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Manganese carbonate minerals and their alteration products in Silurian metalliferous nodules from the region of Asaritsa peak, West Balkan Mountain

Манганови карбонатни минерали и продукти на тяхната промяна в силурски металоносни конкреции от района на вр. Асарица, Западна Стара планина

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Abstract. The studied Silurian nodules have hard light cores and dark shells. The cores consist of quartz with disseminated zonal carbonate mineral and pyrite. Zones in the carbonate have a variable composition from Mn-containing siderite, ankerite and dolomite to mixed Fe-Mn carbonate and Fe-containing rhodochrosite. The nodule shells are composed of quartz, chlorite, sericite, goethite, Mn-Fe oxyhydroxides and siderite. Fe-Mn oxyhydroxides in the nodule shells are formed due to an alteration of the carbonate minerals and inherited their composition. The formation 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. These alteration changes can be related to the influence of later magmatic activity in the area. An example of this activity is the presence of an igneous bodies established on both sides of the section.

Keywords: Silurian, metalliferous nodules, manganese carbonate minerals, alteration, West Balkan.

Introduction

The depletion of traditional resources and high growth of world economy led to defining many strategic metals as critical elements for the EU (COM (2020) 474). The deep-sea polymetallic nodules are a high perspective new raw material and can be a potential source for REE and other critical elements (Hein et al., 2013). Bulgaria participates in nodule research in the Clarion-Clipperton Zone, North Pacific Ocean as a member state of the Interoceanmetal Joint Organization (IOM) and the first results for the resources of polymetallic nodules in the IOM license area have already been reported (Stoyanova et al., 2021). Our attention is also focused on the search of metalliferous nodules in other geological environments, in order to describe their occurrence and test whether they contain critical elements. The first data for nodules in Silurian sequence from the region of Asaritsa, West Balkan Mountain were presented by Hikov et al. (2020). This study is focused on manganese carbonate minerals in the polymetallic nodules and their alteration during the geological history of this West Balkan section.

Geological setting

The study area is a part of the Svoge Unit (Dabovski, Zagorchev, 2009), which is the northernmost fragment of the Srednogorie Zone and is thrust to the

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north over the West Balkan Unit. The pre-Mesozoic basement of the unit is a Palaeozoic, mainly shale succession, which is a part of the Palaeozoic Balkan Terrane (Yanev, 2000). The Llandoverian sedimentological succession is built up mostly of dark grey to black cherts (lydites), organic-rich shales, and siliceous shales of the Saltar Formation (Sachanski, Tenchov, 1993). The chronostratigraphical range of the chert-shale succession has been determined to span the upper Hirnantian Stage of the Upper Ordovician Series to the lower Telychian Stage of the Llandovery Series, based on graptolites (Sachanski, 2017, and references therein). In the middle of this sequence, Sachanski reported one undisturbed section (Asaritsa), which includes the upper part of the Aeronian and the lowermost part of the Telychian (Llandovery Series). The section also contains a 6-m thick interval of graptolite-barren pale-coloured shale. It has been recognized as a parastratotype for the middle part of the Saltar Formation.

The Asaritsa section is exposed southwest of the village of Yablanitsa, about 800 m west-southwest of Asaritsa Peak. The section begins with black siliceous shales with graptolite taxa that could be attributed to the *convolutus* Zone and black shale, which is attributed to the *sedgwickii* Zone – uppermost Aeronian. Upwards the succeeding level is represented by a ~6.5m thick graptolite-barren pale shale. Several levels with nodules occur within the pale shale interval, as the first one, situated 40 cm above the base of the package, is 20 cm in thickness. This interval is covered by grey siliceous shales followed by dark grey to black shales. *Parapetalolithus palmeus* and *Spirograptus guerichi* are documented at the base of the latter, being characteristic for the *guerichi* Zone – lower Telychian (Sachanski, 2017). On both sides of the section, igneous bodies have been established, intruded lit-par-lit in the Lower Paleozoic sediments. Two sills are observed, with a thickness of 0.5–1.5 m. The rocks are affected by hydrothermal alteration and are crossed by thin quartz veins and interspersed pyrite is observed.

Methods

Mineralogical and petrological characteristics of polymetallic nodules and host sediments were studied in thin and polish sections. X-ray Diffraction (XRD) in the Institute of Physical Chemistry of Bulgarian Academy of Sciences and Raman spectroscopy in the Sofia University were used to characterize the carbonate and Mn-Fe oxyhydroxide minerals. The mineral composition was studied by SEM EDS analyses in the Belgrade University, Serbia. Additionally, some samples were studied by QEMSCAN (Quantitative Evaluation of Minerals by SCANning electron microscopy) in the Department of Earth Sciences, Geneva University, Switzerland. Trace elements content in minerals was determined by LA-ICP-MS at the Geological Institute of Bulgarian Academy of Sciences.

