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SIMULATION METHOD FOR X-RAY QUANTITATIVE ANALYSIS OF CLAY SAMPLES

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Abstract. Complete diffractograms of theoretical mixtures of kaolinite, illite, chlorite and quartz were calculated by use of the simulation program of Weiss and Krajíček (1979). Relations between the mineral composition, chemical composition and X-ray intensities have been studied, and the multiplication factors for the pairs of reflections have been found. Calculated X-ray relative intensities were plotted against the content of clay components in the theoretical mixtures. These plots may be used directly for X-ray quantitative analyses of samples composed of similar minerals (kaolinite, illite, chlorite and quartz).

INTRODUCTION

In clay studies or in petrological studies aimed at geological correlation of sediments in lateral or vertical profiles, it is very desirable to have quantitative data on the distribution of clay minerals.

For the last thirty years X-ray diffraction has become the most powerful tool for mineral identifications and quantitative determinations. Many papers and handbooks (e.g. Zevin and Zevialova 1974) have been published, especially since the work of Alexander and Klug (1948). Nevertheless the current knowledge on quantification of clay minerals is poor and a wholly reliable method of quantitative determination of clay components in rocks is still lacking (see chapter 7 in the book ed. by Brindley and Brown, 1980).

Schoen *et al.* (1973) showed that all simple techniques not based on the separation of individual standard clay minerals or on the separation of clay mineral concentrates followed by calculation of very complicated equations (Salyn, Drits 1973) must include at least approximate knowledge of two important factors – structure factor and Lorentz-polarisation constant for each Bragg angle. These two factors may be represented by multiplication factor used to relate the intensity of two peaks of a determined pair of minerals. Other factors shown by various

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versions of the general formula describing the intensity of diffractions (compare for example Azaroff, Buerger 1958, p. 201 and Chessin 1963, p. 529) are also important, but may usually be neglected if the same technique and X-ray equipment are applied.

In clay mineral determinations some difficulties arise because of the overlapping of the reflections suitable for analysis from the point of view of the peak position and intensity. To avoid these difficulties, clay samples may be treated in one or other way well known to clay mineralogists. For example, Böhman (1979) routinely uses glycolation and hydrazine saturation of oriented aggregates. From glycolated samples the intensities areas of smectite (17 Å) and illite (10 Å) peaks and the sum of kaolinite and chlorite peaks (7 Å) can be measured. From samples saturated with hydrazine, 7 Å peak due to the nonexpanded phase (chlorite) can be obtained. Smectite, illite, kaolinite and chlorite peaks are summed and their partitions are taken directly, to visualize clay mineral variations*, neglecting other coefficients influencing X-ray intensities. Various investigators (Schoen *et al.* 1973) have used a multiplication factor as high as seven and as low as two for an illite – glycolated smectite pair of reflections and factors ranging from four to one for kaolinite–illite pair of reflections, based on intuitive conclusions regarding the composition or crystallinity of their samples. The multiplication factor for chlorite – other mineral pair could not be predicted because of the large variation in the chemical composition of chlorites.

Other uncontrolled factors also may influence X-ray intensities from raw and treated aggregates. They are: mineral segregation due to shape and size of clay particles, mixed-layering incorporated in most illites and other mixed-layer phases frequently present in clays, unknown rate of intercalation of clay by organic solvent (especially of kaolinite by hydrazine) during X-ray measurement, other, like coefficients depending on chemical composition, crystalline perfection and particle size.

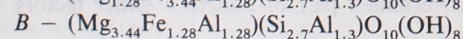
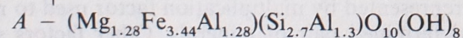
Many sources of error have been satisfactorily recognized in the literature and do not need to be studied again.

The aim of this paper is to show the changes in diffraction intensities with composition of mineral mixtures and with chemical composition of the components, as well as to indicate a promising quantitative approach to X-ray phase analyses based on simulation.

