

Simulation of XRD patterns as an optimal technique for studying glacial and interglacial clay mineral associations in bottom sediments of Lake Baikal

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ABSTRACT: A new method is proposed for modelling complex X-ray diffraction patterns effectively. The method is based on the calculation of the interference function of the one-dimensional disordered crystals with finite thickness. First, we calculated the diffraction effects from structures of individual mineral phases with different layer defects modelled according to the Reynolds' algorithm. To fit the theoretical to the observed XRD patterns more accurately, we then used a specially developed optimization procedure. This iterative procedure selects the optimal set of chemical and structural parameters (probability and domain size) and yields consistent solutions.

The composition of the clay component in bottom sediments of Lake Baikal relates strongly to glacial/interglacial climate cyclicity. Besides changes in the relative abundance of illite and illite/smectites between glacial and interglacial periods, significant differences are observed in the crystal chemistries and structures of layered minerals. A change from chlorite during glacial periods to chlorite-smectite during interglacials is probably indicative of the weathering processes in the watershed. Changes in the degree of ordering, in domain size and grain-size distribution of illite-smectites imply differences in genesis of this mineral phase in different palaeoenvironments. These findings further strengthen the case for using clay minerals in the sedimentary record of Lake Baikal as palaeoclimate indicators.

One of our findings was that none of the fractions separated by Stokes' settling is representative of the bulk sample for either the glacial or interglacial intervals. For the interglacial sample, illite-smectite was concentrated in the <2 µm fraction whereas, for the glacial sample, most of illite-smectite is contained in the <1 µm fraction. The selective use of one fraction is yet another potential source of uncontrolled errors that has to be avoided. We suggest using X-ray patterns of bulk samples as a preferred method of analysis of Lake Baikal (and other) sediments.

KEYWORDS: X-ray diffraction, modelling, illite-smectites, Lake Baikal, climate change.

CLAY MINERALS IN LAKE BAIKAL AS PALAEOCLIMATE INDICATORS

The sedimentary record of Lake Baikal is a palaeoclimate archive of global importance. The climatic record from Lake Baikal, situated at high

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latitudes (52–56°N) in Central Asia, is extremely valuable for reconstructing palaeoclimate in the Northern Hemisphere (Kuzmin *et al.*, 1993; BDP-93 Members, 1995). The international Baikal Drilling Project (USA, Russia, Japan, Germany), which started in 1989, aims to recover the record of changes in ecosystems and climates in central Asia (Kuzmin *et al.*, 1993; BDP-93 Members, 1995). At present, the continuous 5–10 Ma records of climate change in continental interior Asia are available from the Lake Baikal sedimentary archive (BDP-96 Members, 1998; Williams *et al.*, 1997; BDP-98 Members, 2000).

The main palaeoclimate proxy in the Lake Baikal record is the biogenic silica content, reflecting changes in diatom production in response to changes in climate (Williams *et al.*, 1997). It has also been found that climate changes affect not only the ratios of biogenic and terrigenous components in sediments, but also the clay mineral composition (Melles *et al.*, 1995; Yuretich *et al.*, 1999). It is suggested that erosion dominates during cold periods, whereas chemical weathering and soil formation intensify during warm periods. The detailed stratigraphy of the Baikal record is already established, based on diatom and biogenic silica responses with centennial (Karabanov *et al.*, 2000a,b) and millennial (Karabanov *et al.*, 1998, Prokopenko *et al.*, 2000) resolution. The results from sedimentary and palaeoproductivity records indicate that throughout the entire Pleistocene, the Lake Baikal basin has remained remarkably stable in terms of volume, size, drainage system, catchment area, etc. This long-term stability has created a unique opportunity for detailed studies of Lake Baikal clay mineral associations in any chosen period of the Pleistocene, with resolution up to 250 years, to trace the entire Plio-Pleistocene history of chemical processes in the Lake Baikal catchment basin. Analysis of clay minerals reveals watershed responses to glacial/interglacial climatic cycles and, importantly, their rate. The timing of changes in clay mineral association relative to other Lake Baikal proxy records would greatly contribute to understanding the dynamics of weathering processes and their effect on the chemical balance of Lake Baikal and possibly on authigenic clay formation processes.

The multi-component composition of Baikal sediments has been studied by a number of workers. Rateev (1954) described clay minerals in the surface layer of sediments from Southern Baikal

and identified montmorillonite, illite, chlorite and kaolinite. G.S. Goldyrev listed the same mineral association for the late Quaternary sediments and interpreted the differences in the degree of alteration of illite as a response to the processes of soil formation in the watershed (Goldyrev, 1982). The pronounced difference in clay mineral associations between silty clay and diatomaceous ooze was first mentioned in 1995: in cores 305 and 333, the greater smectite content associated with greater biogenic silica content was thought to reflect soil formation during warm periods (BDP-93 Members, 1995). Later studies revealed similar relations between the abundance of clay minerals and palaeoclimate indicators in long boreholes BDP-93-1 and BDP-93-2 (Melles *et al.*, 1995; Kashik & Mazilov, 1997; Yuretich *et al.*, 1999). However, all the above works used a conventional approach to clay mineral investigations, separating fine fractions by Stokes' settling. Kashik and Mazilov (1997), who used the <1 µm fraction, prepared the oriented mounts by centrifugation. Yuretich *et al.* (1999) used the <2 µm fraction and prepared the oriented mounts by smearing. Melles *et al.* (1995) also used the <2 µm fraction but prepared the oriented mount by vacuum filtering. A synthesis of studies on the <2 µm fractions has shown that significant differences in numerical values and certain inconsistencies exist between American and German datasets due to different preparation methods and analytical conditions (Yuretich *et al.*, 1999). These are serious shortcomings for using clay mineral associations as a possible proxy of palaeoclimate and palaeoenvironmental changes. We sought to avoid these shortcomings by designing the optimal analytical technique. In order to do this we selected two typical glacial and interglacial samples, and separated three different fine fractions in order to study their composition. Here, we present a new technique based on the simulation of complex X-ray diffraction (XRD) profiles for studying the composition and structure of clay minerals in the multi-component bottom sediments of Lake Baikal.

