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Lazulite and Ba, Sr, Ca, K-rich phosphates–sulphates in quartz veins from metaquartzites of Tribeč Mountains, Western Carpathians, Slovakia: Compositional variations and evolution

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ABSTRACT

The phosphate–sulphate mineralization occurs in quartz veins in Lower Triassic metaquartzites of the Tribeč Mts., Central Western Carpathians, Slovakia. The mineralization comprises of lazulite, Ba, Sr, Ca, K-rich phosphates–sulphates and barite in an association with muscovite, hematite, locally rutile, zircon, chlorite and tourmaline. The most widespread lazulite forms up to 10 cm large pale to deep blue aggregates in massive quartz. Electron-microprobe analyses show a relatively uniform composition with $Mg/(Mg+Fe) = 0.85$ to 0.93. The Mössbauer spectroscopy reveals 11–30% Fe^{3+}/Fe_{total}. Possible primary goedkenite–bearthite binary s.s. shows the highest known Sr contents worldwide: $Sr/(Sr+Ca) = 0.67–0.71$; Mg, Ba and REE contents are negligible. The lazulite is replaced by a secondary association of Ba, Sr, Ca, K-rich phosphates–sulphates: gorceixite, rarely goyazite, crandallite, svanbergite, jarosite and a rare phase, close to $(Ba,K,Sr)(Fe^{3+},Al)_3[(OH,H_2O)_6(PO_4)(SO_4)]$ composition (Ba,Fe,S,P-phase). Gorceixite exhibits more restricted compositional variations between gorceixite–goyazite and gorceixite–crandallite s.s.: $Ba/(Ba+Sr) = 0.73–0.99$, $Ba/(Ba+Ca) = 0.78–0.99$ and $(P-1)/[(P-1)+S] = 0.84–0.99$. On the contrary, the secondary Sr, Ca-dominant phosphates–sulphates of the crandallite and beudantite groups show wide compositional variations and complex quarternary solid–solution series between goyazite–crandallite and svanbergite–woodhouseite with $Sr/(Sr+Ca) = 0.16$ to 0.99 and $(P-1)/[(P-1)+S] = 0.07$ to 0.97. The K, Ba-dominant phosphates–sulphates of the alunite and beudantite groups occur along jarosite–Ba,Fe,S,P-phase s.s. line with $Ba/(Ba+K) = 0.07$ to 0.56, $Fe/(Fe+Al) = 0.55$ to 0.99, $P/(P+S) = 0.14$ to 0.57 and elevated Sr and Ca (up to 0.24 and 0.12 apfu, respectively). The compositions indicate a close relationship and mutual substitutions between the crandallite, beudantite and alunite groups. Unlike to analogous phosphate-bearing assemblages in the Alps, investigated phosphate–sulphate association doesn't contains REE, Y and Sc minerals but it is rich in Ba-phases (barite, gorceixite). The peak metamorphic conditions of the host rocks estimated using the Kübler index of phyllosilicates point to anchizone/epizone boundary, i.e. ca. 270–350 °C. Fluid inclusions study constrained the minimum formation temperatures of the lazulite to 144–257 °C and of the superimposed sulphate–phosphate mineralization to 175–289 °C. Lazulite crystallized from brines of the system $H_2O–Na–Mg–Cl–CO_2$ with a salinity of 17.2 to 19.8 wt.% NaCl eq. We propose, that the studied mineralization originated from fluids enriched in elements from breakdown of feldspars, biotite, apatite and other phosphates in underlying Hercynian granites. The fluids passed upwards into the metaquartzites and precipitated discrete minerals, due to absence of any suitable sink for the elements among rock-forming minerals.