METHOD

A simulation program for calculating the full line profiles of the X-ray diffraction pattern, developed by Weiss and Krajiček (1979), has been used to simulate theoretical mixtures of mineral in a desired range of °2θ. The following structural and chemical data have been used: quartz according to Smith and Alexander (1963), kaolinite according to Drits and Kashaev (1960); dioctahedral illite – one

layer polytype $\begin{vmatrix} 5.0 \\ 1.0 \end{vmatrix}$ theoretically derived by Dornberger-Schiff *et al.* (1980) of the formula $K_{1.5}(Al_{3.8}Fe_{0.2})(Si_{6.5}Al_{1.5})O_{20}(OH)_4$, trioctahedral chlorite – one layer polytype $\begin{vmatrix} u & u & u \\ e & o & e \\ 3 \end{vmatrix}$ theoretically derived by Weiss *et al.* (1981) of the formulae:



* Procedure used by Sedimentary Petrology Group IGCP Project 124.

To assure the unique influence of iron on peak intensities the same orthorhombic unit cell parameters: $a = 5.390$ Å, $b = 9.366$ Å, $c = 14.166$ Å were adopted for chlorites A and B.

In order to make the data more realistic, corresponding to those obtained by X-ray diffraction from hand pressed aggregates, an experimentally determined correction for partly preferred orientation has been made. The calculated intensities for kaolinite, illite and chlorites were corrected for preferred orientation using a computer program (see Weiss and Krajiček 1979). The application of this procedure is very important for quantitative analysis.

Smectite, which largely occurs in sedimentary rocks, could not be taken into consideration because single crystal data are not available and polytypes are not derived. Quartz was used as a dilutant to produce realistic chemical and mineralogical compositions comparable with clay and clay fractions, which are very rarely free of quartz in particle separation.

RESULTS

Computer calculations were tabulated (e.g. Table 1) and plotted in computed X-ray tracings of mixtures made of quartz, kaolinite, illite and chlorite (Figs 1 and 2). The data supplied the choice of intensities (Table 2) used for further considerations.

The proportions of minerals used for simulation (a in Table 3) were compared with those obtained from the calculated intensities of 100 quartz, 001 kaolinite, 001 illite, 002 chlorite, expressed as per cent of the sum of the reflections (b in Table 3), and similarly from 001 kaolinite, 001 illite and 002 chlorite (c in Table 3).

The data collected in Table 3 show big discrepancies between the intensities of reflections expressed in per cent of the sum of intensity and per cent of clay mineral content.

DISCUSSION AND CONCLUSIONS

The biggest discrepancies are attributed to those mixtures which are characterized by the greatest variations in multiplication factor (structure factor and Lorentz-polarisation factor). In our case high (F)² and L.p. values are common for chlorite, low for kaolinite and illite. It is easily possible then to overestimate the chlorite content twice (2c Table 3) and four times (1c Table 3), depending on the content ratio of chlorite to other components. Illite may be heavily underestimated (2c Table 3), but kaolinite may be overestimated (1c Table 3) or underestimated (3c Table 3). Also quartz does not necessarily give its real (10%) content value (b Table 3). The correct results may be, however, obtained by application of multiplication factors, which from our data for mixtures 2 and 6 are easily found from relative intensities (Table 2) for the two groups of mixtures differing in the chemical composition of chlorite A and B (Table 4).

It may be reminded that Brown (1955) was the first who studied the dependence of the structure factor for 001 reflections of chlorite-type structure for a unit cell on the (Mg, Fe) content of the octahedral sheets. He has shown a similar relationship for mica interlayer, octahedral composition and F_{001} values.

It should be noticed that a lower iron content in chlorite B than in chlorite A is reflected in lesser discrepancies between a and b or c values (mixtures 5–8,

Table 3) and it illustrates the importance of chemical composition (Fe content). The Fe to Mg content ratio in chlorite affects the intensity ratio of basal reflections (Table 5) and it may be used as a criterion for evaluation of the intuitive or real multiplication factor used frequently in quantification of clays.

