Clays and Clay Minerals, Vol. 48, No. 1, 57–62, 2000.

PHASE ANALYSIS OF CLAYS USING AN EXPERT SYSTEM AND CALCULATION PROGRAMS FOR X-RAY DIFFRACTION BY TWO- AND THREE-COMPONENT MIXED-LAYER MINERALS

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Abstract—X-ray phase analysis of clays is difficult because these materials generally consist of a mixture of different phases, *i.e.,* mixed-layer minerals, individual clay minerals (non mixed-layer), and associated minerals, such as calcite and quartz. The analysis requires knowledge that presently is incorporated in a computer-based expert system. This expert system is capable of a) identification of associated minerals; b) identification of individual clay minerals; c) identification of the nature of the mixed-layer minerals; d) approximate structural characterization of the mixed-layer minerals; and e) precise structural determination of the mixed-layer minerals by comparison of experimental X-ray diffraction (XRD) patterns with calculated patterns for different models. Accuracy of the conclusions drawn by the expert system has been verified with literature data. Programs for the structural characterization of mixed-layer minerals must allow a) modification of the structural characteristics, abundances, and order-disorder distribution of the layers; b) modification of the distribution of the sizes of coherent scattering domains; and c) consideration of mixed-layer clays with more than two components. Two programs were written to calculate the XRD patterns of two- and three-component mixed-layer minerals consisting of any layer type and without any limitation in the order-disorder relationships.

Key Words—Clay Analysis, Expert System, Mixed-Layer Minerals, Phase Analysis, XRD.

INTRODUCTION

Clays present several difficulties in their structural characterization for at least two reasons. One reason is that clays generally consist of a mixture of different phases, *i.e.,* mixed-layer minerals (MLMs), individual clay minerals (non mixed-layer), and associated minerals, such as calcite or quartz. However, the main difficulty is that mixed-layer minerals can yield an infinity of X-ray diffraction (XRD) patterns, depending on the nature of the layers they contain, the proportion (or abundance), and the nature of layer stacking.

One partial solution to the problem of phase analysis and structural characterization of clays was well explained by Moore and Reynolds (1997). This book provides a set of theoretical XRD patterns, but cannot describe the extensive diversity of natural samples. A computer program to calculate theoretical X-ray patterns of MLMs is required to do this. The structural characteristics, *i.e.,* the abundance of each type of layer, the stacking arrangement of successive layers as described by the Reichweite, R (Jadgozinski, 1949), and the junction probabilities of Markovian statistics, are determined from the comparison of observed and calculated data. A computer program, NEWMOD (Reynolds, 1985), was written for this purpose and is widely distributed.

However, the phase analysis and structural characterization of clays still has some difficulties. For example, they require a detailed knowledge of mixed-layer clay minerals which non-specialists may not have. To reproduce an observed XRD pattern, approximate starting values for structural parameters involved in the calculation may not be available. On the other hand, experienced clay mineralogists may want to calculate theoretical diffraction patterns of models not available in NEWMOD as, for example: 1) calculation of the XRD pattern of an MLM not part of the database of NEWMOD; 2) calculation, for given R and abundance values, of all possible stacking arrangements, from segregation to maximal possible degree of ordering (MPDO); 3) use of a lognormal crystallite-size distribution of stacking arrangements of layers, as proposed by Drits *et al.* (1997a); 4) calculation of three-component mixed-layer minerals, which do occur in nature (Drits *et al.,* 1997b), without any restriction on the abundance of each component.

A new and more general approach was introduced a few years ago for problems where the influence of many parameters must be understood to reach a solution. This is the use of expert systems. These are interactive computer tools where information of "experts" is introduced as part of the "knowledge base". The user provides answers to questions posed by the program, and these answers allow the expert system to move automatically through the knowledge base to produce conclusions. The more complicated the problem, the more useful is the expert-system approach. There is no requirement of a deep understanding of the subject by the user. In fact the user learns the role of each question, *i.e.,* the way experts think. The first expert system for clay characterization was proposed

by Plançon and Zacharie (1990) for defining defect structures of kaolinite samples.

The aims of this paper are to describe: 1) an expert system for phase analysis of clay minerals, including a first approach for their structural characterization, and 2) the calculation programs for the refinement of the structural characterization of MLMs for two- and three-component systems. The calculation programs include the most recent description of mixed-layer clay minerals, without limiting the type of layers involved or the nature of the order-disorder of their distribution.

