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STRUCTURAL CONSIDERATION OF ZIRCONIUM PHOSPHATE AND ITS ORGANIC COMPLEXES

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INTRODUCTION

In order to explain the difference of properties between montmorillonite and pyrophilite, Edelman and Favejee(E-F) (1940) proposed a structure for montmorillonite different from that suggested by Hofman *et al.* (1933), Marshall (1935) and Hendricks (1942). The characteristic properties for montmorillonites could be readily explained on the basis of the structure proposed by E-F, but there was negative evidence based on the X-ray powder diffraction data and chemical and thermal analysis data (Brown, 1950; Grim, 1968). These phenomena were more adequately explained on the basis of a compromise structure for montmorillonite proposed by McConnell (1950). Though the structure corresponding to the E-F structural hypothesis did not exist in fact, the hypothesis could effectively explain the adsorption property of montmorillonite.

In the course of studies on intercalation complexes, the authors recognized that the structure of zirconium bis-(monohydrogen orthophosphate), hereafter called zirconium phosphate or ZrP, was analogous to that of E-F type montmorillonite and they attempted to form its organic complexes as described in this paper. These results are expected to be helpful for the further investigation of the structure of montmorillonite and of the formation process of its organic complexes.

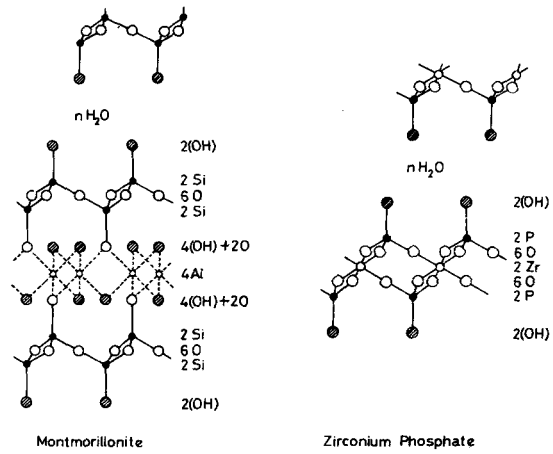


Fig. 1. Schematic presentation of the structure of montmorillonite suggested by Edelman and Fevejee, and that of zirconium phosphate.

STRUCTURAL ANALOGY

The crystal structure of the α-form of ZrP was determined by Clearfield and Smith (1969) by single crystal X-ray analysis. The existence of several other forms of ZrP has been considered due to the difference on the method of linking the layers together, and due to the amount of hydrated water (Clearfield *et al.*, 1968, 1973). Zirconium atoms lie in planes and form hexagonal arrays within these planes, phosphate groups being situated above and below each zirconium layer. Three oxygen atoms of the phosphate are bonded to three different zirconium atoms. The fourth oxygen bears a hydrogen atom and points toward an adjacent plane.

In the structure of montmorillonite postulated by E-F, half the tips of silica tetrahedrons pointed away from the silicate sheet and these tips were replaced by OH instead of O, whereas Hofman *et al.* (Hofman *et al.*, 1933; Marshall, 1935; Hendricks, 1942) considered that all the tips pointed in the same direction and toward the center of the sheet. In Figure 1 the schematic structure of montmorillonite by E-F is compared with that of ZrP. The scheme for ZrP was drawn in accordance with the representation of E-F for comparison. Although SiO_4 tetrahedra are substituted for PO_4 tetrahedra, similarities between the two structures can be summarized as follows: In both of them,

(1) The tips of tetrahedra of the interlayer surfaces point away from the layers.

(2) OH Groups are contained on layer surfaces.

(3) Zeolitic cavities where water molecules are trapped are formed between the adjacent layers.

In order to explain the ion exchange capacity of montmorillonite, E-F posturated that only some of the H ions with OH tips could be exchanged. This concept of selecting site is also adaptable to the discussion on the ion exchange of ZrP. When ZrP is titrated with NaOH, a half-exchanged phase, $Zr(NaPO_4)(HPO_4)$, appears before a fully exchanged phase, $Zr(NaPO_4)_2$, is obtained (Clearfield *et al.*, 1969b).

ORGANIC COMPLEXES OF ZrP

One of the reasons why E-F postulated the structure described above was to explain the marked organophilic character of montmorillonite. Therefore, it will be reasonable to expect that ZrP will have similar organophilic properties. As a matter of fact, it was found that various kinds of polar organic molecules could be adsorbed in the interlayer spaces of α- and γ-ZrP. The basal spacings of these complexes are summarized in Table 1 together with the method of sample preparation.

