Clays and Clay Minerals, Vol. 34, No. 3, 323–329, 1986.

QUANTIFICATION CURVES FOR THE X-RAY POWDER DIFFRACTION ANALYSIS OF MIXED-LAYER KAOLINITE/SMECTITE

KATSUTOSHI TOMITA

Institute of Earth Sciences, Faculty of Science, Kagoshima University
Kagoshima, 890, Japan

HIDEWO TAKAHASHI

Department of Geology, Faculty of Education, Kagoshima University
Kagoshima, 890, Japan

Abstract—X-ray powder diffraction patterns for many interstratified kaolinite/glycolated smectites were calculated by changing combinations of probabilities and transition probabilities of two component layers. Reichweite = 0 and Reichweite = 1 structures were investigated. The calculated d-values were plotted, with P_{KS} (the probability that a smectite layer succeeds a kaolin layer given that the first layer is a kaolinite layer) and P_{SK} as the axes of coordinates. These d-values were then linked into equal d-value curves on a graph. Four equal d-value diagrams for mixed reflections ranging from 34.0 to 17.1 Å, from 8.5 to 7.2 Å, from 6.13 to 5.68 Å, and from 3.540 to 3.401 Å were constructed. Two examples of identifying natural kaolinite/smectite minerals using these diagrams are presented.

要旨 — カオリナイト／スメクタイト（エチレングリコール処理したもの）混合層鉱物について、構成層の存在確率および継続確率をいろいろ変えて、多くのX線粉末回折曲線を計算した。 Reichweite＝0 と Reichweite＝1 の構造について計算を行なった。 計算で得たd－値をP_{KS} （最初の層がカオリナイト層で、スメクタイト層がカオリナイト層に継がる確率）とP_{SK} を座標軸にとった図にプロットした。 これらのd－値のうち等しいd－値を結んで等d－値曲線図を作成した。 34.0－17.2Å、8.5 －7.2Å 、 6.13－5.68Å と3.540 －3.401Å の４つの等d－値曲線図を作成した。 天然産の２つのカオリナイト／スメクタイト混合層鉱物を例にとって、これらの曲線を用いて積層パラメータの決定を行なった。

Key Words—Ethylene glycol, Interstratification, Kaolinite/smectite, Mixed-layer quantification, X-ray powder diffraction.

INTRODUCTION

The occurrence of interstratified kaolinite/smectites (K/S) in nature was first reported by Sudo and Hayashi (1956); such minerals were subsequently confirmed by Altschuler *et al.* (1963). These minerals have since been described in acid clays in Japan (Shimoyama *et al.,* 1969), in Tertiary clays of Yucatan (Schultz *et al.,* 1971), and in hydrothermal deposits of Lower Silesia (Wiewiora, 1971, 1973). Since then, many occurrences of K/S have been described. These minerals have also been synthesized (Urabe *et al.,* 1979; Środoń, 1980). Studies of the nature of layer sequences of such mixed-layer minerals, however, are few: Sakharov and Drits (1973), Cradwick and Wilson (1978), Kohyama and Shimoda (1974), and Tsuzuki and Sato (1974). Sakharov and Drits (1973) and Reynolds (1980) reported calculated X-ray powder diffraction patterns for K/S, but these patterns do not cover the entire range of composition and ordering types represented by naturally occurring interstratified minerals. Tomita and Takahashi (1985) devised X-ray diffraction quantifi-

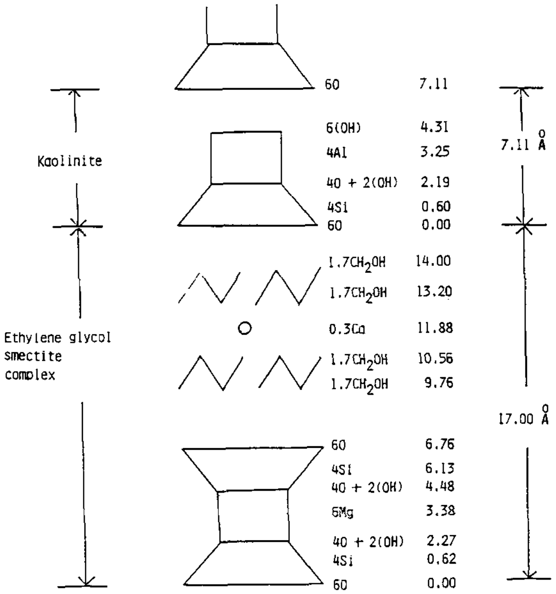

Figure 1. Model of kaolinite and glycolated smectite layers used in calculation of X-ray powder diffraction patterns.