Results

Polymetallic nodules crop out in several levels of the Asaritsa section. The largest nodules (12×8×5 cm) are in the first level. There are also smaller nodules with elliptical to spherical shape and diameter from 2 to 6 cm. The nodules have a hard core composed of quartz with evenly disseminated carbonate mineral (~20%) and pyrite (~1%). The carbonate minerals are rhombohedral with sizes usually up to 50 μm, rarely to 70 μm, and show zonal growth on SEM-BSE images (Fig. 1a.). The carbonate core is rimmed by a transitional zone, where the carbonate is transformed into unidentified mixed phases. In the outer zone, the carbonate minerals are completely replaced by Mn-Fe oxyhydroxides with variable composition, preserving the zonation of the carbonate minerals. Pyrite is partly to completely replaced by goethite. The nodule shells are black and built up of several thin layers consisting of quartz, chlorite, sericite, goethite, Mn-Fe oxyhydroxides and siderite. Smaller nodule-like forms with light cores and an irregular shape are also found. They consist mainly of quartz, muscovite ± chlorite. Their shells are black and identical in composition with the shells of the nodules. During the study, it was established that these are parts of sedimentary rocks, around which Mn-Fe oxyhydroxides are deposited in pores and cracks.

X-ray Diffraction of nodules shows that the nodule cores are composed of quartz, siderite, birnessite, goethite and less muscovite and chlorite. Quartz, muscovite, chlorite, goethite, birnessite and less siderite and jacobsite are established in the nodule shells. Birnessite and traces of todorokite are found in single Mn-rich nodule samples. To more precise determination of the nodules mineral composition, some of the samples were examined by Raman spectroscopy. In this way, the carbonate minerals rhodochrosite and siderite were established and the presence of todorokite was confirmed.

SEM-EDS study shows that zones in the carbonate have variable composition from Mn-containing siderite, ankerite and dolomite to mixed Fe-Mn carbonate and Fe-containing rhodochrosite, by prevailing Mn-containing siderite (Fig. 1b). There is no established regularity in the composition of the cores and peripheries of the crystals. The phases that are rich in Fe and Mn do not contain Ca and Mg, while in the poorer ones, the latter increase and reach ankerite and dolomite. The manganese

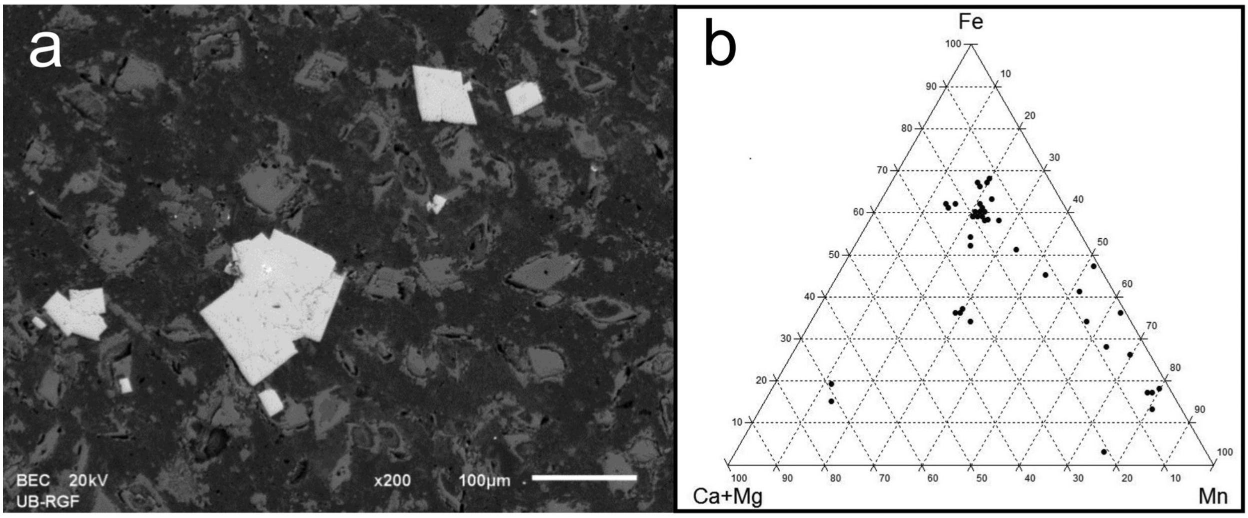

Fig. 1. *a*) BSE image of nodule core with zonal carbonate minerals and pyrite among quartz; *b*) composition of carbonate zones from the nodule cores from Asaritsa

