Chemistry for Sustainable Development **10** (2002) 387–401

Ecological and Mineralogical Characterization of the Phosphorites from the Khubsugul and Dzabkhan Phosphorite-Bearing Basins of Mongolia

MARINA V. CHAIKINA[1], J. AMGALAN[2], F. BATTSETSEG[3], A. DORJPALAM[3] and D. BAYARAA[4]

[1]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)*

E-mail: chaikina@solid.nsk.su

[2]*Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences,*
Pr. Mira 54-26, Ulaanbaatar 51 (Mongolia)

[3]*National University of Mongolia,*
Ikh Surguulin Gudamy 1, P. O. Box 46/337, Ulaanbaatar 210646 (Mongolia)

[4]*State Pedagogical University,*
Baga Toiruu-14, Ulaanbaatar 210648 (Mongolia)

Abstract

The composition of minerals, the structure of apatite and the content of ecologically controlled elements in the phosphorites from the Khubsugul (KhPB) and Dzabkhan (DPB) phosphorite-bearing basins of Mongolia are investigated. The structural chemical and mineralogical classification of the phosphorites is performed. With respect to the mineralogical composition, the major part of phosphorites belongs to the cherty and carbonate-siliceous types. The phosphate substance of the KhPB and DPB deposits is represented by hydroxylcarbonatefluoroapatite. As regards the ratio of the major components, the apatites comprising these phosphorites belong to the first subgroup of the alkaline type, *i. e.* are phosphorus-deficient with respect to the stoichiometric composition. The content of trace elements in phosphorites was estimated using the dimensionless universal characteristics, *i. e.* ecological index of phosphates, which was 1.186 for the phosphorites of the Khubsugul deposit and 1.643 for the Burenkhan deposit, which means their ecological safety and suitability for use as fertilizers without chemical processing and enrichment. The proposed classification and ecological evaluation are necessary for solving the problem concerning the choice of an optimal technology of phosphorite processing, including mechanochemical treatment as the simplest and ecologically safest one. The classification can be useful for solving the genetic problems and for the search for new phosphorite deposits.

INTRODUCTION

There are two world's largest phosphorite-bearing basins in Mongolia: the Khubsugul (KhPB) and Dzabkhan (DPB). More than 30 large and small deposits of phosphorites are explored in the former and about 20 in the latter, with the mean phosphate content of 15 to 28 % P_2O_5; in some cases it reaches 39–40 % P_2O_5 [1–5]. The predicted resources of the Khubsugul and Dzabkhan phosphorite-bearing basins are more than 4.5 and 1.2 billion tons of ore, respectively [3–5]. The development of the deposits of phosphate ores using optimal methods of their processing should play an important role in improving the economical status of Mongolia surviving the difficulties of the transition to the market economy. The importance of a multi-aspect investigation of phosphate ores and of the development of optimal processing methods for the most rapid development is evidenced by the instructions of the Government of Mongolia to the Mongolian Academy of Sciences on the development of the project "Phosphorite". This investigation was carried out within the bounds of the Agreement on collaboration between the Siberian Branch of the RAS and the Mongolian Academy of Sciences.

In order to achieve economical reasonableness of the usage of phosphate ores, the existing methods of processing put forward strict requirements to the quality of raw material, determined as the phosphate content and the presence of harmful admixtures, which causes additional consumption of raw material and brings complications into the processing [6]. A substantial part of the phosphorite ores of the KhPB and DPB, processed by conventional methods, must be enriched to obtain concentrates with P_2O_5 content of 28–30 % [7].

The choice of enrichment and processing procedure is determined by the specificity of mineral composition and type of apatite comprising the phosphorite [8, 9]. The ecological aspect is another important item in characterizing the phosphate raw material and fertilizers made of it. Phosphate ores contain a broad variety of trace elements; some of them pass into the fertilizers during manufacture, are brought into soil, get assimilated by plants and thus bring danger for human health in the case of the increased content [10].

One of the promising methods of processing the phosphorites of the KhPB and DPB is mechanical activation for the purpose of obtaining ready-to-use fertilizers. During mechanochemical processing of phosphate ores, all the admixtures and elements and trace fully remain in the fertilizer and pass into soil. Because of this, a detailed investigation of the ores of the Khubsugul and Dzabkhan phosphorite-bearing basins, which are unique in the scale and structural features of apatite in phosphorites of them, and the content of trace elements has not only the scientific interest but is urgently needed for reasonable and efficient development of the deposits. The major part of works considering the KhPB and DPB is dedicated to the studies of ore genesis, character of their bedding, interconnection of the phosphate substance with other minerals, *i. e.* mainly to the problems related to geology and geochemistry [1–5]. The authors of [1, 11] investigated the changes of the phosphate substance of the ores from the Khubsugul basin formed in sea water and had survived numerous transformations and interactions with the accompanying minerals during the subsequent long period of existence on land (for 500–800 mln years), under great pressure and increased temperature.

The substantial and chemical composition of the phosphorites from the KhPB and DPB is reported in most detail in [1, 3]. On the basis of the data of chemical analysis of more than 1000 samples of phosphorites for the content of the major components – P_2O_5, CO_2, CaO, F^-, MgO, Al_2O_3, Fe_2O_3, Na_2O, K_2O, SiO_2 – the author of the monograph [1] did not manage to compose a full general characteristics of the chemical nature of the KhPB phosphorites because of large nonhomogeneity of their chemical composition. The chemical and substantial composition is characterized in [1] on the basis of the classification of phosphate ores from the KhPB with respect to the texture and structural modifications of phosphate substance and the accompanying minerals; in the group of chemogenic and fragmental debris, the author classified the subgroups: aphanitic phosphorites, granular, sandstone, coarse, among which the modifications of the carbonate and siliceous composition are revealed [1].

In [1], only the data on deposits and phosphate occurrence of the Khubsugul basin are embraced, except very large Burenkhan deposit which was discovered later [4]. Publications concerning chemical and mineralogical characteristics of the phosphorites of the Dzabkhan phosphorite-bearing basin, which was discovered twenty years later than the KhPB, are very scarce [3, 5]. The authors of [12] report the data on the content and distribution of trace elements in some deposits of the Khubsugul phosphorite-bearing basin.

The authors of [10] proposed a procedure of the overall ecological evaluation of the content of ecologically monitored elements (EME); we used this procedure in the present investigation.

The goal of the present work is comparative characterization of the mineralogical and chemical composition of phosphorites of the Khubsugul and Dzabkhan phosphorite-bearing basins of Mongolia, which are the richest in resources and promising for development; ecological evaluation and structural chemical classification of the apatites comprising them. In addition to research interest, these data can serve as the basis for the recommendations related to an optimal technology of processing, in particular mechanochemical processing, as the simplest and ecologically safest method.

EXPERIMENTAL

The samples of the phosphorites of characteristic diversities from the largest and better explored deposits of the KhPB (Burenkhan, Zhankhay and Ongilignur) and DPB (Alagiyn-Daba and Tsakhir-Ula) were investigated. We also used the literature data on the chemical composition of phosphorites from some KhPB deposits and on the content of trace elements in them [1, 10, 12]. Petrographic investigation of the texture and structure of phosphorites was performed by studying the polished sections with the help of optical microscope at a 100–400-fold magnification. Chemical analysis for macrocomponents was performed in the geological laboratory of Mongolia according to the manual for the analysis of phosphate ores [13]. Apatite monofractions were isolated by means of centrifuging the phosphorites in heavy liquids at the Laboratory of Physical Chemistry of ICCT, MAS. Trace elements Mn, Cu, Zn, As, Pb, Hg, Cd, Co, Ni, Cr, Ba, Sr, V, U, Th, Y and rare earths were determined by X-ray spectral, fluorescent, atomic absorption, γ-spectral and photometric techniques [3, 10, 12]. The content of phosphate soluble in 2 % citric acid solution (CASP) and in ammonium citrate with pH 9 (ACSP) was determined according to the State Standard (GOST) [14].