EXPERT SYSTEMS FOR PHASE ANALYSIS OF CLAY MINERALS

The complexity of the phase analysis of clays makes them obvious candidates for the application of expert systems. Two approaches were made previously by Garvie (1993, 1994) and Drits and Plançon (1994). The contribution of Garvie is based on a very large collection of systematically calculated X-ray patterns: the role of the expert system consists of comparing the experimental pattern with calculated ones, and the quality of the fit measured as a "fit index". The result is a small number of possible mixed-layer minerals, the most probable one having the largest fit index. This approach has a weakness: even a large number of calculated patterns cannot match the infinite variety of mixed-layer minerals based on the individual characteristics of the layers (chemical composition, atomic coordinates, site occupancies), the relative proportion of each layer, and the way they stack. The list of possible MLMs generated by the program of Garvie has a 20% range for the proportion of the main layer. In fact, this expert system does not work as a human expert. The approach of Drits and Plançon (1994) was intended to mimic human experts as described by Moore and Reynolds (1997). Drits and Plançon also added an original part for the quantitative evaluation of the structural parameters of mixed-layer minerals. Nevertheless one problem lies in the design of the expert system, which is composed of three separate parts, each devoted to a family of MLMs, *i.e.,* a) mica-smectite and mica-vermiculite, b) MLMs containing chlorite layers, and c) other MLMs (*e.g.,* kaolinite-smectite, *etc.*). In general, the user must use these three parts when only one provides the solution. Perhaps more important is the absence of preliminary tools to identify the associated non-clay minerals in the sample. Finally, there is no computing tool to allow the user to verify the identification of the interstratified mineral and the quantitative evaluation of its structural parameters.

The expert system presented here corrects these difficulties and provides a complete computational method to solve the problem of phase analysis of clays. It consists of five programs that may be used separately but are normally used consecutively. The individual functions are: a) identification of associated minerals, b) identification of individual clay minerals, c) identification of the nature of the MLMs, d) structural characterization of the MLMs, and e) calculation of theoretical diffraction patterns in the common and special case of MPDO for two component MLMs.

Description of the expert system

Data required by the expert system. The phase analysis is founded on the comparison of XRD patterns recorded for three states of the sample: air-dried, heated to 350°C, and solvated with ethylene glycol. To eliminate the contribution of the reflections other than 00*l*, the patterns are recorded by reflection from oriented clay-aggregate samples. In these patterns, the *d*-values of all reflections are measured.

Identification of associated minerals. This step of phase analysis is performed by the ASSOCMIN program with two options corresponding to: a) the introduction of experimental data, *i.e.,* all the *d*-values of reflections whose positions and intensities do not change after glycolation or heating, and b) the identification of the associated minerals. This part compares the observed data from the first part with the *d*-values of the 40 most commonly associated minerals (carbonates, sulfates, oxides, *etc.*). If at least one experimental reflection coincides with a reflection of an associated mineral (taking a small uncertainty into account), the associated mineral is displayed with all *d*-values and relative intensities. This allows the user to decide if the mineral is present in the sample. The data of associated minerals are contained in a text file which can be modified by the user.

Identification of individual clay minerals. The program INDVCLAY displays a list of individual clay minerals (kaolinite, chlorite, *etc.*) for phase analysis. Upon choosing a clay mineral from the list, the program displays the main features of the XRD pattern of that mineral, its behavior after heating or ethylene-glycol treatment, and the minerals that can be confused with it. The program then allows the user to check the presence of the mineral in the sample by introducing the *d*-values of successive 00*l* reflections (at least two). The coefficient of variation CV proposed by Bailey (1982) is then calculated, displayed, and used as the criterion of occurrence in the sample. The cases for R = 1 with the superreflection missing and R = 1 with a missing reflection in the series are treated.

Determination of the nature of the mixed-layer clay minerals. The use of the NATMIX program is an unambiguous determination of the nature of the mixed-layer clay minerals. The program makes decisions based on the comparison of three patterns, *i.e.,* air-dried, ethylene-glycol solvated, and heated to 350°C. For example, if in a given sample there are differences

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between the air-dried and the ethylene-glycol solvated pattern for some of the peaks, then the sample contains layers which swell with ethylene glycol, *i.e.,* smectite or vermiculite layers. If, after heating, only a rational series (or nearly rational) of reflections near 10, 5, 3.3 Å is observed, then the swelling layers have collapsed with a thickness near 10 Å.