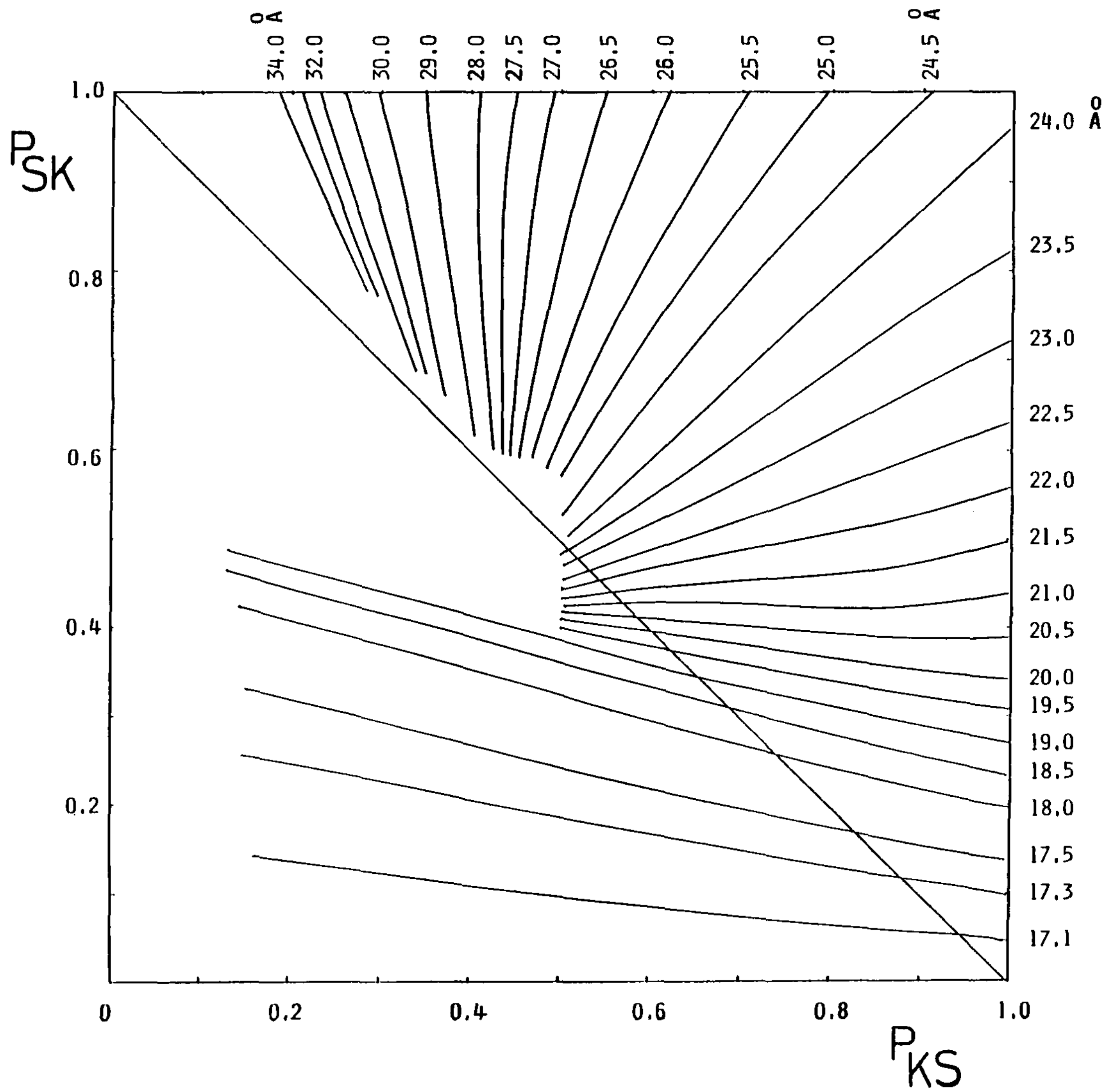

Figure 2. Diagram of equal d-value lines for 34.0–17.1-Å reflection for quantification of kaolinite/glycolated-smectite interstratifications. P_{KS} is probability that a smectite layer succeeds a kaolinite layer given that the first layer is a kaolinite layer. P_{SK} is similarly defined.

cation curves for mica/smectite and chlorite/smectite interstratifications that are useful for the rapid quantification of layer sequences in many interstratified minerals. In the present investigation, X-ray diffraction quantification curves were constructed for K/S interstratifications. These curves can be used to determine the probabilities of occurrence of two component layers and their junction probabilities in R=0 and R=1 structures. The equation of Kakinoki and Komura (1965) was used. The identification plots were prepared in the same way as those prepared for Tomita and Takahashi (1985) for interstratified mica/smectite and chlorite/smectite.