The computer data may serve to establish a relation between the content of

Table 1

Mixture of quartz (10%) + kaolinite (30%) + illite (30%) + chlorite-A (30%)

<i>hkl</i>	<i>d</i>	<i>I</i>	<i>D(P)</i>	<i>2TH(P)</i>	<i>I(P)</i>	<i>IABS(P)</i>	<i>IREL(P)</i>
001	14.167	47	14.167	6.238	36	2.74	35
001	10.080	19	10.073	8.778	15	1.12	14
001	7.131	45					
002	7.083	100	7.093	12.478	100	7.78	100
002	5.040	7	5.040	17.598	5	0.41	5
003	4.722	15	4.721	18.798	11	0.89	11
020	4.668	1					
020	4.525	1					
110	4.475	2					
020	4.463	1					
111	4.433	2	4.440	19.998	4	0.30	4
111	4.433	1					
110	4.361	3	4.362	20.358	4	0.26	3
100	4.255	13	4.255	20.878	10	0.78	10
111	4.158	3	4.160	21.358	4	0.28	4
111	4.112	2	4.122	21.558	3	0.21	3
022	3.898	2	3.890	22.858	4	0.33	4
112	3.898	1					
111	3.883	2					
021	3.839	3	3.841	23.158	3	0.25	3
021	3.729	1	3.727	23.878	2	0.17	2
112	3.623	3					
002	3.566	29					
004	3.541	52	3.543	25.138	46	3.75	48
111	3.369	2					
022	3.367	8					
033	3.360	18					
101	3.343	19	3.344	26.658	55	4.49	58
011	3.343	44					
023	3.320	1					
113	3.320	2					
112	3.136	1					
112	3.125	6	3.126	28.556	5	0.40	5
112	3.086	1					
113	2.901	7	2.901	30.816	5	0.46	6
005	2.833	6	2.833	31.576	5	0.46	6
114	2.821	1					
022	2.743	2	2.742	32.656	2	0.15	2
023	2.698	2	2.697	33.216	2	0.22	3
130	2.695	1					
130	2.603	1	2.603	34.456	2	0.15	2
201	2.603	1					
200	2.574	1	2.574	34.856	2	0.21	3
131	2.574	1					
131	2.524	1					
112	2.520	1					
004	2.520	1					
132	2.519	10	2.519	35.634	13	1.17	15
202	2.519	5					
113	2.514	2					

minerals in mixtures and the relative intensity of the reflections. Such a graph has been drawn (Fig. 3) for 001 reflections because they are the strongest of all and, with an exception of 001K and 002Ch, do not overlap with each other and with *hkl* reflections. Each line has been based on four points representing the contents of 5, 30, 80, 100 per cent of mineral in mixture and it seems to reflect well the relationship between reflections relative intensity and mineral content.

