THE PHOSPHATE MINERALS ON BULGARIA - DISTRIBUTION AND GENESIS

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Introduction. Костов (1993) propose for the phosphate, arsenate and vanadate minerals the formules $A_m[XO_4]_pZ_q.xH_2O$ and $A_mB_m[XO_4]_pZ_q.xH_2O$ (where $[XO_4]$ is $[PO_4]$, $[AsO_4]$ and $[VO_4]$; Z is OH, F, Cl, O; A and B – metals.

Practically all natural minerals of the phosphorus are phosphates with anisodesmic structure made by tetrahedral radicals $(PO_4)^{3-}$ (Kostov, Breskovska, 1989). More than 30 cations react with the phosphorus to form minerals. About 100 minerals contain iron, more than 60 - aluminum, about 60 - calcium, 45 - manganese, etc.

The easily generate in the superficial conditions, the broade spectrum of the cations and the isomorphism between them destine the riche and diversity of the posphate minerals. The possibility for the cation isomorphism between phosphorus and sulphur is the cause for the formation of the about a 11 minerals (ardealite, svanbergite, hinsdalite, orpheite, corkite, woodhouseite etc.).

Discussion. The latest monographic overview on the minerals of Bulgaria dates back to 1964 (Костов et al.). In this monography are described the next phosphates and that sort with additional anions: apatite, wavellite, moraesite, vivianite, cacoxenite, xenotime, monazite, pseudo-malachite, pyromorphite, corcite, hinsdalite, plumbogummite, dumontite, torbernite, autunite, uranocircite, phosphuranylite. In the followed period have been discovered: churchite, anapaite, andrewsite, orpheite, turqouise, faustite (cupro-), rosherite, chalcosiderite (alumo-), augelite, ardealite, landesite, variscite, florencite-(Ce), svanbergite, woodhouseite, taranakite, newberyite, brushite, basetite, fluellite, laubmanite, strengite. So far total with the variety of the apatite (carbonat-fluorapatite, carbonate-hydroxylapatite, hydroxylapatite), pyromorphite-Ca and corcite (Cu containing) are 52 (Минчева-Стефанова, Костов, 2001). This is the 1/6 part of the described phosphate minerals for the world and show possibility for the new minerals for Bulgaria and enlarge the their diversity.

The territorial and quantitative distribution of the phosphates in Bulgaria is irregular (Fig. 1). The apatite is the most frequently found, taking also in account his occurrence as an accessory rock-forming mineral. A significant part of the phosphates is concentrated in the Eastern Rhodopes (Chala, Madzharovo, Obichnik etc.), and only few or some single species - in the Central (Chelopech, Assarel) and Eastern (Duni, Sv. Agalina) Srednogorie. Most of the so far established phosphates in Bulgaria have been found during the investigation of ore mineralizations and wall-rock alterations of regions of intensive hydrothermal-metasomatic and supergene processes.

The phosphate minerals (Table 1, Fig. 1) be found in the differents genetic type deposits: magmatic, metamorphic, sediments (phosphorites), pegmatites and alpide type veins, hydrothermales, suppergenes, biogenes.

The dates of the suppergene are predominate. The convergence of the formation in number of cases indicate though (apatite, turqouise, florencite, variscite, svanbergite etc.) (Kunov, 1999). In the last ten years in the porphyry copper deposit Assarel and in the epithermal deposits and occurrences Chelopech, Bakadzhic, Duni, Klisoura, Obichnik are established woodhouseite-svanbergite solid solutions (possible some hypogene, other supergene). The correct genetic interpretations have an important theoretical and practical value.

Conclusions. One modern and contemporary interpretation of the know dates and discover of the new dates could be used for the enlargement and multiplication the knowledge in the geochemistry and the mineralogy of the posphate minerals of Bulgaria. In many cases it is possible to expect that the phosphates could be used as indicators for the discovery of the occurrences of divers metals.

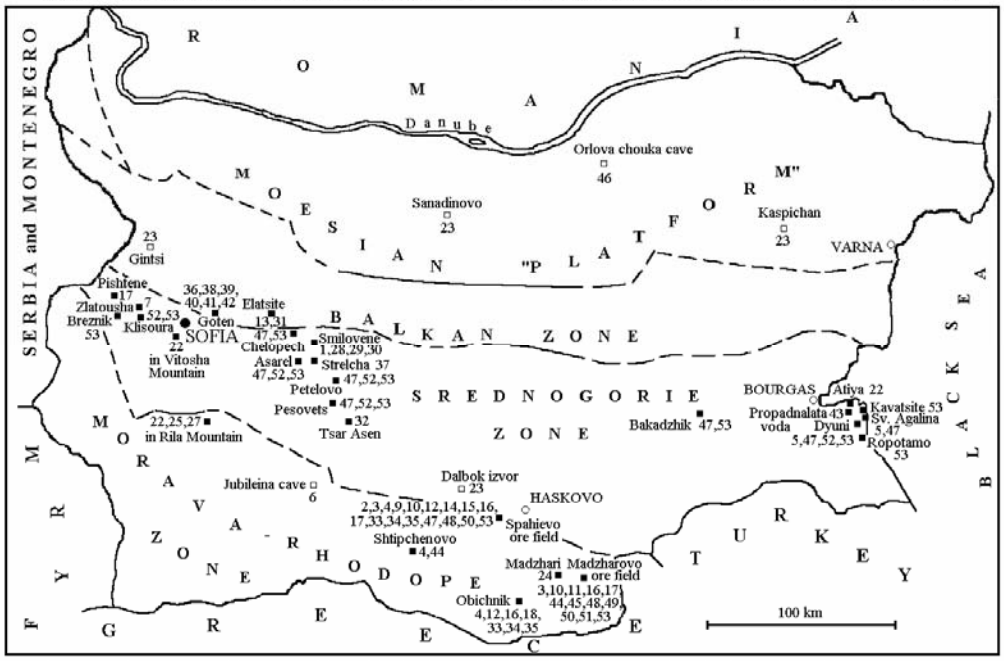
In the world science attach great importance to the geochemistry of the phosphorus also of the its migration and concentration. This interest is not accidental; it first of all is provoked by the actuality of the problems, connected with the interaction between the man and the surroundings. That somewhat account the place of the investigation of the phosphate minerals in the complete study of the problems of the phosphates in the surroundings.

