Experience of Stadial Analysis for Investigating Ultramicrocrystalline Rock (The Case of Structureless Phosphorites of the Okino-Hubsugul Basin)

A F Georgievskiy¹, V M Bugina¹

¹Peoples’ Friendship University of Russia (RUDN University), Moscow, Russia

E-mail: georgievskiy-af@rudn.ru

Abstract. Any sedimentary rock is a complex natural formation, which was formed under the influence of many processes. One of the aims of lithologists is the occurrence and study of these processes, which is necessary for targeted searches for mineral resources associated with sedimentary rock. Analysis of order of mineral crystallization (stadial analysis) is the most successful method to solve the problems. That analysis is a brunch in lithology science aimed at reconstructing the geological history of rock. The step-by-step analysis includes methods of prospecting, optical and electronic microscopy, and diagnostics of the material composition of minerals. However, the researcher receives basic information about the processes of rock formation through microscopic observations of the features of minerals: their shapes, sizes, composition, interrelations, as well as structural and textural features. In the course of such observations, “indicator components” of rock are established with obvious signs of duration and conditions of its formation: sedimentary “indicator components” (biogenic detritus, allothigenic fragments, tufogenous material), dia- and katagenetic (nodule concretions and other varieties), metagenetic “indicator components” (crystalloblasts etc.). Further analysis of the secondary alterations in the mentioned components and their minerals allows us to make series of consistent mineral formation and, thereby, reconstruct main stages and conditions of rock formation. This, in turn, provides the key to understanding the regional geological processes that took place in sedimentary basins.

1. Introduction
The foundations of analysis of order of mineral crystallization were laid in the middle-end of the last century thanks to the works of scientists [1-9]. Its applied meaning is shown in listed publications [10-16]. The methodology of analysis, its methods and techniques, as well as methods for solving problems are considered in textbooks of Japaskurt [17,18]. As shown in all these works, the main (initial) object of study is the mineral individual (grain, crystal) with its external and internal features, the changes of which can be recorded by optical observations. At the same time, there are number of rock types with a colloidal submicrocrystalline (aphanitic) structure invisible to optics. This rock includes most bauxites, manganolites, ferrolites, many silicites (lydites, phitanites, cherty flints), as well as phosphorites. In this case, electronic microscopic studies of rock using scanning electron microscope (SEM) and transmission electron microscope (TEM) become effective methods of stadial analysis. Each of those apparatus has its own capabilities and therefore their application is dictated by
research tasks, mineral composition and rock structure. A performance potential of TEM for studying phosphorites is clearly shown in papers [19-22].

The successful application of TEM for the stage-by-stage mineralization analysis of cryptocrystalline rocks demonstrates the results of the study of aphanitic phosphorites of the Okino-Khubsugul basin. It is located on the Southeastern Sayan Mountains in the border areas of Mongolia and Russia. Here, among the sediments of the Ediacaran system, more than a dozen phosphorite deposits have been identified, among which the large ones (with commercial reserves) include Burenkhan, Khubsugul, Ukhagol and Kharanur [23-26]. The main types of ore deposits are layered aphanitic phosphorites, which were formed as a result of early diagenetic phosphatization of carbonate and clayey sediments [27]. Macroscopically, that is a rock composed of monomineral phosphate laminae alternating with thin bed of dolomite rock. The thickness of the laminae is from the first mm to 10-20 cm. In the thin sections, the phosphate is isotropic with an aphanitic (homogeneous, structureless) structure. Of the secondary processes, catagenic dolomitization, calcification, silicification, dynamic metamorphism and karst changes are strongly marked.

2. Materials and methods
The aim of this work is to evaluate the effectiveness of the use of order of mineral crystallization analysis in the study of cryptocrystalline phosphate secretions by TEM methods. The factual material for the study was more than 50 samples of sedimentary-diagenetic, metamorphosed and karst phosphorites picked up during prospecting of the main deposits of the Okino-Khubsugul basin. Samples were studied in the laboratories of RUDN and RGGRU using optical (POLAM L-213M) and scanning (EMMA-4) electron microscopes. Electron microscopy was carried out using replicas - graphite films obtained by vacuum deposition.

3. Results and discussion
Phosphate, isotropic in thin sections, at 10 000 magnification, is a complex crystalline aggregate of fluorapatite mineral. As studies have shown, the mineral went through a difficult transformation from a gel-like to crystalline state and is divided into three groups that correspond to non-metamorphosed, metamorphosed and karst (infiltration-metasomatic) phosphorites. An analysis of the ultra-microstructures of these groups makes it possible to establish the nature of its change at various stages of phosphorite formation. Phosphate mineral phases are connected with the pre-metamorphic stage, forming a sequential crystallizing series: jelly substance (Figure 1); radial spherulite and fan-shaped isolations of needle-shaped crystallites (Figure 2); well-formed crystals of long columnar habit, grouped into spherulitic formations (Figure 3); prismatic drusoid crystals filling the space between the

**Figure 1.** The jelly phase of the phosphate substance of the aphanitic phosphorites of Okhino-Khubsugul basin. (TEM, 7500’)

**Figure 2.** Unclearly shaped needle-like crystallites (1.5-3µ) of the initial stage of crystallization of a jelly substance. (TEM, 7000’)

**Figure 3.** Well-shaped crystals of columnar habit (1.5-3µ), grouped into spherulitic formations. (TEM,10500’)
spherulites (Figure 4); aggregates of short-columned crystals formed during the recrystallization of radial forms with (Figure 5) and without relicts of original structures (Figure 6).

It is interesting to note that the identified phosphate components and the established order of their mineral formation are almost similar to those that were identified by Baturin et al. [28-30] in modern and quaternary ocean phosphorites. Using the data of those researchers, it is possible to clarify the time of formation of the phosphate components of the identified series. Obviously, by analogy with young phosphorites, the transformation of a jelly substance into crystalline radial and spherulitic aggregates occurred during lithification. The formation of the remaining components of phosphate proceeded in early and late catagenesis. Further phosphate transformation was associated with dynamic metamorphism and alteration processes. Under dynamic metamorphism, primary ultramicrostructures were transformed under the influence of directional pressure into homogeneous aggregates of strongly elongated prismatic crystals, whose sizes are by an order of magnitude larger than crystalline individuals of non-metamorphosed phosphorites (Figure 7). In aggregates, alternation of zones with oriented and non-oriented crystal placement is observed, which led to a micro-flaky (shale) structure of phosphate.

Under the influence of weathering processes, phosphate changes were diverse. For this purpose, a sample of monomineral phosphorite with a rim of weathering at the edges was studied. A consistent electron microscopic examination of the sample from the center to the periphery showed that phosphate becomes structureless upon weathering (Figure 8).
Karst phosphate looks absolutely different. It consists of a jelly and crystalline substance. The jelly phase composes the cellular framework of phosphorites. Crystalline phosphate, in the form of a diverse aggregates of needle-columnar crystals of apatite, grows like a drusoid on the walls of numerous micropores (Figure 9).

4. Conclusions
According to electron microscopy, aphanitic (structureless) phosphate is a complex cryptocrystalline aggregate, the individual crystalline phases of which were formed throughout the history of the formation of the rock: sedimentogenesis, dia- and catagenesis, as well as metamorphism and weathering processes.

TEM and SEM methods can effectively use the order of mineral crystallization (stadial) analysis for rock composed of cryptocrystalline mineral aggregates.

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