1. Introduction

Lazulite and other aluminium-rich phosphate (± sulphate) minerals belong to specific phases of many late-magmatic (mainly pegmatitic), metamorphic, hydrothermal and sedimentary systems under various P-T conditions, from early-diagenetic and anchimetamorphic to ultra-high pressure facies (e.g., Pecora and Fahey, 1950; Chopin et al., 1993; Rasmussen, 1996; Morteani and Ackermand, 1996, 2004, 2006; Bernhard, 1998). Therefore, study of their associations, textural relationships, compositional variations, association with metamorphic index minerals (mainly Al_2SiO_5 polymorphs, staurolite, chlorite),

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alteration and breakdown products enable us to better constrain the origin of the phosphates together with the host-rock evolution and fluid-rock interactions.

Lazulite with Sr-, Ca-, Al-bearing phosphate (±sulphate) phases (goyazite, crandallite, svanbergite, palermoite, bearthite–goedkenite solid solution, apatite, augelite, celestite) in association with kyanite, staurolite, tourmaline, garnet, rutile, jadeite, phengite, etc. were described in several low- to high-grade quartzitic metamorphic rocks or quartz veins, especially in the Alps (Cortesogno et al., 1987; Chopin et al., 1993; Morteani and Ackermand, 1996; Bernhard et al., 1996). Moreover, lazulite in association with Sc, Y, REE-bearing phosphates, namely pretulite, xenotime-(Y) and florencite-(Ce) as well as other phosphate, oxide and silicate minerals were described in the Austrian Alps (e.g., Bernhard et al., 1998; Bernhard, 2001). Analogous lazulite plus kyanite, andalusite, tourmaline, dumorthierite, augelite, amblygonite, berlinite, trolleite, goyazite, svanbergite, crandallite, apatite, celestite, anhydrite mineralization occur in Proterozoic metaquartzites in Brazil and Madagascar (Morteani et al., 2001; Morteani and Ackermand, 2004, 2006).

In this study we present occurrences of lazulite in association with rare goedkenite and other Ba,Sr,Ca,K-rich phosphate–sulphate minerals in Lower Triassic metaquartzites of the Tribeč Mountains, Slovakia.

2. Geological setting

The described quartz veins with phosphate–sulphate mineralization occurs in Lower Triassic (Scythian) metaquartzites of the Lúžna Formation in the Tatricum Superunit.

The Tatricum Superunit represents a Paleozoic to Mesozoic thick-skinned thrust sheet, one major Alpine structural component of the Central Western Carpathians. In the south-western block of the Tribeč Mountains, it is composed of Hercynian tonalites to granites of Mississippian (Carboniferous) age and their Permo-Mesozoic para-autochtonous sedimentary cover, comprising Permoscythian siliciclastic sediments and Middle Triassic to mid-Cretaceous carbonate sequence.

The Lower Triassic (Scythian) Lúžna Formation is a dominant member of the Tatric sedimentary cover in Tribeč Mountains (Fig. 1). The formation usually immediately overlies the granitic rocks of the Zobor-Tribeč granitic massif, only locally thin slices of strongly sheared slaty metaarkoses occur below, probably of Upper Permian age. It consists of bedded, grey, pink or white, fine to coarse-grained metaquartzites, rarely metaarkoses, with thin intercalations of sandy slates. The metaquartzites are very silica-rich, they contain around 95 wt.% SiO_2 in average (Zuberec et al., 1991). The metaarkoses show increased contents of K-feldspars and fine-grained white mica (Ivanička et al., 1998). Basal layers are often coarse-grained, monomict conglomerates with quartz pebbles. Planar cross-bedding and rippled lamination is rarely preserved. The sequence represents continental sediments of braided rivers (Mišík and Jablonský, 2000).

The whole post-Hercynian sequence of the Tribeč Mountains is affected by Alpine very-low grade to low-grade metamorphic overprint, probably of Cretaceous age (Ivanička et al., 1998). The metamorphism partly erased primary sedimentary textures, caused recrystallization of the clay fraction and growth of muscovite, tourmaline, hematite and other minerals accompanying the lazulite and Ba,Sr,Ca-bearing phosphate–sulphate mineralization.

