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Garnet (REE+Y)-bearing mineral association in pegmatite from the Chepino lithotectonic Unit, Western Rhodopes

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(REE+Y)-съдържаща минерална асоциация на пегматитов гранат от Чепинската литотоектонска единица, Западни Родопи

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Abstract. Large pegmatite body/bodies are outcropping in the “Suhata Reka” quarry, near the town of Rakitovo. Their bulk mineral composition with dominant K-feldspar (40%), plagioclase (30%), quartz (25%) and mica (≤ 5%) is complemented by (REE+Y)-bearing association of primary and secondary accessories. Zircon, monazite, xenotime, scarce apatite and noticeable amount of garnet are among the pegmatite primary minerals. The cm-sized almandine-spessartine crystals contain numerous fractures which host secondary (REE+Y)-bearing phosphate (xenotime, cheralite) and silicate minerals (e.g. REE-epidote). Formation of the late-stage REE-mineralization in garnet is due to its hydrothermal alteration and redistribution of REE+Y in the secondary phases.

Keywords: pegmatite, garnet, xenotime, ‘Suhata reka’ quarry, SW Bulgaria.

Introduction

Large pegmatite accumulations are exploited for the ceramic industry in the ‘Suhata Reka’ quarry, SW from the town of Rakitovo in Western Rhodopes (Fig. 1A). They form large intrusive bodies with sharp contacts (Fig. 1B, C) in the metamorphic rocks of the Chepino Lithotectonic Unit, in this area represented by metagranitoids, migmatised gneisses (biotite and two-mica), amphibolites and marbles (Fig. 1B, C; Sarov et al., 2009). The zircon U-Pb age of the pegmatite is 68.7±1.3 Ma (Grozdev et al., 2023). Besides the typical pegmatite minerals such as coarse-grained K-feldspar, plagioclase, quartz and mica, the studied rocks contain diversity of minor accessory minerals, which concentrate significant amounts of incompatible elements (e.g., REE, Y, Th, U etc.) with strategic importance. Garnet crystals and accumulations of various sizes are commonly encountered in the field (Fig. 1 D, E) and represent important hosts for secondary silicate-phosphate mineralization.

The present study is focused on the mineral composition and chemical characteristics of the garnet (REE+Y)-bearing association of accessory minerals in the pegmatites from the outcrop in the ‘Suhata Reka’ quarry.

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Materials and methods

Representative pegmatite samples were processed in polished and double-polished thin sections. Microscopic and BSE observation on the mineral relationships was performed prior to compositional studies by electron microprobe analyses (EPMA) and LA-ICP-MS. The EPMA were done using Cameca SX100 at the Joint Laboratory of Electron Microscopy and Microanalysis, Department of Geological Sciences (Masaryk University) and Czech Geological Survey in Brno, Czech Republic. Wavelength-dispersive mode with an accelerating voltage of 15 (or 20) kV, a beam current of 5–20 nA and a beam size 2–5 μm were applied with natural and synthetic standards. Minor and trace elements incorporation have been determined by New Wave Research 193 nm Excimer laser UP-193FX attached to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma mass spectrometer in the LA-ICP-MS Laboratory of the Geological Institute (BAS, Sofia). Analytical conditions include 7–10 Hz and 50 μm ablation craters. External (NIST 610 and NIST 612) and internal (EPMA contents) standards were used for compositional characteristics.

Results

Occurrence and mineral composition. The pegmatite forms a large body/bodies, more than 40 m wide and at least 100 m long (Fig. 1). The pegmatite lacks typical zonal distribution of minerals in the large scale; characteristic pegmatite textures similar to graphic

