

## BLACK POWELLITE FROM MOLYBDENUM–URANIUM DEPOSIT

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New data on black powellite from a Mo-U deposit, South Kazakhstan are given. Bipyramidal crystals of the mineral have been found in intimate association with uranium minerals of the oxidized zone, including uranyl-arsenate mica (uramarsite) and uranyl silicate uranophane-beta. X-ray diffraction, infrared spectroscopy, differential thermal analysis (DTA), analytical scanning electron microscopy (ASEM), electron microprobe, X-ray fluorescence analysis (XRFA), and laser spectrography have been performed to examine the mineral. Two varieties of powellite have been identified: crystalline in uranophane and amorphous in uranate. The causes of black color of powellite are discussed. This coloration of powellite can be prospecting guide for deposits of radioactive elements. 9 figures, 10 references.

Keywords: powellite, uramarsite, uranophane, uranate, Mo-U deposit Bota-Burum, South Kazakhstan.

Tetragonal bipyramidal black crystals of 0.3–1 mm in size, whose chips are translucent in red attracted attention of mineralogists, when they studied oxidized zone of the Bota-Burum Mo-U deposit, South Kazakhstan. Isolated crystals are sealed in crystalline uranate (Fig. 1) (Sidorenko *et al.*, 2007). Intergrowths of these variably oriented crystals cover a surface (Fig. 1c) or heal cracks in host carbonated felsite porphyry. Regular black bipyramids were identified as inclusions in radiant aggregates (Fig. 2) of amber-coloured uranophane-beta (matrix mineral was determined by X-ray diffraction).

The composition of black mineral from various assemblages (various mineral matrices) was examined using electron microprobe, X-ray fluorescence analysis (XRFA) and laser spectrography. The compositions of the black crystals from various assemblages (uranate and uranyl-silicate) are the same; Ca and Mo are mineral-forming elements. X-ray element-distribution maps for a sample of uranate assemblage are shown in Fig. 3. The chemical composition of these black bipyramids was investigated with a JXA-8100 (JEOL, Japan) electron microprobe. Similar contents of Ca and Mo were

established in various samples. The compositions of the mineral from uranyl-silicate and uranate assemblages are as follows, wt. %: 26.91 CaO and 73.12 MoO<sub>3</sub>; and 26.63 CaO and 73.69 MoO<sub>3</sub>, respectively. These correspond to the composition of powellite and the formula CaMoO<sub>4</sub>. Iron less than 1% was detected in the first analysis that is caused by oxide films; insignificant content of other elements (Cu, U, Pb, Y, As) is due to the admixture of uranyl and clay minerals.

The luster of crystals ranges from adamantine to resinous, more frequent sub-metallic. Microscopically, bipyramidal crystals with adamantine luster are characterized by imperfect and rough faces. However, there are some differences in optical properties of powellite from various assemblages. The crystals included in uranophane-beta (call them "silicate") are *anisotropic*, whereas those disseminated in uranate are *isotropic*. Infrared spectra of powellite from these assemblages are substantially different (Fig. 4). Such distinction in IR spectra reflects the structural state of the mineral and can be resulted from both variable conditions of formation and post-crystallization history of the mineral. This fact caused separated description of each

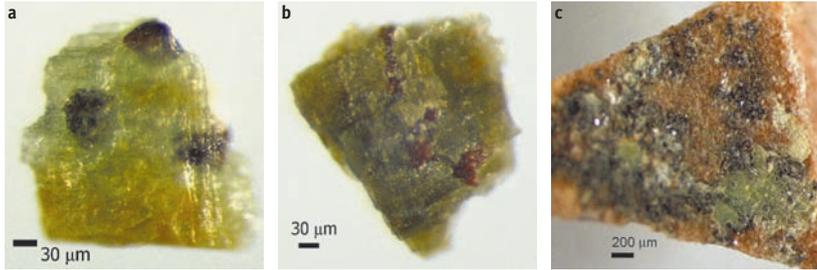


Fig. 1. Black powellite from uranate assemblage. (a, b) Isolated bipyramidal crystals included in uranarsite; (c) intergrowths of crystals covering surface of the rock.