X-ray phase analysis was performed with the JIB instrument (Japan) ($\mathrm{Cu}K_{\alpha}$ radiation, Ni filter, $U = 40$ kW, $I = 40$ mA). The infrared spectra were recorded with Specord-75 DR instrument, samples were pressed as tablets with dried KBr. Thermal analysis was performed with a Q-1500 D instrument within temperature range 25–900 °C. ESR spectra were recorded with Radiopan SE/X-2544 (Poland) at room temperature ($\lambda = 3.2$ cm, $f_{\mathrm{mod}} = 100$ kHz) before and after irradiation at the experimental stand of the Institute of Nuclear Physics, SB RAS, equipped with the ELV-6 electron accelerator. The energy of accelerated electrons during irradiation was 1.4 MeV, the absorbed dose was 3 Mrad. The irradiation of samples was necessary to increase the intensity of spectra for the purpose of more exact interpretation of the paramagnetic centers initially present in the sample.

RESULTS AND DISCUSSION

Texture and structural characterization of the phosphate ores

For reasonable usage of phosphate ores, it is necessary to know the chemical composition of phosphorites and minerals comprising the ore, as well as the character of their interconnection in the rock itself. The degree of intergrowing and phase state of the minerals in phosphorite affect the enrichment and other properties of the ores. According to the data of petrographic investigations, the phosphorites from the KhPB and DPB are characterized by different forms of the occurrence of phosphate substance and by the variety of texture combinations of phosphate and accompanying minerals [1, 3–5, 11]. The variety and intricacy of the intergrowth of minerals comprising phosphorites can be seen in a brief description of the polished sections of the ores from different deposits of the KhPB and DPB (Fig. 1).

One of the examples of various combinations of minerals and the character of their interaction can be the polished sections from the Burenkhan deposit of the KhPB (see Fig. 1, *a* and *b*). The first one of them shows the phosphatic-sandy rock in which the phosphate and quartz-sand parts are mixed with each other. The sandy regions are composed of fragments cemented by fine crystalline quartz; in some places, the cement substance is fine crystalline phosphate and clay material (see Fig. 1, *a*). Quite a different combination of minerals is observed in the second section (see Fig. 1, *b*), in which the pelleted phosphorite is strongly cabronatized; calcite replaces

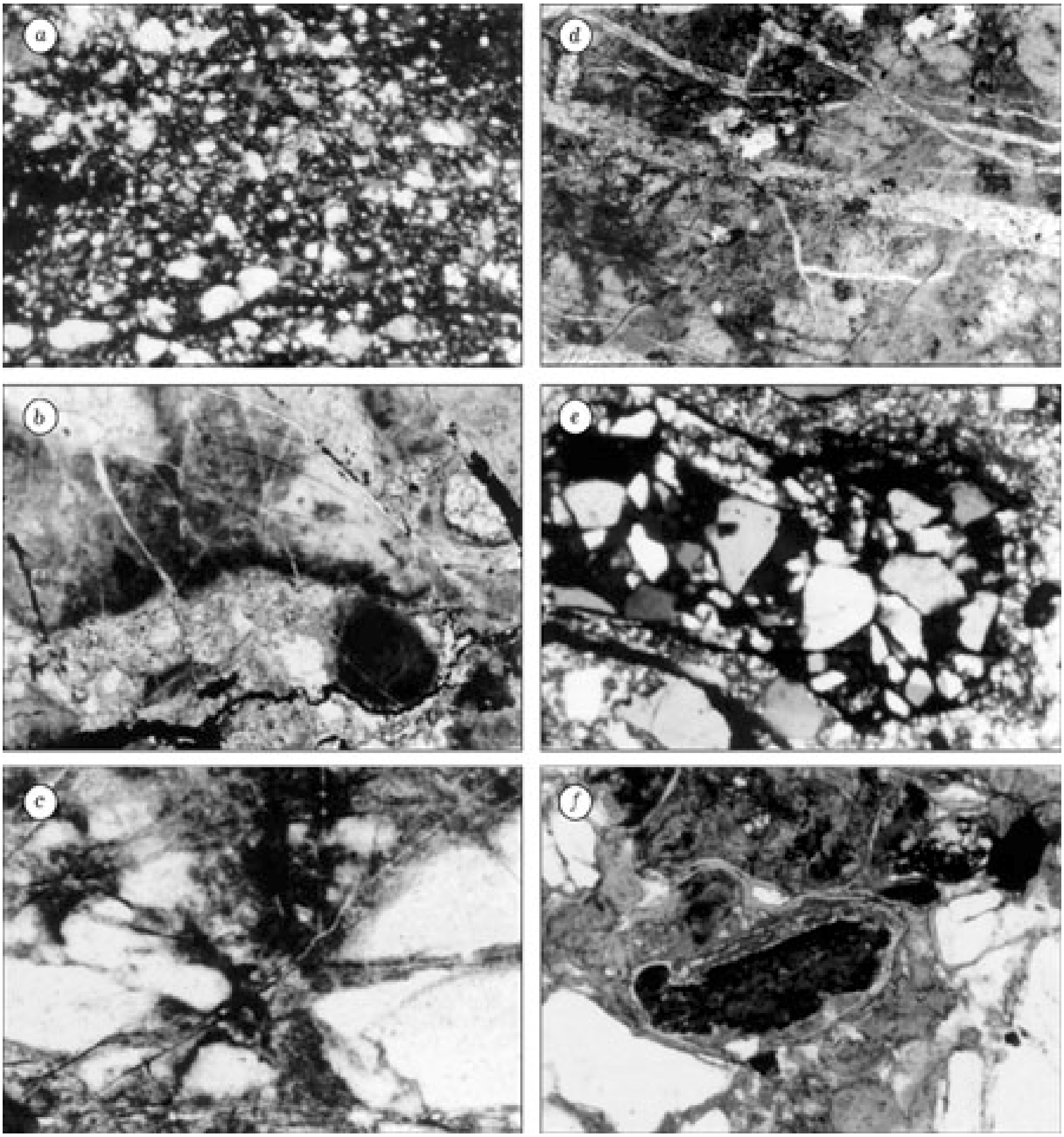

Fig. 1. Micrographs of the polished sections of phosphorites from the deposits: Burenkhan (*a*, *b*), Ongilignur (*c*), Zhankhay (*d*), Alagiyn-Daba (*e*) and Tsakhir-Ula (*f*): *a* – 100-fold magnification (without analyzer), light-coloured particles – quartz fragments, dark background – sandy phosphate cement; *b* – 400-fold magnification (analyzer), phosphate grains and clots (dark parts) in calcite; *c* – 400-fold magnification (without analyzer), apatite (light particles) is crystallized from amorphous phosphate (dark); *d* – 200-fold magnification (without analyzer), amorphous (dark) and decolourised phosphate (gray) with calcite insertions and quartz veins; *e* – 200-fold magnification, quartz sandstone grains (white) in the mass of amorphous phosphate (dark background); *f* – 400-fold magnification, phosphate grains (dark) and quartz grains (white), crustified at the edges with phosphate, in the phosphate amorphous cement.

the space between the pigmented phosphate clots in which typical oncolites are observed, included into the mass of the structureless (aphanite) phosphate. The rock is closely penetrated by cracks, cured by calcite or filler with iron hydroxides.