PREPARATION OF IDENTIFICATION PLOTS

X-ray powder diffraction profiles of interstratified structures were calculated using the equation of Kakinoki and Komura (1965). The integrated intensity and the intensity maximum position were calculated by an electronic computer, using a slightly modified program from Takahashi (1982). Although uncertainties exist in the Lorentz factor at very low values of 2θ (Reynolds, 1983), the Lorentz-polarization factor for the oriented samples was applied for the calculation. A value of N = 20 was chosen to obtain stable calculated peaks and to diminish ghost peaks which are common in the low 2θ region if a small N is used (Sato,

https://doi.org/10.1346/CCMN.1986.0340313 Published online by Cambridge University Press

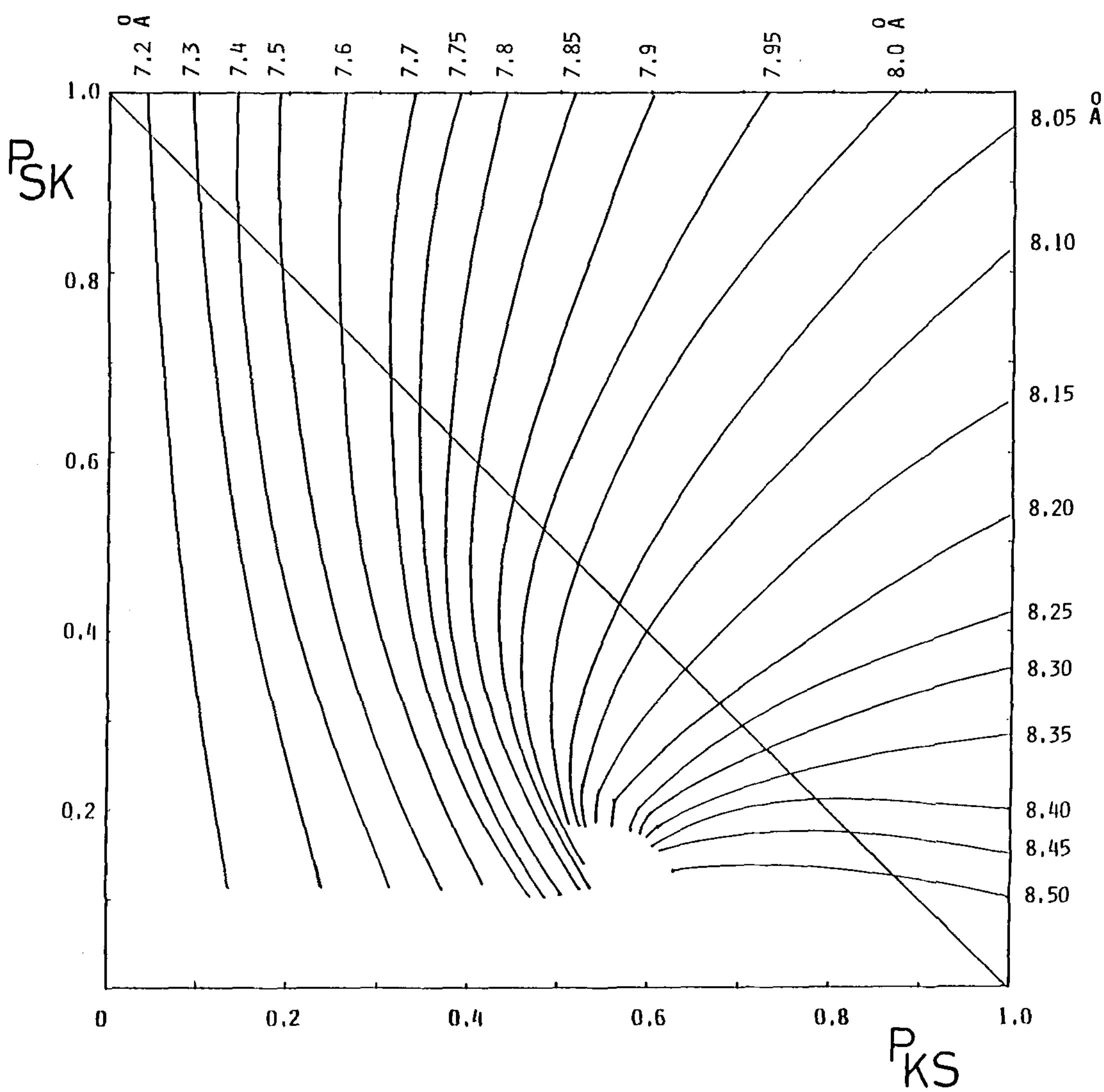

Figure 3. Diagram of equal d-value lines for 8.50–7.2-Å reflection for quantification of kaolinite/glycolated-smectite interstratifications. P_{KS} is probability that a smectite layer succeeds a kaolinite layer given that the first layer is a kaolinite layer. P_{SK} is similarly defined.