MATERIALS AND METHODS

Two samples from BDP cores of Pleistocene sediments from Academician Ridge were selected for our studies. Sample A was silty clay, deposited at the Baikal bottom during the last glacial period. Sample B was a diatomaceous ooze typical of a warm interglacial period (Bezrukova *et al.*, 1991;

Colman *et al.*, 1995). In Table 1 the relative chemical composition obtained by X-ray fluorescence (XRF) analysis is given for both samples. 'Interglacial' sample B has a high biogenic silica content due to the presence of diatom valves, which nearly doubles the Si/Al ratio compared with 'glacial' sample A. The biogenic silica content in sample B is estimated at ~20–25% according to infrared (IR) spectroscopy.

The mineral composition of the original samples and their fine granulometric fractions were studied by X-ray powder diffraction and IR spectroscopy. The XRD patterns were obtained using a DRON-4 diffractometer (Cu-K α radiation, graphite monochromator). The diffraction patterns were first scanned from 2 to 65°2 θ with a step size of 0.05° and a counting time of 10 s. For more detailed study of the composition and structure of the clay minerals, three fine granulometric fractions were separated (<1 μ m, <2 μ m, <5 μ m) by Stokes' settling in water (Ehrmann *et al.*, 1992). Then the water suspension was saturated with MgCl₂ solution. The precipitate obtained was washed repeatedly with distilled water by centrifuge and dried at 60°C. Oriented samples were prepared by centrifuging onto a glass microslide at 8000 rpm.

For modelling purposes, the oriented mounts were prepared by transferring the suspension of bulk sample in distilled water onto a petrographic slide and drying at room temperature. The samples were then placed in a desiccator in an ethylene glycol-rich atmosphere for 24 h at room temperature. The diffraction pattern of glycolated samples for modelling was scanned from 2° to 35°2 θ with a step size of 0.05° and a counting time of 32 s.

An independent semi-quantitative estimation of the mineral composition of samples was made using IR. For reference standards we used the spectra of pure minerals and their mixtures in different

proportions. Spectra were obtained using a Specord-75IR spectrometer. The clay fraction content (chlorite, illite, smectite, kaolinite) was estimated from the absorption band of the OH-stretching vibrations in the region of 3300–3700 cm⁻¹. To eliminate interfering absorptions from molecular water (when necessary), samples of smectite and amorphous silica were heated for 1.5 h at 350°C directly in a KBr pellet. The pellets were subsequently pressed until transparent.

ANALYTICAL RESULTS

Bulk sample analysis

The clay component of both samples consisted of chlorite, illite and mixed-layer illite-smectites. Non-layered minerals were represented by plagioclase, quartz and amphibole. X-ray diffraction patterns for both of the bulk samples are characterized by broad peaks with low intensity (Figs 1a, 2a). The excessive breadth of the diagnostic peaks is caused by the fine particle-size of all mineral phases. The XRD pattern of the diatomaceous ooze (Fig. 2a) has especially weak diagnostic peaks. This is due to the contribution of X-ray amorphous biogenic silica which dilutes sample B as shown by the broad halo at 15–33°2 θ (Fig. 2a).

The IR spectrum of biogenic silica in contrast to the spectrum of crystalline quartz is represented by broad unresolved bands with maxima at ~470, 800, 940, 1090 and 3440 cm⁻¹ (Fig. 3, dotted line). The characteristic band of crystalline quartz with two maxima at 778 and 798 cm⁻¹ in diatomaceous ooze (sample B) exhibits a well defined shoulder on the high-frequency side. The presence of biogenic silica is also clearly manifested by a wide absorption band between 900 and 1200 cm⁻¹ with a maximum around 1090 cm⁻¹ typical of amorphous silica.

TABLE 1. Chemical composition of samples (bulk sample and <1 μ m fraction), wt.%.

| Sample | SiO ₂ | TiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | CaO | Na ₂ O | K ₂ O | Loss on ignition | Total |
|---------------------------|------------------|------------------|--------------------------------|--------------------------------|------|------|-------------------|------------------|------------------|-------|
| A glacial <1 μ m | 49.48 | 0.767 | 18.65 | 9.69 | 2.75 | 1.59 | 2.37 | 3.42 | 9.91 | 98.63 |
| Bulk sample | 56.73 | 0.860 | 17.33 | 8.54 | 2.80 | 2.04 | 1.61 | 3.30 | 6.80 | 100.0 |
| B interglacial <1 μ m | 63.46 | 0.499 | 13.15 | 6.71 | 1.47 | 1.18 | 1.81 | 2.22 | 9.5 | 100.0 |
| Bulk sample | 68.58 | 0.550 | 11.01 | 5.32 | 1.78 | 1.59 | 1.76 | 1.76 | 7.40 | 99.75 |