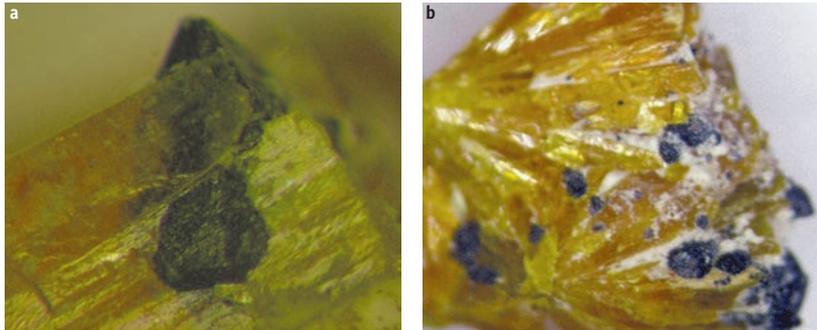


Fig. 2. (a) Inclusions of bipyramidal crystals black powellite in segregations of yellow  $\beta$ -uranophane; (b) black powellite associated with talc from uranophane-beta assemblage.

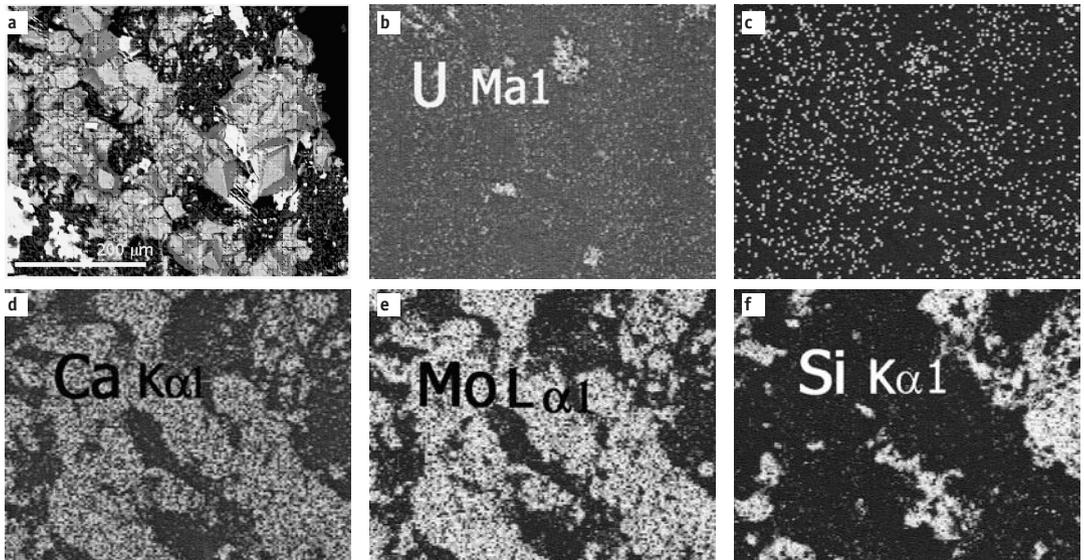


Fig. 3. (a) BSE image of intergrowths of metamict powellite crystals (grey) with grains of uranate (white) in silicate matrix (black); (b–f) X-ray element-distribution maps of U, As, Ca, Mo, and

variety of powellite. Anisotropic Ca-molybdate with IR spectrum of powellite was studied in more detail. Despite initial object for research, isotropic variety was examined in less detail due to extremely small amount.

The aim of this study is to explain rare black color of powellite. There are few reasons for change of typical color of a mineral: (1) disseminated mineral micro-admixture (for example, pink coloration of quartz is caused by the microphase of goethite); (2)

isomorphous impurity; (3) structural damages caused by radioactive emanation (for example, smoky coloration of quartz), which can be removed by ignition to restore primary color of mineral.