Determining the nature of the mixed-layering also allows the refinement of the characterization of the layer composition and structure by proposing additional experiments. For example NH_4^+ micas can be identified by infrared spectroscopy, or the distinction between dioctahedral and trioctahedral layers can be made by measurement of the *d*-value of the 060 reflection in a pattern recorded for a non-oriented sample, *etc.*

Note that this part of the expert system is not limited to the identification of two-component mixed-layer minerals. However, data seldom appear in the literature concerning three-component systems.

The fundamental difference between this system and the first version of the expert system (Drits and Plançon, 1994) is that the new approach covers the entire family of mixed-layer clay minerals and not just a portion of them. Another difference is that the present system determines the nature of MLMs, the structural determination being isolated in the following step. The description of the way the expert system works is found in Plançon and Drits (1994).

Structural characterization of the mixed-layer minerals. This step, performed by the STRUCMIX program, determines the mean abundance of each layer in the MLM and the range of interaction (the Reichweite) between these layers. For a mineral identified in the preceding step by NATMIX, the expert system proposes experimental *d*-values for some reflections located in different *d*-value domains. For example, for an MLM mica-glycolated smectite, the *d*-value must be provided for the reflection located between 17–10 Å, the *d*-value in domain 10.0–8.45 Å, and the *d*-value in domain 5.7–5 Å (if it exists). These values are used in two ways. In most cases, they are introduced into a calculation based on the principle of Méring (1950) as refined by Drits *et al.* (1994). Drits *et al.* showed how the *d*-values of some reflections change with the abundance of each type of layer and the Reichweite. This method was analysed by Drits *et al.* (1994) and Drits and Plançon (1994) in the first version of this expert system. Both studies used calculated patterns of MLMs from the literature with specific compositions and Reichweites. They showed that the evaluation of structural parameters from the rule of Méring was satisfactory. In some cases the structural parameters are obtained from an abacus like that for illite-smectite by Watanabe (1981).

Calculation of XRD patterns of mixed-layer minerals. The two previous steps using NATMIX and STRUCMIX provide information on the nature and structural parameters of mixed-layer mineral(s) occurring in a sample. However, because these steps work with only a few peak positions, they can suffer from a lack of precision and/or accuracy. To confirm the nature and structure of the MLM requires the calculation of a theoretical XRD pattern and the fitting of the calculated pattern to the experimental pattern. This is the purpose of the CALCMIX program, which works for two component systems and, in the case of MPDO, for any structural composition of each layer.

CALCMIX offers a menu from which the user can choose the components of the MLM (for example NH_4^+-rich illite-ethylene-glycolated exchanged smectite) and then the program requests the abundance of one of the two layers and the Reichweite. The program calculates the pattern, and displays the calculated intensities *versus* 2θ. To this point, the program appears similar to NEWMOD (Reynolds, 1985) but an important difference is that the structural characteristics of the layers (atomic coordinates; temperature factors; nature of the octahedral, tetrahedral, and interlayer cations; site occupancies) are not included in the text of the program, but are in separate text data files so that they may be easily modified by the user. Different possible distributions of crystal thicknesses and experimental parameters characterizing the XRD pattern also are in user-accessible text files. The result of the calculation is written to a text file that can be used as input data by graphics programs commonly available. Note also that the menu offers a "personal mixed-layer mineral" option that allows the calculation of any two-component MLM whose structural characteristics are defined in text files as described above. This program intends to improve the user interface and to be as user-friendly as possible.

CALCULATION PROGRAMS FOR ACCURATE STRUCTURAL CHARACTERIZATION OF TWO- AND THREE-COMPONENT MIXED-LAYER MINERALS

The theoretical basis for the calculation of diffraction patterns for two- and three-component systems already exists (*e.g.,* see Drits and Tchoubar, 1990, for a bibliography). For the calculation of the diffraction pattern by one-dimensionally disordered structures, there is the widely used NEWMOD program for two-component mixed-layer clays. We know of two programs that can calculate diffraction patterns for three-component systems: 1) an expanded NEWMOD version for a special case where a third component substitutes in a random way for the minor component of a two-component system, and 2) a program written by Drits and Sakharov (1976), but which is not distributed. Compared to NEWMOD, the purpose of the