The curves from figure 3 may be used directly for X-ray quantitative deter-

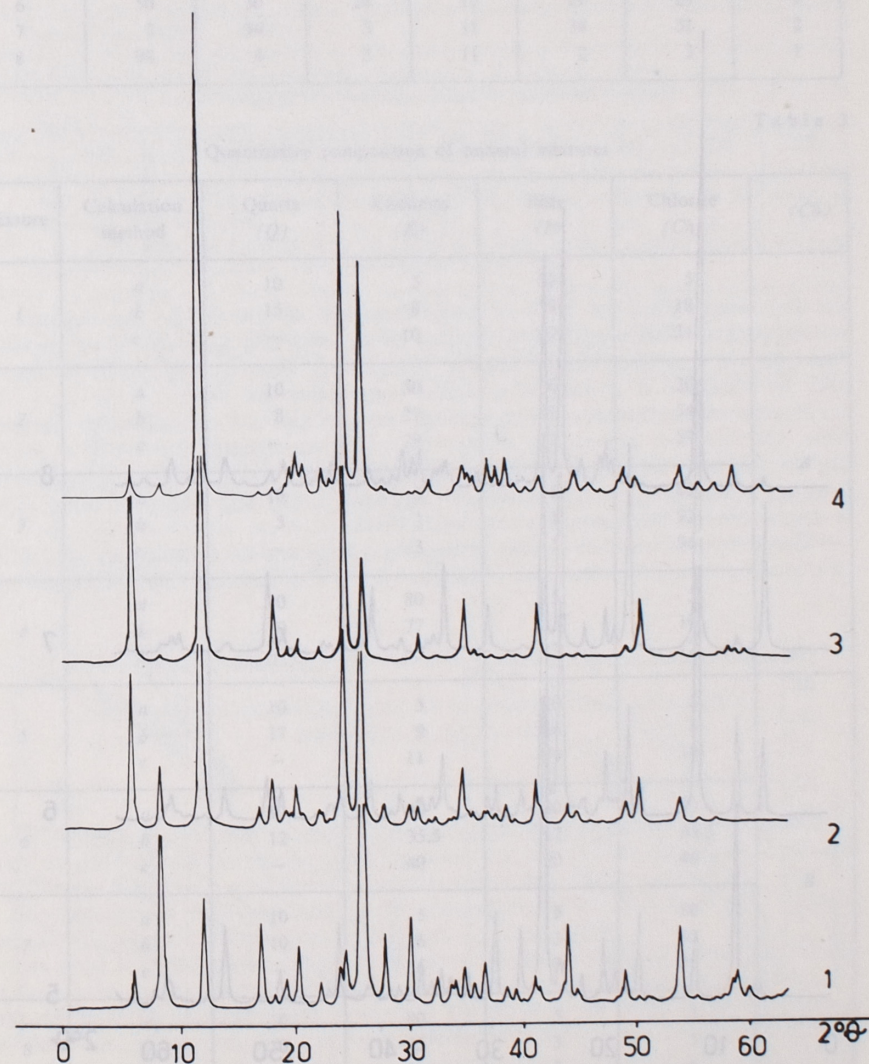


Fig. 1. Computed diffractograms of mineral mixtures 1-4 (see Table 3)

mination of the three studied clay minerals forming mixtures in which quartz may also be present, provided that the investigator knows the chemical composition of chlorite (Fe content), for example, from X-ray relative intensities (Table 5).

The ideology of the plots in figure 3 enable one to use it directly when integral intensities measured from X-ray tracings are related to the strongest reflection in the tracing. It may be $002Ch+001K$ for the sum $Ch+K \geq 60\%$ (Fig. 3) or $003I+101Q$ for the other cases. In mixtures of $K+I+Ch+Q$ only one of the two reflections may be the strongest, so figure 3 may be applied

