

Article

The Potential for REE and Associated Critical Metals in Karstic Bauxites and Bauxite Residue of Montenegro

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Abstract: Research for critical raw materials is of special interest, due to their increasing demand, opulence of applications and shortage of supply. Bauxites, or bauxite residue after alumina extraction can be sources of critical raw materials (CRMs) due to their content of rare earth elements and other critical elements. Montenegrin bauxites and bauxite residue (red mud) are investigated for their mineralogy and geochemistry. The study of the CRM's potential of the Montenegrin bauxite residue after the application of Bayer process, is performed for the first time. Montenegrin bauxites, (Jurassic bauxites from the Vojnik-Maganik and Prekornica ore regions from the Early Jurassic, Middle Jurassic-Oxfordian and Late Triassic paleorelief) are promising for their REE's content (around 1000 ppm of Σ REE's). More specifically, they are especially enriched in LREEs compared to HREEs. Regarding other CRMs and other elements, Ti, V, Zr, Nb, Sr and Ga could also be promising. In bauxite residue, the contents of Zr, Sr, V, Sc, La, Ce, Y, Ti and Nb are higher than those in bauxites. However, raw bauxites and bauxite residue as a secondary raw material can be considered as possible sources of CRMs.

Keywords: bauxite residue; REE; critical metals; Montenegro; bauxites; mineralogy; geochemistry



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1. Introduction

From economical point of view, red karstic bauxites can be considered as a potential mineral raw material for obtaining the REEs. World demand for rare earth elements has been on the rise for years, due to their usage in high-tech applications. REE supply in global market is limited, as China is almost the exclusive global supplier. Significant attention is paid to REE's resources of the United States, when it comes to domestic deposits, a global perspective and world production [1,2], as well as in European and other countries.

Apart from REEs, other trace elements such as vanadium, scandium, gallium, lithium, molybdenum, etc., are important for the exploration of karstic bauxites, as they can be found in considerable amounts and are of economic value. European Commission regularly publishes a list of critical mineral resources (CRM) in the European Union. The last published list of CRM (2020) contains 30 different mineral resources [3]. Some of them, such as: titanium, rare earth elements (light and heavy), vanadium, scandium and gallium are found in karst bauxites deposits in Montenegro and/or in secondary resources red mud—bauxite residue. The bauxite as CRM is included in the list for the first time.

The presence of rare earth elements in significant contents, in the explored deposits and occurrences of Jurassic bauxite in the Vojnik-Maganik and Prekornica ore regions, as well as in bauxites of other bauxite formations in Montenegro has been confirmed by recent studies [4–6]. In this way, a basis has been created for more detailed research for CRMs in Montenegro.

The possibility of extraction of rare earth elements and other critical elements from bauxite residue from the Aluminium Plant Podgorica which is about 7.5 million tons is under investigation. According to Montenegrin legislation, bauxite residue is classified as a technogenic mineral raw material [7].

Rare Earth Elements (REE) in Karstic Bauxites

Bauxites represent residual deposits formed mostly in humid tropical to sub-tropical climates (e.g., [8,9]) and can be subdivided, according to bedrock lithology, into karstic and lateritic types [10–16]. Similar to bauxites, Ni laterites and karstic nickel deposits can be considered as potential resources for critical metals (CM), REEs, Sc and platinum group elements (PGE) exploration [17–20]. Moreover, REE resources on Gran Canaria are significant, especially in Miocene alkaline felsic magmatic rocks and their associated paleosols [21].

Karstic bauxites are enriched in V, Co, Ni, Cr, Zr and occasionally in REE [4,10,22–46]. For example, the Las Mercedes karstic bauxites in the Dominican Republic contain extremely high contents of REEs [47]. The most abundant hydrated alumina oxide minerals in karstic bauxite are böhmite and diaspore [8,9,48]. The vertical distribution of trace elements and REEs in Montenegrin karstic bauxite deposits, particularly those of Jurassic age, show that REE were mobile during deposit formation [49–55]. The REEs generally occur in association with bastnäsite group as the most abundant authigenic REE minerals [14,56–58], while REE phosphates such as monazite-(Nd), monazite-(La) and Nd-rich goyazite are less abundant [52,53,59]. There is a great variety of authigenic REE minerals among the deposits. Their composition depends on fluorine contents. High content of bastnäsite and hydroxylbastnäsite minerals group in Bosnia and Herzegovina, Montenegro and Greece karstic bauxite were connected with fluorine-poor environment [52–54]. The formation of authigenic REE minerals in the deeper part of karstic bauxite deposits, depends on the REE content of the weathered parent rock, the intensity of leaching by surface water and the behaviour of basement limestone as an efficient geochemical barrier [19]. High contents of light REE relative to the heavy REE have been detected in the basal part of the Montenegrin Jurassic bauxites, with very low silica content. By studying REEs in Jurassic bauxite deposits Zagrad from Montenegro, it is determined that the deeper parts of the deposit with authigenic minerals exhibit very strong enrichment in all REEs, especially LREEs [4]. The major carriers of REE and the presence of residual and authigenic monazite and xenotime, clearly indicate that part of REE minerals were redeposited from primary sources, and the rest are formed during an early diagenetic stage, under oxidizing conditions.

This review paper focuses on the presentation of Montenegrin bauxite formations, their mineral composition and geochemical characteristics, principally based on previously published data, as well as an assessment of the potential for REE and associated critical metals exploitation. Moreover, a preliminary attempt to assess the CRM's potential of Montenegrin bauxite residue after the application of Bayer's process is made for the first time.

2. Geological Setting

2.1. Karstic Bauxites of Montenegro

All deposits and occurrences of karstic bauxites in Montenegro belong to the Dinaric metallogenetic province [60–62]. They are located in the metallogenetic units of High Karst, in the Adriatic zone in the coastal area, as well as in the area of the Durmitor metallogenetic subzone, in the area of Sinjavina [15] (Figure 1).