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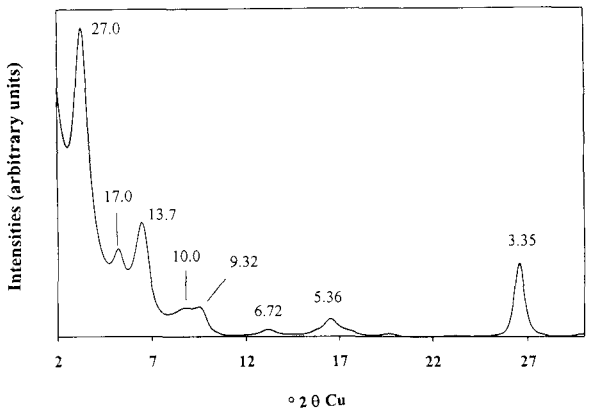

Figure 1. MLM2C-calculated XRD pattern of the two-component mixed-layer mineral illite-smectite, the smectite being intercalated with ethylene glycol, for R = 2, W_I = 0.7, p_{SS} = 0.1, p_{SSI} = 0.15, p_{SII} = 0.20 (I for illite, S for smectite). *d*-values of reflections are expressed in Å.

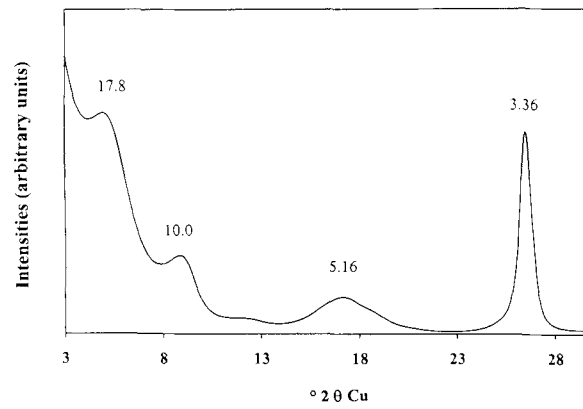

Figure 2. MLM3C-calculated XRD pattern of the three-component mixed-layer mineral illite-smectite-vermiculite, the swelling layers being intercalated with ethylene glycol, for R = 1, W_I = 0.68, W_S = 0.24, p_{SS} = 0.35, p_{SV} = 0.06, p_{VS} = 0.20; p_{VV} = 0.40 (I for illite, S for smectite, V for vermiculite). *d*-values of reflections are expressed in Å.

computer program proposed here for two-component mixed-layer minerals, named MLM2C, is: 1) to extend the range of stacking order from segregation to MPDO without any restriction, 2) to account for new descriptions of the distribution of the number of stacked layers, 3) to include any kind of layer (the type and content of layers can be modified), 4) to improve the user interface for the data input, and 5) to reduce the calculation time of the diffraction pattern because it is previously compiled. The MLM3C program calculates three-component mixed-layer minerals. MLM2C and MLM3C have common parts, some of them also common to CALCMIX. The junction parameters for which the user must provide a value are chosen such that their value may range from 0 to 1. These parameters may depend on the values of some previously input parameters (see case of R = 2, below). The programs check the coherence of the data. If the junction probabilities are not in the correct range, the program stops, indicating the reason for the termination of the calculation.

Features of MLM2C

The calculation can be done for four values of the Reichweite, for R = 0, 1, 2, for all cases of the stacking arrangement (from segregation to MPDO), and for R = 3 in the case discussed below. For R = 0, for the description of the stacking sequences, the user provides only the abundance of one of the two components (between 0–1). Classically calling A the major layer and B the minor layer, this requires either the abundance of the A component, W_A, or the abundance of the B component, W_B. For R = 1, the calculation requires one additional p_{ij} junction parameter; *i.e.,* the probability for a *j* layer to follow an *i* layer; the program asks for the p_{BB} value, *i.e.,* the probability for a B layer to follow a B layer. For R = 2, the calculation requires, in addition to the two previous parameters (W_A and p_{BB}), two p_{ijk} junction parameters (probability for a *k* layer to follow an *ij* pair) which depend on W_A (*e.g.,* p_{BBA} for $p_{BA} \geq 0.5$ and p_{BAA} for $W_{BA}/W_{AA} < 1$, where W_{BA} is the abundance of BA pairs, and W_{AA} the abundance of AA pairs). For R = 3, and not MPDO, there are theoretically four independent additional parameters to provide. This program treats only the useful case for which probability parameters p_{ij} and p_{ijk} are those of MPDO for R = 2. In addition to W_A there is only one additional p_{ijkl} parameter needed; this parameter depends on W_A. An illustration of the use of MLM2C is shown in Figure 1 for an MLM illite-smectite, the smectite being intercalated with ethylene glycol, for R = 2, W_I = 0.7, p_{SS} = 0.1, p_{SSI} = 0.15, p_{SII} = 0.20 (I for illite, S for smectite).

