The Crystallization of "Allophane" under Hydrothermal Conditions

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Allophane, a hydrous silica-alumina mineral, is classified into mineral allophane, soil allophane and "precipitation allophane"¹⁾ from their ways of occurrence. They are almost X-ray amorphous and show the similar thermal behavior characterized by mullite formation at 900～1000°C under atmospheric condition.

In hydrothermal synthesis experiments, crystallization of some amorphous materials, gels or glasses, occurs at fairly low temperatures. In such a condition, phase assemblages more stable than the reactants may easily be formed. An attempt has been made to observe structural differences of allophane and consequently to establish a picture of structural classification of X-ray amorphous minerals by applying the crystallization method under hydrothermal conditions.

The general procedure was to allow samples of allophane to react with water over the range 200～500°C at 1000 atm. H_2O and then to quench into water. The type of pressure vessel used was of the "test-tube" bomb²⁾. Running was made for two weeks at maximum. The products were then examined with an X-ray diffractometer.

Soil allophane from Kanuma³⁾ and Imaichi⁴⁾, mineral allophane from Bihoro⁵⁾ and precipitation allophane from Asama⁶⁾ and Fukazawa⁷⁾ were used for the experiment⁸⁾. Synthetic silica-alumina gels prepared by the homogeneous precipitation method over the chemical composition range of $2SiO_2\cdot Al_2O_3$-$SiO_2\cdot 5Al_2O_3$ were kindly supplied for this investigation by Dr. J. Ossaka. The thermal properties of these gels has been studied by Ossaka and found to be identical with those of the natural allophanes⁷⁾. The aluminosilica gel was also prepared from synthetic zeolite, Type A⁹⁾, by destructing the framework with hydrochloric acid and then washing sodium ion off with water. The mole ratios of SiO_2/Al_2O_3 of these starting materials are illustrated in Fig. 1.

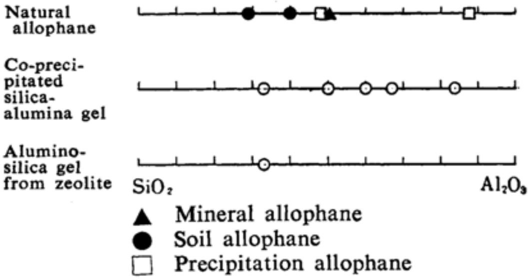

Fig. 1. The chemical composition of the starting materials.

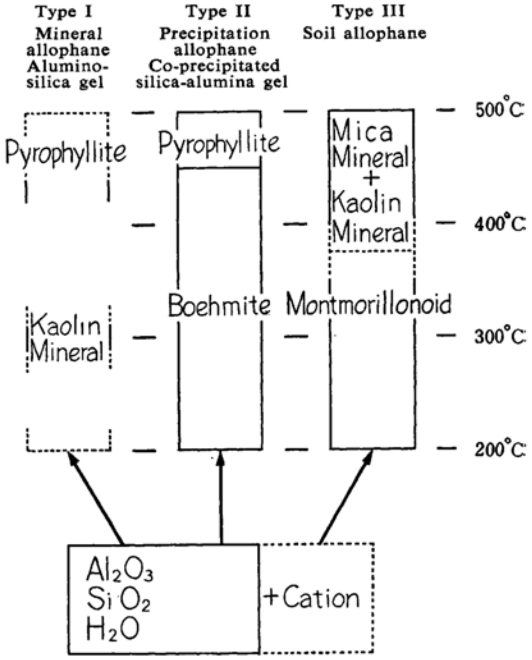

Fig. 2. Diagrammatic representation of phase assemblages obtained from the various starting materials.

The experimental results are summarized diagrammatically in Fig. 2. Owing to the poor crystallinity of the products, the prcise phase determination was somewhat difficult for several specimens. As indicated in Fig. 2, the crystallization process of the starting materials in this investigation are classified into the following types.

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1) This amorphous mineral found from mineral spring was classified by J. Ossaka into a variety of the species of allophane.

2) R. Roy and E. F. Osborn, *Econ. Geol.*, **47**, 717 (1952).

3) T. Sudo and J. Ossaka, *Japanese J. Geol. Geogr.*, **22**, 215 (1952).

4) R. Morimoto, J. Ossaka and T. Fukuda, *Bull. Earthq. Res. Inst.*, **35**, 359 (1957).

5) H. Minato, *Advances in Clay Sci.*, **2**, 350 (1960).

6) J. Ossaka, ibid., **2**, 339 (1960).

7) J. Ossaka, read before the Annual Meeting of the Mineralogical Society of Japan, Tokyo, June, 1959.

8) The authors are indebted to Dr. J. Ossaka and Dr. H. Minato of the University of Tokyo who kindly supplied the specimens for the experiment.

9) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *J. Am. Chem. Soc.*, **78**, 5963 (1956).

Type I: From the materials of this type, a kaolin mineral was formed at 300°C, and then pyrophyllite was obtained at 430°C. The mineral allophane and the aluminosilica gel appeared to crystallize in this manner.

Type II: The two samples of precipitation allophane and all the co-precipitated silica-alumina gels with various compositions were classified into this type. It should be noted that, from these samples, only a boehmite phase appeared in the temperature range between 200 and 450°C and above 450°C pyrophyllite was formed.

Type III: The three samples of soil allophane yielded a montmorillonoid phase in the region from 200 to 350°C. The (0 0 1) spacing was 15 Å and expanded to 18 Å when treated with glycol. Above 400°C, a mica and a kaolin mineral were obtained together.

Important factors controlling what phases crystallize from the amorphous minerals may be considered to involve (i) SiO_2/Al_2O_3 ratio, (ii) impurity cations and (iii) the gel structure. It is probably possible to remove SiO_2/Al_2O_3 ratio out of the major factors on the following basis. Each of the three specimens with the almost same ratio of 2:1, including aluminosilica gel, soil allophane and one of co-precipitated silica-alumina gels, gave a product of its own phase. Such was the case also with mineral allophane, precipitation allophane and co-precipitated gel of the same SiO_2/Al_2O_3 ratio of 1:1. The products of type III were obtained only from soil allophane. It is considered that their formation may be effected by the presence of a considerable amount of cation impurities which have been contained in every soil allophane. On the contrary, all the starting materials of the types I and II are chemically free from any cations. It is thus reasonable to assume that gel structure plays a role in deciding the product from the starting materials of the similar chemical composition.

From the preparation method previously mentioned, it is suggested that the co-precipitated gels are homogeneous mixtures of the two species of gel particles, silica and alumina, finely dispersed in each other. This concept is supported by the experimental result that the materials of the type II do not yield an aluminosilicate phase but an alumina mineral, boehmite, in the lower temperature range. Thus the precipitation allophane is possibly considered to be structurally identical with the co-precipitated gel.

Mineral allophane showed the same crystallization behavior with an aluminosilica gel prepared from the zeolite. It is obvious, therefore, the mineral allophane is probably an aluminosilicate with four-coordinated aluminum.

As it is well known, our present knowledge is insufficient to discuss the gel structure precisely. From the above results, however, we may now recommend that study on crystallization under hydrothermal conditions will be applicable to deduce a structure of X-ray amorphous mineral. In this way natural allophane of this investigation can be classified into three groups.

The detailed description of this work will be given elsewhere in near future.

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