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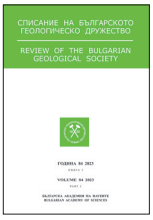

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Posušje bauxites in Bosnia and Herzegovina: A source of critical raw materials and a paleoclimatic marker

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Боксити от Посушье в Босна и Херцеговина: източник на критични суровини и палеоклиматичен маркер

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Abstract. The present study provides geochemical and geochronological data about Posušje bauxites in Bosnia and Herzegovina with the aim to characterize them as Critical Raw Materials (CRMs) sources and to put constraints on the time and genesis of the deposit. Boehmite is the bauxites' main Al-bearing mineral, while gibbsite is a minor constituent. Hematite is the dominant Fe-phase, whereas goethite is rare. The chemical analyses indicate that the Al_2O_3 content ranges from 49.6 to 63.0 wt %, Fe_2O_3 varies from 16.5 to 33.7 wt % and the SiO_2 content is usually <0.5 wt %. TiO_2 content ranges between 2.6 and 3.2 wt %. Typical trace elements are V (353–787 ppm), Cr (498–1055 ppm), Zr (382–558 ppm), Sc (42–72 ppm), and Ga (40–47 ppm). The sum of REEs is 357–1112 ppm. The U-Pb zircon dating indicates an age of Posušje bauxite formation at 56.6±0.5 Ma. This age closely aligns with the global climatic event that occurred approximately 56 Ma ago, called Paleocene–Eocene Thermal Maximum (PETM).

Keywords: bauxite, Posušje, geochemistry, U-Pb zircon dating, Paleocene–Eocene thermal maximum.

Introduction

Bauxite deposits worldwide are the main source of aluminum. They result from intense chemical weathering and are subdivided into two main types: 1) lateritic bauxites derived by *in situ* lateritization of underlying aluminosilicate rocks, and 2) karst bauxites developed on carbonate bedrock during the emersion phase (e.g., D'Argenio, Mindszenty, 1995). Although karst-type deposits account for less than 12% of global bauxite reserves (Yang et al., 2023), they constitute the predominant deposit type in Europe. Bauxite was defined as a Critical Raw Material (CRM) by the EU in 2020. Furthermore, the bauxite deposits may also hold economic value for other CRMs, such as gallium (Ga), tita-

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nium (Ti), and Rare Earth Elements (REEs), among others. This heightened interest in researching and exploring European bauxite deposits is particularly focused on, but not confined to the Late Cretaceous-Paleogene-Neogene Mediterranean belt stretching from Spain through France, Italy, Hungary, Croatia, Bosnia and Herzegovina, Greece and some closely situated countries. Part of this belt includes the Jajce and Posušje deposits in Bosnia and Herzegovina, which are studied within the framework of the AGEMERA Horizon Europe project: Agile Exploration and Geo-modelling for European Critical Raw Materials. In the present study, we provide geochemical and geochronological data for the Posušje bauxite deposit. The main aim is to characterize the bauxite as a CRM source and to constrain the time of formation, geological setting and mineral-geochemical peculiarities. Furthermore, as karst deposits form under specific climatic conditions – warm and humid – they are informative for both global and local climate changes and may serve as markers for processes that induce such changes (e.g., volcanism, tectonic processes).

Geological setting, sampling and methods

The Posušje deposits are located in the south-western part of Bosnia and Herzegovina and geologically belong to the eastern parts of the Adriatic-Dinaric Carbonate Platform (ADCP). In the broader Posušje area, the ADCP carbonates were deposited from the end of the Lower Jurassic through the Cretaceous periods until the late Paleogene (Hrvatović, 2005; Dragičević et al., 2019).

Posušje is a historic bauxite mining area, known for more than 100 years (Dragičević et al., 2019; Bilić et al., 2023, and references therein). The area comprises over 1000 bauxite deposits and occurrences around Posušje village. The bauxites form irregular bodies with different sizes and shapes and are interpreted to have been formed on the paleosurface of Upper Cretaceous rudist limestones. The sequence is covered by Paleocene–Eocene Liburnian limestones, followed by Eocene foraminiferal limestones (hanging wall).