1973). The calculation was based on the model shown in Figure 1; the Sato and Kizaki (1972) model was used which employs a smectite component expanded with ethylene glycol. Similar results were obtained when XRD patterns were calculated using the model of Reynolds (1980). A value of 17 Å for an ethylene glycol-smectite layer was used. The 16.6–17.2-Å range found in natural smectites (Środoń, 1980) was not taken into account in order to simplify the calculations. Diffraction intensities were calculated for many combinations of probabilities and transition probabilities for kaolinite and glycolated smectite layers. Equal d-value line diagrams from 34.0 to 17.1, 8.50 to 7.2, 6.13 to 5.68, and 3.540 to 3.401 Å were constructed from the calculated data and are shown in Figures 2, 3, 4, and 5, respectively. In these illustrations, P_{KS} is the probability of a smectite layer following a kaolinite layer, assuming that the first layer is a kaolinite layer. P_{SK} is the probability that a kaolinite layer succeeds a smectite layer, assuming that the first layer is a smectite layer.

APPLICATION OF IDENTIFICATION PLOTS TO NATURAL MINERALS

Many occurrences of K/S have been described, but precise d-values for these minerals after treatment with ethylene glycol have generally not been reported. As examples of the practical application of this method, a specimen investigated by Akai (1974, sample T183)