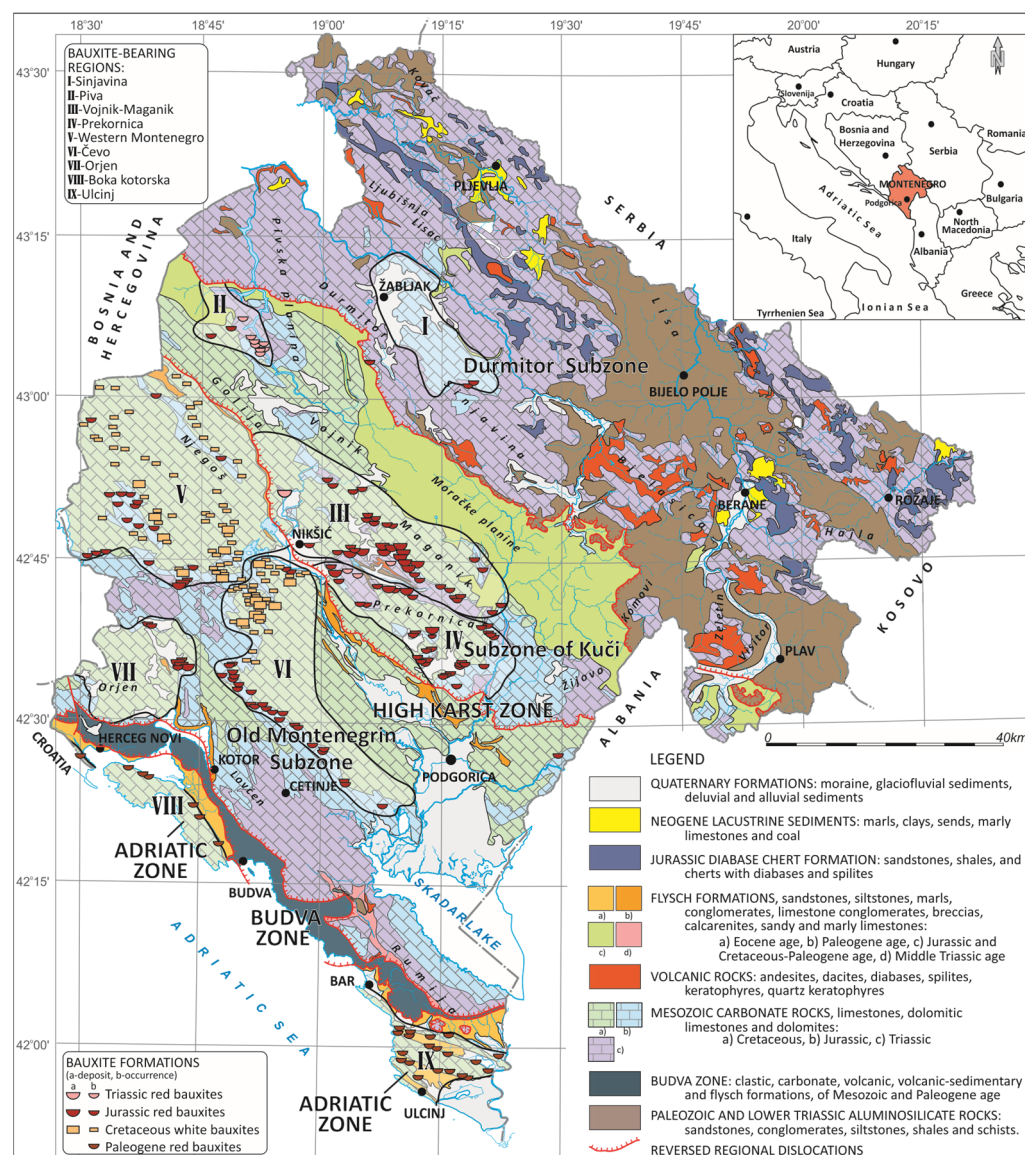


Figure 1. Geological map of Montenegro (after Mirković, et al., modified [63]), with bauxite-bearing regions, bauxite formations, deposits and occurrences of karstic bauxites (after Pajović [15]).

The territory of Montenegro is built of different types of sedimentary, igneous and metamorphic rocks. Most of the terrain is built by Mesozoic formations of carbonate composition. They are developed in the northern, central and coastal part of Montenegro. Magmatic and clastic aluminosilicate rocks are much less presented. Paleozoic geological formations are presented by sedimentary and metamorphic rocks. They are located mainly in the north-eastern part of Montenegro. Cenozoic rocks of carbonate and clastic composition occur here and there in all regions of Montenegro [64] (Figure 1).

The red karstic bauxites occur in three stratigraphic levels in the Middle Triassic, Jurassic and Paleogene, while the white karst bauxites are of Cretaceous age [16,64–66].

Triassic bauxites were discovered in the wider area of Nikšićka župa, in Gornje polje near Nikšić and in Piva (Piva, Vojnik-Maganik and Prekornica bauxite-bearing regions, Figures 2 and 3). The underlying bed of the Triassic bauxite is formed by Anisian limestones, reef Ladinian limestones or Ladinian volcanogenic-sedimentary formation. In their immediate hanging wall, there are terrigenous Raibel sediments, and then early diagenetic dolomites of the Carnian stage.