content in the carbonate minerals is as follows: rhodochrosites (31–40.50%), mixed Fe-Mn carbonates (17–27.70%), siderites (7.50–19%), ankerites (14.60–17.80%), dolomites (6.3–7.8%). Fe-Mn oxyhydroxides predominate in the nodule shells and their composition largely inherited the composition of the carbonates. Mn-rich oxyhydroxides contain Mn (42.6–61.7%) and Fe (0.9–9.5%), mixed phases have Mn (21–40.7%) and Fe (19.8–34%), Fe-rich phases have Mn (2–13.3%) and Fe (30.4–40.5%). Veins of goethite, containing little amount of Mn, are also observed.

The alteration of the carbonate minerals observed on the periphery of nodules, is also found in fine veins and in the halos around them. The QEMSCAN element maps show addition of Mn and depletion of Mg and Ca, while Fe remains immobile. A similar alteration is observed around the nodule-like forms with light cores. The QEMSCAN element maps show that their black shells are enriched in Mn and Fe. Later veins of chlorite, goethite, phengite type of mica and Mn- and Fe-rich carbonates are found in and around the sample.

LA-ICP-MS study show that carbonate minerals are poor in impurities, having very low content (in ppm) of Rb (up to 26.6), Sr (13.4–69.2), Y (2.2–39.8), Ba (28–95.8) and LREE (La 2.1–9.8, Ce 2.3–15.8, Pr 1.2–2.1, Nd < 17). Fe-Mn oxyhydroxides which form mostly after carbonate minerals are richer in impurities: Co (22–289), Ni (63.7–231), Zn (56.6–283), Y (11.7–55), La (12.2–38.5), Ce (16.9–102.5), Pr (0.96–11.1), Nd (21–52.5), sometimes Ga (<42), Sm (<33.6) and Dy (<16.8).

Discussion and conclusions

The study of the Silurian nodules reveals their polystage formation. The grain-size, mineral composition and geochemical features of the sediments point to a remote and weathered source land. Overall, it is concluded that the sediments were deposited in an open-sea environment, away from the wave zone at the edge of the continental shelf (Sachanski, Tenchov, 1993; Milakovska et al., 2022) in a normal to oxidizing environment.

In the Asaritsa section, the highest Aeronian graptolitic strata are separated from the lowest Telychian graptolitic strata by a graptolite-barren interval of pale shale. Similar successions are known and characteristic for different sections around the world but with variations, concerning their lithology and stratigraphic range. When constructing the eustatic sea-level curves, Loydell (1998) and Johnson (2006) have associated this sharp lithological change with sea-level drop around the Aeronian/Telychian boundary. The presence of nodules at several stratigraphic levels suggests short periods of very low sedimentation rates or breaks in sedimentation to allow them to grow (Loydell et al., 2015).

The formation of the nodules with high Fe and Mn content is related to diagenetic processes and synchronous/postponed siderite/rhodochrosite formation. Siderite forms under reducing, waterlogged, conditions of low to negative Eh values and high pH (6–10) values (Krauskopf, 1979) as well as higher concentration of ferrous iron. Rhodochrosite has larger stability field than siderite under reducing conditions and increase in the amount of CO_3^{2-}

and both carbonate minerals can coexist with pyrite (Maynard, 2014). The formation of Fe- or Mn-rich zones in carbonate minerals probably depends on the local concentration of Fe^{2+} and Mn^{2+} in the pore waters.

Later, most likely as a result of hydrothermal activity, carbonate minerals were oxidized and altered into Fe-Mn oxyhydroxides. Iron and manganese from the carbonates remain in place, while Ca and Mg are mobile and are almost completely extracted. There is also an influx of Fe and Mn that fill cracks and pores in the sediments and nodules. In addition, veins with goethite, chlorite, micas, clay minerals and quartz are also deposited. These alteration changes can be related to the influence of later magmatic activity in the area. On both sides of the section, igneous bodies have been established. The rocks are affected by hydrothermal alteration and are crossed by quartz veins. Preliminary data indicate a Late Paleozoic age for these igneous rocks. The magmatic activity led to the metasomatic replacement of carbonate minerals with oxyhydroxides, during which Ca, Mg and C are extracted while Mn and Fe, probably mobilized from the host sediments, are partially added. Addition of some trace elements as Co, Ni, Zn and LREE is also established. This process occurred in an oxidizing environment and probably low temperatures, where carbonates and sulfides were unstable but it was probably short-lived because it was not fully completed. Elucidating the chemistry of magmatic bodies will give us more solutions to the mechanism of the observed alteration changes.

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