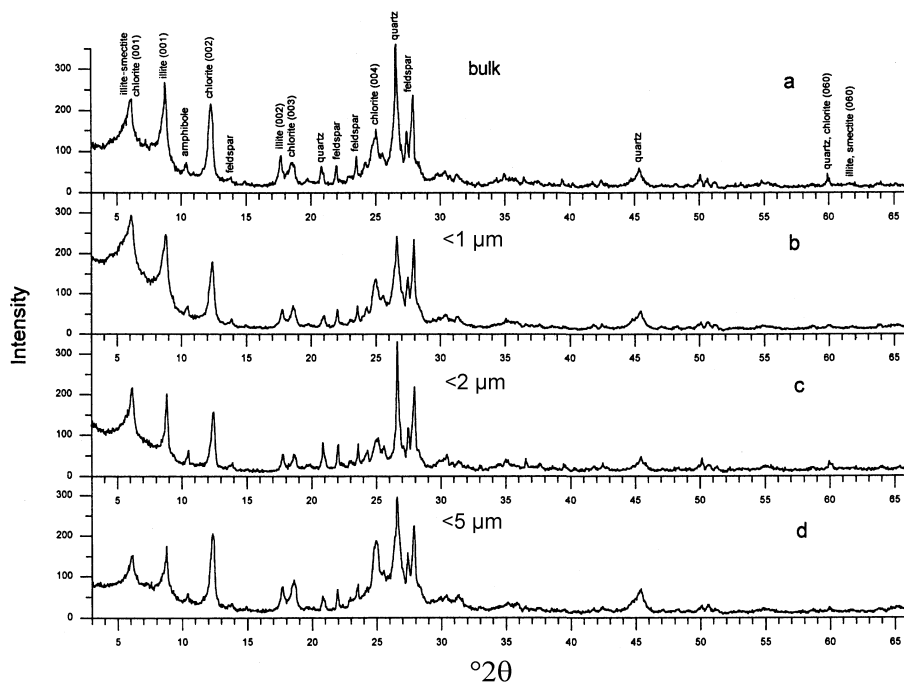


FIG. 1. Experimental XRD patterns of sample A (glacial silty clay – air-dried): (a) bulk sample; (b) $<1 \mu\text{m}$ fraction; (c) $<2 \mu\text{m}$ fraction; (d) $<5 \mu\text{m}$ fraction. The profile of the $<2 \mu\text{m}$ fraction is the closest to that of the bulk sample.

Infrared spectroscopy was used to identify kaolinite; XRD is not sensitive to minor amounts of kaolinite due to stronger chlorite peaks. The kaolinite content does not exceed 1–2% in either sample. In all of the fractions examined, kaolinite content was similar to that of the bulk sample. None of the samples contained significant amounts of organic matter.

Analysis of separate fractions

Comparison of the XRD patterns of different clay mineral distributions revealed differences between the fine fractions of the glacial silty clay (sample A, Fig. 1b, c, d) and the interglacial diatomaceous ooze (sample B, Fig. 2b, c, d). In both samples differences in composition between each of the fractions and the bulk samples were observed.

The $<1 \mu\text{m}$ fraction in glacial sample A is significantly enriched in clay minerals compared with the bulk samples. This enrichment is especially evident for illite-smectite as seen on the XRD pattern (Fig. 1b) and on the ethylene glycol

saturation profile (Fig. 4a). The $<2 \mu\text{m}$ fraction of sample A is the most representative of the bulk sample as seen from the close similarity of their XRD patterns (Figs 1c, 4b). Compared to the bulk sample, the $<5 \mu\text{m}$ fraction of sample A has a lower illite-smectite content and significantly higher chlorite content (Figs 1d, 4c) which indicates the detrital genesis of chlorite.

The distribution of clay minerals in fine fractions of the diatomaceous ooze (interglacial sample B) is significantly different from that in glacial clay. Unlike sample A, the $<1 \mu\text{m}$ fraction is the most representative of the bulk sample B (Figs 2b, 4d). In sample B the $<2 \mu\text{m}$ fraction is strikingly different from the bulk sample due to the pronounced enrichment in illite-smectite (Figs 2c, 4e). The $<5 \mu\text{m}$ fraction of sample B has a small illite-smectite content and a greater chlorite content, probably detrital (Figs 2d, 4f).

The reason for the observed differences is not clear, but it is evident that none of the fractions is preferable to the bulk sample because it would not be equally representative of both glacial and