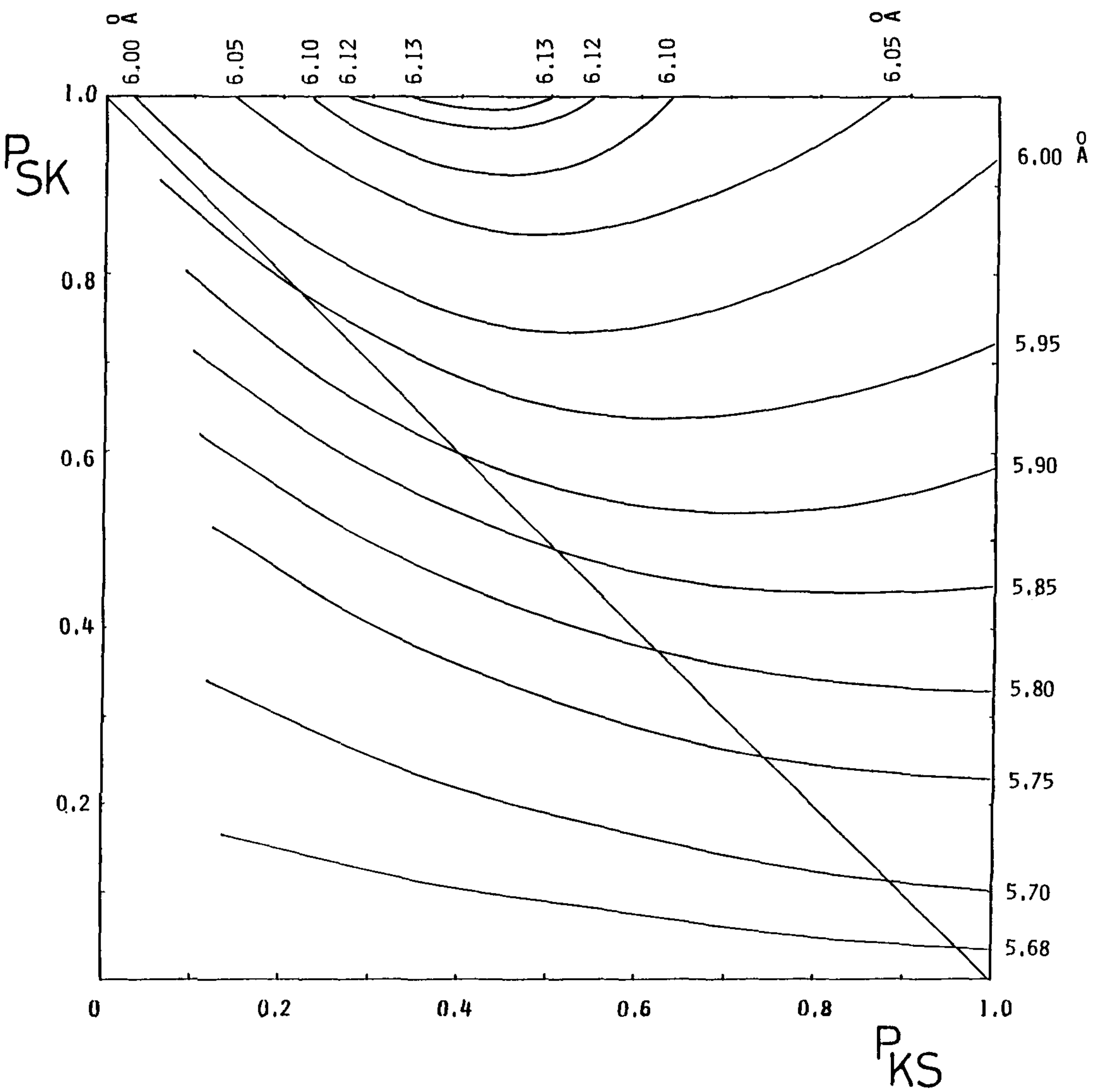

Figure 4. Diagram of equal d-value lines for 6.13–5.68-Å reflection for quantification of kaolinite/glycolated-smectite interstratifications. P_{KS} is probability that a smectite layer succeeds a kaolinite layer given that the first layer is a kaolinite layer. P_{SK} is similarly defined.

and the Becal sample studied by Schultz *et al.* (1971) were examined. For a two-component interstratification of layers K and S, assuming P_K to be the frequency of occurrence of K, P_S is that of S, and $P_K + P_S = 1$; if P_{KS} is the probability that S succeeds K, given that the first layer is K, P_{KK}, P_{SS}, and P_{SK} are similarly defined, thus:

$$P_{KK} + P_{KS} = 1,$$
$$P_{SK} + P_{SS} = 1,$$
$$P_K P_{KK} + P_S P_{SK} = P_K,$$
$$P_K P_{KS} + P_S P_{SS} = P_S,$$
$$P_S P_{SK} = P_K P_{KS}, \text{ and}$$
$$P_K/P_S = P_{SK}/P_{KS}.$$

Sample T183 showed XRD reflections at 17.7 and 7.4 Å. The 17.7-Å contour in Figure 2 was traced along a 17.7-Å line, and the tracing paper was placed on the diagram shown in Figure 3. The 7.4-Å contour was then traced in the same way. From the intersection of the two lines shown in Figure 6 at point A, P_{KS} and P_{SK} values of 0.22 and 0.345 were obtained, respectively. All remaining probabilities and junction probabilities for nearest-neighbor ordering were obtained from these data, as follows: $P_K:P_S = P_{SK}:P_{KS} = 0.345:0.22 = 0.61:0.39$. Accordingly, $P_K = 0.61$, $P_S = 0.39$, $P_{KS} = 0.22$, $P_{KK} = 0.78$, $P_{SK} = 0.345$, and $P_{SS} = 0.655$, where P_K is the probability of the existence of a kaolinite layer, P_S is that of a smectite layer, and P_{KS} is

https://doi.org/10.1346/CCMN.1986.0340313 Published online by Cambridge University Press

