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Application of an XRD-Pattern Calculation Method to Quantitative Analysis of Clay Minerals

X－선 회절도형 계산방법을 이용한 점토광물의 정량분석

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ABSTRACT: An XRD quantitative analytical method using calculated XRD patterns was discussed in this study. Deep-seabed sediments commonly contain smectite, illite, chlorite, and kaolinite, and XRD pattern of each clay mineral of appropriate chemical composition was simulated by using an XRD pattern calculation method. Theoretical peak intensities of specific reflections of four clay minerals (the 001 reflections of smectite and illite, the 004 reflection of chlorite, and the 002 reflection of kaolinite) were measured from calculated patterns, and MIF (mineral intensity factor) value of each phase was determined from the intensities of calculated patterns. The peak intensities obtained from experimental XRD patterns of sediments were corrected using the MIF values so that the calibrated intensity values for the specimens are linearly proportional to the weight fraction of each phase, which is normalized to 100 wt%.

The MIF method can provide accurate quantitaive results without the necessity of correcting the factors by the mass abosorption coefficient of each phase. This method excludes the necessity of standard specimens having compositions that are similar to those of clay minerals in the sediment samples. Therefore, quantitaive analysis using XRD calculation method can be utilized for the specimens, for which the standard specimens are very difficult or impossible to obtain. This quantitative method can provide rapid, routine analysis results for a large number of samples which occur in similar geological environments.

요약: 점토광물들은 지질환경에 따라 다양한 화학성분을 갖게되는데, 화학성분의 변화는 X-선 회절도형 회절선 intensity에도 영향을 미치기 때문에 점토광물들의 정확한 정량분석을 위하여서는 유사한 화학식을 갖는 표준시료를 필요로 하게된다. 대부분의 경우 특정성분의 표준시료를 확보하기 어렵지만, X-선 회절도형 계산방법을 응용하면 표준시료를 사용하지 않고 점토광물들의 정량분석을 실시할 수 있다.

대부분 심해저 퇴적물은 smectite, illite, chlorite, kaolinite 등 점토광물들을 함유하고 있는데, 특정한 화학성분을 갖는 이러한 네가지 점토광물들의 X-선 회절도형을 NEWMOD프로그램을 이용하여 계산하였다. smectite와 illite의 001 회절선, chlorite의 004회절선, kaolinite의 002회절선의 이론적 peak intensity들을 계산된 X-선 회절도형으로부터 구하여 각 광물들의 MIF(Mineral Intensity Factor)값을 결정하였다. 실험에서 얻어진 시료의 peak intensity는 MIF값을 이용하여 교정하면 peak intensity값과 각 광물들의 wt%가 비례하도록 된다. 각 광물들의 wt% 총합계는 100wt%가 되도록 설정한 후 각 광물들의 구성비율을 이용하여 정량화 하였다.

이러한 정량분석방법은 분석하려는 광물의 화학식과 거의 비슷한 표준시료를 준비하지 않아도 되기때문에, X-선 회절도형의 계산방법을 이용한 정량분석은 표준시료를 구할 수 없거나 구하기 힘든 경우 유용하게 사용될 수 있다. 회절도형계산을 이용한 정량분석 방법은 서로 비슷한 지질환경에서 산출된 점토광물들을 대량으로 빠른 시간내에 분석하는데 이용할 수 있다.

INTRODUCTION

Powder X-ray diffraction (XRD) is one of the most widely-used analytical methods used for identifying constituents in the samples that consist of mixtures of minerals. XRD is also used for quantitative characterization of each constituent in the samples. External or internal standards can be used for quantitative analysis (e. g., Copeland and Bragg, 1958 ; Klug and Alexander, 1954, Pawloski, 1985), and methods without using standards were also introduced (e. g., Zevin, 1977 ; Geohner, 1982).

