Application of the solid solution model for the description of the mineral composition of lake Baikal bottom settings

A V Oshchepkova 1, 2, a, V A Bychinskiy 2, b and E A Luk’yantseva 1, c
1 Irkutsk State University, Irkutsk, Russia
2 Institute of Geochemistry SB RAS, Irkutsk, Russia

E-mail: a oshepkova-anasta@mail.ru, b val@igc.irk.ru, c ekaterina-lukyanceva@mail.ru

Abstract. The study of clay minerals, accumulated in the Baikal bottom settings, provides valuable information about climate changes in Asia during the Cenozoic Era. However, the depth of a sedimentary section does not allow conducting mineralogical studies at a pitch providing a reconstruction of the paleoclimate record with high resolution. Earlier, the mineral composition of the Baikal sediments has been calculated on the basis of the results of a chemical analysis [1]. At a preliminary stage the simplex-method, used in this approach, requires the determination of a chemical composition of the clay sedimentary components and the calculation of conditional stoichiometric formulas of mixed-layer aluminosilicates, being the markers of the most important paleoclimate episodes. In this article the improved method for calculating the mineral composition of sediments is used to determine the mixed-layer minerals of a solid solution model, is represented. It allowed eliminating the preliminary stage of clay matter chemical composition calculation and computerizing the determination of minerals stoichiometric formulas, corresponding to warm and cold climate episodes in the reconstruction of paleoclimate changes.

Introduction
The bottom settings of Lake Baikal store information about paleoclimate changes in Asia during the Cenozoic Era. A successful implementation of the project "Baikal Drilling" made it possible to get core samples of Baikal settings up to 600 meters deep [2]. Settings of the Academic ridge, exposed by wells BDP-96 and BDP-98 are of the great interest. The ridge is separated from the lake shores by two deep-water basins. Therefore its settings are formed with the substance, coming from the water layer. It allowed to determine the periods of "warming-cooling", cohering with the marine isotope curve, by the content of biogenic silica in the settings [3].

The study of material composition of Lake Baikal bottom settings, including their clay component, is an important part of paleoclimate reconstructions. It has been established that during the cooling period physical erosion predominated. It was characterized by coarse-grained settings, containing minor amounts of clay material. In warm climate conditions, chemical weathering processes become more active, and, respectively, soil formation processes, related to clay formation, intensify [4, 5]. Low salinity of Baikal water and low temperature prevent a mineral formation in the water layer, and as a result, the setting is formed of fine grain material, brought from the catchment basin. The great thickness of sedimentary layer makes a detailed X-ray phase analysis long-lasting and expensive. Therefore, before starting a detailed mineralogical analysis, it is advisable to use computational methods based on data of settings chemical composition [1, 6].
Calculation of the mineral composition of Baikal bottom settings, based on the data of a chemical analysis

In the works of E.P. Solotchina [5], G. Muller [7], the results of studies of a mineral composition of Baikal settings are presented. Due to the X-ray phase analysis, layered aluminum silicates, quartz and plagioclase (mainly, albite) were found in the deep-water settings of the Academic ridge. Potash feldspar and amphibole were found only in trace amounts. Clay minerals are presented as illite, chlorite, smectite, muscovite, kaolinite, being the main components of hemipelagic settings of the lake during the interglacial and glacial periods [5, 8]. Muscovite and chlorite are considered to be detrital minerals, brought out from the bed rock of the catchment area, the great amount of which indicates the climate cooling. Mixed-layer minerals – illite and smectite, formed in soil, increase in number during warm climate periods. It allows identifying the warm and cold climate periods based on the proportion of these mineral groups.

Previously, an algorithm has been developed to calculate the mineral composition based on chemical analysis data, and it applies the simplex-method, a significant limitation of which is the application of classical crystallochemical formulas of minerals. But mixed-layer minerals are interlaid minerals that are two- or three-layered aluminum silicates with adsorbed elements in the interlayer space. Due to the erratic chemical composition, the formalism of a mineral description is based on the application of variable coefficients in the stoichiometric formula that excludes the use of simplex-method in these calculations. In works [1, 6] it has been shown that if a total setting mineral composition is known, it is possible to calculate the total chemical composition of clay minerals, and on the basis of the latter to determine conventional stoichiometric formulas of the main groups of mixed-layered aluminum silicates: smectite, chlorite and illite. In this approach, the correlation of the total setting chemical composition with the data of the X-ray phase analysis is an obligatory stage of the calculation. As the X-ray phase analysis was performed for a restricted number of samples from the key horizons, it is hard to apply the simplex-method for the whole sedimentary section. The conventional stoichiometric formulas of clay minerals, calculated for samples corresponding to warm and cold periods, may add considerable error to results of mineral composition calculation for the same Holocene-Pleistocene settings from other cores taken in basins with different conditions of sedimentary accumulation.