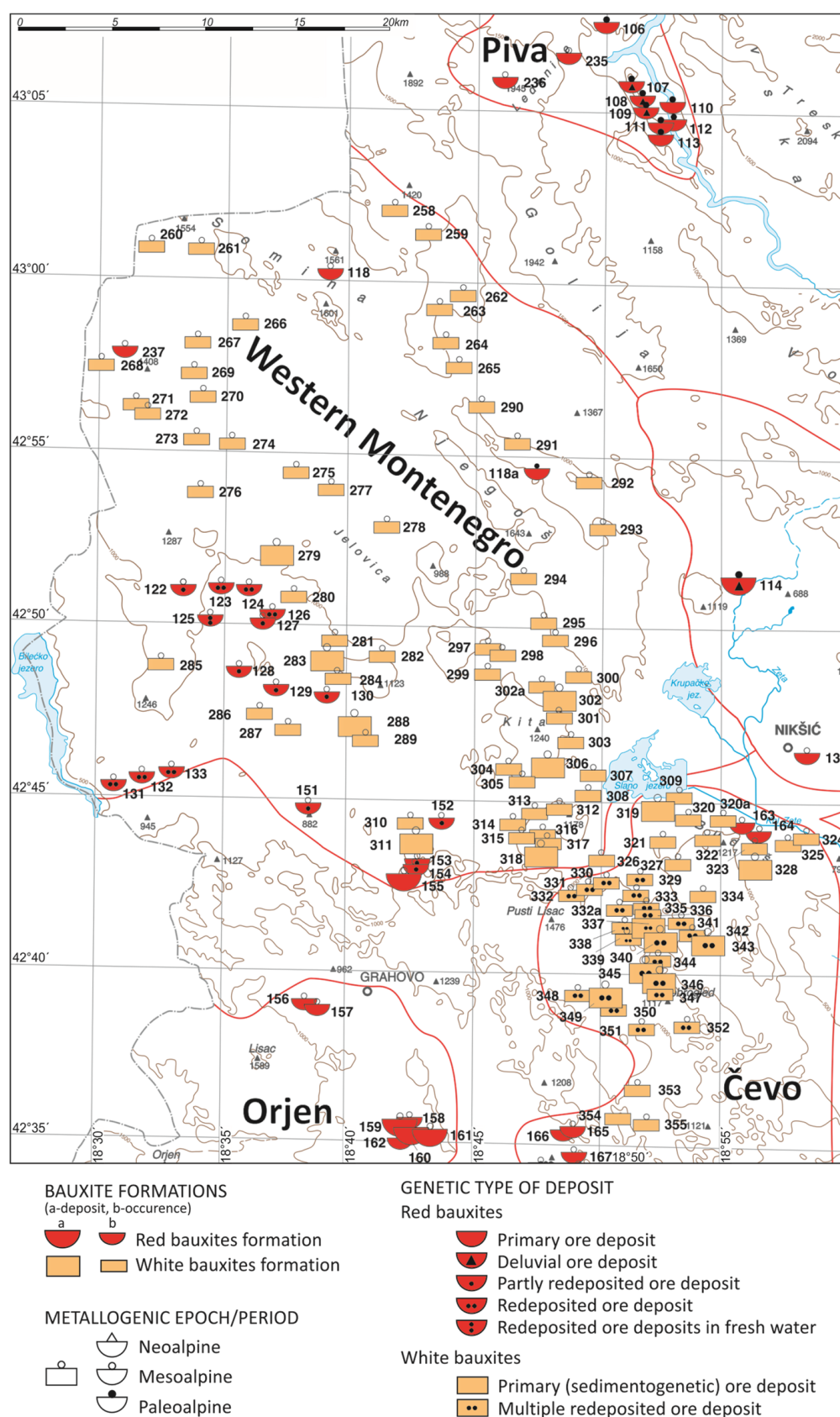


Figure 2. Deposits and occurrences of karstic bauxites of Piva, Western Montenegro and part of Čevo bauxite-bearing regions (after Pajović [15], modified). The legend is the same for Figures 3 and 4. The list of deposits (capital letters) and occurrences of karstic bauxites of Montenegro shown on

Figures 2–4, (according to Pajović [15], supplemented): **I—Red Bauxites.** (a) Triassic ore deposits and occurrences: 106 Goransko, 107 Seljani, 108 Rudinice, 109 Crvena stijena, 110 Dubljevići, 111 Rudinički brijeg, 112 Bezubačke strane, 113 Bukove strane, 114 GORNJOPOLJSKI VIR, 115 Seoca, 116 Žljebovi, 117 Ploče; (b) Jurassic ore deposits and occurrences: 118 Čurilo, 118a G. Srijede, 119 Provalija, 120 Konate I, 121 Konate II, 122 Crvena šuma, 123 Macavare, 124 Selina, 125 Lastva (Morišta), 126 Crveni do, 127 Milovići, 128 Dugi do, 129 Zaljuta (Pandurica), 130 Štrpca (Tupan), 131 Mrkajići (Kapić), 132 Savina gradina, 133 Grepca (Viluski Broćanac), 134 Trebjesa, 135 Raskrsnice, 136 Lokva Milankovac, 137 Strašnica (Gornje Vuče), 137a Ivankovac, 138 Javorak, 139 Rozin vrh I, 140 Rozin vrh II, 140a Saladžakova greda, 140b Krnja jela, 140c Meteris, 141 Laz, 142 LIVEROVIĆI, 142a Bunić, 142b Dubrava, 143 ZAGRAD, 144 Lokva, 145 KUTSKO BRDO, 146 PODPLANINIK, 147 ĐURAKOV DO, 148 BIOČKI STAN, 149 SILJEVAC, 150 Velja Lazba, 151 Maočići, 152 Bajov do, 153 Đelovi do II, 154 Đelovi do I, 155 CRVENA KITA, 156 Vrage, 157 Kovačev do, 158 Čukin do, 159 M. DUBOVA GLAVA, 160 V. DUBOVA GLAVA, 161 GNJILAVI DO, 162 Vukova Lazina, 163 Budoški do, 164 Nuga Borkovića, 165 Danave, 166 Ranjeva vlaka, 167 Jasen, 168 Lastva (Dobra gora), 169 Bojanje brdo (Nerim), 170 Bebin do, 171 Jama Vojvodina, 172 Čukovac, 173 Lipa, 174 Proseni do, 175 Dobra voda, 176 Pejovići, 177 Alužice, 178 Prediš, 179 Lješev stup, 180 Malošin do, 181 ŠTITOVO I, 182 ŠTITOVO II, 183 Repište I, 184 Repište II (Branik), 184a Vodni do, 185 BOROVIK, 186 Raline (Bršno), 187 BRŠNO, 188 Buavice, 189 Seoca (kod Crvenjaka), 190 CRVENJACI, 191 Đelova glava, 192 BOROVA BRDA, 193 Matijaševića pod, 194 Čukar II, 195 Čukar I, 196 Smrekova glavica, 197 Prolom, 198 Međugorje, 199 Javorje, 200 Alina lokva, 201 Mrkalj do, 202 Tijesno ždrijelo, 203 Javorak, 204 Košuća glava, 205 Željeva duga, 206 Pino selo, 207 Đević bor, 208 Zamršten, 209 Crveno katunište, 210 Crvena rupa, 211 Bijela stijena, 2011a Osojnik, 212 Kamenik, 213 Barni do, 214 Crveni ugao, 215 Crvena glavica, 216 Jelenak, 217 Strana (Crnač do), 218 Crveno prlo, 219 Crnač do, 220 Podgrabovlje, 221 Brotnjik, 222 Smrekova glavica, 223 Vranja ulica, 224 Pantelijev vrh, 225 Seoca, 226 Kosača, 227 Dužički krš, 228 Stavor, 229 Oštra glava, 230 Grabova glavica, 231 Češljari I, 232 Češljari II, 233 Veliki Vezac, 234 Benkani, 235 Kovioc, 236 Ružica, 237 Kovači; (c) Paleogene occurrences: 238 Žvinje, 239 Klinci, 240 Petrovići, 241 Krtola, 242 Kovači, 242a Ukropci, 242b Lješevići, 243 Komina, 243a Kurtina, 244 Kunje, 245 Duškići, 246 Povara, 247 Mala Gorana, 248 Velika Gorana, 249 Krute, 249a Kruče, 250 Mavrijan, 251 Mali Kručić, 252 Bijela gora, 253 Kolonza, 253a Lišnjani, 254 Klezna, 255 Briska gora, 255a Ambula, 256 Zoganje, 257 Darza, 257a Sv. Đorđe. **II—White Bauxites:** 258 Korito, 259 Zaljutnica, 260 Biteljica, 261 Stolovan, 262 Javljen, 263 Goslić, 264 Prisoje, 265 Vita Stijena, 266 Suvo polje, 267 Krnja jela, 268 Kovači, 269 Brekovac, 270 Bucari, 271 Vagani, 272 Kaluđerska glavica, 273 Baljački do, 274 Koprivice, 275 Smrdelj, 276 Stražnica, 277 D. Dubočke, 278 Brezov do, 279 ČISTA VLAKA, 280 Miljanići, 281 Prigradina, 282 Grebnice, 283 ČALOVE KOSE (METERIZ), 284 Dolovi, (Liverovo polje), 285 Razvršje, 286 Tupanska ravan I, 287 Tupanska ravan II, 288 DUBRAVČEV DO, 289 Raškovo brdo, 290 Gornje Srijede, 291 Žgurlini, 292 Grabova glava, 293 Kita, 294 Bukarov do, 295 Trnovac, 296 Cerovi do, 297 Zukva (Trepča), 298 Mujova glavica, 299 Pasji brijeg, 300 Pobijen kamen, 301 Studena, 302 PODKITA, 302a Rujnova glava, 303. Krstac, 304. Ranjeva vlaka, 305. Kruščice I, 306. KRUŠČICE II, 307. Slano, 308. Vonjin do (Ponikvica), 309. Orlina (Čelinski do), 310. Božurevo brdo, 311. ĐELOVI DO, 312 Goslić (Katunište), 313 Lipova glavica (Osoje), 314 Golubinja, 315 Stražnik (Veliki čoš), 316 Lazine (Brestica), 317 Gradac (Brestica), 318 PLITKI DO (BRESTICA), 319 ŠIROKA ULICA, 320 Spavade, 320a. Krivodo, 321 Zanoetna glavica, 322 Svinji doli, 323 SZ od Medjedjeg, 324 Carev most, 325 Pandurica, 326 Srni do, 327 Maletin do, 328 MEĐEĐE, 329 Riđa Lokva, 330 Bijeli do, 331 Pusti Lisac, 332 Pusti Lisac II, 333 Lola, 334 Borova brda, 335 Padnurica II, 336 Crveno razdolje, 337 DIONICE (Bijele poljane), 338 Lazine, 339 Aluga, 340 DOBRI POD, 341 Ljeskovi doli I, 342 Ljeskovi doli II, 343 JELINA PEČINA, 344 Trebovinjski pod, 345 STUDENAC, 346 PAPRAT, 347 Dobrogled, 348 Gola glava, 349 PAKLARICA, 350 Katunište, 351 Čumovica, 352 Vujkovo ždrijelo, 353 Šumova greda, 354 Stražnik, 355 Dolovska korita.