The structure and chemistry of most clay minerals vary significantly from sample to sample according to geological environments, and their XRD intensity profiles vary. It is extremely difficult to obatin very accurate quantitative data of clay minerals using XRD methods. One of the most serious problems encountered in conducting quantitative analysis of clay minerals using standard is that accurate structure and chemistry of clays are very difficult to characterize because of their small particle size and occurrence as mixtures. Therefore, well-defined clays are extremely difficult to obtain to use them as standard minerals, and the chemistry and structure of clay minerals in specimens are very difficult to be characterized.

The difficulty of obtaining appropriate standard clay minerals can be partially overcome by utilizing XRD pattern calculation methods. Reynolds (1967) and Reynolds and Hower (1970) introduced the concept of XRD pattern calculation of mixed-layer clays and monomineralic phases. XRD patterns can be calculated based on model structures and experimental conditions, and the effect of structral variation, chemistry, crystal size, and mixed layering on the XRD profiles of clays can be investigated by comparing calculated patterns with experimental ones. Simulated XRD paterns of various clays have been produced successfully by many investigators in order to interpret XRD patterns of various clay minerals (e. g., Perry and Hower, 1970 ; Nadeau et al., 1976 ; Nadeau et al., 1984a, 1984b ; Altaner and Bethke, 1988 ; Ahn, 1991). Calculated one-dimensional XRD patterns are especially useful for interpreting and analyzing complicated experimental XRD patterns.

Most quantitative analytical methods of mixtures of clay minerals are based on the concept that the abundance of a mineral in a mixture sample is related with the diffraction intensity of the same mineral in a standard specimen. Calibration of peak intensities by empirical methods gives very accurate values. However, the difficulty of finding an appropriate standard mineral whose structure and chemistry are identical to those of the same mineral in the sample prevent using empirical methods. The easy access to personal computers made it possible to calculate XRD patterns and intensities by modeling the structures of clays, and XRD pattern calculation method can be applied to quantitative analysis of samples consisting of several clay minerals. Reynolds (1985a) showed that good agreement was attainable between experimental and simulated profiles for kaolinite, illite, smectite, and mixed-layer illte/smectite.

This study intends to formulate a method for quantitative analysis of clay minerals in deep-seabed sediments, which commonly contain four types of clays minerals, namely smectite, illite, chlorite, and kaolinite (Hein, 1979 ; Jung et al., 1991). A computer calculation method was utilized not only to overcome the difficulty of finding appropriate standard minerals but also to take into account the chemical composition in quantitaive analysis of clay minerals.

XRD PATTERN CALCULATION PROGRAM

X-ray diffraction profiles of smectite, illite, chlorite, and kaolinite were calculated using the NEWMOD program written in True Basic for Macintosh computer (Reynolds, 1985b). The NEWMOD program is based on

the same basic theroy as the MOD-series programs (Reynolds and Hower, 1970; Reynolds, 1980), and it is strengthened by adding a recursive routine which computes the statistical matrices (Bethke and Reynolds, 1986). NEWMOD program package includes associated programs, PLOTTER, PLOTMOD, MIXER, and MIX, which are used to handle the calculated intensity data files.

The number of Al atoms per four tetrahedral sites of the model structures are 0, 0.5, 1.0, and 0 for dioctahedral smectite, illite, trioctahedral chlorite, and kaolinite. Such approximate values are satisfactory for the purpose of comparing caculated XRD patterns; the scattering power of Al and Si are not very different, and therefore slight difference of Al content does not result in significant changes in 00ℓ reflection intensities. Atomic scattering factors are calculated based on the method by Wright(1973).

The program assumes that crystals are oriented along the basal plane so only 00ℓ reflections are produced in the resulting XRD profiles. The basal spacings of 16.9, 9.98, 14.0, and 7.2Å were used for ethylene-glycolated smectites, illite, chlorite, and kaolinite. The NEWMOD program is originally made for the XRD pattern calculation of mixed-layer clays. Therefore, two identical clay components are assumed to be randomly interstratified(R=0) in 50 : 50 proportion in order to calculate patterns of monomineralic phases. Instrumental parameters and structural variables used in the calculations are in Table 1.