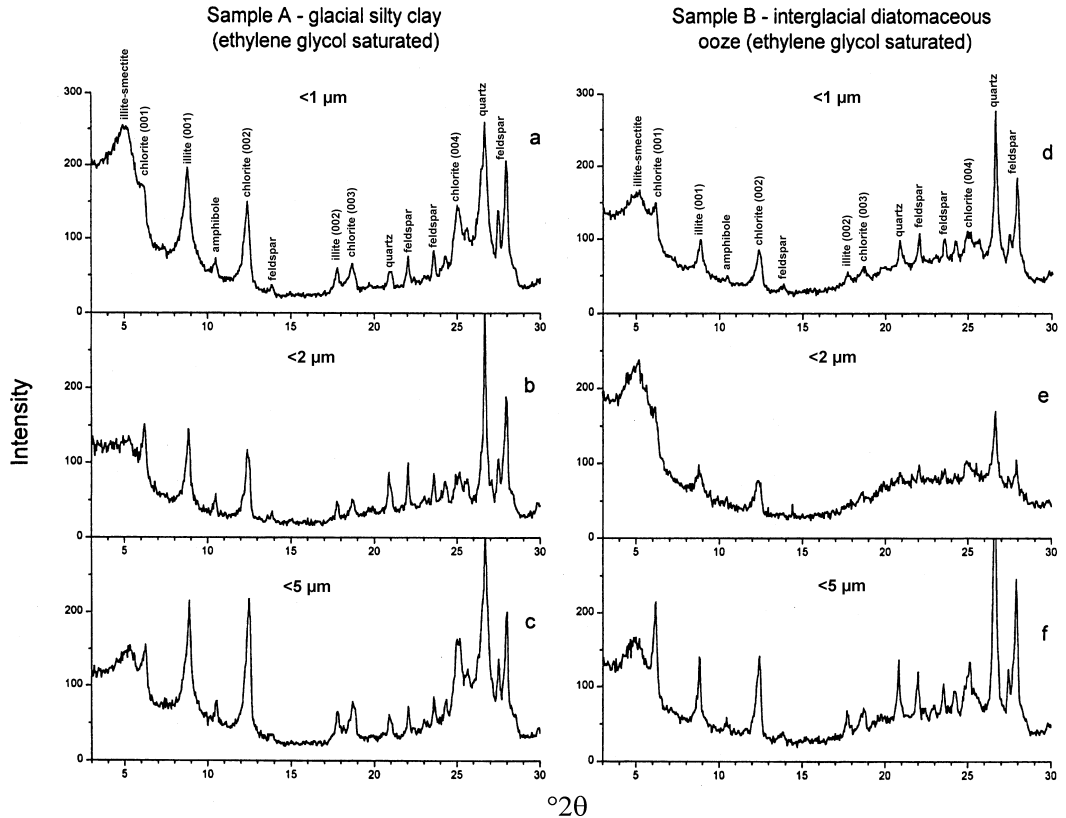


FIG. 4. Experimental XRD patterns for ethylene glycol-saturated fractions of sample A (a–c) and sample B (d–f). The chlorite and illite-smectite diagnostic lines are clearly separated. Note the enrichment of the coarser fraction in chlorite.

of calculation of the interference function of one-dimensional disordered crystals with finite thickness (MacEwan, 1958; Reynolds, 1967, 1980), or (2) the matrix formal approach of calculation of the diffraction effects from structural models with various layer defects (Hendricks and Teller, 1942; Kakinoki and Komura, 1952, 1954; Drits and Sakharov, 1976; Drits and Tchoubar, 1990). In both cases the calculated diffraction pattern is compared with the experimental pattern.

The most widely used software package to perform the modelling is the NEWMOD program, developed by Reynolds (1985), using the algorithm he had proposed previously (Reynolds, 1980). This approach calculates XRD patterns for possible structural models of two-component mixed-layer systems (Drits and Sakharov, 1976; Reynolds, 1980). However, this conventional algorithm with two-component systems does not provide enough

detail for unambiguous modelling of XRD patterns of mixed-layer minerals, and therefore other workers have been forced to modify it. Some researchers use three-component models – illite-smectite-vermiculite (Weir and Rayner, 1974; Drits *et al.*, 1997; Sakharov *et al.*, 1999). Other authors (Lanson and Besson, 1992; Lanson and Velde, 1992) assumed that the complicated profile is caused by the presence of several two-component illite-smectite series. They proposed decomposing the spectrum into several diagnostic zones and distinguishing the component peaks for each of these zones. However, with this approach the choice of the number of zones, the choice of the position of maxima and widths of the component peaks is rather arbitrary and depends on the nature of the samples studied. As a result Gharrabi *et al.* (1996) suggested different parameters for decomposing the spectra. We find these approaches rather forced and

subjective. In cases when samples contain more than just mixed-layer minerals, this type of modelling, based on decomposition of the spectra, yields inadequate results (Solotchina *et al.*, 1999b, 2000).

The full XRD profile for multi-component clay samples, among which the mixed-layer minerals such as illite-smectite are abundant (which is the case with the Baikal samples), may be regarded as multi-parameter systems with strongly correlated parameters. The question of a reliable and unambiguous solution arises even if a reasonable fit between model and experiment is achieved. In order to address this problem we have designed a more efficient algorithm.

We developed an approach involving optimization of the variables in the models of composition of clay mineral associations. The algorithm is based on a formal analysis of the correspondence between the theoretical and experimental profiles, and on the optimization of the parameters by methods of nonlinear programming. Our approach is, in a sense, similar to the trial-and-error optimization procedure suggested by Pevear and Schuette (1993) to fit models to experimental XRD patterns. However, our algorithm takes into account a larger number of variables and is more effective because of greater sensitivity to low-amplitude local extremes of spectral curves (which is extremely important for characterizing mixed-layer mineral phases) and, at the same time, is less sensitive to trends. This combination results in a more monotonous fitting process. Another advantage is a fast optimization at the same time, allowing the use of a large number of parameters. Our computer package consists of several subroutines: the first step includes preliminary individual simulations of the main mineral phases in the composition selected: illite, muscovite, chlorite and kaolinite (if present) to find a close match with the observed XRD pattern in terms of breadth and intensity of diagnostic lines. Then using Pearson's VII function we approximated the peaks of non-layer minerals, such as quartz, amphibole and feldspar. For interglacial Lake Baikal samples we added an experimental profile of an additional component – biogenic silica (Baikal diatoms) – in the proportion corresponding to the biogenic silica content of the sample modelled. We ran the simulation of the mixed-layer phase last among the main components, because it is the most complex phase. The next subroutine is an iterative procedure. It includes

summation of the individual patterns of the components and the refinement of parameters. The parameters of chemical composition are selected manually. The other two groups of parameters are calculated using an automatic optimization procedure. The following sections deal in detail with each of the above procedures.

Modelling individual components

The structural model for each of the components is simulated using the Reynolds algorithm of (Reynolds, 1980, 1985). For each of these components (illite, muscovite, chlorite and kaolinite) the number of parameters is set. The parameters are subdivided into two groups. The first group defines the chemical composition. The second group of parameters controls the distribution of domains (areas of coherent scattering) by size.

