Petrography and geochemistry of Cretaceous bauxites from Jajce, Bosnia and Herzegovina

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Abstract. The study presents petrographic and compositional data of Late Cretaceous bauxite deposits in the area of Jajce, Bosnia and Herzegovina. Results indicate that bauxites exhibit ooidic to pisodinic textures enclosed within a pelitomorphic matrix. Most of the deposits are boehmitic but in some localities, a considerable quantity of diaspore is identified. Hematite is the dominant Fe-mineral, while kaolinite, goethite and calcite are minor. The accessory minerals are represented by anatase, rutile and zircon. Al2O3 content ranges between 54.32–61.05 wt % and is negatively correlated to Fe2O3. Rare earth elements (REE) show variable concentrations, reaching up to 1353 ppm. The chondrite normalized patterns reveal negative Eu anomaly in all and positive Ce anomaly in almost all samples. Ce anomaly shows negative correlation with REE. Bauxites from the Jajce area represent valuable mineral resource with potentially valuable quantities of REE and Sc. Mineralogy and geochemical signature indicate a complex petrogenetic history.

Keywords: bauxites, critical raw materials potential, Jajce, Bosnia and Herzegovina, AGEMERA project.

Introduction

Mining of bauxite in Bosnia and Herzegovina has a long history which is dated back to the first half of the 20th century when it has represented an important part (up to 50%) of the country’s export (Brkljača, 1999). One of the most productive bauxite localities over the past decades is a broader area around Jajce (Dragićević et al., 2019), encompassing three major deposits: Bešpelj, Crvene Stijene and Poljane. The bauxites themselves form irregular bodies with a range of sizes and shapes that are mostly predefined by the paleo relief of the Albian limestones of the footwall (Pavičić et al., 2018). In the hanging wall there are diverse lithologies of the Santonian age, but carbonate clastic rocks (breccia or conglomerate) predominate.

Previous works on the bauxite of the Jajce region were mostly focused on the local geology and exploration of new deposits, with only few publica-
...tions, notably by Dragičević (1981) and Palinkaš et al. (1993) addressing mineralogy and geochemistry of the Cretaceous bauxites are known. Important reports on mineralogy and chemistry of the Jajce bauxites were published by Trubelja (1984) and Trubelja and Mutić (1991), although they deal with only Palaeogene bauxites. The lack of detailed mineralogical studies and geochemical data on the potential of the bauxites as a source of gallium, REE, Ti, Zr etc. motivated the present study that is also a contribution to the Horizon Europe AGEMERA (Agile Exploration and Geo-modelling for European Critical Raw Materials-CRMs) project aiming the unravelling of the European potential for CRMs. The study presents new data on mineralogy and major and trace element geochemistry of Cretaceous bauxites in the area of Jajce. Along with the evidence for potentially valuable enrichments of Al, Ti, REE and Zr, the study offers a substantial opportunity to contribute to the understanding of the genetic history of the deposits.

Analytical methods

Petrographic and XRD analyses were done at the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Croatia. The XRD analyses were preformed by Malvern Panalytical Empyrean diffractometer using 0.5° divergent and anti-scatter slits, 0.03 and 0.04 rad soller slits, CuKα radiation, 45 kV, 40 mA and a PIXcel 3D detector. The measurement time per step was 78.8 seconds with the step size of 0.0130°2θ. The XRF analyses were performed by EDXRF Epsilon 3XLE instrument (PANalytical) using the Omnian 3SW software, at the Faculty of Geology and Geography, Sofia University, Bulgaria. Loss on Ignition (LOI) was determined at 1000° C and was calculated as a percentage by weight of the starting sample weight. Trace elements in the same samples were measured 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.

Petrography

Petrographic studies of the Jajce bauxites reveal that all deposits share relatively similar textural and mineralogical characteristics. Ooidic to pisoidic textures dominates (Fig. 1a). Particles of microcrystalline and ooides are fixed in a pelitomorphic matrix. Pisoides range in size up to 2 mm and are often completely hematized. Large grains (up to 2 cm) of former ooidic bauxites are often present and form conglomeratic textures (Fig. 1a). Other elements of resedimentation can be observed in form of ooides and ooides are fixed in a pelitomorphic matrix. Particles of microcrystalline and ooides are fixed in a pelitomorphic matrix. The main Al-bearing mineral phase in all samples is boehmite; diaspor is observed only in the Crvene Stijene localities, whereas gibbsite is not detected (Fig. 1b). Hematite is the only Fe-bearing mineral with traces of goethite detected only in one sample from the Bešpelj locality. Minor and accessory minerals like kaolinite, calcite, anatase, rutile and zircon are detected in almost all samples.