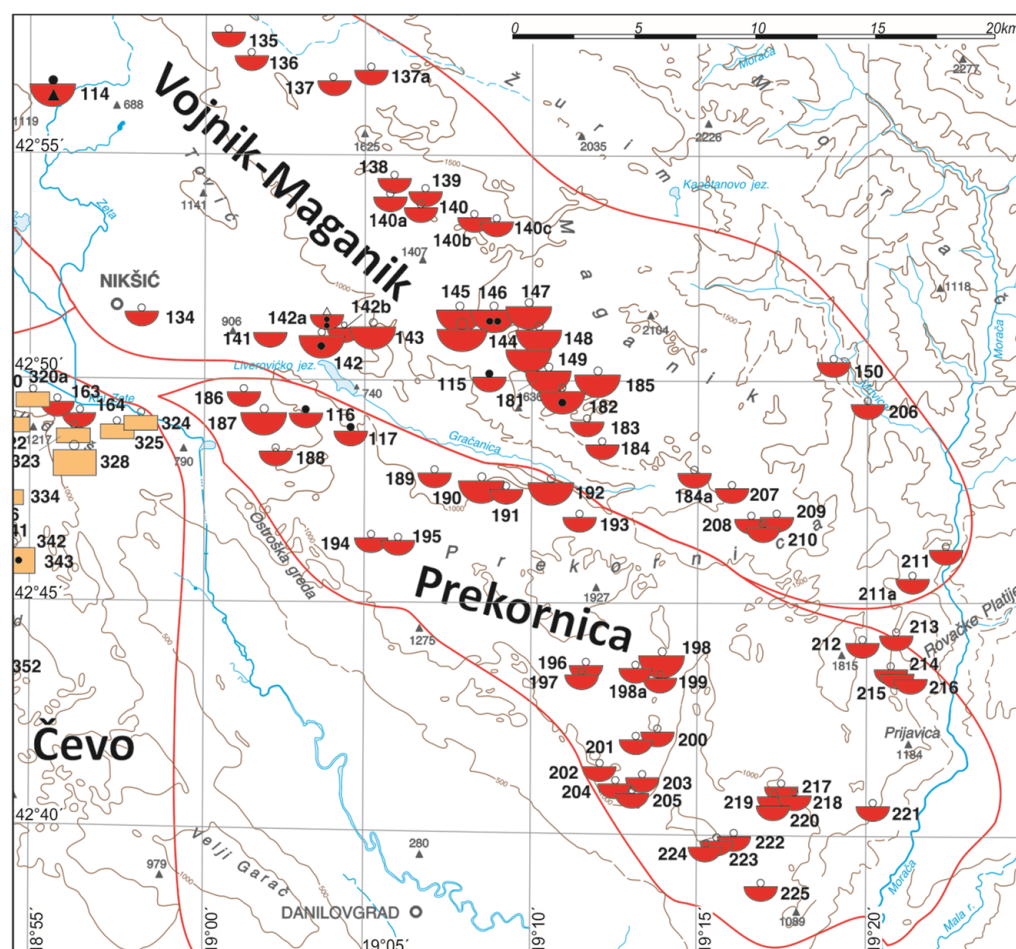


Figure 3. Deposits and occurrences of karstic bauxites of Vojnik-Maganik and Prekornica bauxite-bearing regions (after Pajović [15], modified).

Jurassic bauxites in Montenegro are widespread in the area of the High karst zone, and are present on the terrains of Sinjavina and Durmitor—in the Durmitor tectonic unit. During the Jurassic, the High karst zone was differentiated into two complex anticline forms: the subzone of Kučii in the northeast and the Old Montenegrin subzone in the southwest [67]. Jurassic bauxite deposits and occurrences belong to Vojnik-Maganik, Prekornica, Western Montenegro, Orjen and Čevo bauxite-bearing regions, (Figures 2 and 3). The paleorelief of Jurassic bauxite in Montenegro consists of karstified limestones and rare dolomites of the Late Triassic, Liassic and Dogger-Oxfordian age. Their hanging wall of Kimmeridgian-Titon age, is represented by different types of limestone and rarely present dolomites.