The diffraction lines of non-layered minerals are simulated by Pearson's VII function (Hall *et al.*, 1977). For illite-smectites, in addition to the parameters of chemical composition and domain size, we added the third group of parameters – the probability parameters describing the composition of the layers, the number of layers of different type and their stacking sequences in a mineral structure. The contents of each layer type and their stacking sequences are given by probability parameters: W_i – concentration of a layer type; P_{ij} , P_{ijk} , P_{ijkl} – probabilities of their ordering in a crystal (Drits and Sakharov, 1976; Drits and Tchoubar, 1990; Reynolds, 1980).

In order to combine all components into the multi-component model we used the procedure of summing the contribution of individual components taking into account their weight factors. Weight factors are calculated using the set of linear equations from the intensities of the diagnostic peaks of individual phases (Reynolds, 1989). In this step we could also refine the parameters for each of the components and chose the optimal (identified by the least-squares method) weight factors describing the contributions of these components into the full profile. For instance, this may be necessary for correcting the overlapping peaks of kaolinite and chlorite. If needed, the calculation of weight factors and summation may be repeated to account for manual changes in parameters of these phases. From there on, we worked only with a full diffraction profile of the multi-component model, and not with the profiles of individual phases.

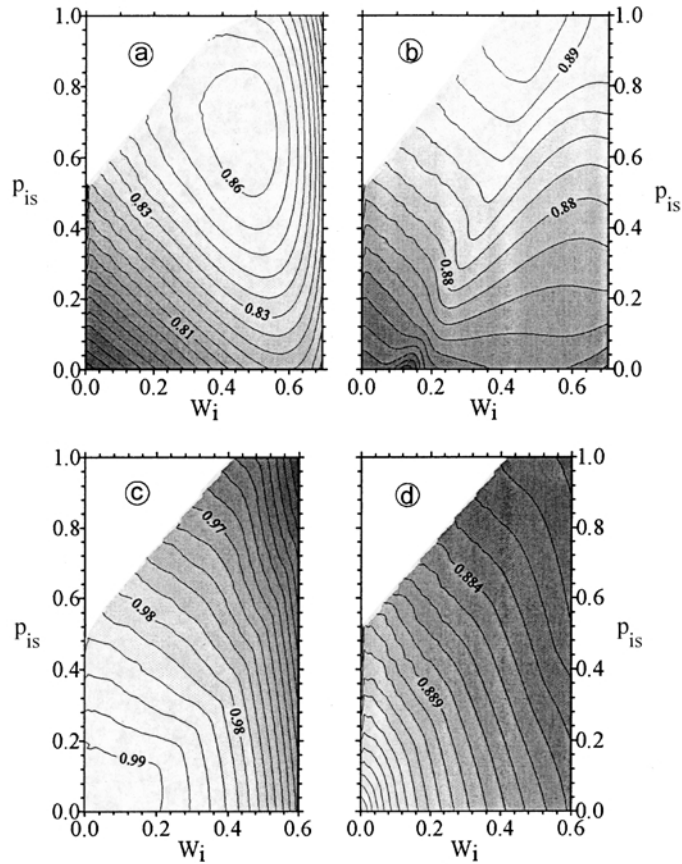


FIG. 5. The projection of maxima of coefficients of correlation between experimental and theoretical XRD patterns of glacial silty clay (a,b) and diatomaceous ooze (c,d) onto the plane of W_i – p_{is} parameters (the plane of concentration equates to a degree of ordering, where the subscripted i stands for the illite and the subscripted s for the smectite component) reduces the multi-dimensional distribution of correlation coefficients to two-dimensional distribution. (a,c) correlations for the entire profiles; (b,d) correlations in the moving range with a width of 20. The figure demonstrates clearly that the probability parameters for the main mixed-layer components of these samples are substantially different.

For complex multi-component systems, in order to estimate the degree of fitting between the experimental and simulated profiles, we used standard deviation of profiles and standard deviation of local curvatures of profiles as measures of discrepancy between the profiles. To calculate local curvatures we first used running averages to smooth the profiles and then for each point of the profile (except for the boundary points) we used moving range and local polynomial approximation of the profile to compute curvatures. The use of discrepancies of local curvatures to estimate the degree of fitting between the profiles gives

significant advantages over the conventional use of discrepancies of entire profiles because of higher sensitivity to mismatches between the extremes of the profiles and low sensitivity to trends. It is precisely these advantages that allow use of the effective algorithms of non-linear programming for optimization of parameters. The use of these algorithms minimizes the exhaustive search of parameters as opposed to methods of complete or adaptational exhaustion, used, for instance, in a genetic algorithm of Pevar and Schuette (1993). The use of conventional discrepancy to estimate the degree of fitting between the experimental and

simulated profiles is effective only in simple cases, which basically reduce to finding parameters of a single component, whose properties are known to a large extent.