The major part of the minerals of phosphate ores survived substantial changes since the formation moment. For example, a polished section of the phosphorite from the Ongilignur deposit of the KhPB is shown in Fig. 1, c; the relicts of primary dark-brown amorphous phosphate mass of possibly organogenic origin loose their colour during gradual crystallization forming blocks between the cracks. The formation of both the carbonates and the quartz is observed along the cracks (see Fig. 1, *c*). A phosphorite sample from the Zhankhay deposit of KhPB is composed of the aggregates of fine crystalline decolourized apatite and dark-brown phosphate with the insertions of the smallest calcite crystals; at the same time, quartz clusters are observed; they also fill the cracks (see Fig. 1, *d*).

A complicated combination and tight intergrowth of minerals is also observed in the samples from two phosphorite deposits of the DPB. A polished section of the phosphorite from the Alagiyn-Daba deposit is shown in Fig. 1, *e*. It is composed mainly of the grains of quartz sandstone of different sizes and shapes, included in fine crystalline quartz and the brown mass of the amorphous phosphate. Scattered mica particles are observed among the quartz grains of the rock. A polished section of the phosphorite from the Tsakhir-Ula deposit is shown in Fig. 1, *f*. The rock is a sandy phosphorite composed of quartz particles of various sizes and shapes, held together by the amorphous phosphate. The bulk is a structureless phosphate forming the growth crust over the grain boundaries; this means that crustification process is observed both along the quartz grain boundaries and around the darker particles of iron-containing phosphate, also held together by the amorphous phosphate mass. The pyrite particles and iron hydroxide crystals are scattered over the rock (see Fig. 1, *f*). The residues of the ancient marine organisms were observed almost in all the sections; these were the spicules of sponges, fragments of sea shells, *etc.*; they were substituted with quartz, calcite, or phosphate. In some cases the colouring of the phosphate substance was due to the presence of the organic matter which is often an accumulator of the trace elements [8].

The above description of the polished sections gives only an approximate picture of the intricacy of composition and fineness of intergrowth of various minerals, but it cannot embrace the entire variety of the compositions and structures of these complicated rocks. They have been described in more detail in monographs and reviews [1, 3–5, 11]. A quantitative ratio of minerals in the phosphorites from the KhPB and DPB and their mineralogical characterization have been performed on the basis of the data of chemical analysis and physical methods of investigation described below.

Characterization of the mineral composition of phosphorites

When investigating 30 deposits and phosphate occurrences at the KhPB, the author of [1] marked two features of their chemical nature: prevalence of carbonate phosphorites, and a close connection of the phosphate substance with dolomite. However, later discovered Burenkhan deposit, as well as other deposits of the KhPB and the phosphorites from the DPB [3–5], depending on the occurrence of the productive packets together with the rocks of the carbonate or siliceous composition, exhibited a broad variety of the mineral composition with the trend towards the phosphorites of the cherty type.

According to the data of chemical analysis shown in Table 1, in the major part of the investigated samples of the phosphorites from the Alagiyn-Daba and Tsakhir-Ula deposits of the Dzabkhan basin, the main components accompanying phosphate was silicon oxide. In the samples with the mean phosphate content of 20–22 % P_2O_5, the fraction of silicon oxide reached 40 %; in not so rich samples it was more than 50 % (sample No. 12 in Table 1). The major part of phosphorites from these deposits contained less than 5 % of carbonate minerals.

The deposits of the KhPB are characterized by the trend to increased carbonate content in the phosphorites of deposits situated at the North-West of the basin [1, 3–5, 11]. For example, the main minerals accompanying apatite were dolomite and calcite in the phosphorites of the Khubsugul deposit situated at the western shore of the Khubsugul Lake, and the Uleindaban deposit, which lies to north-west of it (see Table 1, samples No. 49, 50, 54). In the Burenkhan deposit, situated in the southern part of the KhPB, predominant are the phosphorites of cherty type, and more rarely of carbonate-

TABLE 1

Chemical composition of the phosphorites from KhPB and DPB, % mass

Sample No.	Deposit	CaO	P_2O_5	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	MnO	SO_3	c.l.	H_2O	CO_2	F
1/27	AD	41.30	30.0	20.8	0.26	0.84	1.75	0.24	0.39	0.23	0.01	–	0.88	–	1.02	1.8
2/17	AD	31.82	25.4	37.8	–	0.86	1.26	0.49	0.14	0.32	–	–	–	–	0.4	0.47
3/11	AD	31.11	23.67	39.24	0.1	0.96	1.62	0.58	0.12	0.33	0.17	0.1	2.0	0.05	0.4	1.27
4/19	AD	31.11	23.7	39.2	–	0.96	1.62	0.58	0.12	0.53	–	–	–	–	0.4	1.27
5/6	AD	30.4	22.5	37.5	0.04	1.8	2.2	0.10	0.28	0.24	0.03	–	1.25	–	1.40	1.43
6/20	AD	29.05	21.2	42.7	–	1.53	2.47	0.3	0.1	0.3	–	–	–	–	0.4	1.68
7/34	AD	31.7	21.4	38.34	0.08	1.85	1.14	0.12	0.36	0.39	0.01	–	1.43	–	1.42	0.85
8/36	AD	35.4	21.4	32.40	0.08	1.79	1.43	0.22	0.35	0.29	0.025	–	1.37	–	1.49	0.83
9/40	AD	30.43	20.5	39.27	0.07	1.02	2.19	0.08	0.35	0.19	0.03	–	1.74	–	2.17	1.85
10/3	AD	27.70	20.15	–	–	–	–	–	–	–	–	–	–	–	–	–
11/38	AD	31.2	18.7	40.34	0.05	1.07	2.14	0.07	0.42	0.19	0.015	–	2.69	–	2.19	1.15
12/16	AD	24.39	18.5	53.0	–	0.64	0.45	0.34	0.10	0.18	–	–	–	–	0.4	0.40
13/30	AD	30.40	17.8	42.3	0.06	1.9	2.24	0.08	0.38	0.26	0.01	–	1.72	–	2.14	1.44
14/9	TsU	44.3	36.5	10.90	0.24	0.85	1.55	0.27	0.39	0.24	0.01	–	0.87	–	1.08	2.2
15/35	TsU	40.9	29.5	18.00	0.06	1.90	2.93	0.52	1.65	0.40	0.03	–	3.10	–	1.10	1.45
16/41	TsU	43.0	29.0	16.80	0.12	1.14	1.40	1.60	0.45	0.30	0.03	–	2.30	–	2.10	1.60
17/29	TsU	41.52	27.6	4.86	0.05	1.22	3.47	0.52	0.74	0.43	0.04	–	3.12	0.04	1.1	1.63
18/39	TsU	39.4	25.8	19.33	0.29	2.35	2.48	0.17	0.45	0.41	0.14	–	3.15	–	0.15	2.08
19/10	TsU	31.82	25.35	37.8	0.1	0.86	1.26	0.49	0.14	0.32	0.07	0.1	1.78	0.14	0.4	0.47
20/12	TsU	31.46	23.45	33.0	0.1	1.28	0.6	0.93	0.08	0.36	0.15	0.1	8.74	0.14	7.78	1.06
21/33	TsU	34.14	23.4	31.92	0.54	1.18	2.18	0.54	0.49	0.35	0.02	–	1.15	–	1.34	2.07
22/31	TsU	32.4	21.4	37.12	0.09	1.08	1.17	0.11	0.47	0.39	0.01	–	1.19	–	1.43	0.94
23/32	TsU	31.2	21.4	38.4	0.06	1.05	1.18	0.24	0.19	0.22	0.19	–	2.04	–	1.15	1.07
24/42	TsU	29.05	21.15	42.71	0.11	1.53	2.47	0.30	0.10	0.30	0.19	0.1	2.24	0.17	0.4	1.68
25/4	TsU	27.2	20.7	48.60	0.05	0.60	0.96	0.3	0.19	0.37	0.05	0.1	1.1	0.11	1.23	0.23
26/8	TsU	26.6	20.5	42.1	0.06	1.17	2.68	0.08	0.41	0.34	0.02	–	1.67	–	2.24	0.49
27/28	TsU	30.10	17.5	39.4	0.09	0.85	1.95	0.25	0.22	0.34	0.01	–	2.49	–	1.17	0.88