Cretaceous, white bauxites were formed during the Early Cretaceous on a karst paleorelief built of limestone, dolomitic limestones and dolomite of Liassic, Doggerian, Tithonian and Berriasian-Barremian age. Over the white bauxite, limestones of the Late Cenomanian were deposited. They were discovered in the Western Montenegro and Čevobauxite-bearing regions (Figure 2), in the domain of the Old Montenegrin subzone.

Paleogene bauxites were formed in the coastal part of Montenegro within the Adriatic zone. They are known mainly as of Eocene age, and less frequently as Lutetic bauxites in the literature. Deposits and occurrences of Paleogene bauxites in the area of Luštica and Grbalj and between Bar and Ulcinj (Figure 4) are located on a paleorelief built of Late Cretaceous limestones and dolomites, while their hanging wall is made up of Middle Eocene limestones.

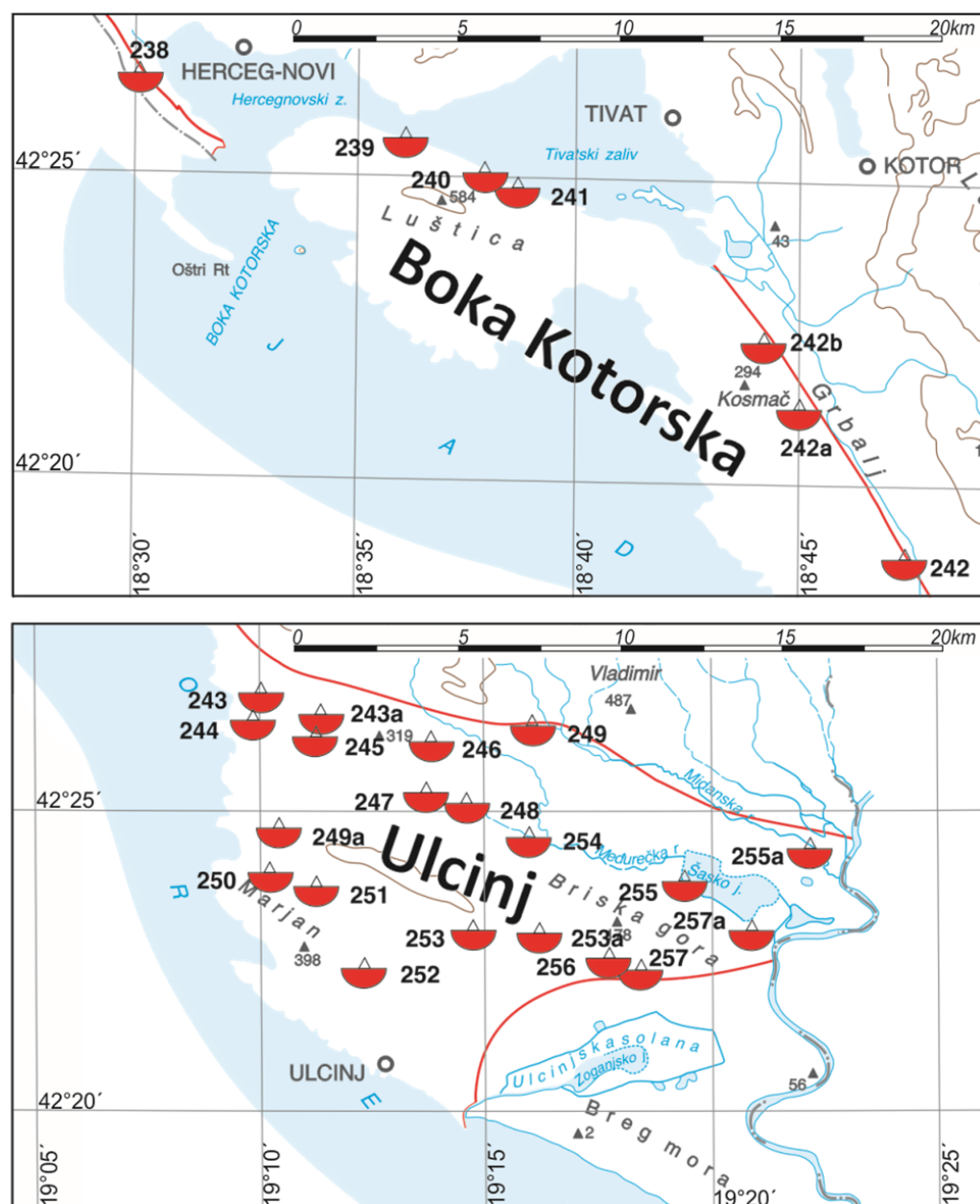


Figure 4. Occurrences of karstic bauxites of Boka Kotorska and Ulcinj bauxite-bearing regions (after Pajović [15], modified).

Triassic bauxites have been poorly explored, primarily due to their high SiO_2 content. On the contrary, Montenegrin Jurassic bauxites in general have been thoroughly investigated. Some Cretaceous bauxite deposits, especially in the area of Bijele poljane and Trubjela, have been investigated in more detail. Paleogene bauxites have not been thoroughly evaluated as a potential economic resource.

According to previous explorations, Montenegrin bauxites are characterised by variable geological characteristics and chemical composition, as well as a complex mineral composition. Detailed information on the geological setting, mineralogy and geochemistry can be found in [15,68–75] and references therein.

Most researchers agree that laterite bauxites are formed ‘in situ’, from aluminosilicate igneous, sedimentary and metamorphic rocks, on land, in humid tropical and subtropical climates. The genesis of karstic bauxite is still controversial in terms of: the place and conditions of bauxitisation, the origin of the parent material and its transport to karstic

areas. When it comes to the origin of the parent material from which bauxites originated in Montenegro, interpretations are also different [61,68,71,72,76].