Optimization of parameters

As a first step in the optimization procedures, the preliminary parameters are set based on crystallochemical considerations for each of the components clearly visible in the experimental XRD profile. The second step includes automatic calculations of optimal probability parameters, defining the layering sequences in the structure and the degree of ordering. In case the profile for one of the components is complicated, an additional step is taken to evaluate the initial parameters prior to the automatic optimization. In this additional step we revealed statistically non-perspective areas for the selected parameters in order to narrow the perspective areas for the optimal solution. In order to do this, the multidimensional matrix of average correlation coefficients in moving ranges of different widths is computed in the space of W_i-p_{is} parameters, where the subscripts i and s stand for the illite and smectite components (for illite-smectite), respectively. The use of ranges with different widths makes it possible to check the match/mismatch of the positions of a particular peak in experimental and theoretical profiles (Fig. 5a, b). The use of this method prevents the loss of potential solutions, because losses may occur due to the interfering effects of other mineral components. Usually, three different widths of moving ranges are enough for this procedure. The first width equals the whole range of angles ($^{\circ}2\theta$) on the diffraction profile and actually does not differ from standard deviation. The width of the second moving range corresponds to the breadth of local peaks on the XRD pattern. The recommended third width for the moving range equals the width of individual peaks at the level 0.5–0.7 of their amplitudes. The average correlation is calculated using the weight factors, which strengthen the contribution of certain peaks. The correlation coefficients calculated using small range widths make it possible to check the convergence of the shapes and positions of local peaks on theoretical and experimental profiles. This process does not consider the amplitudes of different peaks, because relative amplitudes can be corrected later using either the parameters not engaged in the process of

formal optimization, or the additional contribution from other mineral components.

The local extremes of the distributions of correlation coefficients are compared for all three widths of ranges. If the local extremes coincide at all widths, they are used as initial values for the next step of automatic optimization of parameters for accurate fitting. If the extremes do not coincide, then the whole set of chemical composition parameters used for this mineral phase has to be changed. If the extremes do not coincide for the new set of parameters, again, the component has to be changed, i.e. a different mineral phase has to be selected. The latent features of these multi-dimensional distributions of correlation coefficients may be found by the calculation of divergence fields of distribution gradients (i.e. using a Laplacian operator). These features can be used for isolating the areas prior to automatic fitting. Therefore, it is necessary to perform a preliminary analysis of the character of the multi-dimensional distribution of correlation coefficients aimed at finding the maxima of this distribution. For more convenience in the analysis we reduced the multi-dimensional distribution of correlation coefficients to a two-dimensional distribution by projecting the maximum values of correlation coefficients onto the plane of W_i-p_{is} parameters (the plane concentration-degree of ordering). This method makes it possible to localize the extreme values in a rather narrow zone. In addition, this zone is independent of changes in other parameters.

In the second step of the optimization procedure, the probability parameters of a mixed-layer phase and the parameters defining the domain-size distribution are computed automatically. The function of domain-size distribution affects the diffraction pattern in a complex manner, which might create considerable difficulties for automatic computation of the parameters of the diffracting domains. Reynolds (1985) used a set of relative probabilities to describe the occurrence of domains with different numbers of layers. We described the probabilities of domain-size distribution using the sum of two exponential functions with controlled amplitudes, slope and location of maxima. This way of describing the distribution function is a significant improvement. On the one hand, this function closely approximates the natural domain distributions, on the other hand, the instability in solutions of the domain distribution is minimized.

To compute the probability and the domain-size parameters we solve the system of non-linear equations. In these equations the right hand side consists either of: (a) discrepancies of curvatures in the observed and the modelled profiles, calculated in the moving range (breadth of local peaks); or (b) discrepancy of the entire profiles. The system is solved using the Levenberg-Marquardt method (Gill *et al.*, 1981).

In order to diminish the ambiguity of the solution, unlike in the algorithm of Pevear and Schuette (1993), we do not include the parameter Sigma star (σ^* , orientation parameter) (Reynolds, 1986; Walker, 1993) and concentrations of Fe and K in the automatic optimization procedure. There are two main reasons for this. Firstly, we include a larger number of parameters in our automatic procedure: in addition to the complete set of the parameters defining layering sequences we include the function of domain-size distribution. The influence of the latter on the theoretical diffraction pattern in the area of low angles is similar to the influence of σ^* (in part this is also true for Fe concentration). This might create non-uniqueness of solution and thus might slow or prevent convergence of the solution. To facilitate the process of automatic optimization and in order to fully control the uniqueness of a solution, we control the parameters σ^* and concentrations of Fe and K separately from the optimization procedure, i.e. these parameters are selected manually or using an automatic exhaustion. Secondly, the above parameters have little effect on the location of the peaks in theoretical diffraction patterns, whereas they strongly influence the relative intensity of these peaks. Therefore, if the discrepancies of curvatures are used as the right hand side of the equations, the rough estimates of these parameters do not lead to the failure of convergence in the process of computing the probability parameters and the domain-size parameters. This makes the process of progressive iterative optimizing of the parameters convergent.

If necessary, our algorithm allows some of the parameters to be fixed or limited to certain areas of their potential values. This feature may be used to either facilitate the convergence of the optimization process or check the hypotheses on non-uniqueness of solutions. For the most complex mixed-layered phases which always create the most difficulties for modelling, our algorithm includes exhaustion of the complete set of the probability parameters

(Solotchina *et al.*, 1999b, 2000). This allows us to check if there is another potential solution in terms of optimal parameters and thus to control the ambiguity of the solution. The fine fitting of the simulated to experimental XRD patterns is reached by progressive iterative optimization of parameters until the optimal fit is found. In the course of parameter fitting for one of the components, the contribution of other components may be changed automatically or manually at every iterative step in order to better fit the profiles.

The algorithm presented above allows complete deciphering of the experimental XRD profiles. For each of the components, the composition and structure can be identified with a high degree of confidence. Besides, the resultant quantitative estimates for each mineral phase of the clay component in the sample are especially important for constructing the clay mineral abundance profiles in Lake Baikal palaeoclimate reconstructions (Melles *et al.*, 1995; Solotchina *et al.*, 1998, 1999a; Yuretich *et al.*, 1999; Kuzmin *et al.*, 2000).