Chemistry

Major elements of the Jajce bauxites reveal compositional variations: Al₂O₃ ranges from 54.32 to 61.05 wt.%, Fe₂O₃ from 23.02 to 29.60 wt.%, and SiO₂ from 0.57 to 1.75 wt.%. With this composition the Jajce bauxites correspond to the ferritic bauxite (Fig. 1c). TiO₂ content range between 2.28–2.73 wt.% and MgO does not exceed 0.25 wt.%. A relatively higher content of the CaO (0.13–0.73 wt.%) is detected only in samples from the Bešpelj and Skakavac localities, reflecting the presence of calcite. Selected trace element concentrations are presented in Table 1. Compared with the average continental crust the bauxites show general depletion in Cs, Rb, Ba, K and Sr. REE concentrations vary, with most samples having ΣREE under the 500 ppm sum of REEs (Table 1). However, the sample from the Skakavac locality has significantly higher REE content (1353 ppm), which indicates high potential for possible extraction. Chondrite normalized REE patterns show enrichment of light rare elements (LREE) relative to heavy rare earth elements (HREE). Negative Eu anomaly is evident in all samples and positive Ce anomaly in almost all samples except in the Skakavac locality where Ce anomaly has negative character. It is evident that the Ce anomaly has a negative correlation with ΣREE. The negative Eu anomaly is constant through all samples and shows no correlation with other REEs. Moderately enriched Sc content (up to 60 ppm) also represents potentially valuable resource as it is listed as critical raw material for EU.

Discussion and conclusion

This study provides detailed petrographic and geochemical data on Cretaceous bauxites from the Jajce area. The results show that bauxite deposits vary in quality and some of them are enriched in valuable
Table 1. Concentrations of selected trace elements in bauxite form Jajce (in ppm)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Sc</th>
<th>Ga</th>
<th>As</th>
<th>Y</th>
<th>Zr</th>
<th>Nb</th>
<th>Mo</th>
<th>La</th>
<th>Ce</th>
<th>Nd</th>
<th>ΣREE</th>
<th>LREE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-0607</td>
<td>Skakavac</td>
<td>57.0</td>
<td>43.4</td>
<td>135.1</td>
<td>87.5</td>
<td>464</td>
<td>43.0</td>
<td>6.16</td>
<td>368.1</td>
<td>244.1</td>
<td>390.0</td>
<td>1353</td>
<td>1174</td>
</tr>
<tr>
<td>A-0614</td>
<td>Poljane</td>
<td>50.7</td>
<td>46.3</td>
<td>93.8</td>
<td>40.1</td>
<td>465</td>
<td>45.8</td>
<td>9.39</td>
<td>43.8</td>
<td>265.5</td>
<td>36.9</td>
<td>399</td>
<td>365</td>
</tr>
<tr>
<td>A 0609</td>
<td>Bespelj</td>
<td>52.5</td>
<td>36.2</td>
<td>123.5</td>
<td>49.9</td>
<td>463</td>
<td>46.3</td>
<td>5.10</td>
<td>68.7</td>
<td>258.0</td>
<td>84.9</td>
<td>502</td>
<td>450</td>
</tr>
<tr>
<td>A 0611</td>
<td>CrvStijene</td>
<td>48.8</td>
<td>36.1</td>
<td>99.8</td>
<td>31.5</td>
<td>474</td>
<td>45.9</td>
<td>12.7</td>
<td>26.7</td>
<td>240.0</td>
<td>23.1</td>
<td>324</td>
<td>301</td>
</tr>
</tbody>
</table>

Fig. 1. a, ooidic to conglomerate texture of the bauxite from the Bešpelj locality; b, XRD spectra of major, minor, and accessory minerals; c, classification of bauxites based on major elements after Aleva (1994)

REE and Sc. The negative Eu anomaly is constant showing no correlation with other REE and probably reflects the characteristics of the source material. Variations in the Ce anomaly is caused by the same processes that had affected the total sum of the REE. All these geochemical characteristics indicate complex and multi-phase petrogenetic history of bauxite formation. Further geochronological and
in-situ EPMA and LA-ICP-MS investigation will be carried out to link the whole rock geochemistry with specific minerals and better resolve questions regarding the sources and genesis of bauxites from the Jajce region.

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