### Black powellite associated with uranyl silicate

The crystals are uniaxial, with refractive index more than 1.780. The density of po-

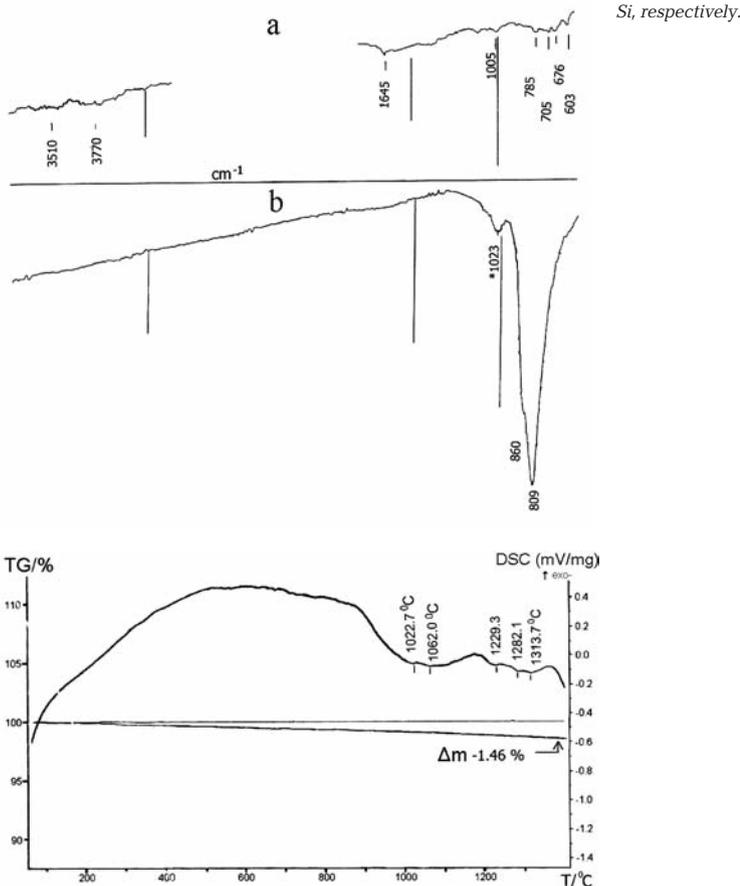
wellite measured with microvolumetric method by Vasilevsky ranges from 4.023 to 4.195 g/cm<sup>3</sup>; the average value (six measurements) is 4.128 g/cm<sup>3</sup> that is much less than in handbooks [4.54–4.23 (Feklichev, 1977); 4.25–4.52 (Lazarenko, 1963)]. The density becomes typical of powellite 4.249 g/cm<sup>3</sup> after one hour ignition at 600°C.

X-ray powder diffraction pattern of the crystals from silicate assemblage corresponds to well-crystallized powellite with insignificant admixture of -uranophane (X'Pert PRO Panalytical diffractometer; CuK radiation). The tetragonal unit-cell dimensions of black powellite are:  $a = 5.227 \text{ \AA}$ ,  $c = 11.428 \text{ \AA}$ ,  $c/a = 2.186$ . Sharp X-ray diffraction pattern was remained after ignition of powder up to 700°C; no changes of the unit-cell dimensions were documented:  $a = 5.229 \text{ \AA}$ ,  $c = 11.430 \text{ \AA}$ ,  $c/a = 2.186$ .

IR spectrum recorded with a SPECORD 75 IR spectrometer is typical of powellite (Fig. 4) characterized by insignificant admixture of silicate (talc).