These complexes can be classified into three different types according to the ways of attaching organic molecules to the phosphate layers:

Type I. Complexes containing hydrogen bonds
Type II. Complexes containing ionic interactions
Type III. Complexes containing covalent bonds

In Type I complexes, the interaction between organic molecules and the phosphate layers is attributed to the

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Table 1. Basal plane spacings of organic complexes of ZrP

Type of complexes	Complex forming substance	Method of formation*	Basal plane spacings, Å: Complex with α-ZrP (7·6 Å)	Basal plane spacings, Å: Complex with γ-ZrP (12·3 Å)
I	methyl alcohol	a		12·7
	ethyl alcohol	a		16·6
	iso-propyl alcohol	a		19·4
	ethylene glycol	a	10·3	13·4
	diethylene glycol	a	10·5	13·2
	acetone	a		14·4
	N,N-dimethylformamide	a	10·7	16·5
	dimethyl surfoxide	a	11·3	15·8
II**	n-butylamine	b	18·8	21·5
	pyridine	b	10·9	
III	ethylene oxide	c		18·4
	propylene oxide	c		24·5

* a = immersed in large excess of liquids at room temperature for one day. b = immersed in large excess of 1 M aqueous solutions for one day. c = immersed in large excess of 2 M aqueous solutions for one day and then thoroughly washed with pure water.

** See also a reference (Michel and Weiss, 1965).

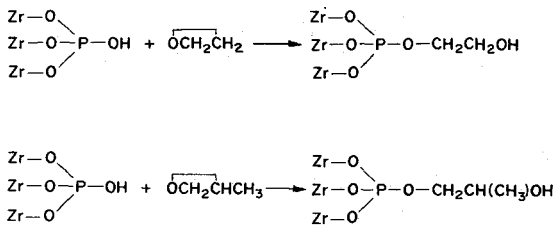
formation of hydrogen bonds such as $\gtrless P—O^- H^+ \cdots O\lessgtr$, and some contribution of a molecular sieving effect of zeolitic cavities must be taken into account. Organic species in Type I complexes are so loosely bonded to the phosphate layers that they were easily desorbed when the complexes were left in air or washed with water. Therefore, the X-ray diffraction patterns were taken on samples covered with a thin polyethylene film to protect the immersed samples from dryness.

For Type II complexes, a number of amine complexes of α-ZrP had been prepared by Michel and Weiss (1965) before the structure of α-ZrP was determined by Clearfield and Smith (1969a). The bonding interaction contained is ionic:

$$\gtrless P—O^- \cdots H_3N^+C_4H_9.$$

Details of formation mechanism for Type II complexes will be published elsewhere in the near future.

The complexes belonging to Type I and II are sorption complexes. The complexes of a different type were formed by the reaction of ethylene and propylene oxides with γ-ZrP. These epoxides adsorbed in the interlayer space from the aqueous solutions undergo ring-scission and form glycol esters with the phosphate groups of the layers:



As reported in a previous paper (Yamanaka *et al.*, 1973), the formation of the P—O—C ester bond was confirmed by a number of evidences. Type III complexes are considered to be organic derivatives of ZrP rather than sorption complexes.

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REFERENCES

Brown, G. (1950) A Fourier investigation of montmorillonite: *Clay Minerals Bull.* **4,** 109–111.

Clearfield, A., Blessing, R. H. and Stynes, J. A. (1968) New crystalline phases of zirconium phosphate possessing ion-exchange properties: *J. Inorg. Nucl. Chem.* **30,** 2249–2258.

Clearfield, A. and Smith, G. D. (1969a) The crystallography and structure of α-zirconium bis(monohydrogen orthophosphate) monohydrate: *Inorg. Chem.* **8,** 431–436.

Clearfield, A., Duax, W. L., Medina, A. S., Smith, G. D. and Thomas, J. R. (1969b) On the mechanism of ion exchange in crystalline zirconium phosphates. Sodium ion exchange of α-zirconium phosphate: *J. Phys. Chem.* **73,** 3424–3430.

Clearfield, A., Landis, A. L., Medina, A. S. and Troup, J. M. (1973) More on crystalline zirconium phosphates: *J. Inorg. Nucl. Chem.* **35,** 1099–1108.

Edelman, C. H. and Favejee, J. Ch. L. (1940) On the crystal structure of montmorillonite and halloysite: *Z. Krist.* **102,** 417–431.

Grim, R. E. (1968) *Clay Mineralogy* 2nd Edn., Chap. 10. McGraw-Hill, New York.

Hendricks, S. B. (1942) Lattice structure of clay minerals and some properties of clays: *J. Geol.* **50,** 276–290.

Hofman, U., Endell, K. and Wilm, D. (1933) Kristallstruktur und Quellung von Montmorillonit: *Z. Krist.* **86,** 340–348.

Marshall, C. E. (1935) Layer lattices and base-exchange clays: *Z. Krist.* **91,** 433–449.

McConnell, D. (1950) The crystal chemistry of montmorillonite: *Am. Miner.* **35,** 166–172.

Michel, E. and Weiss, A. (1965) Kristallines Zirkonphosphat, ein Kationen-austauscher mit Schichtstruktur und innerkristallinen Quellungsvermögen: *Z. Naturforsch.* **20b,** 1307–1308.

Yamanaka, S., Kanamaru, F. and Koizumi, M. (1973) Organic derivative of γ-zirconium phosphate: *Nature Phys. Sci.* **246,** 63–64.

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