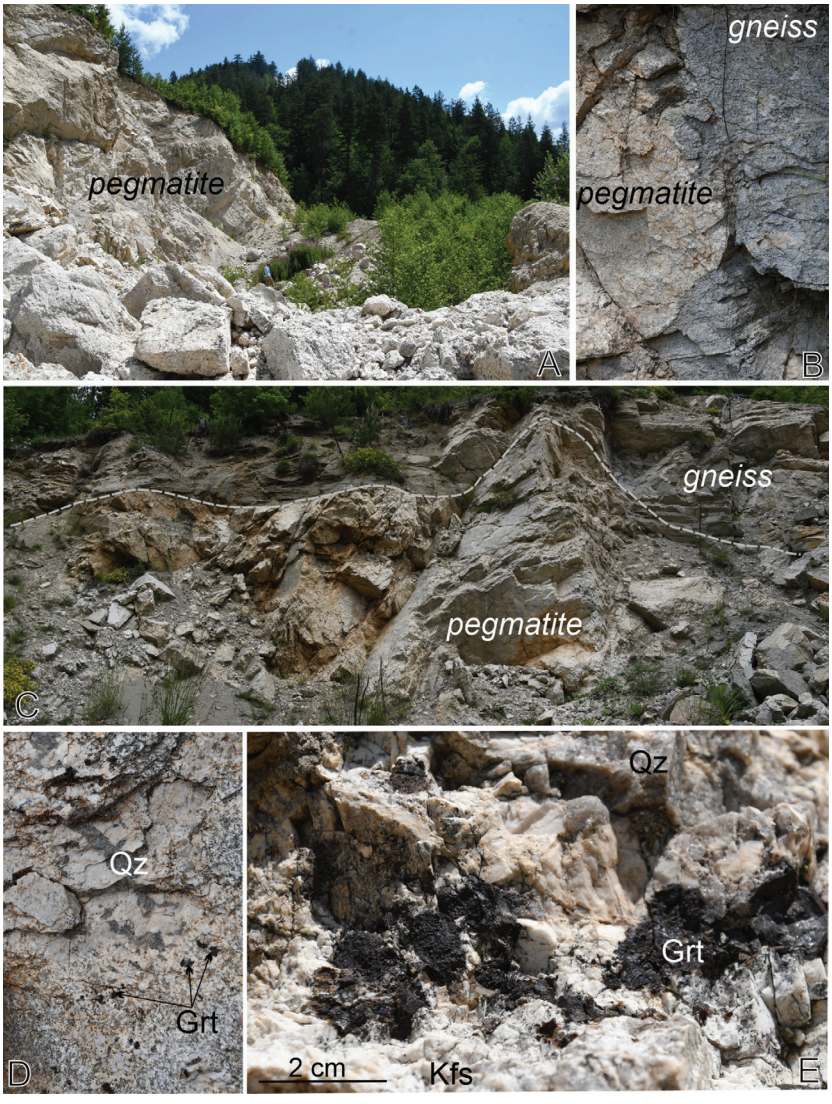

Fig. 1. Photographs of the pegmatite outcrop and field relationships: *A*, general view in the 'Suhata Reka' quarry; *B–C*, sharp contacts of the pegmatite with the host rocks of the Chepino Litotectonic Unit; *D*, typical transition to the coarse-grained texture of the pegmatite; *E*, cm-sized garnet crystals. Abbreviations as in Fig. 2.