The content and mode of occurrences of REEs and other trace elements in the bauxite deposit of Montenegro are directly related to the composition and origin of the parent material, as well as the conditions and duration of bauxitisation and the other factors. The source material for the Triassic bauxites originates from the products of the Middle Triassic volcanism, the volcanic ashes and/or the weathering crust formed on the rocks of igneous origin, while Jurassic red bauxites are originated from the volcanic ashes, related to the igneous-tectonic processes and the volcanoes to follow during the 'opening' and 'closing' of the Jurassic ophiolitic trough. A smaller quantity of the source material can come from the weathering crusts of mainly basic rocks [15,16]. The value of Eu/Eu^* versus $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios indicates shales, UCC and andesitic rocks as possible source rocks, or protolith of the Zagrad deposit Jurassic bauxite [4]. The binary plot of Eu/Eu^* vs. Sm/Nd indicates that the parental material for the bauxite was derived from a combination of a clastic material derived from shales and/or upper continental crust and, probably, distant andesitic volcanic source. Jurassic paleo-geographical and paleo-tectonic processes in the Mediterranean indicate that the source material most likely originates from ophiolites complexes, which are suprasubduction oceanic island-arc type ophiolites, with intensive extrusive volcanism [5,77]. It is possible that the volcanic ash or/and material from weathered crust of this complex are parent materials from which Jurassic karstic bauxites in Montenegro were formed. The source material of white Cretaceous bauxites mainly comes from the weathering crusts on the igneous basic rocks, and in rare cases, from the volcanic ashes. Origination of the white bauxite facies is related to the circulating, lacustrine, oxygen-rich environments, while the pyritised bauxites originated in a reducing environment. In the region of Bijele Poljane, however, the deposits of white bauxites were formed by mixing of various colored clays with redeposited sandy-gravelly material which originates from the deposits of the red Jurassic bauxites in the same region. That is why such deposits are rightfully called 'complex' deposits of the white bauxites [15,65]. The source material of the Paleogene bauxites probably comes from the volcanic ashes and/or the weathering crusts of basic rocks, and to a smaller extent also from the weathering crusts of ultra-basic rocks [15].

2.2. Rare Earth Elements (REE) in Montenegrin Karstic Bauxites

Previous researchers have investigated the REE content of Montenegrin bauxites including [15,49,50,53,57,68,74,76,78–80]. These studies have focused on the study of geological structure and structural characteristics of bauxite-bearing terrains, as well as geological, structural morphological, chemical and geochemical characteristics of karstic bauxite deposits. The deposits of red and less white bauxites from which this raw material was or is being exploited have been investigated in detail.

Recent national exploration projects include the following: Metallogenetic-prognostic map of the bauxite-bearing region Vojnik-Maganik, 1:50,000 (MPMVM), 'Metallogenetic-prognostic map of the bauxite-bearing region Western Montenegro', 1:50,000 (MPMWM) and 'Exploration of rare earth elements in ore regions Vojnik-Maganik and Prekornica (REEVMP)', as well as the international project 'REEBAUX-Prospects of REE recovery from bauxite and bauxite residue in the ESEE region'. A summary of the occurrences of the samples is given in Tables 1–3.

Table 1. Origin and information of bauxite samples from Montenegro (Radusinović [5]; REEBAUX [6]).

Bauxite Formations	Paleorelief Age	Data from Project	Bauxite-Bearing Region/Label	Number of Deposits/Occurrences	Sample ID/Sample Sequence	Type of Sample	Number of Samples
Triassic	Middle Triassic	REEBAUX *	Piva (PI-II/1)	1	CGBX 01	composite	1 (6 i.s.)
			Vojnik-Maganik (VM-III/1)	1	CGBX 24-CGBX 29	individual	6 (av.)
		REEBAUX *	Vojnik-Maganik (VM-III/2)	7	CGBX 02-CGBX 07; CGBX 30-CGBX 36	composite; individual	6 (56 i.s.) + 7 i.s. (av.)
Jurassic	Late Triassic	REE VMP *	Vojnik-Maganik & Prekornica (VMP-III&IV/1)	24	004-160	individual	157 (av.)
		MPM VM **	Vojnik-Maganik (VM- III/3)	27	G 001-G 206	individual	206
		REEBAUX *	Prekornica (P-IV/1)	2	CGBX 08; CGBX 09	composite	2 (18 i.s.)
	Liassic	REE VMP *	Vojnik-Maganik & Prekornica (VMP- III&IV/2)	7	001-003; 161-215	individual	58 (av.)
		REEBAUX *	Prekornica (P-IV/2)	1	CGBX 10	composite	1 (4 i.s.)
		REE VMP *	Vojnik-Maganik & Prekornica (VMP III&IV/3)	6	216-252	individual	37 (av.)
	Dogger-Oxfordian	MPM VM **	Vojnik-Maganik (VM - III/4)	4	G 210-G 232	individual	23 (av.)
		REEBAUX *	Western Montenegro & Orjen (WMO-V&VII/1)	5	CGBX 11-CGBX 14; CGBX 37-CGBX 45	composite; individual	4 (25 i.s.) + 9 i.s. (av.)
		MPM WM **	Western Montenegro (WM-V/1)	7	2-23, 32-74, 84-112, 122, 213	individual	94 (av.)
		REEBAUX *	Western Montenegro & Čevo (WMC-VI/1)	8	CGBX 15-CGBX 21; CGBX 46-CGBX 55	composite; individual	7 (61 i.s.) + 10 i.s. (av.)
Cretaceous	Liassic, Doggerian, Oxfordian, Early Cretaceous	MPM WM **	Western Montenegro & Čevo (WMC-VI/2)	17	1,25-28, 75-83, 113-121,124	individual	25 (av.)
		REEBAUX *	Boka Kotorska (BK-VIII/1)	4	CGBX 22	composite	1 (9 i.s.)
Paleogene	Late Cretaceous	REEBAUX *	Ulcinj (U-IX/1)	8	CGBX 22	composite	1 (18 i.s.)

Research projects: REEBAUX—Prospects of REE recovery from bauxite and bauxite residue in the ESEE region (data from 2019); REE VMP—REE exploration in bauxites of Vojnik-Maganik and Prekornica bauxite-bearing regions (data from 2014–2016); MPM VM—Metallogenetic-prognostic map of Vojnik-Maganik bauxite-bearing region, 1:50,000 (data from 2000); MPM WM—Metallogenetic-prognostic map of Western Montenegro bauxite-bearing region, 1:50,000 (data from 2015). Analytical method: * ICP ES/MS, Li-borate fusion; ** ICP-ES/MS, Multi-acid digestion; i.s.—individual sample; av.—average content.

Table 2. Sampled bauxite deposits and occurrences.

Bauxite-Bearing Region/ Label	Data from Project	Label and Name of Deposits/Occurrences
Piva (PI-II/1)	REEBAUX	108 Rudinice
Vojnik-Maganik (VM-III/1)		114 GORNJEPOLJSKI VIR
Vojnik-Maganik (VM-III/2)	REEBAUX	142 LIVEROVIĆI, 143 ZAGRAD 3, 147 ĐURAKOV DO, 148 BIOČKI STAN, 182 ŠTITTOVO II, 187 BRŠNO
Vojnik-Maganik & Prekornica (VMP-III & IV/1)	REE VMP	137 Strašnica (Gornje Vučje), 137a Ivankovac, 138 Javorak, 140 Rozin vrh II, 140a Meteris, 141 Laz, 142 LIVEROVIĆI, 143 ZAGRAD 1&3, 145 KUTSKO BRDO (Palež, Lokve, Šunčeva dolina, Crvene ornice) 147 ĐURAKOV DO 2, 148 BIOČKI STAN, 181 ŠTITTOVO I, 182 ŠTITTOVO II, 187 BRŠNO, 207 Đečić bor, 208 Gornji i Donji Zamršten, 209 Crveno katunište, 210 Crvena rupa, 187 BRŠNO, 188 Buavice

Table 2. Cont.