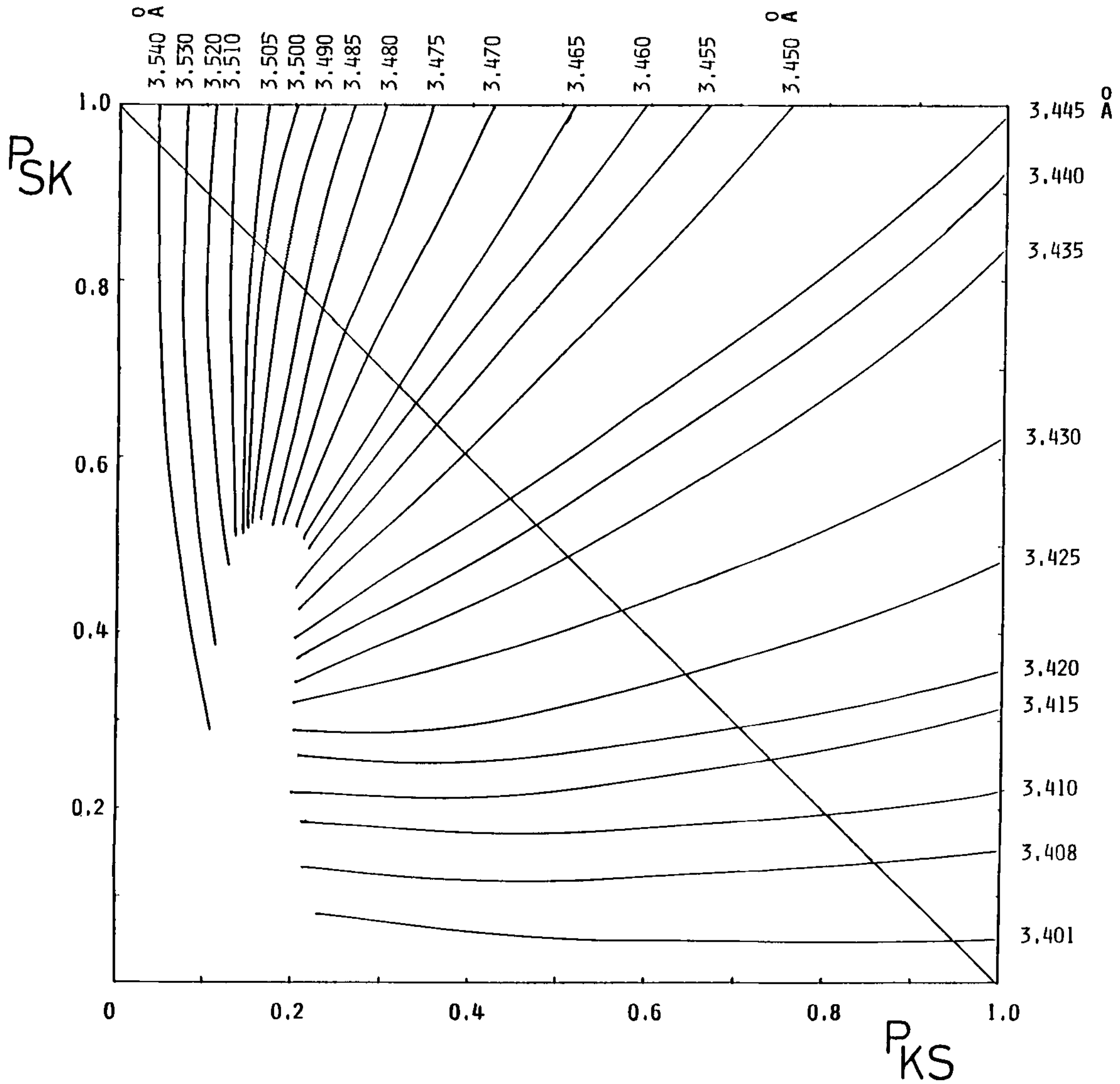

Figure 5. Diagram of equal d-value lines for 3.540–3.401-Å reflection for quantification of kaolinite/glycolated-smectite interstratifications. P_{KS} is probability that a smectite layer succeeds a kaolinite layer given that the first layer is a kaolinite layer. P_{SK} is similarly defined.

the probability that a smectite layer succeeds a kaolinite layer, assuming that the first layer is a kaolinite layer. P_{KK}, P_{SK}, and P_{SS} are similarly defined.

The Becal sample showed XRD reflections at 20.0 and 7.9 Å. In the same way as described for sample T183, P_{KS} and P_{SK} values of 0.44 and 0.435 were obtained at the intersection of the 20.0- and 7.9-Å lines shown in Figure 6 at point B. From these values, P_K: P_S = P_{SK}:P_{KS} = 0.435:0.44 = 0.497:0.503 were obtained. Accordingly, $P_K = 0.50$, $P_S = 0.50$, $P_{KS} = 0.44$, $P_{KK} = 0.56$, $P_{SK} = 0.435$, and $P_{SS} = 0.565$.

The XRD patterns of the samples Becal and T183 and their calculated XRD patterns are shown in Figure 7. Differences in intensities are due to the differences of chemical compositions and orientations of samples.

For samples not showing high d-spacings (i.e., 17 Å), interstratified structures can be determined by using the proper two diagrams among the remaining three diagrams.