Table 1. The phosphate minerals in Bulgaria

Species	Formula	Space Group	Firstly Occurrence	Authors
Be-(Al, Fe)-Mg Assemblages				
Axial				
1. Moraesite	$Be_2PO_4(OH)_4.4H_2O$	*Cc*	Smilovene	Ivanov, Arnaudov, 1964
2. Augelite	$Al_2PO_4(OH)_3$	*C2/m*	Spahievo ore field	Kunov et al., 1986; Kunov, 1996
3. Wavellite	$Al_3(PO_4)_2(OH)_3.5H_2O$	*Pcmn*	Madzharovo ore field	Angelov, 1960
Planar				
4. Plumbogummite	$Al_3Pb(PO_4)_2(OH)_5.H_2O$	*R3m*	Shtipchenovo	Kostov, 1960
5. Florencite	$Al_3Ce(PO_4)_2(OH)_6$	*Fddd*	Sv. Agalina	Kunov et al., 1992
6. Taranakite	$Al_3(PO_4)_2(OH)_3.5H_2O$	*R3c*	Jubileina cave	Fillipov, 1979
7. Overite	$AlCa\,Mg(PO_4)_2(OH).4H_2O$	*Pcaa*	Zlatousha	Ferdov, Kunov, 2001
8. Newberyite	$MgHPO_4.3H2O$	*Pbca*	(?)	Shopov, 1999
(Pseudo)Izometric				
9. Rosherite	$Be_3Ca(Mn,Fe)_2(PO_4)_3(OH)_3$	*C2/c*	Spahievo ore field	Gadzheva, Matanova, 1980
10. Variscite	$AlPO_4.2H_2O$	*Pcab*	Spahievo ore field	Kunov, 1977
11. Gelvariscite			Madzharovo ore field	Todorov, 1984
12. Strengite	$FePO_4.2H2O$	*Pcab*	Obichnik	Kunov, Mandova, 1997
13. Fluellite	$Al_2PO_4(OH)F_2.7H2O$	*Fddd*	Elatsite	Tokmakchieva, 1994
14. Lazulite	$Al_2MgPO_4(OH)$	$P2_1/c$	Spahievo ore field	Patrikova, 2000
Li-Fe-Mn Assemblages				
Axial				
15. Laubmanite	$Fe_3Fe_6^{3+}(PO_4)_4(OH)_{12}$	*Pbma*	Spahievo ore field	Kunov et al., 1997
16. Cacoxenite	$Fe_{24}Al(PO_4)_{17}(OH)_{12}.O_6(H_2O)_{24}.51H_2O$	$P6_3/m$	Madzharovo ore field	Breskovska, 1961
Planar				
17. Vivianite	$Fe_3(PO_4)_2.8H2O$	*C2/m*	Madzharovo ore field	Kolkovski (Kostov et al., 1964)
(Pseudo)Izometric				
18. Landezite	$Fe_3Mn_9(PO_4)_2(OH)_3.9H2O$	*Pbcn*	Obichnik	Kunov, Mandova, 1997
Na-Ca-Ba Assemlages				
Axial				
19. Ningyoite	$(Ca,U,Ce)_2(PO_4)_2.1\text{-}2H_2O$	*P222*	Depression (?)	Belova et al., 1986
Planar				
20. Anapaite	$Ca_2Fe(PO_4)_2.4H_2O$	*P1*	Sofia district	Ruskova, Alexiev, 1971
21. Brushite	$CaHPO_4.2H2O$	*A2*	Magura cave	Fillipov, 1980
(Pseudo)Izometric				
22. Apatite	$Ca_5[PO_4]_3(OH)_3.(F, Cl, OH)$	$P6_3m$	Rila Mountain	Zlatarski, 1882
23. Fluorapatite	$Ca_5[PO_4]_3(OH)_3.F$	$P6_3m\ P6_3m$	Sanadinovo,Kaspichan	Nacheva, Kokev, 1966
24. Hydroxylapatite	$Ca_5[PO_4]_3.(OH)$	$P2_1a$	Madzhari	Todorova et al., 1972