28/25	Bkh	54.5	41.1												0.06	2.09
29/26	Bkh	54.96	40.2												0.87	2.85
30/24	Bkh	54.8	40.3												0.51	2.74
31/46	Bkh	46.71	33.5	10.08	–	0.86	1.2	1.89	0.4	0.1	–	–	–	–	0.44	2.26
32/47	Bkh	46.6	32.7	8.1	–	0.64	0.96	1.5	1.0	0.15	–	–	–	–	2.50	2.35
33/48	Bkh	55.7	39.1	0.85	–	0.32	1.05	0.3	0.29	0.29	–	–	–	–	0.6	2.9
34/49	Bkh	55.0	39.9	–	–	–	–	0.2	–	–	–	–	–	–	0.95	2.8
35/50	Bkh	53.2	38.8	–	–	–	–	–	–	–	–	–	–	–	0.86	2.75
36/51	Bkh	54.96	38.5	–	–	–	–	–	–	–	–	–	–	–	0.87	2.34
37/52	Bkh	54.4	39.65	–	–	–	–	–	–	–	–	–	–	–	1.25	2.85
38/15	Bkh	53.0	39.1	0.85	–	0.32	1.05	0.3	0.29	0.29	–	–	–	–	0.6	2.9
39/13	Bkh	45.76	35.2	8.36	–	0.76	0.97	0.84	0.5	0.1	–	–	–	–	4.4	2.41
40/23	Bkh	52.7	38.3												1.7	2.39
41/5	Bkh	40.6	32.6	23.46	0.07	0.8	0.43	0.3	0.22	0.2	0.03	0.1	1.4	0.09	1.13	0.09
42/44	Bkh	49.86	33.8	9.88	–	0.79	0.89	0.84	0.7	0.2	–	–	–	–	1.1	2.52
43/45	Bkh	49.71	28.7	2.46	–	0.45	0.82	3.15	1.8	0.1	–	–	–	–	6.05	2.01
44/1	Zhkh	47.97	36.7	10.5	0.05	0.05	1.46	0.1	0.01	0.04	0.01	0.1	1.97	0.03	1.28	0.16
45/2	Zhkh	45.5	33.98	10.93	0.05	0.05	1.98	0.3	0.04	0.14	0.07	0.1	5.54	0.02	5.24	0.12
46/14	Ong	44.5	32.5	12.3	–	0.72	1.06	1.2	2.1	0.3	–	–	–	–	2.52	2.6
47/22	Ong	54.8	39.7												0.8	2.81
48/43	Ong	49.19	32.6	5.03	–	0.26	0.86	1.36	0.6	0.1	–	–	–	–	0.44	2.35
49*	Khb	41.39	21.73	–	–	1.02	0.52	8.49	–	–	–	–	–	–	16.53	–
50*	Khb	43.87	20.75	5.12 (i. r.)	–	1.1	0.61	4.03	2.15	2.15	–	–	–	–	20.15	1.88
51*	Tsag	47.10	29.50	2.87	–	0.87	0.76	4.10	2.36	1.08	–	–	–	–	9.41	2.80
52*	Tsag	45.22	27.65	2.20 (i. r.)	–	1.79	0.89	4.80	1.89	1.30	–	–	–	–	12.68	2.08
53*	Uhgk	39.20	25.30	20.46	–	1.0	0.71	2.60	2.43	0.43	–	–	–	–	4.36	2.18
54*	Uld	43.68	21.30	0.73 (i. r.)	–	traces	0.28	8.40	0.82	0.49	–	–	–	–	23.25	1.95

Note. AD – Alagiyn-Daba, TsU – Tsakhir-Ula, Bkh – Burenkhan, Zhkh – Zhankhay, Ong – Ongilignur, Khb – Khubsugul, Tsag – Tsagannur, Ukhg – Ukhagol, Uld – Uleindaban deposits; i. r. – insoluble residue; c. l. – calcination loss at 900 °C.

*For data [1].

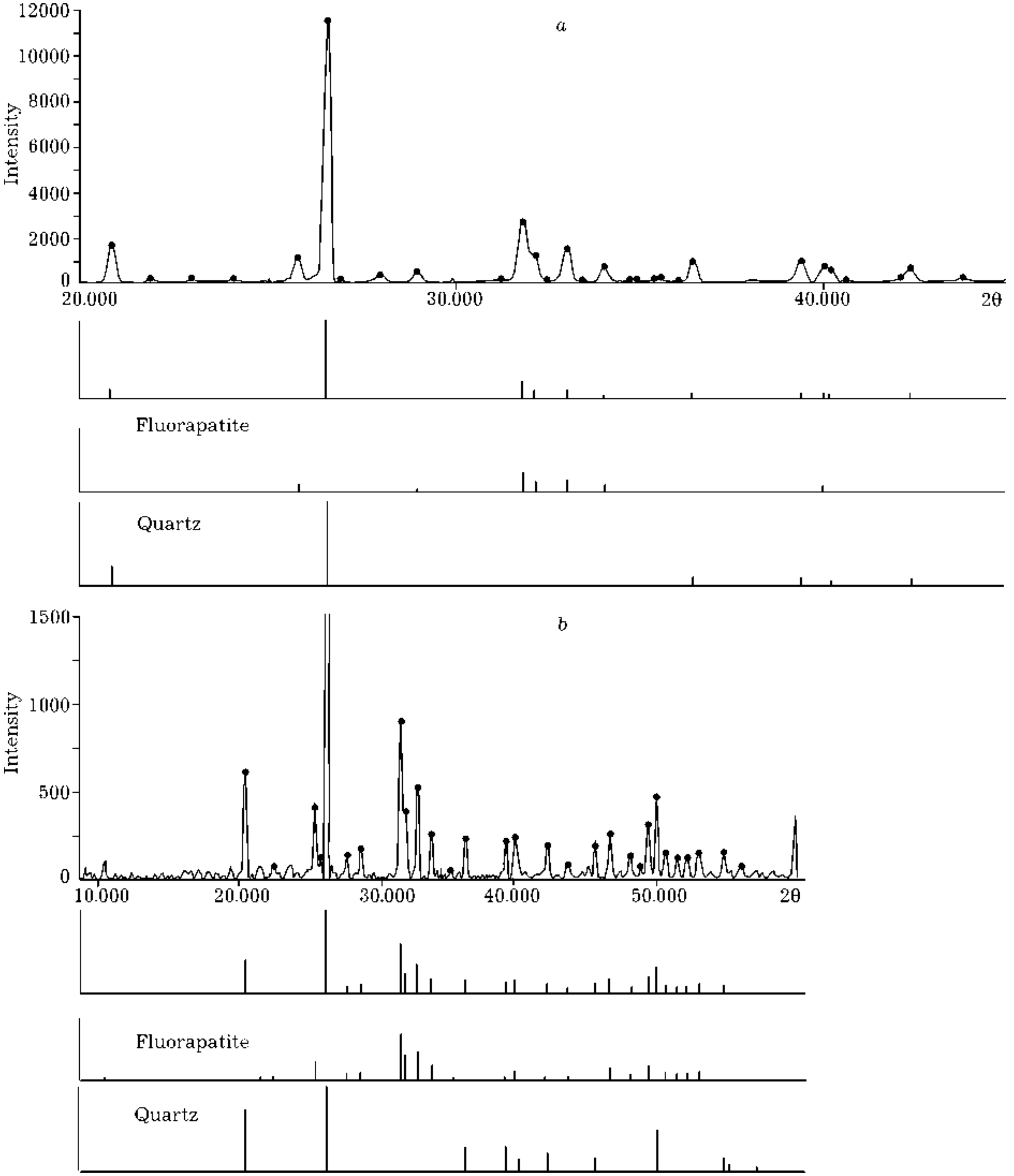

Fig. 2. X-ray diffraction patterns of the phosphorites from the Tsakhir-Ula deposit (*a*) (sample No. 25, see Table 1), and Alagiyn-Daba deposit (*b*) (sample No. 6, see Table 1).

siliceous composition, and substantial fraction of ores is characterized by high content of phosphate (see Table 1, samples No. 28–43).