Table 1. Parameters of instrument and samples used in the XRD pattern calculations.

Wavelength of X-ray	1.5418Å
Divergence slit	1.0 degree
Goniometer radius	20 cm
Soller slit 1 (incident beam slit)	6.6 degrees
Soller slit 2 (diffracted beam slit)	2.0 degrees
sample length	3.0 cm
θ compensating slit	0
$\bar{\mu}$(mean sample absorption coefficient)	45 cm^2/g
σ^*(standard deviation of the orientation function)	12
Low N	7
High N	14

XRD PATTERN CALCULATION RESULTS

Effect of Chemistry on XRD Profiles of Clay Minerals

The 00ℓ intensities of clay minerals are strongly dependent on the total scattering power of the octahedral layers. XRD pattern profiles of clay minerals are strongly affected by the chemical changes such as the substitution of Fe in octahedral sites of clay minerals. XRD pattern calculation method can be used to evaluate the effect of the chemical substitution on the intensity of the 00ℓ reflections. The relationship between composition and 00ℓ reflection of clays is investigated by utilizing the XRD pattern calculation method.

Smectite : Calculated XRD paterns of dioctahedral and trioctahedral smectites (Ahn, 1991) showed that XRD patterns of ethylene-glycolated specimens are more useful than those of hydrated specimens in obtaining informations about the composition; ethylene-glycolated smectites show stronger intensities for the 002 and 003 reflections than hydrated smectites do. Intensities of 00ℓ reflections of smectite are strongly dependent on the chemistry of cations in the octahedral sheet. The intensity of the 002 reflection increases with increasing Fe in ethylene-glycolated smectites, but that of 003 reflection decreases with increasing Fe.

Chlorite : Various cations can incorporate in octahedral cation sites of chlorite, and both trioctahedral and dioctahedral chlorites are well known. Most chlorites are trioctahedral, and there is a continuous solid solution between the Mg and Fe species. XRD patterns of chlorite can be more complicated because

of the variable distribution of cations between the octahedral sites of the 2 : 1 layers and the hydroxide layers at the interlayers.

The effect of chemistry on XRD patterns is illustrated in Fig. 1. The intensities of 00ℓ reflections change drastically by the substitution of Fe for Mg in octahedral sites. Systematic changes in the 00ℓ intensities occur with increasing Fe in the octahedral sites. The 00ℓ reflections with $\ell = 2n+1$ become weaker with increased Fe substitution.

Illite : XRD pattern calculation of illite showed that the 002 reflections are strongly affected by the change of Fe content in the octahedral sites (Fig. 2). The 002 reflections are almost nonexistent when Fe content is 1.7 per formula unit. The peak intensity ratios of 003/001 also gradually decrease with increased Fe.

XRD Pattern Calculation of a Mixture

Calculated XRD patterns of various clay minerals (Figs. 1 and 2) showed that XRD profiles change considerably with the change of the chemistry. Quantitative analysis using XRD involves measurement of intensities of certain 00ℓ reflections. If the intensity of the peak is sensitive to the chemical changes, acquisition of standard minerals whose chemical composition is similar to the investigated specimen is required for accurate quantitative characterization.

Among the four minerals occurring in deep-seabed sediments, kaolinite may not cause serious problem in finding good standard samples. On the other hand, smectite, illite, and chlorite normally show wide range of solid solutions, and determination of chemistry of each phase in the investigated samples is necessary. However, these three phases in most of sediments cannot be separated or analyzed using electron microprobe because of their small crystal size and intimate occurrence with other phases at a very fine scale in sediments. The chemistry of each clay mineral can be inferred from the previously reported data which were obtained from similar geological environments.