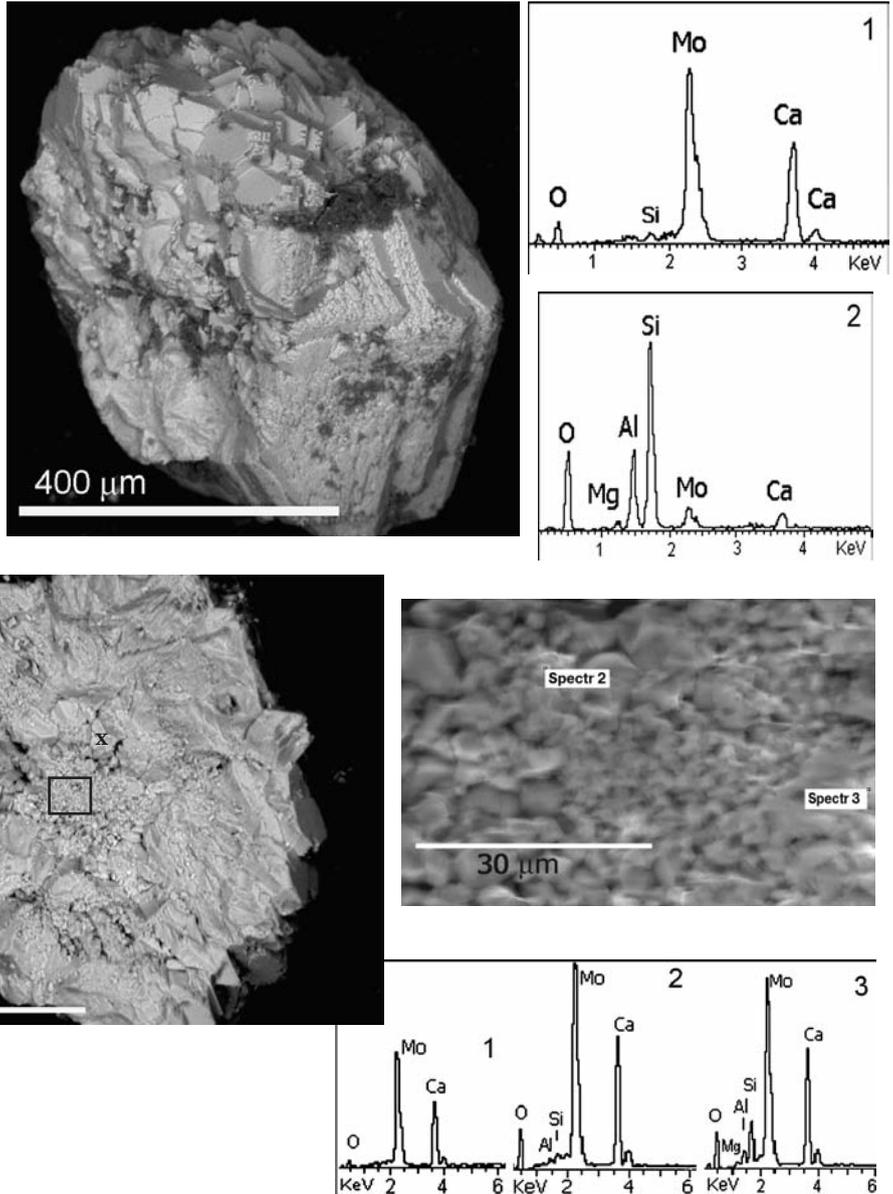
Differential thermal analysis (DTA) of powdered black crystals indicated that a broad exothermal peak with total weight loss of 1.46% (Fig. 5) is observed at DTA curve at heating up to 900°C and the further ignition results in textural and structural ordering. This exothermal peak can be probably caused by that the thermal effect removes stress and elevated potential energy accumulated by crystal.

Analytical scanning electron microscopic (ASEM) study using a JSM 5300 JEOL scanning electron microscope equipped with INCA energy dispersion system was performed to explain black coloration of powellite. The assumption of



Si, respectively.

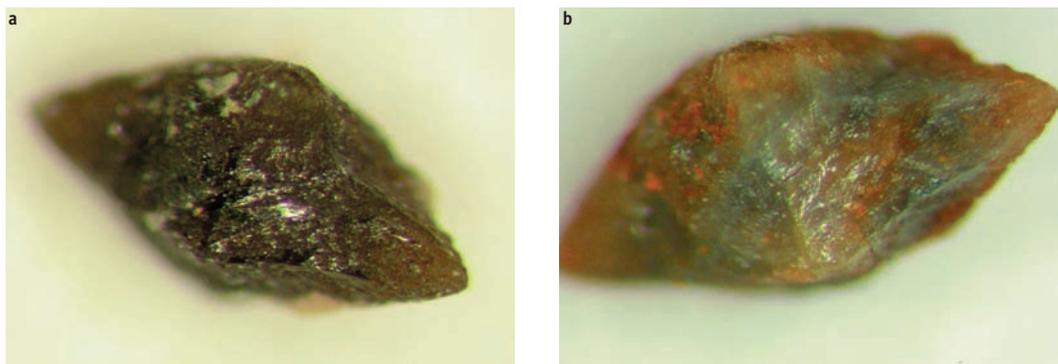
Fig. 4. IR absorption spectra of powellite: (a) metamict (uranate assemblage); (b) crystalline (uranophane-beta assemblage). Asterisk denotes admixture of clay matter.



disseminated highly dispersed mineral phase in powellite resulted in color transformation was checked. No extraneous mineral phases were identified in powellite.