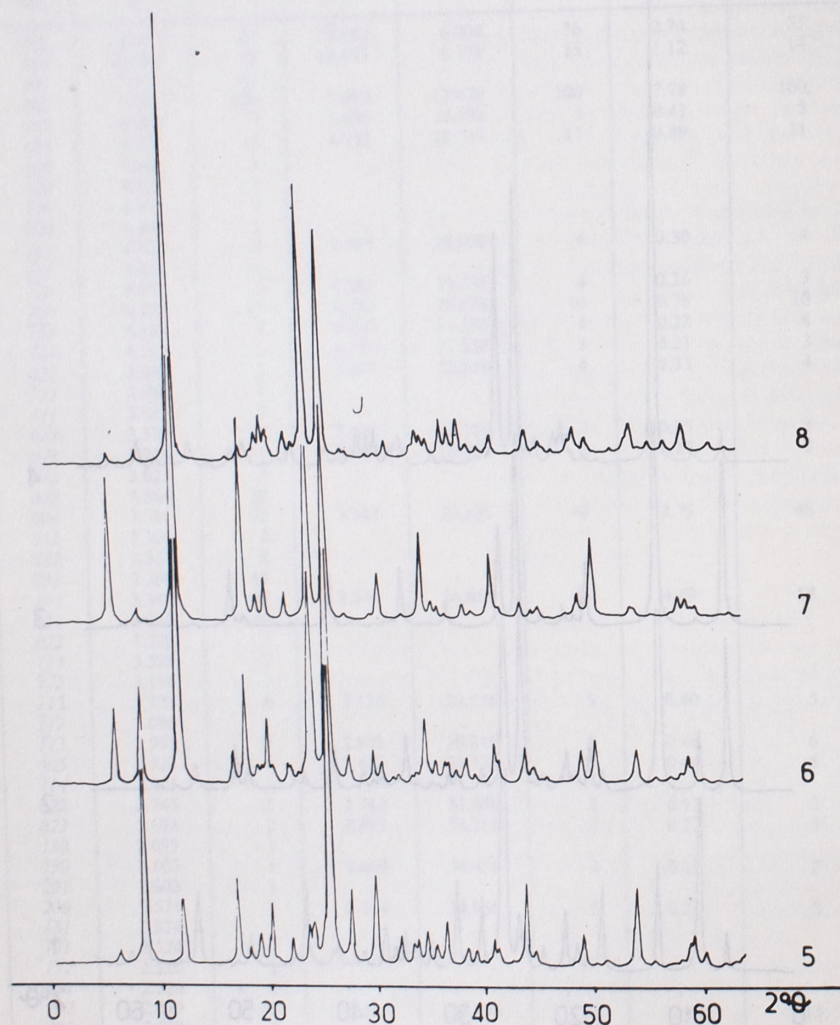


Fig. 2. Computed diffractograms of mineral mixtures 5-8 (see Table 3)

Table 2

Relative intensities from computer charts

Mixture	001K	002Ch	001I	Q	001Ch	003Ch	002I
1	7	15	50	13	8	3	17
2	33	67	14	10	35	11	5
3	3	97	1	5	46	15	—
4	88	12	3	11	6	2	1
5	7	6	50	13	3	4	17
6	50	50	24	17	19	29	9
7	7	94	3	11	34	51	2
8	94	6	3	11	2	3	1

Table 3

Quantitative composition of mineral mixtures

Mixture	Calculation method	Quartz (Q)	Kaolinite (K)	Illite (I)	Chlorite (Ch)	(Ch)
1	a	10	5	80	5	
	b	15	8	59	18	
	c	—	10	69	21	
2	a	10	30	30	30	A
	b	8	27	11	54	
	c	—	29	12	59	
3	a	10	5	5	80	
	b	5	3	1	92	
	c	—	3	1	96	
4	a	10	80	5	5	
	b	10	77	3	10	
	c	—	85	3	12	
5	a	10	5	80	5	
	b	17	9	66	8	
	c	—	11	79	10	
6	a	10	30	30	30	B
	b	12	35.5	17	35.5	
	c	—	40	20	40	
7	a	10	5	5	80	
	b	10	6	3	82	
	c	—	6	3	91	
8	a	10	80	5	5	
	b	10	82	3	5	
	c	—	91	3	6	

Explanation: a — used for simulation, b — from $100Q+001K+002Ch+001I$, c — from $001K+002Ch+001I$

Table 4

Multiplication factors for pairs of the studied clay minerals

Mixtures	Multiplication factor		
	001 Kaolinite 001 Illite	002 Chlorite 001 Kaolinite	002 Chlorite 001 Illite
1-4 (Ch_A)	2.4	2.0	4.8
5-8 (Ch_B)	2.1	1.0	2.1

Table 5

Relative intensities of basal reflections of chlorites A and B

	001	002	003	004	005	006	007	008	009
A	47	100	15	52	6	1	1	—	1
B	36	100	52	72	10	—	4	—	1

for any composition of $K+I+Ch+Q$ (roughly about 10%). As regards the overlapping of 002Ch and 001K, it may be advised that Ch content be measured from 001Ch and also 003Ch relative intensities. 002Ch and 001K intensities may be obtained if hydrazine saturated aggregates are used.

It also seems that there exist limited possibilities of determining kaolinite, illite, chlorite and smectite in sediments containing smectite, if it is not a prevailing component. Smectite and expanding layers of smectite-illite collapse under heating, which makes their structure „illite-like”, but still the plot from Fig. 3 is applicable in those cases when $003I > 001I$.

The proposed method seems promising as the use of a computer allows one to experiment rapidly with such important factors as structure and chemical com-

position of any component and with some correction coefficients, first of all particle orientation. Further efforts will be made to improve the simulation method and apply it for quantification of clays most wide-spread in nature.

The present research has been made within the project MR 1.16.

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SYMULACYJNA METODA W ILOŚCIOWEJ ANALIZIE PRÓBEK ILASTYCH

Streszczenie

W badaniach mineralogicznych lub petrograficznych, zwłaszcza ukierunkowanych na geologiczną korelację profili pionowych lub poziomych, duże znaczenie mają dane ilościowe o rozmieszczeniu minerałów ilastych w osadach.