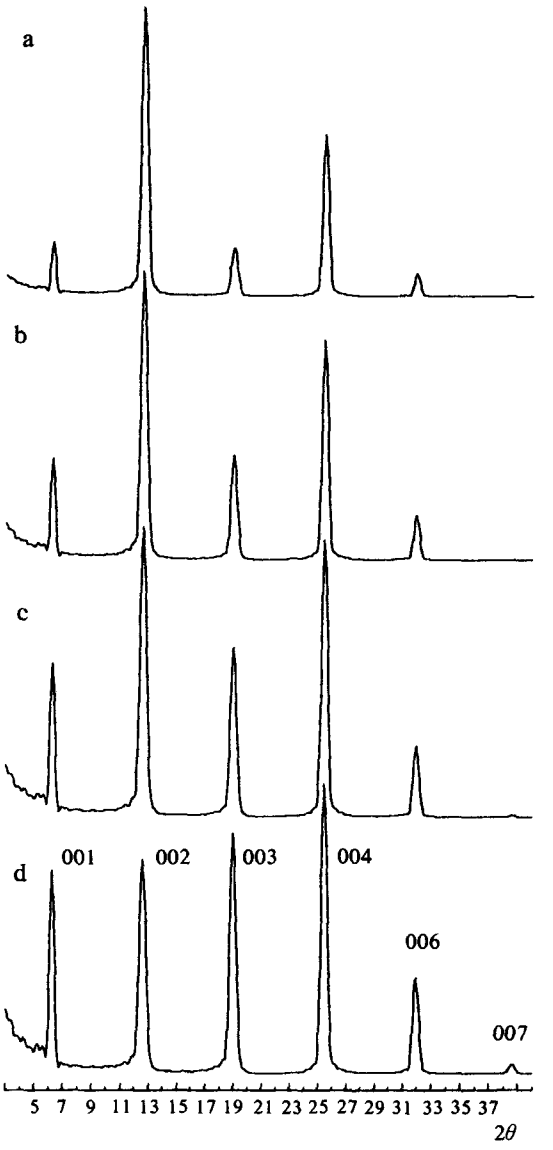

Fig. 1. Calculated XRD patterns (CuKα radiation) of trioctahedral chlorites having octahedral Fe of (a) 2.0, (b) 1.0, (c) 0.5, and (d) 0 per formula. N=7 to 14.

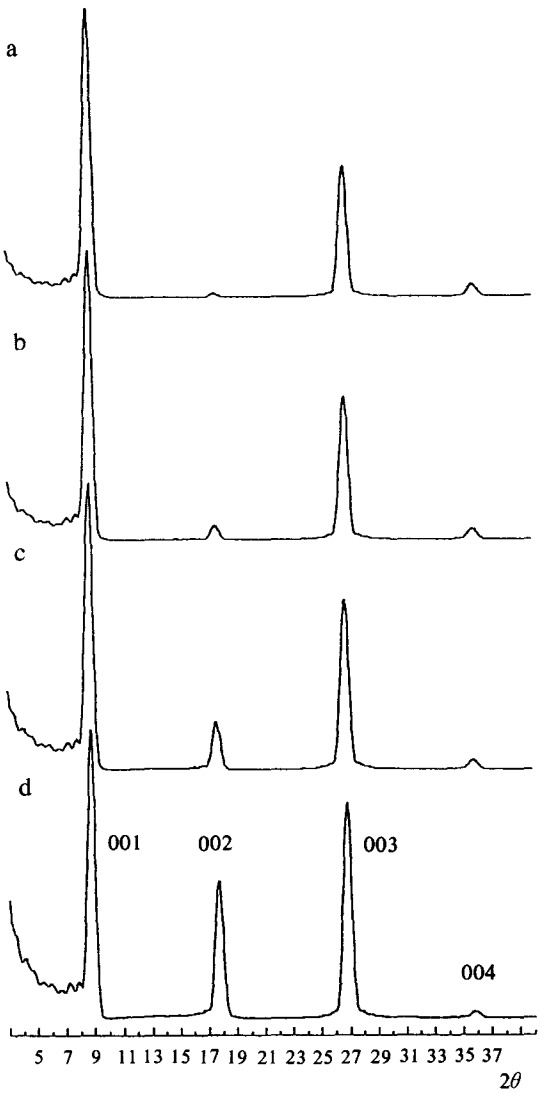

Fig. 2. Calculated XRD patrerns (CuKα radiation) of dioctahedral illites having octahedral Fe of (a) 1.7, (b) 1.2, (c) 0.5, and (d) 0 per formula. N= 7 to 14.