The composition of minerals was identified according to the data of X-ray phase analysis and IR spectroscopy. The XPA data for the samples of phosphorites from the two deposits of the DPB are shown in Fig. 2. These data are also typical for other deposits. In the phosphorite samples of the DPB with the phosphate content at the level of the mean of the deposit, the major apatite-accompanying mineral was quartz; the intensity of its reflections in diffraction patterns several times exceeded

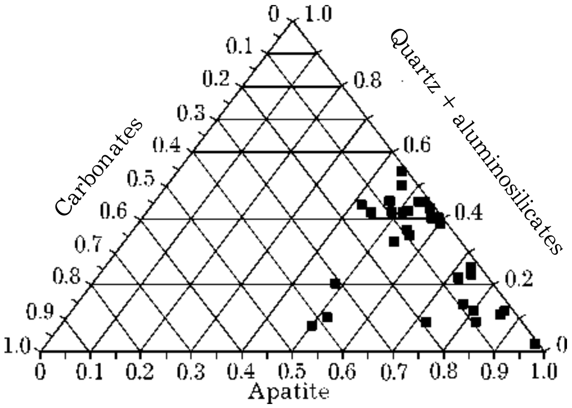

Fig. 3. Mineral composition of the phosphorites from the deposits of KhPB and DPB.

those of the apatite (see Fig. 2, *a*, *b*). In order to obtain a general view of the ratio of minerals in the phosphorites of the KhPB and DPB, we built up a diagram for the three-component system (Fig. 3). For construction of the diagram, proceed from the chemical composition of phosphorite samples, we calculated the content of apatite, dolomite and calcite, minerals of silicon, and aluminosilicates using the data of Tables [15]. All the components in the diagram were reduced to three ones: apatite, the sum of carbonates, and the sum of silicon minerals with aluminosilicates. One can see in the diagram that the major part of the investigated phosphorite samples is adjacent to the side of triangle: apatite − quartz + aluminosilicates, *i. e.* it is mainly siliceous. A part of the phosphorites from the KhPB deposits belongs to typically carbonate ones [1]; however, the phosphorites of the Khubsugul and some other deposits of the KhPB contain carbonate and siliceous minerals, so they can be referred to the siliceous-carbonate type.

A very difficult problem is to reveal structural features and the exact composition of the isomorphous modifications of apatite comprising phosphorites. As one can see in Fig. 1, minerals finely intergrow; to characterize apatite, one should isolate it is an individual phase.

Structural features and composition of the apatite of phosphorites from the KhPB

In order to determine the structural features of the isomorphous modifications of apatite, we isolated the monofractions of phosphate matter from the phosphorites of the Burenkhan and Zhankhay deposits of the KhPB (see Table 1, sample No. 33 and 44). Both samples exhibit the deficit of flouorine with respect to the shoichiometry; hydroxylapatite is observed in the X-ray diffraction pattenrs of the fractions (Fig. 4), though the X-ray diffraction patterns of the initial phosphorite sample of the Burenkhan deposit, from which the monofraction was isolated, exhibited fluorapatite. According to the data of the IR spectroscopy (Fig. 5), the initial sample and the monofraction of the Burenkhan phosphorite contain quartz (absorption bands in the regions of ν_2 and ν_1 470−500 and 790−800 cm^{-1} due to the bending vibrations of the Si−O bonds; stretching vibrations of these bonds are overlapped with the absorption bands of the stretching vibrations of phosphate ion).

Quartz was absent from the monofraction of the Zhankhai sample, though absorption bands in the region of 790−800 cm^{-1} were observed in the initial sample (see Fig. 5, spectrum *1*). The phosphate of both monofractions of phosphorites was partially substituted by the carbonate ion, which is evidenced by absorption bands of the C−O bonds at 720 and 890 cm^{-1} (ν_4 and ν_2 deformation vibrations) and 1400−1450 cm^{-1} (ν_3^1 and ν_3^{11} are stretching vibrations) [16]. In the monofraction and in the initial sample of the phosphorite of the Zhankhay deposit, the stretching vibrations of the C−O bonds were many times more intensive, which was the evidence of substantial extent of the substitution of phosphate for carbonate ion in the apatite structure (see Fig. 5, spectra *1* and *2*).

The IR spectra of the monofractions contained absorption bands of the P−O bonds of apatite at 470, 560−580 and 610 cm^{-1} (ν_4 deformation vibrations) and 970 (ν_1), 1050−1060 and 1100 cm^{-1} (ν_3 stretching vibrations) [16]. Thus, phosphate is represented by hydroxylcarbonatefluorapatite in these samples.

A finer structure of apatite and the state of ions incorporated in it can be revealed by means of ESR. An ESR spectrum of the monofraction of Burenkhan phosphorite after its γ irradiation is shown in Fig. 6. Paramagnetic centres (PC) were observed in the anion sublattice of the comprising apatite both in the position

