Analytical methods

Small fragments of phosphate nodules and associated minerals collected in 2000–2002 were investigated using an optical microscope, electron microprobe and X-ray powder diffraction. The electron microprobe analyses were performed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of University of Warsaw, using a Cameca SX 100 electron microprobe operating in wavelength-dispersive mode with the following conditions.

Phosphate minerals and tourmaline: accelerating voltage of 15 kV, beam current of 10 and 20 nA, respectively, beam diameter of 2–5 μm, peak counting time of 20 s and background time of 10 s. The following standards, analytical lines and crystals were used: phlogopite – F (K_α, TAP), albite – Na (K_α, TAP), diopside – Mg and Si (K_α, TAP) and Ca (K_α, PET), orthoclase – Al (K_α, TAP) and K (K_α, PET), apatite – P (K_α, PET), barite – Ba (K_α, TAP), tugtupite – Cl (K_α, PET), rhodonite – Mn (K_α, LIF), ZnS – Zn (K_α, LIF), $SrTiO_3$ – Sr (K_α, TAP).

Nb–Ta oxides: accelerating voltage of 15 kV, beam current of 70 nA, beam diameter of 2 μm, peak count time of 20 s, background time of 10 s; standards, analytical lines and diffracting crystals were as follows: LaP_5O_{14} – La (L_α, PET), CeP_5O_{14} – Ce (L_α, PET), PrP_5O_{15} – Pr (L_β, LIF), GdP_5O_{14} – Gd (L_α, LIF), REE1 – Dy (L_β, LIF) and Er (L_α, LIF), REE2 – Eu (L_β, LIF), Ho (L_β, LIF) and Tm (L_α, LIF), REE3 – Sm (L_α, LIF) and Yb (L_α, LIF), REE4 – Nd (L_α, LIF), Tb (L_α, LIF) and Lu (L_α, LIF), YAG – Y (L_α, PET), albite – Na (K_α, TAP), Ca (K_α, PET), Mg (K_α, TAP) and Si (K_α, TAP), orthoclase – K (K_α, PET) and (K_α, TAP), phogopite – F (K_α, TAP), pure Sc – Sc (K_α, PET), hematite – Fe (K_α, LIF), rhodonite – Mn (K_α, LIF), rutile – Ti (K_α, PET), zircon – Zr (L_α, PET), cassiterite – Sn (L_α, PET), pure Nb – Nb (L_α, PET), pure Ta – Ta (M_α, TAP), scheelite – W (M_β, PET), Bi_2Te_3 – Bi (M_α, PET), galena – Pb (M_α, PET), ThO_2 – Th (M_α, PET), UO_2 – U (M_β, PET), where REE1–REE4 are silica glass standards, containing the respective lanthanides (Drake and Weill 1972).

The raw data were reduced with the PAP routine of Pouchou and Pichoir (1985), whilst the overlaps of *REE* analytical lines were corrected using the coefficients given by Reed and Buckley (1998).

Chemical formulae of the analyzed phosphates have been calculated on the basis of the respective contents of P atoms per formula unit (*apfu*), with lithium and water calculated by stoichiometry, assuming Li = 1.0 *apfu* in triphylite, Li = Me^{2+} in ferrisicklerite, and no Li in heterosite. Manganese was assumed to be divalent except for heterosite, Fe_{total} only as Fe^{2+} in triphylite, graftonite, beusite, sarcopside and wagnerite-group minerals; in ferrisicklerite, heterosite and kryzhanovskite Fe_{total} was assumed to be Fe^{3+}. For alluaudite and a whitlockite-like minerals the Fe^{3+}/Fe_{total} ratio was obtained assuming the contents of 12 and 7 $(PO_4)^{3-}$ anions, respectively. Water in kryzhanowskite was calculated assuming OH + H_2O = 3 *pfu*. The chemical formula of a dickinsonite-like mineral was calculated using rules for members of the arrojadite-group minerals (Cámara et al. 2006; Chopin et al. 2006). Tourmaline compositions were normalized on the basis of 31(O,OH) anions (F was below detection) and 15 ($Y + Z + T$) cations when Si was below 6 *apfu*; otherwise the normalization was to 6 Si *apfu*. Compositions of biotite, garnet and fergusonite-(Y) were normalized to 22, 12 and 4 O *apfu*, respectively.

The X-ray powder-diffraction patterns were acquired at Faculty of Geology, Geophysics and Environmental Protection, AGH–UST in Cracow, by a Philips PW 3020 E'xpert-APD diffractometer system with a Cu anode and a graphite monochromator, beam at 35 kV voltage and 30 mA current, in the 2Θ range of 3–70° with a registration velocity of 0.01°/s. Quartz was used as an internal standard for the zero-shift calibration. The data were analysed using an X’rayan computer program and X-ray standards in the form of ICDD files (ICDD 2013).

References

CÁMARA F, OBERTI R, CHOPIN C, MEDENBACH O (2006) The arrojadite enigma: I. A new formula and a new model for the arrojadite structure. Amer Miner 91: 1249–1259

CHOPIN C, OBERTI R, CÁMARA F (2006) The arrojadite enigma: II. Compositional space, new members and nomenclature of the group. Amer Miner 91: 1260–1270

DRAKE MJ, WEILL DF (1972) New rare earth element standards for electron microprobe analysis. Chem Geol 10: 179–181

ICDD (2013) PDF-4+ (Database) The International Centre for Diffraction Data, Newrown Square, Pa, USA.

POUCHOU IL, PICHOIR F (1985) “PAP” (ϕ–ρ–Z) procedure for improved quantitative microanalysis. In: ARMSTRONG IT (ed) Microbeam Analysis. San Francisco Press, San Francisco, 104–106

REED SJB, BUCKLEY A (1998) Rare-earth element determination in minerals by electron-probe microanalysis: application of spectrum synthesis. Mineral Mag 62: 1–8