25. Chlorapatite	$Ca_5[PO_4]_3(OH)_3$. Cl	*$P6_3m$*	Vitosha Mountain	Kostov et al., 1964
26. Carbonate-fluorapatite (francolite)	$Ca_5(PO_4,CO_3)_3$.F	*$P2_1/n$*	Haskovo district	Atanasov, 1961
27. Monazite	(Ce,La,Y,Th)[PO_4]	*14/mmm*	Rila Mountain	Alexiev, Tstvetkova, 1962
28. Xenotime	YPO_4	*$P6_222$*	Smilovene	Kostov et al., 1964
29. Rhabdofane	(Ce,La,Nd)$PO_4.H_2O$	*A2/a*	Smilovene	Ivanov, 1968
30. Churchite	$YPO_4.2H_2O$		Smilovene	Ivanov, 1968
Zn-Cu-Pb(U) Assemblages				
Axial				
31. Libethenite	$Cu_2PO_4(OH)$	*Pnnm*	Elatsite	Tokmakchieva, 1994
32. Andrewsite	$Cu_3Fe_6(PO_4)_4(OH)_{12}$	*$B22_12$*	Tsar Asen	Tokmakchieva, 1994
Planar				
33. Turqouise	$CuAl_6(PO_4)_4(OH)_8.4H_2O$	*P1*	Spahievo ore field	Kunov et al., 1977
34. Chalcosiderite (alumo-)	$CuFe_6(PO_4)_4(OH)_8.4H_2O$	*P1*	Spahievo ore field	Kunov et al., 1986
35. Faustite (cupro-)	$ZnAl_6(PO_4)_4(OH)_8.4H_2O$	*P1*	Spahievo ore field	Kunov et al., 1982
36. Dumontite	$Pb_2(UO_2)_3(PO_4)_2.5H_2O$	*$P2_1/m$*	Goten	Kostov et al., 1964
37. Autunite	$Ca(UO_2)_2(PO_4)_2.10\text{-}20H_2O$	*I4/mmm*	Strelcha	Azmanov, 1933
38. Torbernite	$(UO_2)_2Cu(PO_4)_2.8\text{-}12H_2O$	*I4/mmm*	Goten	Koniarov, 1937
39. Metatorbernite	$Cu(UO_2PO_4)_2.8H_2O$	*P4/nmm*	Goten	Koniarov, 1937
40. Bassetite	$Fe(UO_2)_2[PO_4]_2.8H_2O$	*$P2_1/m$*	Goten	Stoynov, Bozhkov, 1991
41. Phosphuranylite	$Ca(UO_2)_4[PO_4]_2.(OH)_4.7H_2O$	*Bmmb*	Goten	Kostov et al., 1964
42. Uranocircite	$Ba(UO_2)_4[PO_4]_2.8H_2O$	*P4/nnc*	Goten	Bonchev, 1923
(Pseudo)Izometric				
43. Pseudomalachite	$Cu_5(PO_4)_2(OH)_4.H_2O$	*$P2_1/c$*	Propadnalata voda	Kostov, 1960
44. Pyromorphite	$Pb_5(PO_4)_3$.Cl	*$C6_3/m$*	Madzharovo	Kolkovski, 1959
45. Pyromorphite-Ca			Madzharovo	Breskovska, 1988
With additional groups				
Planar				
46. Ardealite	$CaH(PO_4)(SO_4).2H_2O$	*C2/c*	Orlova chuka cave	Fillipov, 1983
47. Svanbergite	$SrAl_3(PO_4)(SO_4).(OH)_6$	*R3m*	Spahievo ore field	Kunov et al., 1986
48. Hinsdalite	$PbAl_3(PO_4)(SO_4).(OH)_6$	*R3m*	Madzharovo	Kolkovski (Kostov et al., 1964)
49. Orpheite	$Pb_{10}Al_{20}H(PO_4)_{12}(SO_4)_5.(OH)_{40}.11H_2O$	*$14_1/amd$*	Madzharovo	Kolkovski, 1971
50. Corcite	$PbFe_3(PO_4)(SO_4).(OH)_6$	*R3m*	Madzharovo	Kolkovski (Kostov et al., 1964)
51. Corcite (Cu containing)			Brusevtsi	Tsvetanova, 1993
52. Woodhouseite	$CaAl_3(PO_4)(SO_4).(OH)_6$	*R3m*	Asarel	Velinov et al., 1991

Fig. 1. Firstly and more important occurrences of phosphate minerals Bulgaria (Tectonic scheme of Bulgaria after Dabovski et al., 2002)



■ - in magmatic, metamorphic, pegmatitic and hydrothermally altered rocks; □ - in phosphorite rocks and in caves

Comment: Number 53 is for the mixed phases of the phosphate and phosphate with additional groups minerals, well-knowns also like (aluminium phosphate-sulfate minerals; Stoffregen, Alpers, 1987). Some new data into fig. 1 are results be the French-Bulgarian Program "EGIDE", PAI "Rila 10"

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