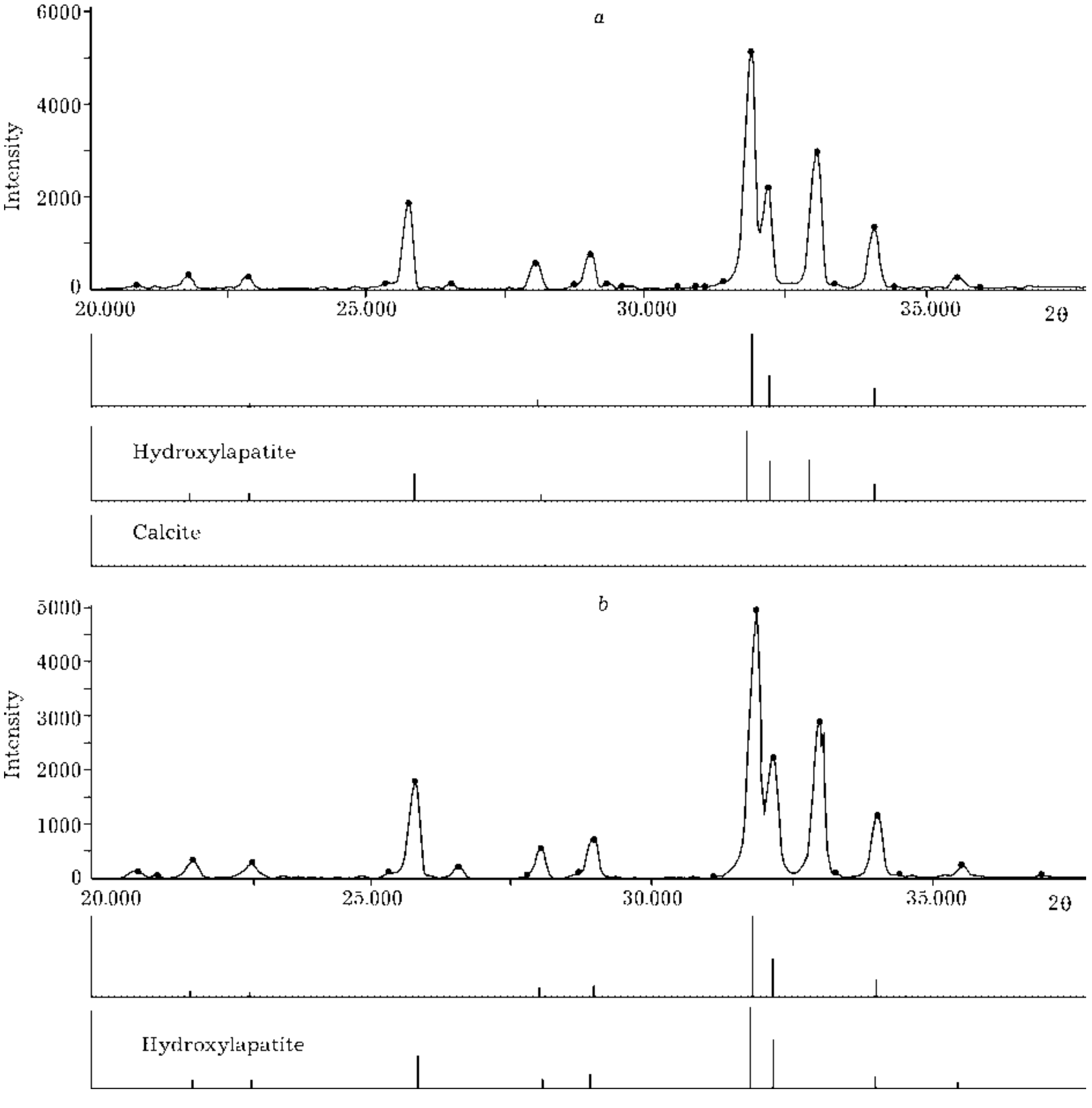

Fig. 4. Diffraction patterns of the monofraction of the phosphate substance isolated from the phosphorites of the Zhankhai (*a*) and Burenkhan (*b*) deposits.

of the phosphate ion and at the 6_3 axis, where monovalent anion is usually localized. Carbonate ion that substitutes phosphate forms PC of two types, CO_3^{3-} and CO_3^-; the former is very intensive (see Fig. 6, *a*, curve *1*). At the 6_3 axis, where fluorine and/or OH^- ion are usually localized, three types of oxygen in the form of O^- were revealed by means of ESR: $OH^-{-}O^-{-}OH^-$, $F^-{-}O^-{-}F^-$, $OH^-{-}O^-{-}V$, where V is a vacancy. As we have mentioned above, the fluorine content of the monofraction of Burenkhan phosphorite is much below the stoichiometry, which agrees with the data of ESR that the substanmtial amount of fluorine is substituted not only by OH^- groups but also by more complicated combinations forming PC.

In the phosphate position, paramagnetic centres PO_3^{2-} (Th) and PO_3^{2-} (U) were recorded (see Fig. 6, *b*), which were due to the substitution of calcium ions in apatite by uranium and thorium in the form of cations; they pull the oxygen of the phosphate tetrahedron so that the PO_3^- ion is formed; capture of an electron by this ion leads to the formation of the paramagnetic center PO_3^{2-} [17]. It should be noted that the uranium and thorium con-

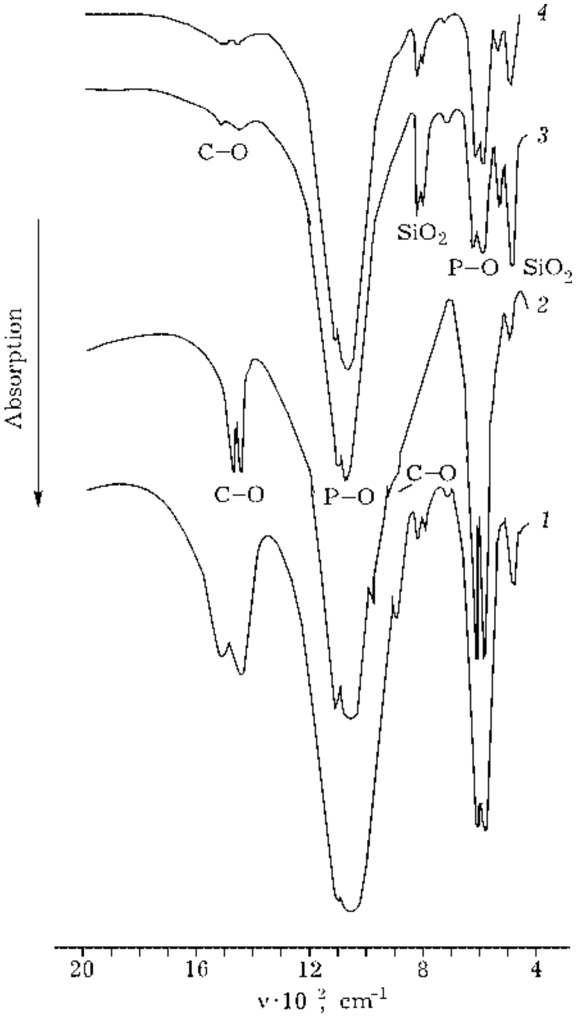

Fig. 5. IR spectra of the phosphorites from Zhankhai (*1, 2*) and Burenkhan (*3, 4*) deposits: *1* and *3* – initial samples, *2* and *4* – after the isolation of phosphate monofraction.

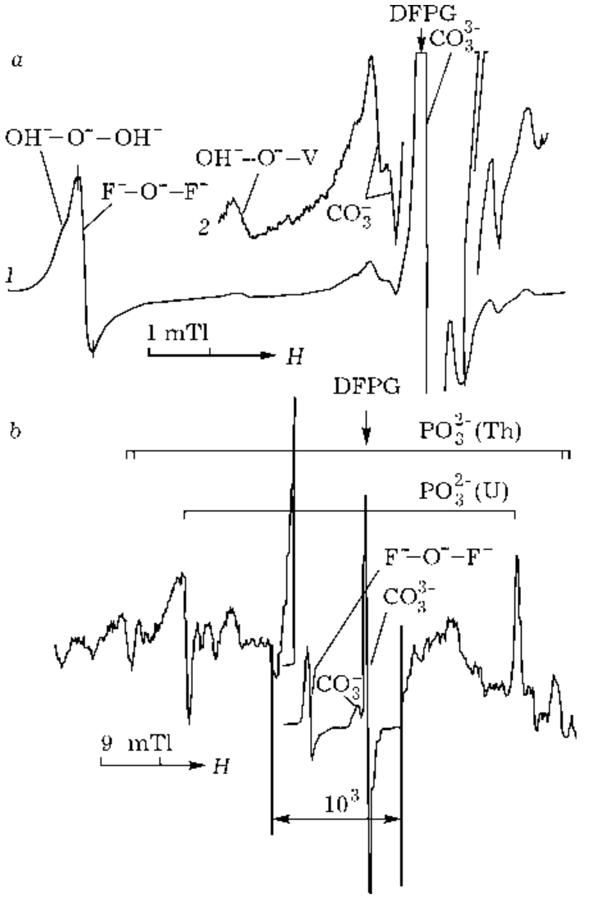

Fig. 6. ESR spectra of the monofraction of phorphorite from the Burenkhan deposit after γ irradiation. Recording conditions: *a* – amplification 1 10^4 (*1*) and 1 10^5 (*2*); *b* – amplification 1 10^5, central region of the spectrum (↔) was recorded at the amplification of 1 10^3.

tent of the samples was thousandth or ten thousandth fraction of per cent, which is much lower than in the phosphorites of other world's deposits [10], but this amount is quite sufficient for the deformation of the phosphate tetrahedron and the formation of the PC PO_3^{2-}.