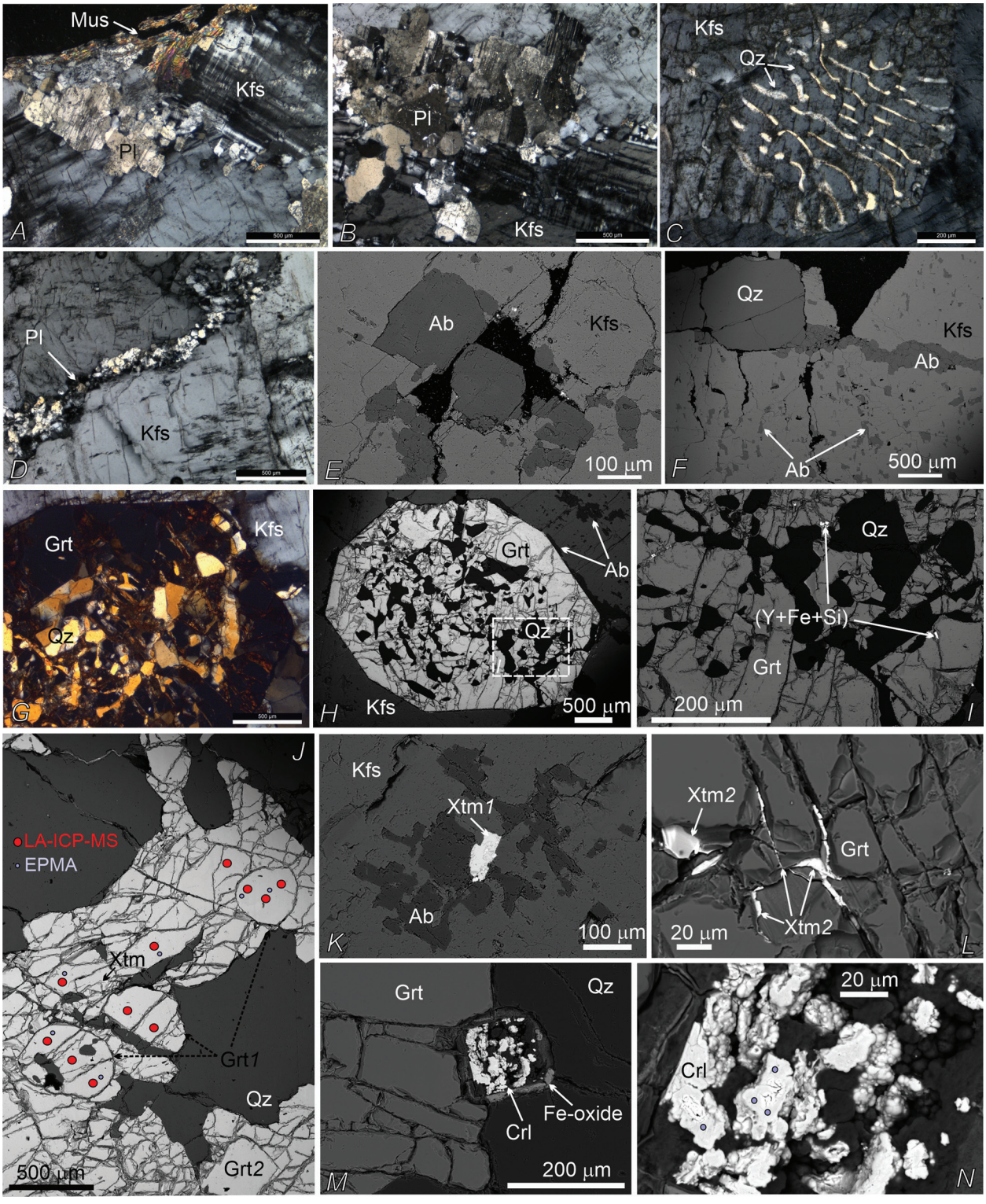

Fig. 2. CPL- and BSE-images of the mineral relationships in the studied pegmatite: *A–D*, K-feldspar, plagioclase and mica pegmatite association; *C*, myrmekitic texture of K-feldspar and quartz; *E*, albite–K-feldspar association; *F*, albite crystals and veinlets within K-feldspar; *G–H*, euhedral garnet/quartz nodule; *I–J*, part of large garnet/quartz intergrowths, showing relics of relatively older garnet (Gar1) in later (Gar2) matrix. The circles refer to EPMA (violet) and LA-ICP-MS (red) analytical points; *K*, primary xenotime grain in K-feldspar; *L*, secondary xenotime, formed as crack-fillings in the garnet; *M*, complex cheralite/Fe-oxide nest at the garnet rims; *N*, detail of (M), showing the botryoidal morphology of cheralite aggregates. Abbreviations: Ab, albite; Crl, cheralite; Grt, garnet; Kfs, K-feldspar; Mus, muscovite; Pl, plagioclase; Qz, quartz; Xtm, xenotime.

(feldspar/quartz) intergrowths, albite-dominated areas and transitions to coarse-grained texture occur rather irregularly within the pegmatite volume (e.g., Fig. 1D). Petrographic study (Fig. 2A–D) of selected samples allowed estimation of the general bulk mineral composition with dominant K-feldspar (40%), plagioclase (30%), quartz (25%) and mica (≤ 5%). Mica is present as both muscovite and biotite. Accessory garnet, Fe-oxides (magnetite/hematite) and pyrite are visible on field. Plagioclase (Fig. 2A–D) occurs as subhedral grains, sometimes forming perthite exsolution in microcline, veinlets (Fig. 2D, F) or anhedral exsolved patches in K-feldspar (Fig. 2F). Garnet is generally rather uncommon, with significant local accumulations of cm-sized crystals and grains (Fig. 1D, E). Monazite, xenotime, zircon and scarce apatite are also typical for the early pegmatite stage. The garnet crystals contain nodule-like cores of garnet-quartz intergrowths (Fig. 2G, H). Garnets are typically characterized by visible alteration (as visible on Fig. 1E) and a brittle deformation that resulted in abundant fractures (Fig. 2H, J). The fractures accommodate some late-stage secondary phases.

