Minerální asociace fosfátů z Čížové u Písku (Česká republika)

The phosphate mineral association from Čížová near Písek (Czech Republic)

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Abstract

An interesting phoshate mineral assemblage was found in temporary open cut 700 m W from Čížová near Písek, southern Bohemia, Czech Republic. Fluorapatite forms abundant white veins up to 1 cm thick and white spherical aggregates in cavities; minor contents of carbonate ions were observed; its empirical formula is $(Ca_{4.95}Al_{0.02}Mg_{0.01}Fe_{0.01})_{\Sigma 5.00}[(PO_4)_{2.82}(CO_3)_{0.18}]_{\Sigma 3.00}F_{0.18}[F_{0.93}(OH)_{0.09}]_{\Sigma 1.02}$ and refined unit-cell parameters are *a* 9.3607(5), *c* 6.8860(9) Å, *V* 522.53(7) Å^3. Leucophosphite was found only as very rare irregular crystals and their aggregates up to 50 - 80 μm in size on hemispherical variscite; its empirical formula is $(K_{0.82}Na_{0.01}\square_{0.17})_{\Sigma 1.00}(Fe_{1.32}Al_{0.61}Ba_{0.04}Ca_{0.02}Mg_{0.01}Cu_{0.01}Zn_{0.01})_{\Sigma 2.02}[(PO_4)_{1.97}(SiO_4)_{0.03}]_{\Sigma 2.00}[(OH)_{0.70}F_{0.03}]_{\Sigma 0.73}.\ 2H_2O$. Meurigite-K forms rare yellow spherical aggregates up to 0.4 mm in size growing on hemispherical green natrodufrénite aggregates; its empirical formula is $(K_{0.60}Ca_{0.09}Na_{0.02}\square_{0.29})_{\Sigma 1.00}(Fe_{6.72}Al_{1.01}Mg_{0.04}Zn_{0.01})_{\Sigma 7.78}[(PO_4)_{5.60}(SiO_4)_{0.25}(VO_4)_{0.11}(AsO_4)_{0.04}]_{\Sigma 6.00}(OH)_{5.84}\ .\ 6.5H_2O$. Natrodufrénite was found as dark green to bluish green aggregates with light green or yellowish green zones forming reniform crusts (1 - 2 mm thick) on rocks; its empirical formula is $(Na_{0.68}Ca_{0.08}\square_{0.24})_{\Sigma 1.00}(Fe^{2+}_{0.96}Zn_{0.03}Mg_{0.01})_{\Sigma 1.00}(Fe^{3+}_{4.42}Al_{0.51})_{\Sigma 4.93}[(PO_4)_{3.86}(SiO_4)_{0.09}(AsO_4)_{0.03}(VO_4)_{0.02}]_{\Sigma 4.00}(OH)_{5.49}F_{0.02}\ .\ 2H_2O$ and refined unit-cell parameters are *a* 25.883(6), *b* 5.152(1), *c* 13.830(3) Å, *β* 111.37(2)° and *V* 1717.2(9) Å^3. Opal as the youngest mineral phase forms thin transparent colourless coatings on older phosphates and tiny irregular or dropstone-like aggregates in cavities. Perhamite was determined as irregular aggregates up to 0.2 mm in size in close association with wavellite; its empirical formula is $(Ca_{3.03}Ba_{0.11}Mg_{0.07}Sr_{0.02})_{\Sigma 3.23}(Al_{7.65}Fe_{0.08})_{\Sigma 7.73}Si_{2.56}(P_{4.38}V_{0.06})_{\Sigma 4.44}O_{23.65}(OH)_{14.17}F_{0.63}\ .\ 8H_2O$. Turquoise forms apple green crusts (0.5 - 1 mm thick) with reniforms surface; its empirical formula is $(Cu_{0.68}\square_{0.29}Zn_{0.21}Fe^{2+}_{0.03}Ca_{0.02})_{\Sigma 1.00}(Al_{5.52}Fe^{3+}_{0.48})_{\Sigma 6.00}[(PO_4)_{3.35}(PO_3OH)_{0.29}(SiO_4)_{0.34}(AsO_4)_{0.01}(VO_4)_{0.01}]_{\Sigma 4.00}(OH)_{7.28}F_{0.09}\ .\ 4H_2O$ and unit-cell parameters are *a* 7.426(8), *b* 7.634(8), *c* 9.91(1) Å, *α* 68.67(8)°, *β* 69.70(8)°, *γ* 65.01(8)° and *V* 461.5(9) Å^3. Two varieties of variscite was observed; variscite I with empirical formula $(Al_{0.98}Fe_{0.01})_{\Sigma 0.99}(PO_4)_{1.00}F_{0.01}$ forms massive white to bluish green aggregates up to 2 cm in weathered quartzite; and variscite II with $(Al_{0.92}Fe_{0.08})_{\Sigma 1.00}[(PO_4)_{0.98}(VO_4)_{0.02}]_{\Sigma 1.00}F_{0.04}$ was found as light green hemispherical to reniform aggregates up to 1.5 mm in size forming crusts with some tens cm^2 in area; both varieties belong to variscite of Messbach type with following unit-cell parameters: I *a* 9.894(1), *b* 9.6586(7), *c* 17.175(2) Å, *V* 1641.2(3) Å^3; II *a* 9.895(6), *b* 9.659(4), *c* 17.206(7) Å and *V* 1645(1) Å^3. Lamellar aggregates up to 0.2 mm in size probably of berlinite were observed in the centre of variscite II aggregates; its empirical formula is $(Al_{0.81}Fe_{0.19}Ca_{0.01})_{\Sigma 1.01}[(PO_4)_{0.99}(VO_4)_{0.01}]_{\Sigma 1.00}F_{0.05}$. Wavellite is the most abundant phosphate in the studied mineral association, it usualy occurs as acicular crystals up to 1 cm in length forming rich spherical aggregates and veins in rock fissures. Its colour is significantly zonal, from yellowish green in the centre of aggregates through greenish blue and blue to colourless part in the marginal part. Yellow wavellite with empirical formula $(Al_{2.78}V_{0.10}Fe_{0.05}K_{0.05})_{\Sigma 2.98}(PO_4)_{2.00}(OH)_{2.16}F_{0.67}.5H_2O$ has unit-cell parameters *a* 9.6184(7), *b* 17.357(2), *c* 6.9893(9) Å, *V* 1166.9(2) Å^3; blue wavellite $(Al_{2.80}V_{0.07}Fe_{0.04}K_{0.04})_{\Sigma 2.95}(PO_4)_{2.00}(OH)_{1.99}F_{0.77}.5H_2O$ and *a* 9.616(1), *b* 17.357(2), *c* 6.991(1) Å, *V* 1166.8(2) Å^3; and colourless wavellite $(Al_{2.85}V_{0.04}Fe_{0.03}K_{0.03})_{\Sigma 2.95}(PO_4)_{2.00}(OH)_{2.07}F_{0.73}.5H_2O$ and *a* 9.613(1), *b* 17.354(2), *c* 6.991(1) Å, *V* 1166.4(3)Å^3, respectively. The studied assemblage of phosphates from Čížová is interpreted as young (subrecent - maximum up to some thousand years) low-temperature (up to 10° C) association; and its origin is connected with weathering of graphite quartzites in depth of few metres under the present surface.

Key words: *phosphates, X-ray powder diffraction, unit-cell parameters, chemical composition, Čížová near Písek, southern Bohemia, Czech Republic*