The results of the investigation of phosphorites of the mentioned deposits of the KhPB and DzPB allow us to conclude that the phosphate comprising them is an isomorphous modification of hydroxylcarbonatefluorapatite with partial substitution of the phosphate tetrahedron for the PC PO_3^{2-}, CO_3^{3-} and CO_3^-; fluorine is substituted by OH^- ions and the PC $OH^- – O^- – OH^-$, $F^- – O^- – F^-$, $OH^- – O^- – V$ incorporating the trace amounts of uranium and thorium occupying the positions of cations. We made an attempt to classify the apatites comprising these phosphorites of Mongolia, on the basis of the data of chemical analysis of the samples containing phosphate more than 30 % P_2O_5 and the isolated apatite monofractions.

Structural chemical classification of apatites

On the basis of investigation of the composition and structure of isomorphous modifications of apatite formed in the acidid, neutral and alkaline media of the phosphate-calcium equilibrium aqueous systems, and the investigation of physicochemical properties of phosphates from different phosphorite deposits of the world, we proposed a structural chemical classification of apatites [18]. The grounds of the classification is the ratio of the ions in the investigated modifications of apatites compared to the stoichiometry, a reference for which is the fluoroapatite $Ca_{10}(PO_4)_6F_2$ with the atomic ratio of ions $(Ca/P)_{at} = 1.67$, $(F/P)_{at} = 0.33$. Under natural conditions, during the precipitation and post-genetic transformation of phosphorites, the comprising apatites always contain from several thousandth to several per cent substituents in different fragments of the lattice [19]. The most widespread and substantial substituent of the phosphate ion in phorphorites is carbonate ion CO_3^{2-}, while calcium in phosphorites is most frequently bound to apatite and carbonate minerals. Interconnection of the composition and character of substitutions in apatite can be revealed on the basis of atomic ratios between the major components: CaO, P_2O_5, F, CO_2: $(Ca-C/P)_{at}$, $(F/P)_{at}$. Taking magnesium carbonates into account, one can use the comparison of $(Ca/P)_{at}$ with $(Ca-C/P)_{at}$ to distinguish calcium belonging to the carbonate minerals and to apatite.

On the basis of the proposed classification, three main structural chemical types of natural apatites have been established; their conventional names are “acidic”, “neutral”, and “alkaline”, similar to the solid phases of apatites formed in different pH ranges in the equilibrium solutions of the systems [18]. The composition of “acidic” apatites is characterized by the ratios $(Ca/P)_{at} < 1.67$ and $(Ca-C/P)_{at} \leq 1.60$; this means that these are the apatites with the lack of calcium, which under natural conditions is substituted by various cations. “Neutral” apatites are close in composition to the stoichiometry with the ion ratio $(Ca/P)_{at}$ ~1.67–1.70, and $(Ca-C)/P)_{at} = 1.62-1.69$. “Neutral” apatites are characterized by small amount of defects in the structure, low content of susbtituent ions, or their equal amount in the anionic and cationic sublattices, and low solubility in 2 % citric acid solution. The “alkaline” type includes the major part of apatites comprising phosphorites.

With respect to the ionic ratio, three subgroups of “alkaline” apatites have been revealed [18]:

I – $(Ca/P)_{at} = 1.7-1.79$; $(Ca-C/P)_{at} = 1.65-1.70$

II – $(Ca/P)_{at} = 1.8-1.9$; $(Ca-C/P)_{at} = 1.70-1.80$

III – $(Ca/P)_{at} \geq 2$; $(Ca-C/P)_{at} > 1.75$

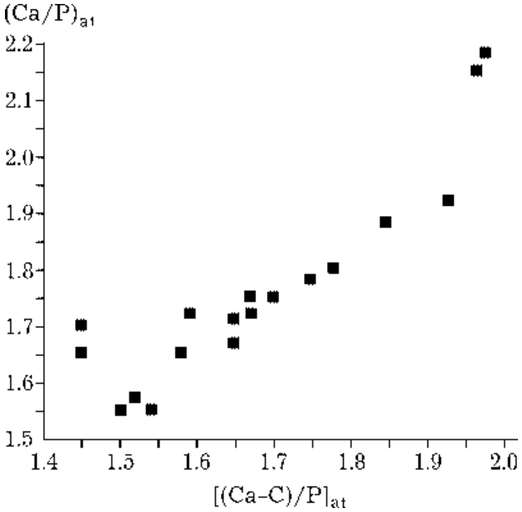

Fig. 7. Structural chemical classification of apatites comprising the phosphorites from the deposits of KhPB and DPB.

With an increase of the $(Ca/P)_{at}$ ratio, the reactivity of apatite usually increases because of substantial substitution of phosphate by carbonate and other ions.

On the basis of the above considerations, we classified the apatites comprising phosphate ores from the deposits of the KhPB and DPB basins. The structural chemical classification of the apatites from six phosphorite deposits of these basins is shown in Fig. 7. Only a small part of samples relates to the calcium-deficient apatites, *i. e.* to the group of “acidic” apatites with $(Ca/P)_{at} < 1.67$, as well as to the group of “neutral” apatites; these are only a few samples from different deposits. The major part of phosphorite samples is composed of the “alkaline” apatites of the first subgroup. This type of apatites is characterised by the 0.5–1.5 % content of carbonate ion that substitutes the phosphate in the structure, relatively low solubility in 2 % solution of citric acid, and the absence of ACSP. The third group of the “alkaline” type includes some modifications of the phosphorites from the Alagiyn-Daba and Tsakhir-Ula deposits. These apatites contain considerable amount of defects in the anion sublattice and the substituents of the phosphate ion; they are well soluble in 2 % solution of citric acid; in principle, they can be used as phosphorite powder.

On the basis of the data reported in [18], one may assume that during the mechanical treatment of the phosphorites from the deposits of KhPB and DPB, the structure of the comprising hydroxylcarbonatefluoroapatite will be destroyed along the prismatic $\{2\bar{1}20\}$, $\{10\bar{2}0\}$ and pyramidal $\{22\bar{1}2\}$ planes, which will provide rather high content of CASP and ACSP, which are standard tests characterizing the efficiency of water-insoluble phosphorus-containing fertilizers.

In order to provide full characterization of phosphate ores and to determine their suitability for one or another processing technology, the ecological evaluation is necessary. The data on the content of trace elements in the KhPB phosphorites and their relation to clarke are reported in [12]. However, an ecological evaluation of the fertilizer taking into account the total content of trace elements is also important. We used the method described in [10] to characterize the phosphorites of Mongolia.

Content of ecologically monitored elements and ecological evaluation of phosphorites

In addition to minerals composed of macrocomponents, such as apatite, quartz, calcite, *etc*., phosphate ore contains a set of impurity elements incorporated as isomorphous substituents or forming their own minerals [8]. During the processing of phosphorites, some trace elements pass into the fertilizers. When introduced into the soil, some impurity elements can be partially assimilated by plants and play a role of microfertilizers, but their high content and the presence of toxic trace elements can lead to hazardous consequences.

No unified regulations for the limiting content of toxic elements in phosphorus-containing fertilizers have been adopted in the world's production and application of fertilizers. Within the recent decade, in many countries only the upper limit for cadmium content of a fertilizer has been adopted; it differs by an order of magnitude for different countries. For example, in the Netherlands, maximal permissible cadmium level in the phosphorus-containing fertilizer is 35 mg per 1 kg of P, while in Australia it is 350 mg per 1 kg of P [20].