Combined BSE observation with EPMA revealed (REE+Y)-bearing association of secondary accessory phosphate and silicate minerals in the garnet fractures – xenotime, cheralite, silicate phase of Y+Fe (Fig. 2I). REE-epidote and chlorite complete the list of garnet-hosted minerals. Xenotime is observed as primary ~ 100 μm long crystals (Fig. 2K) within K-feldspar/plagioclase matrix or as late crack-fillings in the garnets (Fig. 2L). A silicate mineral rich in Y and Fe occurs as small (below 10 μm) irregular grains within the garnet volume (Fig. 2I) and might be gadolinite-Y/rowlandite-Y according to its chemical composition. Cheralite botryoidal aggregate is observed in a complex nest with Fe-oxides rims possibly formed after thorite (Fig. 2M, N) at the garnet/quartz border within large garnet crystal.

Chemical composition. In our study, we focused on the compositional features of the (REE+Y)-bearing mineralization. Pegmatite accessories such as zircon, monazite, xenotime, apatite and garnet are the main minerals concentrating incompatible elements in the studied samples. According to the chemical EPMA data, monazite-Ce reveals strong incorporation of Nd (~11 wt % Nd_2O_3), La (~10 wt % La_2O_3), Th (averaging ~8 wt % ThO_2), as well as 2–3 wt % of Y_2O_3, Pr_2O_3, Sm_2O_3, Gd_2O_3. Minor amounts of ~1 wt % of Dy_2O_3 and UO_2 are characteristic. Xenotime-Y concentrates Yb_2O_3 (12–16 wt %), Er_2O_3 (~6 wt %), Dy_2O_3 (~2 wt %) and lesser quantities of Gd, Sm, Nd, Lu and Tm. The average composition of the garnet is $Alm_{(44–52)}Sps_{(40–45)}Prp_{(3–6)}Grs\text{-}And_{(1–3)}$. Chemical inhomogeneity is observed in some of the crystals, defined by slight variation of cations (Fe-Mn-Mg-Ca) within the dodecahedral site. The central parts tend to incorporate more Y (reaching above 5000 ppm) along with increased Mn-contents, while the rims are slightly Ca-enriched and mostly depleted in REE (due to later processes). The textural features of inner garnet parts of a 2 cm crystal (Fig. 2J), reveal old garnet cores (Grt*1*) in a later garnet matrix (Grt*2*). EMP and LA-ICP-MS study demonstrates that both types have similar chemical characteristics, although some points show increased Mn, Y and HREE contents. Certain trace incorporation (in ppm) of Li (46–200), Sc (200–320), Zn (~80), Ga (20–30), Ge (~40) is characteristic. Garnet is an important host for HREE, with ΣHREE (Gd-Lu) content ranging in the studied samples from 800 (rims) to 4000 (cores) ppm. The ΣREE in the zircon reaches up to 16 590 and averages 8580 ppm, while in apatite varies from 765 to 3760 ppm. Cheralite composition reveals increased amounts of Y_2O_3 (4 wt %), Nd_2O_3 (1.7 wt. %), Sm_2O_3 (1.6 wt %), UO_2 (2.26 wt. %), Gd_2O_3 (2 wt %), Dy_2O_3 (2.1 wt %). Minor quantities (in wt %) of La_2O_3 (0.3), Er_2O_3 (0.7), Yb_2O_3 (0.6) complete the compositional characteristics. Cerium incorporation is below 1 wt % Ce_2O_3. The REE are partitioned between phosphate and silicate minerals. Monazite preferably concentrates LREE and MREE, while zircon and garnet are enriched in HREE, which is also visible by the chondrite-normalized patterns of garnet, zircon and apatite.

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