Chemical analysis data of smectites from DOMES (Deep Ocean Mining and Environmental Study) area indicate that the chemistry of smectites from deep-sea environments is intermediate between that of montmorillonte and that of nontronite (Hein et al., 1979). Hein et al. (1979) showed that smectites from deep-seabed are rich in Fe and Mg but they are dioctahedral. The chemistry of smectites from DOMES area was used in the calculation of smectite from deep-seabed environments. However, the amount of interlayer cations of smectite reported by Hein et al. (1979) is too high. The amount of interlayer cations in smectite ranges normally between 0.3 and 0.4 per formula (Weaver and Pollard, 1973), and cations in the interlayers are assumed to be 0.4 Na per formula in the model structure (Table 2, Fig. 3b).

The chemistry of chlorites from deep-seabed environments are not well known. Analytical electron microscopy (AEM) study of chlorite from Gulf Coast argillaceous sediments showed that chlorites crystallized in diagenetic environments are high in Fe compared to those from metamorphic environments. The composition of Fe-rich chlorite from Gulf Coast sediments was used in the XRD pattern calculation of deep-seabed chlorite (Table 2, Fig. 3d).

The Chemistry of illite apparently does not vary significantly depending on the geological environment (Środoń and Eberl, 1984). Illite is predominantly dioctahedral, and it commonly have slight substitution of Fe and Mg for Al in the octahedral sites. The composition of illite from Gulf Cost Sediments(Ahn and Peacor, 1986) was used in the

Table 2. d(001) and chemistry of model structures of clays used in the XRD pattern calculations.

Clay Minerals	d(001)	Interlayer	Octahedral Sheet	Reference
Smectite	16.9 Å	$Na_{0.4}$	$Fe_{0.6}Al_{1.4}$	Hein et al. (1979)
Illite	9.98Å	$K_{0.6}$	$Fe_{0.6}Al_{1.4}$	Ahn and Peacor(1986)
Chlorite	14.0 Å	$Fe_{1.55}Al_{1.45}$	$Fe_{1.55}Al_{1.45}$	Ahn and Peacor(1985)
Kaolinite	7.2 Å	———	$Al_{2.0}$	Ideal composition