Rentgenowska ilościowa analiza fazowa, mimo pokładanych w niej wielkich nadziei, nie spełniła dotychczas oczekiwań.

Spśród najprostszych technik stosunkowo dobre wyniki przynosi stosowanie intuicyjnych mnożników wyrównujących różnicowanie intensywności refleksów spowodowane przez czynniki niezależne od zawartości minerałów. Niektórzy geolodzy stosują jednak zbyt uproszczone metody oparte na pomiarach jedynie intensywności wybranych refleksów (np. do korelacji osadów trzeciorzędu Europy — IGCP, projekt 124).

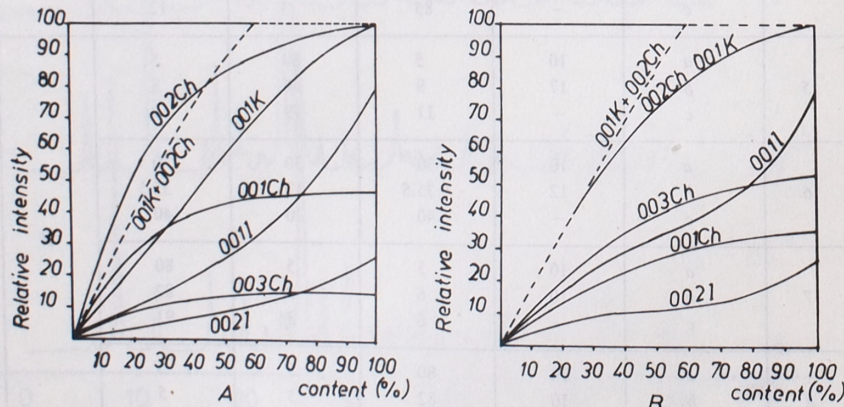
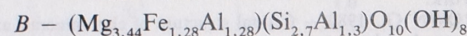
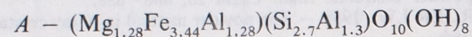


Fig. 3. Relationship between clay mineral contents and relative intensities of basal reflections (001) of chlorite (Ch), kaolinite (K), illite (I) for mixtures 1-4 (A), 5-8 (B)

Zastosowanie metody symulacji komputerowej do analizy ilościowej pozwoliło ocenić błędy wynikające ze wspomnianego uproszczenia. W tym celu obliczono dyfraktogramy: kwarcu według danych strukturalnych Smitha i Alexandra (1963), kaolinitu według danych Drica i Kaszajewa (1960), dioktaedrycznego illitu o wzorze krystalochemicznym $K_{1,5}(Al_{3,8}Fe_{0,2})(Si_{6,5}Al_{1,5})O_{20}(OH)_4$ i strukturze teoretycznego jedno-pakietowego politypu (Donberger-Schiff i in. 1980) oraz trioktaedrycznego chlorytu teoretycznie wyprowadzonego przez Weissa i innych (1981) przy uwzględnieniu dwóch wariantów składu chemicznego (Mg, Fe):



Następnie obliczono dyfraktogramy mieszanin mineralnych (fig. 1 i 2) uwzględniając czynnik orientacji dla preparatów prasowanych pod naciskiem ręki. Intensywności względne obliczone z dyfraktogramów (tab. 2) posłużyły do porównania proporcji minerałów wziętych do analizy z obliczonymi bez uwzględniania korekcji intensywności (tab. 3) i do obliczenia współczynników korekcji intensywności refleksów podstawowych dla par kaolinit—illit, chloryt—kaolinit i chloryt—illit (tab. 4).

Intensywności względne (tab. 2) wykorzystano również do przedstawienia pierwszej wersji prostej metody ilościowej (fig. 3) oznaczania kaolinitu, chlorytu i illitu w osadach zawierających kwarc (około 10%). Warunkiem możliwości bezpośredniego stosowania wykresów przedstawionych na figurze 3 jest skład chemiczny i struktura minerałów nie odbiegająca od danych teoretycznych wziętych do symulacji komputerowej.