Imperfect surface of faces of tetragonal bipyramid is clearly seen under electron microscope. These faces are covered by heads of variable-sized microcrystals (Fig. 6). The inner structure on the fractured surface of bipyramidal crystallites is very

interesting. The secondary emission image shows sheath-shaped character of bipyramidal microcrystal having wide solid layer at the surface, disoriented mosaicism in the intermediate part, and powder-like porous structure in the core (Fig. 7). The dispersivity of crystallite increases toward the core that is like loose submicroblock (polycrystalline) segregation. The composition of calcium molybdate is unchangeable in the whole volume.



In addition to Ca and Mo, traces of U or Pb were locally detected. E.V. Kopchenova and K.V. Skvortsova (1958) identified these trace elements in powellite from Bota-Burum. We suggest that this fact is caused by failure of textural homogeneity of crystals during post-crystallized alteration. Such continuous superegene alteration led to micro-mosaicism and porosity of mineral matter within crystal. The solutions penetrating bipyramidal powellite crystals along microfractures destroyed the central part composed of numerous nuclei. Disorientation of microcrystals generated during growth and further natural selection of larger blocks terminating growing single crystal favored disintegration. Superegene destruction of the powellite crystal was gradual with introduction of trace elements appeared in solutions during superegene transformation (U, Pb, As etc.). We can conclude this on the basis of the texture revealed by ASEM study of crystal chip.

Is it a combination of intrastructural features that is an original cause of unusual black coloration of powellite? According to the handbook (Lazarenko, 1963), the typical pale yellow color of powellite is diagnostic feature of the mineral. Specified structural failures can be removed by heat treatment, which was performed.

Black bipyramidal crystals ignited up to 700°C in air in muffle changed their color to conventional slightly grayish greenish

yellow (Fig. 8). Solid surface on chip of ignited crystal (Fig. 9) indicates compaction of micro-blocky structure of the matter observed in black crystals before ignition (Fig. 7). Point analyses did not show changes in composition of the surface of ignited crystal. Small admixture of Al is observed in the grain core; in wide marginal zones Al peak slightly increases and insignificant Si peak appears; these elements are probably related to the primary admixture of talc.

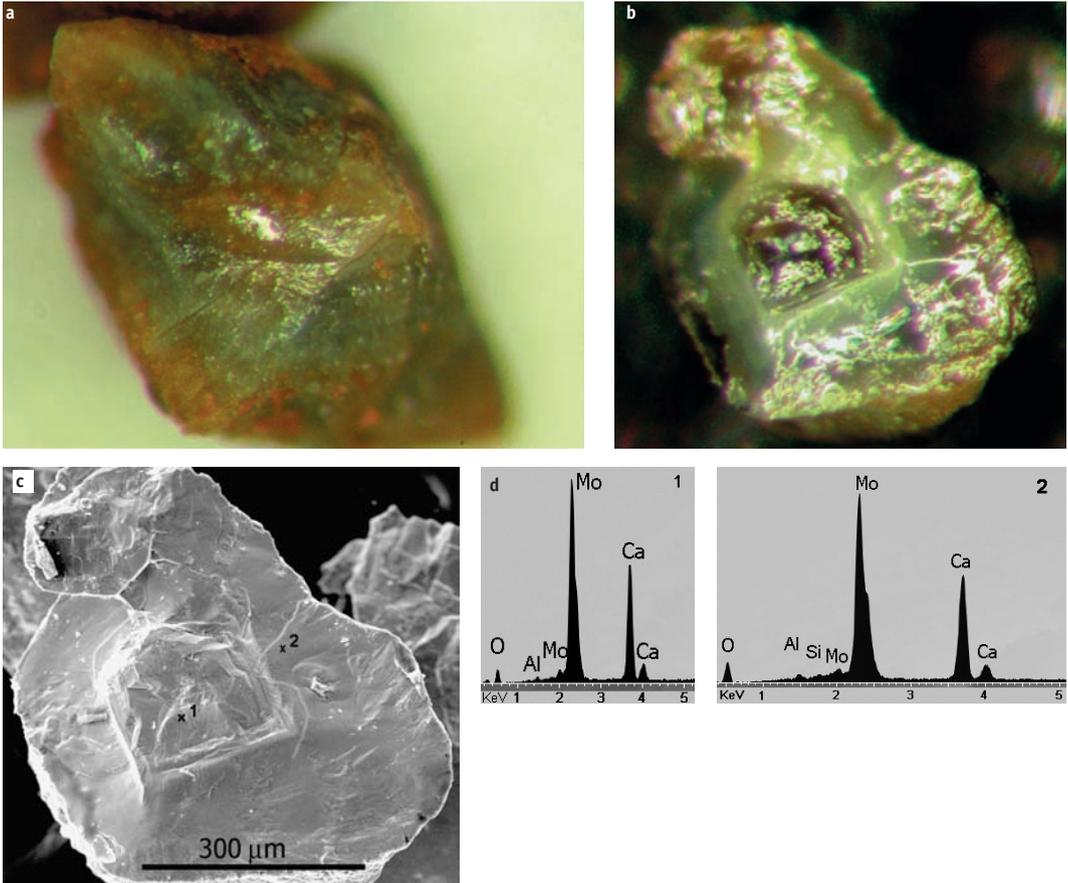
### Black powellite associated with uranate