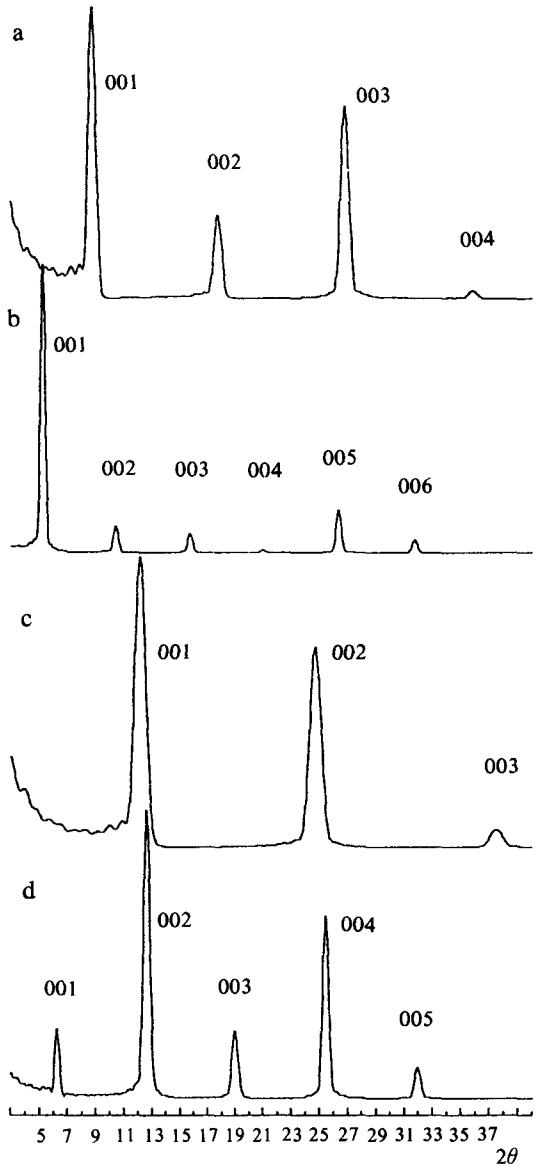

Fig. 3. Calculated XRD patterns (Cukα radiation) of (a) illite, (b) smectite, (c) kaolinite, and (d) chlorite. The composition and interplanar spacing of the minerals are presented in Table 2. N=7 to 14.

XRD pattern simulation of deep-seabed clays (Table 2, Fig. 3a).

Unlike other clay minerals kaolinite is known minor to have fairly uniform chemistry. Although the presence of minor Fe in some kaolinite was reported (Malden and Meadbs, 1967 ; Jepson and Rowse, 1975), the chemistry of most kaolinite does not deviate much from the ideal stoichiometric composition, $Al_2Si_2O_5(OH)_4$. Kaolinite is not known for significant chemical substitution. Fig. 3c shows XRD pattern of kaolinite having the ideal composition.

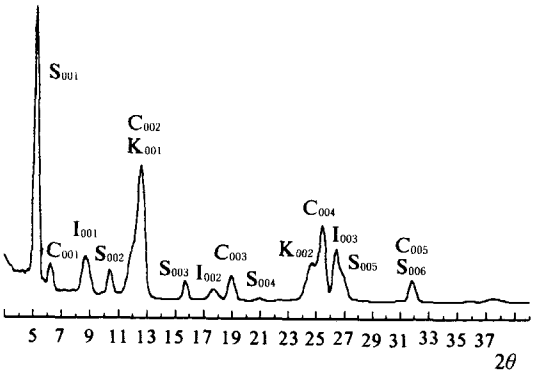

Fig 4. Calculated XRD pattern (CuKα radiation) fo mixtures of one formula unit of illite, smectite, kaolinite, and chlorite, whose structural and chemical parameters are identical to those of the calculated patterns in Fig. 3. N=7 to 14

Fig. 4 shows the calculated XRD pattern of mixtures of smectite, illite, chlorite, and kaolinite, each of which is assumed to be present in one unit formula. XRD pattern calculation by Ahn (1991) showed that the 002 and 003 reflections of smectite and illite are strongly dependent on the scattering power of octahedral cations. Therefore, 001 reflections of both smectite and illite wee used as reference peaks for intensity measurements. The 002 reflection of chlorite and 001 reflection of kaolinite overlap almost completely, but the 004 reflection of chlorite and the 002 reflection of kaolinite are distinguishable. The 004 reflection of chlorite and the 004 reflection of kaolinite were chosen as reference reflections in intensity measurement.

DISCUSSION

Quantitative Analysis Using Calculated X-ray Patterns

The intensity of XRD diffraction by a component A in a mixture is given by the equation (Klug and Alexander, 1974),

$$I_a = K_a \omega_a / \bar{\mu}, \quad (1)$$

Where K_a is a constant of a specific reflection which is dependent on the crystal structure A and experimental conditions ; ω_a is the weight fraction of phase A ; $\bar{\mu}$ is the mass attenuation coefficient of the mixture. If all the phases in a mixture are identified as A, B, C, ···, R, the intensity of a specific reflection from each phase can be given by the equation,

$$I_b = K_b \omega_b / \bar{\mu},$$
$$I_c = K_c \omega_c / \bar{\mu}, \cdots$$
$$I_r = K_r \omega_r / \bar{\mu}.$$