Bauxite-Bearing Region/ Label	Data from Project	Label and Name of Deposits/Occurrences
Vojnik-Maganik (VM- III/3)	MPM VM	137 Strašnica (Gornje Vučje), 137a Ivankovac, 138 Javorak, 139 Rozin vrh I, 140 Rozin vrh II, 140a Meteris, 140b Saladžakova greda, 140c Krnja jela, 141 Laz, 142 LIVEROVIĆI, 143 ZAGRAD 2, 145 KUTSKO BRDO, 146 PODPLANINIK, 147 ĐURAKOV DO 2, 148 BIOČKI STAN, 149 SILJEVAC, 181 ŠTITOVO I, 182 ŠTITOVO II, 183 Repište I, 184 Repište II, 184 a Branik, 184b Vodni do, 186 Raline (Bršno), 187 BRŠNO, 207 Đević bor, 208 Donji i Gornji Zamršten, 209 Crveno katunište, 210 Crvena rupa
Prekornica (P-IV/1)	REEBAUX	190 CRVENJACI, 192 BOROVA BRDA
Vojnik-Maganik & Prekornica (VMP- III & IV/2)	REE VMP	136 Lokva Milankovac, 190 CRVENJACI, 192 BOROVA BRDA, 198 Međugorje, 198a Plačnik (Međugorje) 199 Javorje, 200 Alina lokva,
Prekornica (P-IV/2)	REEBAUX	218 Crveno prlo
Vojnik-Maganik & Prekornica (VMP III&IV/3)	REE VMP	213 Barni do, 215 Crvena glavica, 216 Jelenak, 218 Crveno prlo, 220 Podgrabovlje, 222 Smrekova glavica,
Vojnik-Maganik (VM - III/4)	MPM VM	150 Velja Lazba, 206 Pino selo, 211 Bijela stijena, 2011 a Osojnik,
Western Montenegro & Orjen (WMO-V&VII/1)	REEBAUX	127 Milovići, 132 Savina gradina, 152 Bajov do, 154 Đelovi do I, 160 V. DUBOVA GLAVA
Western Montenegro (WM-V/1)	MPM WM	124 Selina, 125 Lastva (Morišta), 127 Milovići, 132 Savina gradina, 152 Bajov do, 154 Đelovi do I, 155 CRVENA KITA
Western Montenegro & Čevo (WMC-VI/1)	REEBAUX	306. KRUŠČICE II, 328 MEDEDE, 337 DIONICE -Bijeje poljane, 338 Lazine, 343 JELINA PEČINA, 344 Trebovinjski pod, 345 STUDENAC, 349 PAKLARICA
Western Montenegro & Čevo (WMC-VI/2)	MPM WM	274 Koprivice, 297 Zukva, 302 Podkita, 306 Kruščica, 308 Vonjin do, 313 Lipova glava, 316 Lazine-Brestica, 317 Gradac Brestica, 318 Brestica - Plitki do, 330 Bijeli do, 332, Pusti Lisac, 337 Dionice (Bijeje poljane), 341 Ljeskovi doli I, 342 Ljeskovi doli II, 343 Jelina pećina, 349 Paklarica, 350 Katunište (Šašovica)
Boka Kotorska (BK-VIII/1)	REEBAUX	240 Petrovići 242 Kovači-Glavati, 242a Ukropci, 242b Lješevići,
Ulcinj (U-IX/1)	REEBAUX	243a Kurtina, 244 Kunje, 245 Duškići, 248 Velika Gorana, 249 Krute, 250 Mavrijan (Bratica), 257a Sv. Đorđe

Table 3. Bauxite samples data from characteristic deposits/occurrences.

Bauxite for Mations	Paleorelief Age	Project	Deposit/Occurrence	Bauxite-Bearing Region	Sample Sequence	Number of Samples
Triassic	Middle Triassic	REEBAUX	114 GORNJEPOLJSKI VIR	Vojnik-Maganik (VM-III)	CGBX 24-CGBX 29	6
	Late Triassic	REEVMP	143 ZAGRAD 3	Vojnik-Maganik (VM-III)	034-046	13
Jurassic			REEBAUX	182 ŠTITOVO II	Vojnik-Maganik (VM-III)	CGBX 30-CGBX 36
	Liassic	REEVMP	192 BOROVA BRDA	Prekornica (P-IV)	179-187	9
		REEVMP	218 CRVENO PRLO	Prekornica (P-IV)	216-225	10
	Dogger-Oxfordian	REEBAUX	152 Bajov Do	Western Montenegro (WM-V)	CGBX 37-CGBX 45	9
		REEBAUX	160 VELJA DUBOVA GLAVA	ORJEN (O-VII)	CGBX 12	1 (9 i.s.)
Cretaceous	Liassic	REEBAUX	337 BIJELE POLJANE (Dionice)	Čevo (C-VI)	CGBX 46-CGBX 55	10
Paleogene	Late Cretaceous	REEBAUX	248 Velika Gorana	Ulcinj (U-IX)	CGBX 55-CGBX 60	5

3. Sampling and Analytical Methods

3.1. Sampling

At 37 locations along 47 profiles, the recording and sampling of bauxite bodies formed on a karstified paleorelief made of carbonates of Late Triassic, Early Jurassic and Middle Jurassic-Oxfordian age, were performed, and 252 representative channel bauxite samples with identical intervals (1 m), were collected during the REEVMP project implementation [5]. The samples were prepared for different investigation methods by using standard methods. Mineralogical examinations included tests of 64 samples by using XRD method and 34 samples by using SEM-EDS method (JEOL Ltd., Musashino, Akishima, Tokyo, Japan). Geochemical examinations were done by using inductively coupled plasma method ICP-ES/MS (Bureau Veritas, Vancouver, Canada) on a total number of 252 bauxite samples.

