Abstract. Two diorite to monzodiorite sills are recently found among the Silurian sedimentary succession near to Asaritsa peak, West Stara Planina Mountain. Several levels with diagenetic metalliferous nodules occur within shale interval in the sediments. The magmatic rocks are affected by strong propylitic to sericitic alteration (chlorite, sericite, albite and quartz) and only relics of the rock-forming minerals (feldspar, biotite and clinopyroxene) are observed. The bodies are crosscut by thin quartz veins and disseminated pyrite is observed. The chondrite normalized spidergrams show patterns similar to orogenic rocks, with very high peaks of Th and U and depletion in Sr and Ti. The zircon U-Pb geochronology reveals that the magmatic crystallization is during the Carboniferous period – 326.4±3.2 Ma, with low content of xenocryst most probably from the sedimentary basement. The magmatic activity coincides with the Variscan orogeny formed during the late Paleozoic and most probably is related to the evolution of the alkaline Buhovo-Seslavtsi Pluton which is situated just to the south, at a direct proximity. The different composition of the pyrite from the sills and the diagenetic nodules from the sediments is most probably due to their different genesis. While the alterations of the nodules can be attributed to metasomatic processes related to the magmatic activity.

Keywords: Carboniferous sills, metasomatic alteration, Silurian metalliferous nodules.

Introduction and geological setting

The research area is a part of the Svoie Unit which is the northernmost fragment of the Srednogorie Zone and is thrust to the north over the West Balkan Unit. Recently, the Asaritsa Silurian sedimentary succession is a subject of several studies regarding the sedimentology and stratigraphy (Sachanski, 2017; Milakovska et al., 2022) and the manganese metalliferous nodules as a potential source for critical elements (Hikov et al., 2020, 2022). It is exposed in the roadcut of a small forest road SW of Yablanitsa Village, about 800 m WSW of Asaritsa Peak. Several levels with nodules occur within the pale shale interval, as the first one, situated 40 cm above the base of the package, is markedly well sustained, 20 cm thick. The origin of the nodules with Fe- and Mn-carbonates is related to diagenetic processes under reducing conditions of low Eh and high pH values. Later, carbonate minerals were altered into Fe-Mn oxyhydroxides (Hikov et al., 2022). On both sides of the section two sills are observed (with a thickness of 0.5–1.5 m) intruding the sediments (Fig. 1a). The rocks are hydrothermally altered and intersect by thin quartz veins and interspersed pyrite is observed. The focus of the present contribution
is the magmatic and metasomatic activity related to the sills, their age of zircon crystallization and possible relation with the nodules.

Analytical methods
The XRF analyses were performed by EDXRF Epsilon 3XLE instrument (PANalytical) using the Omnia 3SW software, at the Faculty of Geology and Geography, Sofia University, Bulgaria. Trace elements in the same samples and the zircon geochronology were obtained by LA–ICP–MS (PerkinElmer ELAN DRC-e ICP-MS attached to a New Wave UP193FX LA system) at the Geological Institute, Bulgarian Academy of Sciences. XRF analyses were done at the Institute of Physical Chemistry, Bulgarian Academy of Sciences.

Petrology and geochemistry
The magmatic rocks are affected by strong metasomatic alteration (Fig. 1b). Only relicts of the rock forming minerals are found. The rocks are porphyroid with fully crystalized matrix. Feldspars are fully altered to clay minerals, albite and sericite. Relicts of mafic minerals, most probably biotite and clinopyroxene are distinguished based on the morphology of the crystals and alteration minerals. The clinopyroxene is fully altered to chlorite and sometimes needle rutile is observed. The accessory minerals are presented by apatite and zircon. Quartz, albite, chlorite and sericite are additionally proved by the XRD analyses. The metasomatic alteration can be considered as a strong propylitic to sericitic. Thin quartz veinlets (>1mm) and veins (Fig. 1f–h) up to 1 cm in thickness and disseminated pyrite is observed.

The alteration of the rocks reflects to high LOI (6.7–7.2 wt %). The both analyses from the sills show similar SiO₂ (53.9–54.3 wt %), TiO₂ (1.0–1.2 wt %), Al₂O₃ (13.4–14.2 wt %), Fe₂O₃tot (10.3–11.2 wt %) and varied CaO (0.8–2.56 wt %), MgO (5.8–9.9 wt %), Na₂O (1.3–1.9 wt %) and K₂O (1.6–0.2 wt %). The classification of the rocks using classical diagrams with major elements is difficult and that’s why the classification of Winchester and Floyd (1977), using immobile elements is applied (Fig. 1c). The rocks fall in the field of the intermediate, near to that of mafic alkali compositions. It can be conditionally classified as diorite to monzodiorite.