Features of MLM3C

The calculation can be performed for the two values of Reichweite R = 0 and R = 1, for all cases of stacking arrangement (from segregation to MPDO). For R = 0 the two parameters required are the abundance of the major layer, A (*i.e.,* W_A) and the abundance of one of the two other layer components, which are the B and C layers. For R = 1 the calculation requires four additional independent p_{ij} junction parameters. The program asks for the p_{BB}, p_{BC}, p_{CB}, and p_{CC} parameters. An illustration of the use of MLM3C is shown by Figure 2 for an MLM illite-smectite-vermiculite, the swelling layers being intercalated with ethylene glycol, for R = 1, W_I = 0.68, W_S = 0.24, p_{SS} = 0.35, p_{SV} = 0.06, p_{VS} = 0.20, and p_{VV} = 0.40 (I for illite, S for smectite, V for vermiculite). This corresponds to an MLM with minor segregation of smectite and major segregation of vermiculite.

https://doi.org/10.1346/CCMN.2000.0480107 Published online by Cambridge University Press

Common features of the calculation programs

In each of the three programs, the structural features of each type of layer, *i.e.,* layer thickness, atomic coordinates, site occupancies, diffusion factors, and temperature factors are contained in individual files. The names of these files are the input information required to define the nature of the mixed-layer mineral under calculation. The calculation can be performed for any X-radiation and range of 2θ angle. The three programs consider several types of distribution of stacked layers: 1) lognormal distribution of the number of layers in crystallites following the observation of Drits *et al.* (1997a) (in this case, the mean value of the lognormal distribution must be provided), 2) uniform distribution of the number of layers of crystallites between two limits, the minimum and maximum number of layers in the crystallites, and 3) a user supplied distribution of the number of layers of crystallites and an upper and lower limit (in addition to these limits, the user must list the proportion of crystallites for each thickness). Defect-broadening characterized by a mean defect-free distance can also be introduced according to the proposal of Ergun (1970) (the mean number of defect-free cell sequences must be provided). Data concerning experimental conditions can also be modified, *i.e.,* the divergence and soller slits, the radius of the goniometer, the sample length, the σ^* value for the orientation of the particles in the sample (Reynolds, 1985), and, as noted above, the wavelength of radiation and limits of the recorded domain. After the calculation, the parameters are written in a file that is used as default parameters for the next calculation, the results of the calculations are written to a text file for use with any graphics program, and these results are displayed on the monitor with a possible comparison with the experimental data.

CONCLUSIONS

The expert system proposed here is intended to refine the phase analysis of clays. Results were compared against data published in the literature and the system proves to be efficient in the determination of the nature and structural parameters of mixed-layer clay minerals. It provides an original approach that allows the user to obtain a good evaluation of these structural parameters (see references in Drits and Plançon, 1994). The CALCMIX program for calculation of theoretical diffraction patterns, which is included in the expert system, is user-friendly and fast.

The MLM2C and MLM3C programs allow the user to perform improved calculations for diffracted patterns of two- and three-component mixed-layer minerals including the most recent developments in clay-mineral science.

The expert-system package with the two calculation programs, which includes instruction manuals with a detailed description of the different data files, is distributed free of charge, except for the cost of the diskettes and handling and shipping costs. These programs, written in the Delphi language, run on PC computers with Windows 95, Windows 98, or WinNT as an operating system.

ACKNOWLEDGMENTS

The authors thank B. Lanson for checking the expert system and for the wise suggestions he has made for its improvement. We also thank very much D.M. Moore for his comments and the improvement of the language, and R.F. Giese, who helped to correct the English of the last version of this manuscript.

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(*Received 21 September 1998; accepted 26 June 1999; Ms. 98-116*)