Obliczenia komputerowe pozwalają na szybkie eksperymentowanie z wieloma czynnikami decydującymi o intensywności refleksów rentgenowskich. Autorzy mają nadzieję, że uda się im opracować ulepszoną wersję metody, która znajdzie szerokie zastosowanie do ilościowej analizy fazowej najczęściej spotykanych osadów ilastych.

OBJAŚNIENIA FIGUR

Fig. 1. Obliczone dyfraktogramy mineralnych mieszanin 1—4 (tab. 3)

Fig. 2. Obliczone dyfraktogramy mineralnych mieszanin 5—8 (tab. 3)

Fig. 3. Zależność pomiędzy zawartościami minerałów ilastych i względnymi intensywnościami refleksów podstawowych 001 chlorytu (Ch), kaolinitu (K), illitu (I), dla mieszanin 1—4 (A), 5—8 (B)

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МЕТОД МОДЕЛИРОВАНИЯ В КОЛИЧЕСТВЕННОМ АНАЛИЗЕ ГЛИНИСТЫХ ПОРОД

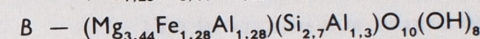
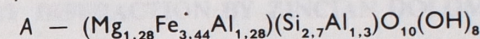
Резюме

В минералогических или петрографических исследованиях, в особенности предусматривающих геологическую корреляцию отложений, важное значение имеют количественные данные, касающиеся распределения глинистых минералов в осадке.

Рентгеновский фазовый количественный анализ пока-что не оправдал ожидаемых эффектов.

Из числа простых примеров сравнительно надежные результаты дает применение интуитивных множителей, выравнивающих дифференцированность интенсивности рефлексов, обусловленную не зависящими от содержания минералов факторами. Однако, некоторыми геологами применяются слишком упрощенные методы, основывающиеся лишь на замерах интенсивности избранных рефлексов (например, при корреляции третичных отложений Европы в рамках проекта I24 МПГК).

Применение метода математического моделирования на ЭВМ для целей количественного анализа позволило определить погрешности, возникающие при упомянутом упрощении. С этой целью были вычислены диффрактограммы кварца, по структурным данным Смита и Александра (1963), каолинита, по данным Дрица и Кашаева (1960), диоктаэдрического иллита с кристаллохимической формулой $K_{1,5}(Al_{3,8}Fe_{0,2})(Si_{6,5}Al_{1,5})O_{20}(OH)_4$ и структурой теоретического однопакетного политипа (Дорнбергер-Шифф и др. 1980) и триоктаэдрического хлорита, вычисленного теоретически Вайссом и др. (1981), с учетом двух вариантов химического состава (Mg, Fe):



Затем были вычислены диффрактограммы минеральных смесей (фиг. 1 и 2) с учетом фактора ориентировки в препаратах, прессованных ручным нажимом. Относительные интенсивности, вычисленные по диффрактограммам (табл. 2), послужили при сравнении пропорций минералов, взятых для анализа, с вычисленными без учета поправки интенсивности (табл. 3), и при вычислении коэффициентов поправки интенсивности основных рефлексов пар каолинит—иллит, хлорит—каолинит и хлорит—иллит (табл. 4).

Относительные интенсивности (табл. 2) использовались также при разработке первого варианта простого количественного метода (фиг. 3) определения каолинита, хлорита и иллита в отложениях, содержащих кварц (около 10%). Для непосредственного применения графиков, представленных на фигуре 3, должно быть соблюдено условие, чтобы химический состав и структура минералов не отличались от теоретических данных, принятых при моделировании на ЭВМ.

Вычисления с помощью ЭВМ позволяют производить быстрые эксперименты со многими факторами, влияющими на интенсивность рентгеновских рефлексов. Авторы выражают надежду, что им удастся разработать усовершенствованный метод, который получить широкое применение в количественном фазовом анализе наиболее распространенных глинистых минералов.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Вычисленные диффрактограммы минеральных смесей 1—4 (табл. 3)

Фиг. 2. Вычисленные диффрактограммы минеральных смесей 5—8 (табл. 3)

Фиг. 3. Зависимость между содержанием глинистых минералов и относительными интенсивностями основных рефлексов 001 хлорита (Ch), каолинита (K), иллита (I) в смесях 1—4 (A) и 5—8 (B)