If same amounts of A, B, C,···, R are assumed to be present in a mixture, then,

$$\omega^o_a = \omega^o_b = \omega^o_c = \cdots = \omega^o_r$$

The intensity contributed by each phase in the mixture can be written as

$$I^o_a = K_a \omega^o_a / \bar{\mu}^o$$
$$I^o_b = K_b \omega^o_b / \bar{\mu}^o, \cdots,$$
$$I^o_r = K_r \omega^o_r / \bar{\mu}^o$$

If the component R is set as a reference phase, the weight fraction and the mass attenuation coefficient of the mixture can be eliminated by dividing the intenstiy I_i by the intensity I_r of the reference phase :

$$\frac{I^o_a}{I^o_r} = \frac{K_a}{K_r},$$
$$\frac{I^o_b}{I^o_r} = \frac{K_b}{K_r}, \cdots,$$
$$\frac{I^o_c}{I^o_r} = \frac{K_c}{K_r}.$$

The intensity ratio between the reference phase R and the other phase is a constant, which is characteristic of each component. Such value can be utilized to correct an observed intensity value to a new intensity value which is linearly proportional to the weight fraction of the reference phase. Such intensity correction factor is known as mineral intensity factor (MIF) (Moore and Reynolds, 1989), and MIF value for each phase can be obtained from the following equations ;

$$MIF_a = \frac{I^o_a}{I^o_r},$$
$$MIF_b = \frac{I^o_b}{I^o_r}, \cdots, \text{etc.} \quad (2)$$

The MIF value is fixed for a specific reflection of a mineral having a specific composition. If mixture specimen containing equal amounts of phases A, B, C,···, and a reference mineral R is prepared, we can measure peak intensities, I^o_a, I^o_b, ···, I^o_r . Values for MIF_a, MIF_b, ···, can be determined from the relationship of the equation (2).

The most commonly used method for quantitative analysis of clay minerals involves peak intensity ratios, and this method gives the relative proportions of the clay minerals normalized to 100 wt%. If all the phases are normalized to a unity, the following equation holds :

$$\omega_a + \omega_b + \omega_c + \cdots = 1. \quad (3)$$

Quantitative estimation is possible without adding any standard to the unknown specimen, if the equation (3) holds. The MIF values can be used for calibration of the diffraction intensity. The weight of each phase can be obtained using the peak intensities calibrated by MIF ; wt% of a phase I equals $[(I_i/MIF_i)/\sum_n(I_i/MIF_i)] \times 100\%$. The method results in the relative proportions of the phases normalized to 100%.

The MIF method is similar to the internal standard method where all phases are

analyzed and it is assumed that the sum of all of the mineral fractions equals 1. In the MIF method, one of the phases to be analyzed is selected arbitrarily as a reference phase. Therefore, there is no need to add internal standard to the mixture.

The MIF values can be obtained much more easily from calcuated patterns than can be determined from experiments. In order to determine MIF values from experiment it is necessary to prepare a large number of standard minerals having specific compositions. However, some of standard minerals may be very difficult or almost impossible to obtain. On the other hand, calculation methods eliminate the necessity of standard minerals, because peak intensities of minerals having specific composition can be calculated.

Quantitative Analysis of Deep-seabed Clays

The 001 reflections of smectite and illite, the 004 reflection of chlorite, and the 002 reflection of kaolinite were selected for the peak intensity measurement of the calculated XRD patterns. The 004 reflection of chlorite and 002 reflection of kaolinite partially overlap, and the 001 reflection of smectite occurs at low-angle region where the Lorentz-polarization factor is significantly high. Therefore, illite was selected as a reference phase in calculating MIFs. The intensity of each reflection used for the MIF value determination should be calibrated on the basis of the same molecular weight in order to obtain MIF values, because each peak intensity of the simulated pattern was calculated based on one formula unit for each mineral. When a calibrated intensity of a phase I is I′, $MIF_i = \frac{I'_i}{I'_r}$. MIFs of clay minerals constituting deep-seabed sediments were obtained by using the intensity of the 001 illite reflection (Table 3).