Distinguishing K/S from halloysite(7Å) and illite/smectite is often necessary. The best test for K/S vs. halloysite(7Å) is the 002 reflection of halloysite(7Å) (3.56 Å) moving toward lower angles in halloysite and higher in K/S. At the other end of the series of clays consisting of nearly pure smectite, infrared spectroscopy is a very sensitive technique for detecting even small amount of kaolinite layers (Jan Środoń, Institute of Geological Sciences, Polish Academy of Sciences, 31002 Krakow, Poland, personal communication, 1986). In illite/smectite samples, a reflection near 5 Å

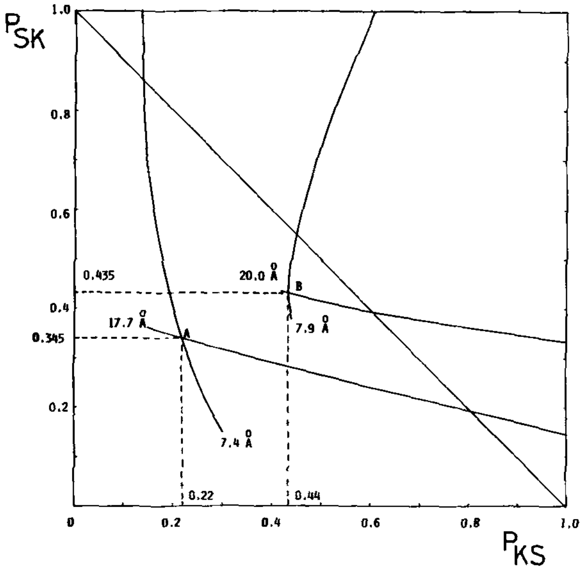

Figure 6. Plots of 17.7- and 7.4-Å lines, and 20.0- and 7.9-Å lines using the diagrams of Figures 2 and 3, respectively, for quantification of the kaolinite/glycolated-smectite interstratifications. P_{KS} is probability that a glycolated smectite layer succeeds a kaolinite layer given that the first layer is a kaolinite layer. P_{SK} is similarly defined.

is characteristic, whereas in K/S samples, a reflection near 5.65–6.13 Å is characteristic.

DISCUSSION

The layer sequences of interstratified K/S were determined easily using the diagrams presented in this study. These diagrams are useful for the rapid quantification of layer sequences of such interstratifications. If an XRD pattern is similar to that of kaolinite and if the reflection at about 7 Å shows larger d-values than that of halloysite(7Å) and expands by treatment with ethylene glycol, the specimen can be identified as an interstratified kaolinite/smectite. But if an XRD pattern is similar to that of smectite and contains a reflection between 14 and 16 Å which moves to 17–18 Å after treatment with ethylene glycol, such a sample will often be identified as smectite, although it may be kaolinite/smectite with few kaolinite layers. Discrete kaolinite in the sample will affect the position of neighboring kaolinite/smectite peak. If an interstratified kaolinite/smectite shows a d-value larger than 17 Å after treatment with ethylene glycol, Figure 2 should be used as one of diagrams for the quantification because the movement of peak position with composition for K/S is large in the low-angle range. If it is impossible to quantify the interstratification of the interstratified mineral by using any combination of two diagrams among the four presented, the sample must contain three or more kinds of layers, or R>1. Diagrams for such samples are in preparation.

A value of 17 Å was used for the ethylene glycol-smectite layer as was used by previous workers, although Środoń (1980) reported a range of 16.6–17.2 Å for natural smectites. Some error (2–3%) may be expected because of this simplification as mentioned by Środoń (1980).

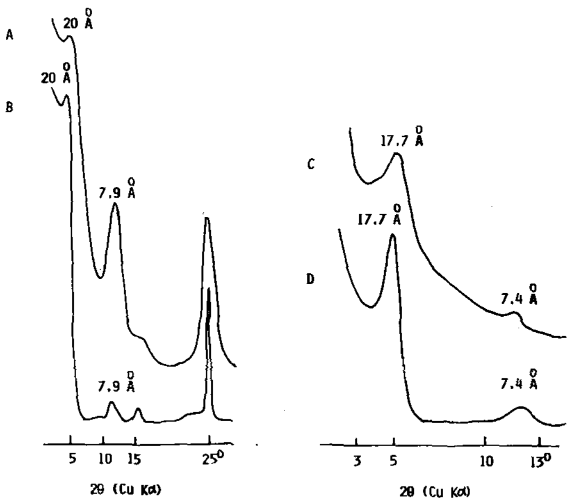

Figure 7. X-ray powder diffraction patterns of kaolinite/smectite samples described by Schultz *et al.* (1971) (Becal) and Akai (1973) (sample T183). A = natural Becal sample; B = calculated pattern of Becal sample; C = natural sample T183; D = calculated pattern of sample T183.