Using the software complex “Selector” [9], the mineral composition calculation can be solved without a preliminary determination of the clay stoichiometry. The physicochemical model calculates a mineral paragenesis depending on the chemical composition and independent variables of the system state (temperature, pressure, volume, activity factors) [10]. Three models of solid solutions are used for a complex mineral phase description: subregular, Darken's quadratic formalism model and model of perfect disordered solid solution [10, 11, 12]. In the work the model of disordered solid solution was taken as the basis to calculate the equilibrium of the following mineral phases: illite, illite-smectite, chlorite. At the final stage, the equilibrium solid solution is calculated into a common conventional formula according to the mole quantity of minerals presented in a solid solution based on methods proposed by A.G. Bulakh [13].

For Baikal bottom settings, the mineral composition is reconstructed; the setting is presented as a mixture of clay minerals (chemical weathering products) and minerals formed under completely different conditions: quartz, feldspar, muscovite, chlorite. The appropriate use of methods of the thermodynamic modeling of non-equilibrium mineral composition requires calculating the metastable Gibb’s potential for xenogenic minerals (muscovite, feldspar). This allows determining the metastable equilibriums and provides a high reproducibility of the physicochemical modeling with data of the X-ray phase analysis.

The principle of the thermodynamic model is a list of potential mineral in equilibrium, composed according to the data of the X-ray phase analysis. The greatest attention has been paid to the formation of the solid solutions of mixed-layered aluminum silicates – illite, smectite, chlorite. The actual isomorphic substitutions (replacements) occurring during the formation of mixed-layer mineral phase, can be described by mathematical methods using the list of minerals, including all variations of its
Results of the mineral composition reconstruction based on solid solution model application.

The presented method for calculating mineral composition is used in the study of bottom settings from the well BDP-96 (the Academic ridge). Samples were taken from 18.45 and 32.59 m deep. The sample from the depth of 18.45 m is characterized by a high content of biogenous silica (39.6 – 46.2 %), and corresponds to the 11th warm interglacial stage according to the marine isotope-oxygen curve; its age is 410 thousand years. The setting from the depth of 32.59 m was accumulated during the 18th cold climate episode of the marine isotope-oxygen curve; its age is 760 thousand years. The biogenic silica content in this sample forms the first percentages [5].

These samples shall be considered as standard samples that allow assessing the calculation accuracy (table 1).

Table 1. Mineral composition of Baikal bottom settings from well BDP-96, mas. %.

| Depth, m | Non-layered minerals | Layered minerals |
|---------|----------------------|------------------|
|         | Quartz | Feldspar | Total | Illite | Illite-smectite | Chlorite | Chlorite-smectite | Chlorite | Kaolinite | Muscovite |
| 18.45   | XRD    | 12.60    | 12.60  | 25.20  | 23.00  | 34.00  | 5.20  | 4.00  | 1.90  | 6.70  |
|         | Calculation | 12.75 | 20.91  | 33.66  | 23.93  | 30.96  | 4.40  | 0.00  | 5.59  |
| 32.59   | XRD    | 17.70    | 16.80  | 34.50  | 0.00   | 31.80  | 4.10  | 6.40  | 2.60  | 20.80 |
|         | Calculation | 26.86 | 19.44  | 46.31  | 13.22  | 22.46  | 5.81  | 0.00  | 11.76 |

Note. XRD – data of X-ray phase analysis; calculation – data received using the software “Selector”.

It should be noted that it is not easy to coordinate the results of X-ray phase analysis with the calculation data and results of chemical analysis. As in any algorithm for a mineral composition calculation minerals with the stoichiometric formula and strictly-defined coefficients are used, while in X-ray phase analysis the phase of mixed-layered minerals are defined as a set of aluminum silicate layers different in structure. Such phases possess an inconstant chemical composition.