The samples for the present study were chosen from Mratnjača, Snižnica, Grečica, Studena Vrila and Judin Ležaj deposits. Analytical techniques employed encompass a suite of mineral-petrographic (microscopy, XRD), geochemical (XRF, LA-ICP-MS) and geochronological (in-situ U-Pb and trace element LA-ICP-MS) analyses. These were performed at Zagreb University (Faculty of Mining and Geology), Sofia University (Faculty of Geology and Geography), the Geological Institute of the Bulgarian Academy of Sciences and ETH-Zurich.

Petrography, geochemistry and geochronology

The bauxites exhibit ooidic to pelitomorphic textures and, in places, also clastic textures. Micro-ooids and spheroids are mostly smaller than 0.1 mm. Remnants of former ooids can occasionally be observed. In some bauxites, pebbles of resedimented bauxite prevail. Boehmite is the main Al-bearing mineral of the bauxites, significantly outweighing gibbsite, while diaspore is absent. Hematite is the dominant Fe-phase in all deposits. Goethite-rich bauxites are rare and appear as isolated layers, with just traces of hematite. Zircon, apatite and calcite are accessory or minor minerals. The X-ray analysis indicated significant amounts of anatase and rutile, whereas kaolinite was detected in only one sample.

Chemical XRF analyses reveal Al_2O_3 content ranging from 49.6 to 63.0 wt %, Fe_2O_3 from 16.5 to 33.7 wt % and SiO_2 content between 0.5 and 4.0 wt %. Based on these major oxide compositions, the studied bauxites are classified as ferritic according to the ternary classification diagram of Aleva (1994). TiO_2 content ranges between 2.6 and 3.2 wt %, while MgO does not exceed 0.3 wt %. The CaO content at Posušje is usually below 0.1 wt %; exceptional instances of 0.5 wt % are attributable to calcite. Typical trace elements are V (353–787 ppm), Cr (498–1055 ppm), Zr (382–558 ppm), and Sc (42–72 ppm). Ga content is in the range of 40–47 ppm. The sum of the REEs varies between 357 and 1112 ppm, with the light REEs (317–1018 ppm) clearly predominating over the heavy REEs.

The U-Pb zircon dating yields a maximum age of ~56 Ma for bauxite formation at Posušje (Fig. 1), although a Late Cretaceous signal (69–92 Ma) is also well preserved. Detrital zircon populations range from 54 to 1080 Ma; however, Phanerozoic to Proterozoic zircons are rare and the Devonian–Silurian ages predominate (Fig. 1).

Discussion

The Jajce and Posušje bauxite deposits in Bosnia and Herzegovina are formed on the Adriatic-Dinaric carbonate platform. Eight bauxite-bearing horizons have been previously identified (Sakač, Šinkovec, 1991) and subsequently confirmed in the adjacent Croatian territory (Ilijanić et al., 2023). These horizons cover a time period from the Triassic (BX1) to the Miocene (BX8). Given its age of 56.6 ± 0.5 Ma, the Posušje bauxites can be classified under bauxite type 5 (BX5), which is of Paleocene/early Eocene age. Significantly, this age of approximately 56 Ma coincides with a well-documented global climatic event in geological history, known as the Paleo-