Isolated powellite crystals (Fig. 1) were identified in uramarsite  $(\text{NH}_4, \text{H}_3\text{O})_2(\text{UO}_2)_2(\text{AsO}_4, \text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ , uranium mica discovered at Bota-Burum (Sidorenko *et al.*, 2007). Black bipyramids are included in lamellar uramarsite.

Microscopically, in immersion liquids, black crystals of powellite recovered from lamellar uranate are isotropic. Despite tetragonal bipyramidal shape, powellite crystals do not demonstrate X-ray diffraction pattern, thus they are X-ray amorphous.

There are no bands of powellite in IR spectra (Fig. 4a). Characteristic bands of water molecules and a molybdenum oxide indicate substantial transformation of the mineral.

Combination of crystal shape of powellite, optical isotropy, X-ray amorphism,



and bands of H<sub>2</sub>O and Mo oxide in IR spectrum shows the metamict state of powellite crystals associated with uranate. Godovikov (1975) reported certain instability of powellite, which "under supergene conditions ... is easily transformed into molybdenum acid and hydromolybdates".

A term "metamict mineral" introduced in mineralogy by Brögger (1896) implies notion "mix otherwise" meaning a mineral, where the arrangement of molecules in the crystal structure differs from that in an initial crystal. In an extreme case, this results in amorphous state of mineral with preserved crystal shape, but with optical isotropy, absence of cleavage, and conchoidal fracture. Thus, the preservation of crystal shape with the failure (to complete destruction) of three-dimensional lattice periodicity in a crystal structure is the major feature of metamict state. Just these fea-

tures are characteristic of black powellite from uranate assemblage. This structural failure can be caused by sufficiently strong radiation that results in the displacement of atoms in the crystal structure of the mineral. Most important lithospheric radioactive elements are U, Th, and <sup>40</sup>K whose decay is accompanied with α-, β-, and γ-emission are attributed to such natural sources of radiation. -component that can displace atoms in crystal structure is the most effective. For example, colored halos around mineral inclusion containing radioactive elements in transparent colorless single crystals of quartz visualize such effect.

X-ray amorphous (metamict) state is characterized by higher potential energy as compared to the same matter but in crystalline state. Heating of metamict mineral releases this energy that is recorded on the DTA curves as exothermal peak at tempera-

ture (temperature of recalescence) lower than that of destruction or melting of the mineral. The similar energy release can cause exothermal effect on the DTA curve of uranophane associated powellite, which lost typical yellowish color (indicating transformation of mineral matter) but preserved ability of diffraction. Probably, maximum transformation leading to complete amorphization occurs in powellite associated with uranate. Unfortunately, due to lack of material, thermal analysis of powellite associated with uranate was not performed.

Ignition of metamict mineral either restores initial crystal structure (recrystallization when minimum fragments of initial structure were preserved in the structure) or results in crystallization of simple oxides of mineral-forming elements. In any case, amorphous matter is devitrified. The similar devitrification of porous, but crystalline matter we observed after ignition of black bipyramidal crystals of powellite associated with uranophane.