SIMULATION RESULTS

The simulation algorithm above was used to examine the composition of the clay component in both samples. Figure 6a,b illustrates the close fit of experimental and simulated profiles. The clay component of glacial sample A contains ~53% of fine dispersed disordered illite-smectite (with domains of 1 to 4 layers). Illite-smectite is estimated to contain 40% illite layers ($W_i = 0.4$) and to be characterized by the following probability parameters of ordering: $p_{is} = 0.1$, $p_{iis} = 0.8$). The K content in illite-smectite is small (0.4 K p.f.u.). The second most abundant component is muscovite (17%), with domains of larger size, up to 24 layers, and with high K content of 1 p.f.u. Illite is present in smaller amounts (10%). It is slightly K-deficient (0.8 K p.f.u.), and the domain-size ranges from 3 to 9 layers. Chlorite contents of up to 14% are found; domain sizes range from 11 to 24 layers.

The clay component of interglacial sample B consists primarily of disordered fine illite-smectite (67%), with domain size from 1 to 4 layers. Illite-smectite with an estimated 35% illite layers ($W_i = 0.35$) is characterized by probability parameters different from those in sample A: $p_{is} = 0.3$, $p_{iis} = 0.5$. The K content in illite-smectite of sample B is slightly lower than in sample A (0.3 K p.f.u.). Muscovite is present in small amounts (~4%); it is

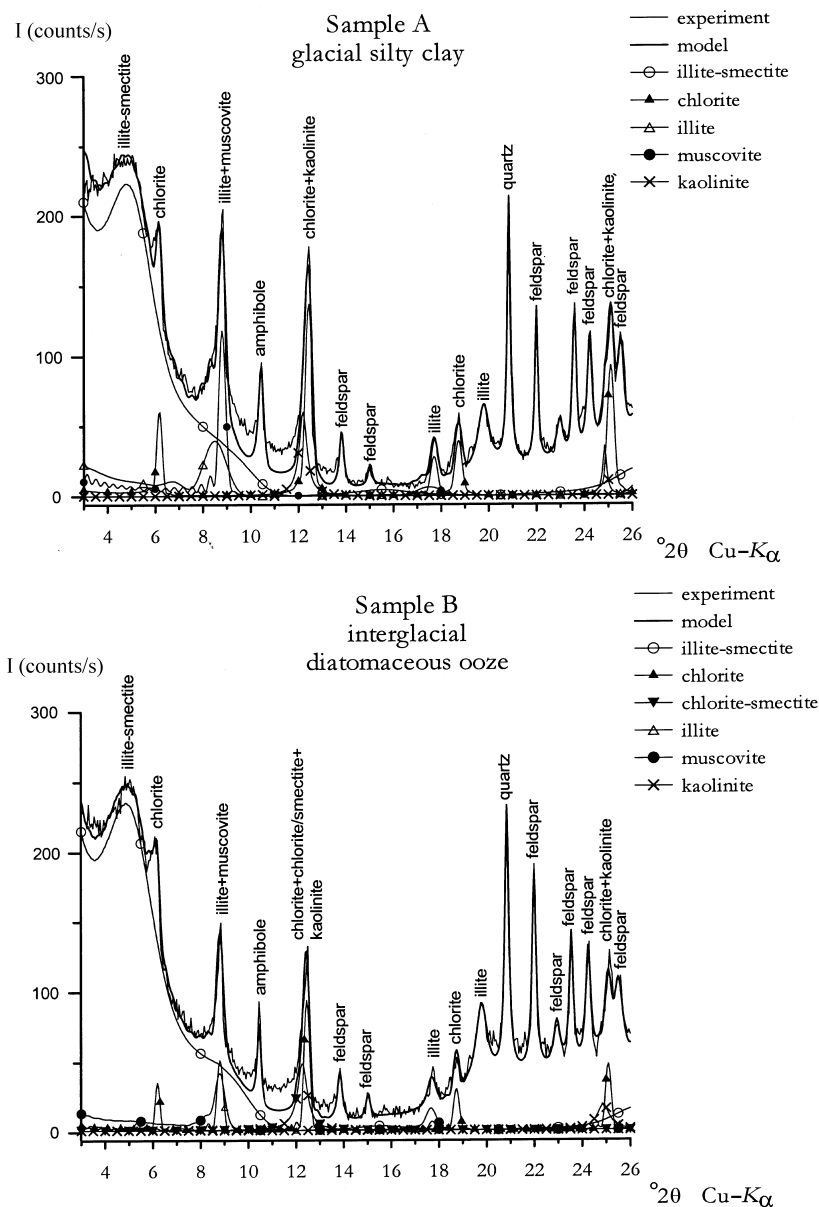


FIG. 6. The results of simulating the XRD pattern of bulk samples. On each plot two profiles at the top illustrate the fit between the model (thin line) and experimental profiles (heavy line). The lines at the bottom indicate the contributions of different layered-mineral phases to the modelled profile. For the interglacial sample B we modelled the filtered XRD pattern: the experimental profile of 30% Baikall biogenic silica was subtracted from the original XRD pattern of sample B prior to modelling.

again characterized by a large domain size of 22 layers and higher (the most abundant are the 25-layer domains). The illite content in sample B

(9.7%) is practically the same as in sample A, with the same K content (0.8 p.f.u.) and similar domain size (1 to 8 layers). The estimated chlorite content

in sample B (9.7%) is lower than in sample A, whereas the domain size is larger: 19 layers or more; the 22-layer domains are the most abundant. In addition, the modelling results suggest that sample B contains 2.7% of ordered mixed-layer chlorite/smectite with 85% chlorite layers ($W_{\text{ch}} = 0.85$). The optimal fit is achieved for this phase when using large domains, from 11 to 17 layers (mostly 14–15 layers). Ordering has the following probability characteristics: $P_{\text{chs}} = 0.8$, $P_{\text{chchs}} = 0.86$, where the subscripted ch stands for chlorite, and subscripted s for the smectite component. Kaolinite is not abundant, and its estimated content in both samples A and B is similar (5.6 and 6.9%).

