

DEMIXING OF SODIUM AND CALCIUM IONS IN MONTMORILLONITE CRYSTALLITES*

(Received 25 February 1975)

Glaeser and Méring (1954) observed that during substitution of calcium for sodium in montmorillonite, demixing of cations occurs; namely, some interlayers contain only sodium ions and others only calcium ions. McAtee (1956) found that sodium-calcium montmorillonite is a randomly interstratified mixture, i.e. the system exhibited nonintegral basal reflections. Francis (1972) reported that polyvinylpyrrolidone (PVP) is adsorbed by montmorillonite and the amount absorbed is higher for sodium-saturated montmorillonite than for calcium-montmorillonite. Since the basal spacing, $d(001)$, of PVP-sodium-montmorillonite is 26 Å and that of PVP-calcium-montmorillonite is 16 Å, it is expected that PVP treatment will provide a simple method to study the distribution of Na and Ca ions in montmorillonite. Such an approach to the problem is reported in the following.

The montmorillonite used in this study was prepared from Clay Spur (Wyoming) bentonite, supplied by Ward's Natural Science Establishment (A.P.I. No. 26). The $<2\ \mu\text{m}$ particles in the calcium form were prepared by the method described by Levy and Shainberg (1972). All the other montmorillonites were prepared from the freeze-dried calcium clay. The sodium-calcium montmorillonites were prepared by equilibrating with NaCl-CaCl₂ solutions of 0.1 and 0.3 N concentrations. The 0.1 N solutions were used to obtain samples up to 40% exchangeable sodium and the 0.3 N solutions for the 60 and 80% sodium saturated montmorillonites. The composition of the sodium-calcium montmorillonites was checked by exchanging the counter-ions with 1 N CH₃COONH₄ (Levy and Shainberg, 1972). Sodium and calcium in the equilibrium solutions and in the CH₃COONH₄ extracts were determined by a Perkin-Elmer 403 atomic absorption spectro-

photometer, at a wavelength of 4227 Å for calcium and 5893 Å for sodium. The sodium montmorillonite was prepared using four washes of 1 N NaCl. The excess NaCl was removed by washings using equal parts of water and ethanol.

Sodium-calcium montmorillonite samples were dried on glass slides from 1% polyvinylpyrrolidone (PVP) (Francis, 1972). The amount of 1% PVP used for 30 mg montmorillonite was 0.5 ml and 1 ml for samples containing $<40\%$ Na and $>40\%$ sodium, respectively.

The X-ray powder diffraction data on the basal spacings of sodium-calcium montmorillonites dried from 1% PVP are listed in Table 1. As calcium was replaced by sodium no diffraction due to sodium in the interlayers was recorded until sodium content $>20\%$. In the samples containing $>20\%$ sodium two distinct reflections of 26.8 Å and 15.5 Å were obtained from samples 4 and 5. The appearance of two peaks indicated that demixing occurred. Both first and higher orders of diffraction were recorded for samples containing 40 and 60% sodium. The higher orders were integral values of the first-order values. At 80% Na saturation the Ca peak became wider, spreading between 16.4-14.7 Å. First-order peaks of Na-Ca montmorillonite dried from 1% PVP are shown in Fig. 1. It is evident that above 20% Na saturation there were two first-order maxima. While not shown in Fig. 1 the sample with sodium saturation above 90% still showed a calcium peak.

From Table 1 and Fig. 1 it is evident that segregation into zones seems to be the dominant type of interstratification, although at 40-80% Na-saturation some random interstratification might be developing between the Ca and Na layers. The concept of interstratification is usually employed in cases where the crystallites are composed of layers of similar clay minerals (MacEwan, Amil and Brown, 1961). In the case of a segregation of the exchangeable ions in the same clay mineral, Glaeser and Méring

* Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

Table 1. X-ray diffraction data on the basal reflections of sodium-calcium montmorillonites dried from 1% PVP*

Sample No.	Saturation %		1st Order		3rd Order		5th Order	
	Na	Ca	d(Å)	d(Å)	d(Å)	d(Å)	d(Å)	d(Å)
1	0-100			15.8		5.21		3.09
2	10-90			15.8		5.21		3.09
3	20-80			15.8		5.21		3.09
4	40-60		26.8	15.5	8.83	5.21	5.21	3.10
5	60-40		26.8	15.5	8.83	5.21	5.21	3.13
6	80-20		26.8	16.4 to 14.7	8.83		5.21	
7	100-0		26.8		8.83		5.21	

* Obtained with a Philips Norelco diffractometer using Ni-filtered CuK α -radiation and scanned at a speed of 1°/min.

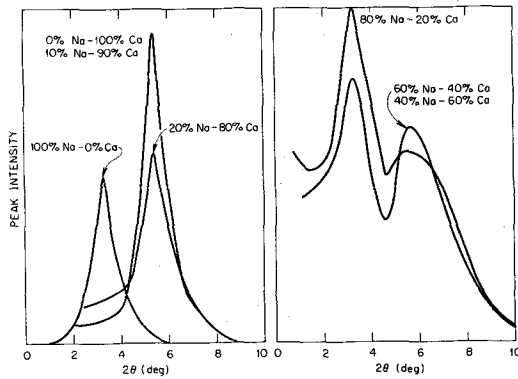


Fig. 1. Profile of first-order basal spacings of Na-Ca montmorillonite dried from 1% PVP.

*The scale of these profiles is twice larger than that of the other profiles.

proposed the concept of demixing, which seems to us more appropriate.

Environmental Sciences Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830, U.S.A.

RACHEL LEVY*
C. W. FRANCIS

REFERENCES

- Francis, C. W. (1973) Adsorption of polyvinylpyrrolidone on reference clay minerals: *Soil Sci.* **115**, 40-54.
- Glaeser, R. and Méring, J. (1954) Isotherms d'hydratation des montmorillonites bi-ioniques (Na, Ca): *Clay Min. Bull.* **12**, 188-193.
- Levy, Rachel and Shainberg, I. (1972) Calcium-magnesium exchange in montmorillonite and vermiculite: *Clays and Clay Minerals* **20**, 35-44.
- McAtee, J. L., Jr. (1956) Determination of random interstratification in montmorillonite. *Am. Miner.* **41**, 627-631.
- MacEwan, D. M. C., Ruiz Amil, A. and Brown G. (1961) Interstratified clay minerals. In *The X-ray Identification and Crystal Structures of Clay Minerals* (Edited by Brown, G.). Mineralogical Society, London.

* On leave of absence from the Agricultural Research Organization, The Volcani Center, Bet Dagan, Israel. This research was made possible by a fellowship given to the senior author by the IAEA under Contract No. AID/csd 1582.