Metamict state is not typical of powellite. Therefore, the following remains undecided: what did lead crystal structure of the examined mineral with heterodesmic interatomic bonds (degree of Ca-O ionic bond is near two times more than Mo-O) to metamict, i.e., amorphous state with the preservation of crystal shape. As aforementioned, transition from crystalline to metamict state as a rule is caused by the irradiation of the own matter of the crystal. In our case, the mineral matrix composed of secondary uranium minerals is a source of radioactive emanation because black crystals of powellite are dipped in it.

Close sizes of powellite grains from different above-described mineral matrices and quite identical shape of bipyramidal crystals indicate simultaneous formation of powellite from different assemblages at the deposit. According to the shape of powellite crystals, the mineral predates uranyl mineralization. Different structural state of powellite (from uranate and uranyl silicate assemblages) can testify to varied duration

of the contact of the mineral with radioactive elements and variable degree of supergene alteration of powellite (for example, hydration, micro-mosaicism etc.). This fact can be explained on the basis of general features and stages of supergene formation of uranium minerals (Belova, 2000; Belova and Doinikova, 2003; Doinikova *et al.*, 2003). Uranate are formed at the later oxidized stage than uranyl silicates. Uranate characterize longer process of uranyl mineralization. Hence, powellite associated with uranate was longer affected by radioactive medium. Powellite from the uranophane assemblage was shorter affected by uranium mineralization that resulted only in the failure of the matter continuity (texture) within crystals but was sufficient for disappearance of anisotropy and ability for diffraction of the mineral. G.K. Krivokoneva (pers. comm.) noted that crystals of powellite associated with uranyl silicate are black only on the surface, whereas inside, they are yellowish white. This observation supports our assumption of radiation nature of black color of the mineral. In other words, longer contact with radiation leads to both failure and metamict radioactive decay that occurs in case of uranate assemblage. Relatively less irradiated powellite from the uranyl silicate assemblage preserves three-dimensional order of crystal structure with high mosaicity.

The distinction in mineral assemblages containing bipyramids of powellite is caused by irregular formation conditions of secondary uranium minerals that were reported by E.V. Kopchenova and K.V. Skvortsova (1958), who studied mineralogy of this deposit for a long period: "Nasturane-sulfide mineralization at the Bota-Burum deposit hosted in altered felsitic volcanic rocks oxidize along highly jointed zones that causes extremely irregular secondary mineralization". Therein and in description of stages of supergene uranium mineralization (Belova and Doinikova, 2003), there was reported that uranium hydroxides and silicates precipitate in neu-

tral and weak-acid media, whereas uranium micas, in acid.

Summarizing the results obtained, we conclude that black color of powellite is related to radiation effect upon the mineral resulted in the transformation of its structure from micro-blocky to the complete loss of three-dimensional order. In other words, blocks of coherent scattering (BCS) decrease and powellite becomes metamict. Radiation medium leads to the failure of definite molybdenum coordination in powellite. In the mineral structure, character of chemical bond changes and coordination polyhedron of molybdenum is distorted with invariability of hexavalent Mo in supergene zone. We suggest that this phenomenon is similar to darkening of phosphate (or arsenate) uranate as a result of pyrophosphate (pyroarsenate) complexes in the crystal structure of this mineral (Belova *et al.*, 1992). The change of black color of powellite to characteristic greenish yellow clearly testifies to radiation origin of structural failure of this mineral and its unusual color.

Thus, black color of powellite can be considered as an indicator of radioactivity of host rocks. Such specific color of powellite can serve as a prospecting guide for deposits of radioactive elements.

Intimate association of powellite with secondary uranium minerals, whose conditions of formation are known, testifies to the stability of powellite in near-neutral and acidic media. This allows recalling numerous publications concerning reasons of metamictisation of minerals, where role of hydration was noted. In our case, revealed micromosaicity favored this process and supergene solution along with other elements introduced uranyl, which was radioactive source in an interblock space of crystallites.

The conclusion on the existence of metamict powellite is an interesting result of this study. Up to date, metamictisation was associated with radioactive elements (U,Th), which form proper minerals or

incorporate by isomorphic substitution into the structure of the other minerals. Probably, small size (few mm) of powellite crystals in comparison with volume of host uranium mineralization played important role. Such significant structural failure was favored by polyvalency of Mo.

The documented amorphization of powellite should attract attention of mineralogists because metamictization of calcium molybdate indicates the possibility of similar transformation for other minerals.

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