ACKNOWLEDGMENTS

This study was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. The authors thank R. C. Reynolds and J. Środoń for many valuable comments and critical review of the manuscript. F. A. Mumpton kindly improved the English of this manuscript.

REFERENCES

Akai, J. (1974) Some examples of weathering product of montmorillonite: *J. Mineral. Soc. Japan* **11**, 87–92 (in Japanese).

Altschuler, Z. S., Dwornik, E. J., and Kramer, H. (1963) Transformation of montmorillonite to kaolinite during weathering: *Science* **141**, 148–152.

Cradwick, P. D. and Wilson, M. J. (1978) Calculated X-ray diffraction curves for the interpretation of a three-component interstratified system: *Clay Miner.* **13**, 53–65.

Kakinoki, J. and Komura, Y. (1965) Diffraction by a one-dimensionally disordered crystal. I. The intensity equation: *Acta Crystallogr.* **19**, 137–147.

Kohyama, N. and Shimoda, S. (1974) On a few specimens called mixed layer kaolinite-montmorillonite: comparisons of observed and calculated X-ray diffraction patterns: *J. Mineral. Soc. Japan* **11**, 99–106 (in Japanese).

Reynolds, R. C. (1980) Interstratified clay minerals: in *Crystal Structures of Clay Minerals and Their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 249–303.

Reynolds, R. C. (1983) Calculation of absolute diffraction intensities for mixed-layered clays: *Clays & Clay Minerals* **31,** 233–234.

Sakharov, B. A. and Drits, V. A. (1973) Mixed-layer kaolinite-montmorillonite: a comparison of observed and calculated diffraction patterns: *Clays & Clay Minerals* **21,** 15–17.

Sato, M. (1973) X-ray analysis of interstratified structure: *Nendo Kagaku* **13,** 39–47 (in Japanese).

Sato, M. and Kizaki, Y. (1972) Structure of a 38-Å interstratified mineral, an illite-montmorillonite mixture: *Z. Kristallogr.* **135,** 219–231.

Schultz, L. G., Shepard, A. D., Blackmon, P. D., and Starkey, H. C. (1971) Mixed-layer kaolinite-montmorillonite from the Yukatan Peninsula, Mexico: *Clays & Clay Minerals* **19,** 137–150.

Shimoyama, A., Johns, W. D., and Sudo, T. (1969) Montmorillonite-kaolin clay in acid clay deposits from Japan: in *Proc. Int. Clay Confer. Tokyo, 1969, Vol. 1,* L. Heller, ed., Israel Univ. Press, Jerusalem, 225–231.

Środoń, J. (1980) Synthesis of mixed-layer kaolinite/smectite: *Clays & Clay Minerals* **28,** 419–424.

Sudo, T. and Hayashi, H. (1956) A randomly interstratified kaolin-montmorillonite in acid clay deposists in Japan: *Nature* **178,** 1115–1116.

Takahashi, H. (1982) Electronic computer's program for calculation of diffracted intensity by close-packed structures with stacking faults: *Bull. Fac. Educ. Kagoshima Univ.* **34,** 1–14 (in Japanese).

Tomita, K. and Takahashi, H. (1985) Curves for the quantification of mica/smectite and chlorite/smectite interstratifications by X-ray powder diffraction: *Clays & Clay Minerals* **33,** 379–390.

Tsuzuki, Y. and Sato, M. (1974) Some structure models of kaolin/montmorillonite random mixed-layer minerals: *J. Mineral. Soc. Japan* **11,** 106–110 (in Japanese).

Urabe, K., Udagawa, S., and Hayashi, T. (1979) Synthesis of kaolin-montmorillonite mixed layer minerals: *J. Mineral. Soc. Japan* **14,** 146–161 (in Japanese).

Wiewiora, A. (1971) A mixed layer kaolinite-smectite from lower Silesia, Poland: *Clays & Clay Minerals* **19,** 415–416.

Wiewiora, A. (1973) Mixed-layer kaolinite-smectite from lower Silesia, Poland: final report: in *Proc. Int. Clay Conf., Madrid, 1972, Vol. 1,* J. M. Serratosa, ed., Div. Ciencias C.S.I.C., Madrid, 101–116.

(Received 3 September 1985; accepted 25 February 1986; Ms. 1517)