DISCUSSION

X-ray analysis shows that clay components of glacial and interglacial sediments of Lake Baikal belong to the same clay association: illite-smectites, illite and chlorite with a minor contribution of kaolinite. The associated non-layer minerals also remain the same: quartz, feldspar and amphibole in small amounts. The distribution of clay minerals in different fractions is slightly different between glacial and interglacial samples. Detrital quartz and chlorite tend to concentrate in coarser fractions, illite and plagioclase appear to be evenly distributed among all fractions. The biggest difference, however, is in the distribution of illite-smectites. In glacial clays, illite-smectites dominate in the finest $<1 \mu\text{m}$ fraction whereas, in diatomaceous ooze, extreme enrichment in illite-smectites is observed in the $<2 \mu\text{m}$ fraction. One of the most evident implications of such differences is that the conventional method of separating a certain fraction by Stokes' settling for X-ray analysis would yield incompatible results for glacial and interglacial sediments of Lake Baikal. Therefore, selective use of one fraction is a potential source of uncontrolled errors that has to be avoided when attempting palaeoclimate reconstructions based on clay mineral assemblage.

The algorithm developed for modelling the XRD patterns yields consistent solutions for the multi-component clay mineral association of Lake Baikal sediments. It deals successfully with the low peak intensity displayed by Baikal XRD profiles, with superposition of diagnostic peaks of layered phases, and it avoids decomposition of spectra into areas by summing the contribution of all layered and non-layered phases at every iterative step of modelling.

One of the most important results of applying a modelling algorithm to clay associations of Lake Baikal is a quantitative estimate of clay mineral abundance. This is especially important for future interpretations of the watershed response to glacial/interglacial cycles because, as shown by our study and previous works, the clay mineral association in Lake Baikal sediments basically remains the same during cold and warm periods and quantitatively only the relative abundance of illite-smectites, muscovite and illite are systematically changing. The efficiency of the method was revealed by modelling the spectra of two different samples from the same interval of 252 cm in the Baikal core BDP-93-2. Despite the analysis and modelling for these samples conducted separately, fitting resulted in a close convergence of the modelled abundance and structure of clay mineral phases: $46.2 \pm 2.6\%$ of illite-smectite containing an estimated $46.5 \pm 2\%$ illite layers; $22.8 \pm 0.8\%$ of chlorite with an estimated 98% of chlorite layers; $4.9 \pm 0.2\%$ of illite; $19.7 \pm 1.3\%$ of muscovite and $6.5 \pm 0.3\%$ of kaolinite (Solotchina *et al.*, 2001).

Another outcome of modelling is the estimate of chemical composition and structure of clay minerals. For instance, detrital chlorite during glacial periods does not contain smectite layers, whereas during interglacial periods this mineral phase is represented by both chlorite and chlorite-smectite with 15% smectite layers. This might be indicative of more active weathering processes in the Lake Baikal watershed during warm periods. Illite-smectites of glacial and interglacial periods also reveal structural differences. The degree of ordering in interglacial illite-smectites is slightly greater than in the glacial sample. Also, the content of smectite layers in interglacial illite-smectites is slightly greater. Different lines of evidence, such as the degree of ordering, the smectite layers content, the pronounced concentration of illite-smectites in the $<2 \mu\text{m}$ fraction and the overall greater abundance of this phase in clay components of interglacial diatomaceous ooze imply differences in genesis of illite-smectite during glacials and interglacial periods.

CONCLUSIONS

The clay component of typical glacial and interglacial intervals in bottom sediments of Lake Baikal is represented by the same mineral association. Quantitative estimates of clay mineral phases are therefore important in revealing the

watershed responses to Pleistocene climatic cycles. The comparative analysis of three different fractions indicates that none of the fractions is equally representative of the clay component of the bulk sample. Modelling XRD spectra of the bulk sample is therefore recommended as the preferred method of analysis of clay component of Lake Baikal sediments. The conventional method of fraction separation by Stokes' settling yields inadequate results and further scatter of data is introduced by the use of different sample preparation techniques.

The new effective algorithm developed by the authors is proposed for modelling the complex XRD patterns. The method is based on the calculation of the interference function of one-dimensional disordered crystals with finite thickness. The algorithm allows complete deciphering of the experimental XRD profiles. For each of the components the composition and structure can be identified. An important part of our new algorithm is the automatic optimization procedure, which allows fine fitting of the simulated to experimental XRD patterns by progressive iterative optimization of parameters for clay mineral phases. This procedure is more time-efficient than an exhaustive search of parameters and allows better control of the uniqueness of the solution.

Our preliminary results of testing the algorithm on typical Baikal glacial and interglacial samples indicate that besides changes in the relative abundance of illite and illite-smectite between glacial and interglacial periods, significant differences are observed in crystal chemistry and structure of layered minerals. A change from chlorite during glacial periods to chlorite-smectite during interglacials is probably indicative of the weathering processes in the watershed. Changes in the degree of ordering, in the smectite layer content and in the grain-size distribution of illite-smectites imply differences in genesis of this mineral phase in different palaeoenvironments. These findings further strengthen the case for using clay minerals as palaeoclimate indicators in the sedimentary record of Lake Baikal.

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