The trace elements include heavy metals, toxic elements and natural radionuclides. The A. I. Sysin Research Institute of General and Communal Hygiene, Academy of Medical Sciences of RF, NIUIF and VIEMS performed investigations on the ecological effect trace elements present in the phosphate raw material, in concentrates of a series of deposits and in phosphorous fertilizers; they found out that the monitoring of 16 elements is sufficient for such an ecological evaluation. These elements are: fluorine, manganese, nickel, copper, zinc, arsenic, strontium, vanadium, chromium, lead, mercury, cobalt, cadmium, uranium, thorium, and yttrium [21]. To estimate the integral effect of ecologically monitored elements, the authors of [21] introduced the summing ecological dimensionless universal parameter K_e, called the ecological index of phosphates:

$$K_e = Q_{16}/(K_{c(P)}K_{t(P)});\ K_t = g_i/g_{i(Cl)};$$
$$Q_{16} = \Sigma\,(K_cK_t)$$

Here K_c is the coefficient of concentration of a chemical element with respect to the Clarke of the Earth's crust; g_i is the content of an element in the sample, g/t; $g_{i(Cl)}$ is the Clarke content of an element, g/t; K_t is the toxicity coefficient of a chemical element. The toxicity coefficient of a monitored element is determined depending on the class of danger of that element [10]. To express K_t numerically, quantitative characteristics of the class of danger have been introduced. The first class of danger includes Hg, Cd, U, Th, and Y; for them, K_t is accepted to be 30 units. The second class includes Mn, Ni, Cu, Zn, As, V, Pb, and Co; for these elements, K_t is 20. The third class includes P, F, Sr, and Cr ($K_t = 10$) [10, 20, 21]. In order to render a universal character to the ecological index, the sum of K_cK_t product for each of the 16 elements is divided by the product $K_{c(P)}K_{t(P)}$ for phosphorus in a given sample [21].

The K_e values calculated for the samples of Mongolian phosphorites are shown in Table 2. The authors of [10, 20, 21] analyzed the data on the content of ecologically monitored elements in 20 deposits of phosphate ores of different genesis and in concentrates of them, in order to reveal which is the fraction of each EME in the Q_{16} value. The calculations

TABLE 2

Content of ecologically monitored elements in the phosphorites of the Khubsugul and Burenkhan deposits, g/t

Deposit	F*	Mn	Ni	Cu	Zn	As	Sr	V	Cr	Pb	Hg	Co	Cd	U	Th	Y	K_e	Ref.
Khubsugul	30	78	23.8	24	39	22.4	1660	26	47	14.3	0.27	12.8	1.6	32	2.8	182.7	1.186	[21]
»		700	95	57	80	10	450	150	100	20	–	23		20	11	–	1.26	[8]
»		880	100	15	10	8	900	40	9	3	–	100	–	10	–	–		[12]
»		980	175	15	1	7	600	10	90	3	–	40	–	1.5	–	–		[12]
Burenkhan	22	142	65.6	43	52	29.0	1068	55	52	11.0	0.32	35.7	2.5	38	4.8	290	1.643	[21]
		280	57	52	98	н/о	769	150	28	23	–	6.5	–	23	10	29		[3]

*In kilogrammes per ton.

demonstrated that the level of ecological index (EI) is determined by the concentration of seven components: fluorine, arsenic, strontium, mercury, cadmium, uranium, yttrium, while other elements account for 2.4 to 10.7 % of the EI. Thus, to simplify the calculation of the ecological index of phosphate products, one can use the K_c and K_t for the seven ecologically monitored elements: $K_э^1 = Q_7 / (K_{c(P)}) K_{t(P)}$. The authors of [10, 20, 21] proposed to evaluate the ground phosphates and phosphorus-containing fertilizers using $K_e = 2.4$ or $K_e^1 = 2.3$. Those kinds of ground phosphates and fertilizers for which $K_e^1 < 2.3$ can be used without the danger of negative ecological effect on the soil and on the quality of agricultural products. One can see in Table 2 that the phosphorite samples from the Khubsugul and Burenkhan deposits are characterized by low ecological index and can be introduced into soil without chemical treatment.

CONCLUSIONS

Mineralogical and ecological characterization, and structural chemical classification of the phosphorites of some deposits of Mongolia is reported. The minerals comprising phosphate ores (apatite, quartz, calcite, dolomite, aluminosilicates, *etc.*) are in close intergrowth, which can create substantial difficulties in phosphorite enrichment.

In the investigated phosphorite samples, except for the phosphorites from KhPB deposits, the major mineral that accompanied apatite was quartz; so, the major part of phosphorites can be related to the siliceous type. According to the classification, the major part of apatites comprising phosphorites of the deposits of KhPB and DPB relates to the first subgroup of the “alkaline” type and to the “neutral” type; these apatites are hydroxylcarbonatefluoroapatite close to francolite. The content of ecologically monitored elements in the phosphorites from the deposits of KhPB and DPB has no danger for their use as the fertilizers without chemical treatment; because of this, they can be processed mechanochemically.

Acknowledgements

The authors thank workers from the Institute of Geology and Geophysics, SB RAS, E. A. Eganov for assistance in describing the polished sections, and L. G. Gilinskaya for ESR measurements; we also thank the researcher from the INP, SB RAS, S. N. Fadeev for γ irradiation of phosphorite samples.

REFERENCES

1 A. V. Il'in, Khubsugulsky fosforitonosny basseyn, Nauka, Moscow, 1973.
2 A. L. Yanshin, M. A. Zharkov, Fosfor i kaliy v prirodye, Nauka, Novosibirsk, 1986.
3 J. Amgalan, in: Agrokhimiya mikroelementov pochv Mongolii i mekhanokhimicheskaya tekhnologiya fosfornykh udobreny, Ulanbator, 1999, p. 144.
4 J. Amgalan, M. Dulamsuren, A. Mijidsuren and A. Bilegbaatar, Report on Scientific Research of Burenkhan Phosphorite during the Years 1995–1996, Ulaanbaatar, 1996.
5 J. Temuujin, A. Mijidsuren, J. Amgalan, *Proc. Mong. Acad. Sci.,* 147 (1998) 12.
6 V. F. Karamyshov, Khimicheskaya pererabotka fosforitov, Khimiya, Moscow, 1983.
7 M. E. Pozin, Tekhnologiya mineral'nykh soley, part 2, Khimiya, Leningrad, 1970.
8 V. Z. Bliskovsky, Veshchestvenny sostav i obogatimost' fosforitovykh rud, Nedra, Moscow, 1983.
9 M. A. Veiderma, *Izv. AN SSSR. Khimiya, geologiya*, 26, 1 (1977) 28.
10 Yu. A. Kiperman, V. I. Skorobogatov, E. F. Antonets *et al.*, Gorny informatsionno-analitichesky byulleten', Moscow, 1995, issue 1, p. 44.
11 E. A. Eganov, Problemy obrazovaniya i razmeshcheniya plastovykh fosforitov, Nauka, Novosibirsk, 1974.
12 J. Amgalan, A. Bilegbaatar, *Chemistry for Sustainable Development*, 4 (1996) 163.
13 V. A. Oknina, Metody khimicheskogo analiza fosfatnykh rud, Goskhimizdat, Moscow, 1961.
14 Udobreniya mineral'nye, GOST 20851–2–75.
15 V. P. Florensky, B. V. Bal'shina, A. N. Lopakov, Raschet khimicheskikh analizov osadochnykh porod, Vysshaya shkola, Moscow, 1964.
16 R. Z. LeGeros, *Bull. Soc. Chem. Franse*, Num. Spec. (1968) 1712.
17 L. G. Gilinskaya, in: Issledovaniye fosfatov kal'tsiya fizicheskimi metodami, Nauka, Novosibirsk, 1979, p. 39.
18 M. V. Chaikina, *Chemistry for Sustainable Development*, 4 (1996) 71.
19 R. G. Knubovets, Kristallokhimiya i svoystva apatita: Obzornaya informatsiya, Ser. Gorno-khimicheskaya promyshlennost', NIITEkhim, Moscow, 1988.
20 Ekologo-geokhimicheskaya otsenka fosfatnogo syr'ya i udobreny, in: Fosfaty na rubezhe XXI veka, Moscow *etc.*, 1996.
21 V. G. Kazak, A. I. Angelov, Yu. A. Kiperman, *Problemy fosfatnoy geologii. Gorny vestnik*, Spec. issue, 96 (1996) 76.