The lazulite and related mineralization is known from over 30 localities of the Lúžna Fm. metaquartzites of the Tribeč Mountains

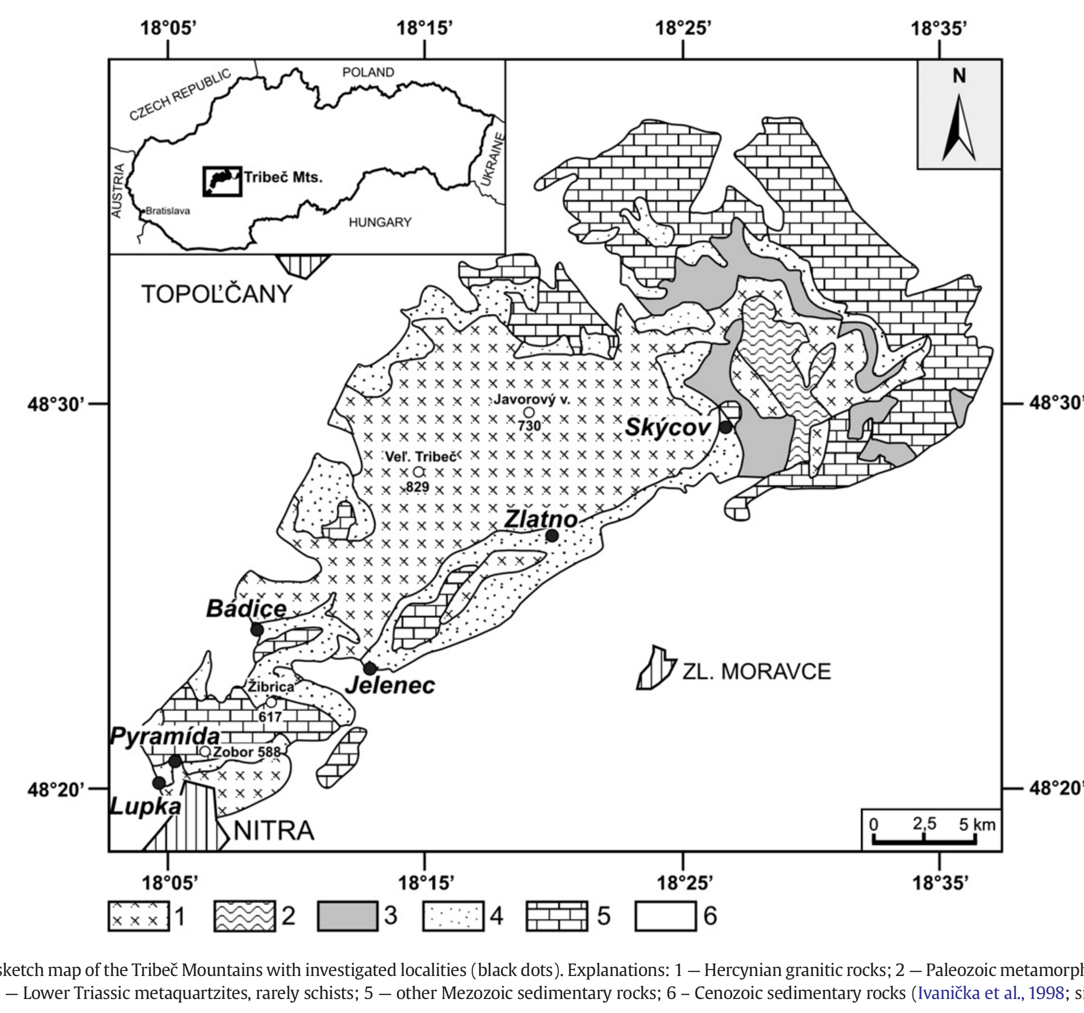

Fig. 1. Geological sketch map of the Tribeč Mountains with investigated localities (black dots). Explanations: 1 — Hercynian granitic rocks; 2 — Paleozoic metamorphic rocks; 3 — Permian metasediments; 4 — Lower Triassic metaquartzites, rarely schists; 5 — other Mezozoic sedimentary rocks; 6 – Cenozoic sedimentary rocks (Ivanička et al., 1998; simplified).