However, in spite of different magnitudes of crystal structures content, evaluated by different methods, the proportions of mixed-layered silicates and non-layered minerals are preserved. The main purpose is not to develop a method of mineral composition precise calculating, but to develop an express method to assess the clay minerals content, which allows identifying cold and warm episodes and decoding climate changes within the region during the studied period. Both methods distinguish invariably of warm and cold climate episodes. The change of illite / illite-smectite proportion turned out to be a reliable indicator of paleoclimate changes; the X-ray phase analysis describes this proportion as the content of illite layers, while the physicochemical models describe it as the increasing of illite content [6].

In simplex-method calculations by a chemical composition of clay part setting the conditional formulas have been calculated, describing the illite-smectite group in aggregate [1]. It has been shown on its base that the content of non-layered minerals along with muscovite and chlorite increases in settings accumulated in cold climate episodes, and illite and illite-smectite prevail in warm climate periods. The conditional formulas of mixed-layered minerals were calculated out of the total clay chemical composition at the first stages of the study, which deprives this approach of universality.
The application of the solid solution model allows determining the conventional formulas of mixed-layered aluminum silicates, related to glacial and interglacial episodes. They were calculated automatically without preliminary calculations. As it was noted above, it is hard to show the structure and composition of mixed-layered mineral, such as illite, with a strict stoichiometric formula. Usually, it is described as K$_{0.75}$(Al$_{1.75}$)Re$_{0.25}$(Al$_{0.5}$Si$_{3.5}$)O$_{10}$(OH)$_2$, where Re – is divalent cations of Mg or Fe, interlayer cations K$^+$ can be partly replaced with Ca$^{2+}$, Mg$^{2+}$, H$^+$, sometimes – with Na$^+$ [5]. The following conventional formulas of mixed-layered minerals are automatically calculated in the solid solution model:

Depth 18.45 m:
illite   K$_{0.5}$Fe Al [Al$_{0.5}$Si$_{3.5}$]$_4$O$_{10}$(OH)$_2$; (23.93 % weight)
illite-smectite K$_{0.013}$Na$_{0.053}$Ca$_{0.106}$Fe$_{0.218}$Mg$_{0.43}$Al$_{1.439}$[Al$_{0.107}$Si$_{3.893}$]$_4$O$_{10}$(OH)$_2$. (30.96 % weight)

Depth 32.59 m:
illite   K$_{0.5}$Fe Al [Al$_{0.5}$Si$_{3.5}$]$_4$O$_{10}$(OH)$_2$; (13.22 % weight)
illite-smectite K$_{0.013}$Na$_{0.074}$Ca$_{0.094}$Fe$_{0.226}$Mg$_{0.426}$Al$_{1.434}$[Al$_{0.109}$Si$_{3.891}$]$_4$O$_{10}$(OH)$_2$. (22.46 % weight)

It is essential to determine the general stoichiometric formula because the layers of various types, separated by different interlayered intervals, alternate in mixed-layered minerals [5].

These peculiarities of mixed-layered minerals structure and composition reflect changes in physical and chemical conditions of weathering process, thus, the mixed-layered phases, related to both warm (illite), and cold (illite-smectite, smectite) episodes, may be formed from the same solid solution.

Conclusions

Thus, the data calculated using the physicochemical model do not give accurate quantitative information about the mineral composition, but these data contain an expressive evaluation of the clay to non-layered minerals proportion, which allows reconstructing the catchment weathering conditions based on chemical composition only.

The mixed-layered minerals were included in the model as solid solutions (a set of minerals), enabling to describe a wide range of aluminum silicate layers proportions. The calculated results were compared with the data obtained by XRD-method (see Table 1). It should be noted that modeling of mineral composition is the way to identify warm and cold climate episodes. Despite the variations of calculated amounts of mineral phases from the XRD-analysis data, high accuracy in identifying the main climate episodes by proportions of clay and detrital phases is preserved. In warm periods the illite content and total amount of clay minerals increase (the amount of illite, illite-smectite, chlorite-smectite), in cold periods, the non-layered minerals (quartz, feldspar) and detrital muscovite and chlorite prevail in settings.

The evaluation of the developed method will be tested on key sections of Baikal deep-water, settings of the Holocene-Pleistocene period. A wider application of the developed method requires a specified list of minerals of illite and montmorillonite solid solutions, which is the main target of further studies.

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