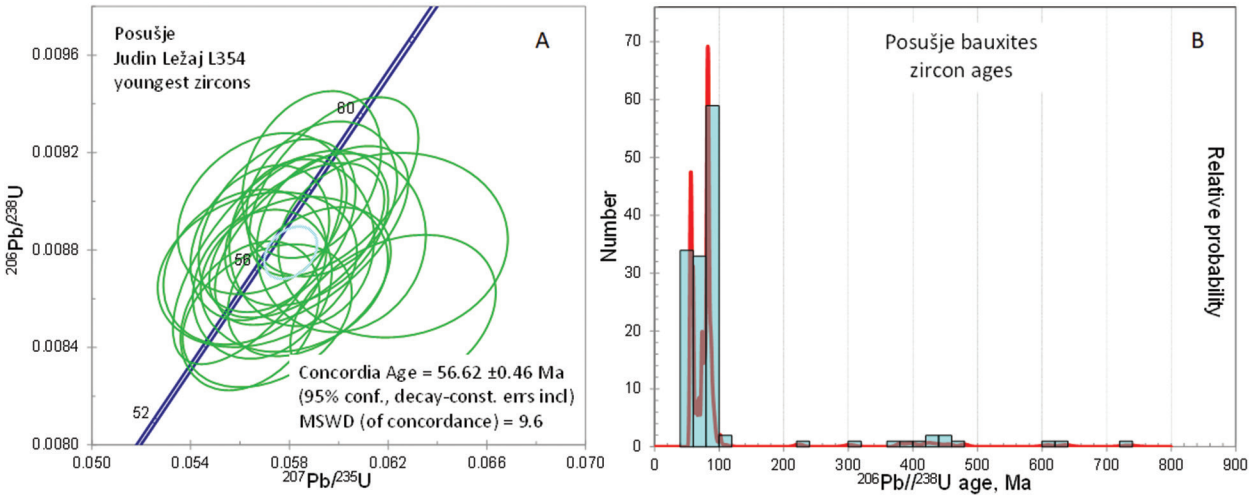

Fig. 1. LA-ICP-MS U-Pb age data for zircons from Posušje bauxites: *A*, concordia age of 56.6±0.5 Ma is calculated based on the youngest zircon population at the Judin Ležaj deposit; *B*, the age distribution and relative probability of all dated zircons are shown, demonstrating well-defined peaks at ~56 Ma and in the Late Cretaceous (<88 Ma), with a minor older population (a single date at 1080 Ma is not shown on the graphic)

cene–Eocene Thermal Maximum (PETM). The PETM stands as the warmest among several brief, very warm periods or "hyperthermals" that occurred in the late Paleocene and early Eocene between 56 and 53 Ma. A warm and humid climate was optimal for bauxite formation when coupled with tectonically controlled subaerial exposure of the carbonate platform. A recent paleogeographic and paleoenvironmental evolution model for the ADCP elucidates the PETM event, the following Early–Middle Eocene Climatic Optimums (~40 Ma) and the final cooling trend at the Eocene/Oligocene boundary (~34 Ma). These events coincided with the continuous drift of the African continent towards Eurasia. The ~40 Ma event culminated in the closure of the western part of the former Neo-Tethys Ocean and was associated with massive volcanic activity (Brčić et al., 2023). According to this model, in the early Eocene period, parts of the ADCP were tectonically exposed. Concurrently, the elevated temperatures during the PETM accelerated hydrological cycles and increased precipitation rates. These conditions were favourable for the development of karst bauxites.

The geological community acknowledges the polygenetic origins of karst bauxites, with two prevalent theories. The first "Detrital Origin" model calls for initial karstification, followed by the deposition and transformation of soil-derived bauxitic material, terra rossa (e.g. Durn et al., 2007). The second "Residual Origin" model accepts that these bauxites are residually generated from the dissolution of the precursor limestone material (Bardossy, 1982; Moresi, Mongelli, 1988). The well-preserved zircons in the Posušje bauxites, largely transported as volcanic ash, are in favor of the new concept for isovolumetric interaction between the carbonate bedrock and airborne material as proposed by Merino and Banerjee (2008). The model combining the terra rossa as the proto-bauxitic material with processes of karst weathering is accepted by Ilijanić et al. (2023) for the Croatian bauxite deposits of the ADCP. Under this paradigm, the parent material of the Posušje bauxites can be regarded as a paleosol derived from the interaction between the carbonate rock and airborne siliciclastic material, whether eolian, volcanic, or even terrestrial in nature.

The mineral-geochemical features of Posušje bauxites position them as a viable source for not only aluminum but also for other CRMs such as Ti and REEs. However, the commercial extraction of these CRMs requires the development of effective processing and metallurgical techniques.

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