The equation (1) shows that the intensity of a phase in the mixture is linearly proportional to its weight fraction, and the intensity is related to the average mass absorption coefficient of the mixture. Therefore, it is not necessary to calibrate for the difference of the mass absorption coefficients between the constituting phases. The mass absorption coefficent of ethylene-glycolated smectite, 45cm^2/g, was also used for the calculation of XRD profiles of illite, chlorite, and kaolinite(Table 4).

Table 4. Calculation of mass absorption coefficient of ethylene-glycolated smectite.

Atoms	[1]No. of atoms	Mo. wt.	[2]Mass absorption coeffi. (cm^2g^{-1})	Mass absorption coeffi. (cm^2g^{-1})
Na	0.4	12	30.30	0.72
Fe	0.6	33.5	304.4	20.70
Al	1.4	37.8	50.23	3.82
Si	4.0	112	65.32	14.76
O	15.4	246.4	11.03	5.49
H	12.2	12.2	0.39	0.01
C	3.4	40.8	4.22	0.35
	tot. mol, wt.=494.7		tot. abs. coeff.=45.85	

1. The number of atoms is based on one formula unit.
2. The mass absorption coefficients are from the International Tables for X-ray Crystallography.

Table. 3. Measured intensity data and calculated mineral intensity factors (MIF) resulting from simulated XRD patterns of deep-seabed clays.

Clay Mineral	Reflection	Measured intensity(cps)	Molecular weight	Corrected intensity	Calculatede MIF
Smectite	001	2330	495	1845	4.1
Illite	001	452	392	452	1.0
Chlorite	004	607	659	361	0.8
Kaolinite	002	920	258	1398	3.1

The quantitative method described in the present paper has several important advantages over the other quantitative analytical methods such as internal or external standard methods. The XRD calculation method does not require standard samples for calibration, because specific reflections of specific phases can be simulated using model structure. Therefore, XRD peak intensities of specific reflection that can be strongly dependent on the composition can be obtained more accurately than can be determined by using inappropriate standard specimens. This analytical method provides routine, rapid quantitative analysis, provided that XRD patterns are carefully calculated.

Same MIFs can be used only for samples from similar geological environments. For samples from different geological environments, new MIFs should be determined to conduct accurate quantitative analysis, because minerals from other environments may have significantly different mineral chemistry and structure.

CONCLUSIONS

Quantitative analysis of clay minerals in the deep-seabed sediments can be conducted routinely and rapidly by applying XRD pattern calculation methods. MIF values can be calculated from simulated patterns of specific minerals whose structure and chemistry can be inferred from their geological environments.

The 001 reflections of smectite and illite, the 004 reflection of chlorite, and the 002 reflection of kaolinite from the calculated XRD patterns were selected for the peak intensity measurement. The peak intensities of calculated XRD patterns were corrected to the identical molecular weight for each phase to obtain the MIF. Normalized weight fraction of each phase can be obtained using the peak intensities calibrated by MIF values ; wt% of a phase I equals $[(I_i/MIF_i)/\sum_n (I_i/MIF_i)]\times 100$ %. This calculation method is based on the concept that weight fraction of each phase is assumed to be linearly proportional to the corrected intensity for each phase. The resulting values represent the relative amount of each clay minerals normalized to 100 wt%.

The XRD calculation method does not require standard samples for peak intensity calibration. Therefore, this method is very useful for quantitative analysis of samples for which appropriate standard sepcimens are very difficult or impossible to obtain. Furthermore, this quantitative method can result in routine analysis for a large number of samples occurring in similar geological environments.

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