On a primitive-mantle normalized diagram, the rocks show well pronounced peaks in LILE (U, Th, almost not Pb) and slight troughs in Nb, Ta and well pronounced of Sr and Ti (Fig. 1d), which is a characteristic feature of orogenic rocks. They show high contents of LILE and gently decreasing LREE chondrite-normalized patterns and almost flat HREE normalized patterns (Fig. 1e). The rocks exhibit weak negative Eu* (0.63–0.65) anomaly and La/Yb(N) ratio ranging from 11.6 to 12.7.

The LA-ICP-MS data reveal that the studied pyrites from the magmatic rocks has variable trace element content. We have established elevated content of As (up to 7530 ppm), Co (up to 670 ppm), Ni (up to 67 ppm), Cu (up to 247 ppm), Sb (up to 465 ppm) and Pb (up to 3600 ppm). The trace element content of pyrite from the sills has distinctly lower Mn, Co, Ni and Cu content in comparison to this from the nodules (Fig. 1i).

Geochronology
An attempt for zircon U-Pb geochronology is made on both samples from the sills. The zircons are rare and only a single grain is separated from one of the samples (3 kg rock sample) and from the other – 17 crystals. The crystals are short to medium prismatic with weak or lack of oscillatory zoning (Fig. 1j) with Th/U ratio from 0.49 to 1.01, typical for intermediate to mafic magmas. Some of the analyses are discordant due to U loss. The magmatic crystallization age is obtained using 6 concordant analyses at 326.4±3.2 Ma (Fig. 1k). Limited content of xenocrysts with ages of 491–518 Ma, 658 Ma and 697 Ma is found.

Discussion and conclusion
The sills intruded in the Silurian sedimentary succession are affected by strong propylitic to sericitic alteration and only relicts of the rock-forming minerals can be observed. The primary composition of the rocks is highly affected by the alteration and the rocks are classified according to the relict mineral identification and immobile elements. They can be conditionally determined as diorite to monzodiorite. The chondrite normalized spidergrams show pattern similar to orogenic rocks, with very high peaks of Th and U and depletion in Sr and Ti. The zircon U-Pb geochronology reveals that the magmatic crystallization is during the Carboniferous – 326.4±3.2 Ma, with limited content of xenocryst most probably from the sedimentary basement. The time of zircon crystalization of the rocks can attribute the magmatic activity to the Variscan/Carboniferous plutons that are widespread in the Balkan, Srednogorie and Kraishche Zone in Bulgaria (330–289 Ma). It belongs to the Variscan orogenic belt formed during the late Paleozoic as a result of the convergence and subsequent collision of the two major paleocontinents Laurasia and Gondwana, including a number of smaller microplates and fragments of magmatic arcs (e.g. Carrigan et al., 2005).
Fig. 1. Geological features of the magmatic and metasomatic activity related to the Asaritsa sills: a, a sill intruded in the Silurian succession; b, macroscopic view of the magmatites affected by strong propylitic alteration; c, classification diagram using immobile elements after Winchester and Floyd (1977); d, primitive mantle normalized spidergram (normalizing values after McDonough and Sun, 1995); e, chondrite normalized REE pattern (normalizing values after Boynton, 1984); f, quartz veins in the sills; g, quartz (Qz) vein – microscopic view; h, pyrite (Py, reflected light); i, diagram comparing specific element concentration of pyrites in the sills and the Silurian sedimentogenic nodules; j, zircon CL images (laser pit 35 µm, ages in Ma); k, LA-ICP-MS zircon Concordia age of the sills.
and reference therein). At the direct proximity of the studied rocks is situated the alkaline Buhovo-Seslavtsi Pluton. The magmatic age of zircon crystallization is 330–310 Ma (Dyulgerov et al., 2016), roughly similar to the age of the sills. On the other hand, the sills have lower alkalis in relation to the rocks of the Buhovo-Seslavtsi Pluton, which can be due to some extent to the alteration. The immobile elements and the pronounced peak of U and Th give some clues for their close evolution.

The different composition of the pyrite from the sills and diagenetic nodules from the sediments is most probably due to their different genesis. While the alterations of the nodules can be attributed to hydrothermal processes related to the magmatic activity.

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