earth montmorillonites and the smooth decrease of acidity with ionic radius accounts for the absence of trapping of these ions by the surface and consequently for the more symmetrical distribution of these cations in the interlamellar space. The exception is beryllium but that may be attributed to its extremely small ionic radius.

The trapping of ions into crystallographic holes may phenomenologically be compared to the formation of cryptates. The stability constants of the alkalicryptates follow the same trend as do the maximal amounts of Ph_3C^+ on the alkalimontmorillonites. They exhibit very high ionic to cavity radius selectivity as may be illustrated by the values from Table 2, taken from Lehn and Sauvage (1971) and Bernabei (1973) and determined for the commerical products Kryptofix (Merck) 222, 221 and 211. As one can see in the table, each cation forms a complex of highest stability when the cavity radius best fits its radius.

The water content and corresponding (001) spacing at which the formation of Ph_3C^+ starts, are indicated in Table 1. The x-ray data at the indicated water contents, indicate that this formation comes from a monolayer in the case of Li–montmorillonite and from a double layer for Ca– and Mg–montmorillonite. For Na– and K–montmorillonite it happens below the monolayer level but the diffractograms for both are not rational (9·5–12·5 interstratification) and there is a rather high discrepancy between the x-ray rata and the water content for K–montmorillonite. This indicates the existence of two kinds of water on the surface depending on the water content: a rather 'normal' water at high levels, a highly dissociated water at lower levels.

These results also seem to be compatible with i.r. observations of clays with water contents. Indeed, Prost (1971) observed that the i.r. adsorption bands of adsorbed water conserve all their spectral characteristics for water contents of 8% and above irrespective of the compensating cation. The spectrum however changes notably at lower water contents. These observations fit well our results because above about 8% for the alkali montmorillonites (and 13% for alkaline earth montmorillonites) no formation of Ph_3C^+ occurs, indicating also the existence of two kinds of water depending on the hydration level.

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