During the REEBAUX project implementation, surveying and sampling of bauxite bodies in Montenegro was performed at 37 sites, on open bauxite outcrops, as well as in the open pits and underground bauxite mines [6]. Sixty representative channel bauxite samples were collected mainly at intervals of 1-m length. From individual samples, 23 composite samples were formed to determine the medium content of REE and other components in selected deposits/occurrences, ore regions (Boka Kotorska and Ulcinj). Different stratigraphic levels, 37 individual samples were formed from five selected deposits. Geochemical examinations were done by using inductively coupled plasma method ICP-ES/MS on a total number of 60 bauxite samples. Mineralogical examinations were performed on 14 samples by using the XRD method.

During the implementation of the MPMVM project, the recorded geological sections of bauxite bodies at 32 sites in total were 232 individual representative channel bauxite samples, collected and prepared for chemical analysis. Moreover, during the realisation of the MPMVM project, 94 samples of white Cretaceous bauxite from 17 localities and 25 samples of red Jurassic bauxites from 7 localities were sampled.

The red sludge samples originate from six vertical exploration drill holes with an average length of 12 m, three from each basin. A total amount of 20 analytical samples were formed from three to four individual samples. Samples were prepared by standard methods, while geochemical tests of 20 bauxite residue samples were performed by ICP-AES/ICP-MS. All exploration activities were done in the frame of the REEBAUX project implementation.

3.2. Mineralogical Analyses

The mineralogy of 64 bauxite samples was determined by optical microscopic observation and powder X-ray diffraction (XRD) at the University of Belgrade, Faculty of Mining and Geology, Belgrade, Serbia, during the REEVMP project implementation. XRD analysis was performed on a Philips PW 1710 powder diffractometer with $\text{CuK}\alpha_{1,2} = 1.54178 \text{ \AA}$ radiation (despite the known limitations for Fe-rich minerals) and a 40 kV, 30 mA. The XRD pattern was recorded over a 2θ interval of $4\text{--}70^\circ$, with a step size of 0.02° and the fixed counting time of 1 s per step. Some samples with high contents of REE were studied by reflected light optical investigations, scanning electron microscope equipped with an energy-dispersive spectrometer (SEM-EDS) and micro-Raman spectroscopy.

The SEM-EDS analyses were carried out at the University of Belgrade, Faculty of Mining and Geology, on polished bauxite samples, under high vacuum conditions on a scanning electron microscope (SEM) type JEOL JSM-6610LV. Mineral images were obtained using back-scattered electrons (BSE) detectors, and tungsten fibre was used as the electron source. The samples were evaporated with carbon on a steamer type BALTEC-SCD-005, and quantitative chemical analyses of individual minerals in the samples were performed on an energy-dispersive spectrometer (EDS) type X-Max Large Area Analytical Silicon Drift. An acceleration voltage of 20 kV was used for analyses. Detection limits are estimated as $2\sigma \sim 0.2 \text{ wt.}\%$. This method was applied for mineral identification and obtaining REE mineral compositions. According to very fine mineral intergrowths in the studied bauxite

and regular presence of sub-microscopic mineral inclusions in REE minerals it was not possible to achieve accurate composition of REE minerals using external standards. Thus, compositions of these minerals were obtained using internal standards and normalisation. However, this mode of the analysis quite well shows differences in the composition of various types of the REE minerals.

In addition, the mineralogy of 14 bauxite samples, collected and selected during the REEBAUX project implementation, was determined by optical microscopic observation and powder X-ray diffraction (XRD) at the University of Zagreb, Faculty of Science, Department of Geology, Zagreb, Croatia. Diffraction data were collected using Philips X'Pert PRO powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 40 kV and 40 mA with divergent slit of $\frac{1}{4}^\circ$ and antiscatter slit of $\frac{1}{2}^\circ$. Diffracted radiation was monochromatized using graphite monochromator.

3.3. Chemical Analyses

Ore samples were crushed to 200-mesh size particles using an agate mill. All samples (REEVMP and REEBAUX projects) were prepared for chemical analyses in the laboratories of AcmeLabs (now Bureau Veritas), Vancouver, Canada. Prepared sample is mixed with $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ flux. Crucibles are fused in a furnace. The cooled bead is dissolved in ACS grade nitric acid and analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and/or inductively coupled plasma-mass spectrometry (ICP-MS). Loss on ignition (LOI) is determined by igniting a sample split, while the measuring of weight loss was done after. Quantitative values of major and minor elements, trace elements, and REEs were determined by using inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry analysing methods, respectively. Total loss on ignition (LOI) values were gravimetrically estimated after overnight heating at 950°C for 90 min. Detection limits for major oxides, such as Fe_2O_3 and K_2O were 0.04%; SiO_2 , Al_2O_3 , CaO , MgO , Na_2O , MnO , TiO_2 and P_2O_5 were 0.01%; for LOI 0.1%; and for Cr_2O_3 , 0.002%. Detection limits for trace elements were: for Ni and Co 20 ppm; for V 8 ppm; for Ba 5 ppm; for Be, Sc and Zn 1 ppm; for Ga, Sr, W, As, La and Ce, 0.5 ppm; for Co and Th, 0.2 ppm; for Ce, Cs, Hf, La, Nb, Rb, Ta, U and Y 0.1 ppm; for Dy, Gd, Sm, Yb, 0.05 ppm; for Er 0.03 ppm; for Eu, Ho and Pr, 0.02 ppm; Lu, Tb and Tm, 0.01 ppm.

Total carbon (C) and sulphur (S) content were analysed on a LECO Elemental Analyser in the laboratories of AcmeLabs (now Bureau Veritas), Vancouver, Canada. Induction flux was added to the prepared sample and it was ignited in an induction furnace after. A carrier gas sweeps up released carbon to be measured by adsorption in an infrared spectrometric cell. Results are total and attributed to the presence of carbon and sulphur in all forms.

Apart from the above mentioned, the results of geochemical analysis of bauxite samples from the MPMVM project are presented in order to compare these older data with newer ones, as well as the content of some elements that were not examined later, primarily lithium (due to the applied sample dissolution method-Li-borate fusion). Classical methods were used for the analysis of major oxides and LOI, while analyses were performed in the Chemical Laboratory of the Geological Survey of Montenegro, Podgorica, Montenegro. Trace elements were analysed by ICP-MS method (4 Acid digestion) in AcmeLabs, Vancouver, Canada. Moreover, the results of the geochemical tests of the MPMWM project are presented with the same goal. For geochemical analyses, a combination of ICP-AES methods for major oxides (Li-borate fusion) and ICP-MS for trace elements (4 Acid digestion) was used. The research were performed in AcmeLabs, Vancouver, Canada.

4. Results and Discussion

According to shape and size of the structural elements of the bauxite structure, the following textures can be found: aphanitic or pelitomorphitic, pisolitic-oolitic, complex conglomeratic and brecciated structure [74]. Extremely rarely, striped, parallel and schistose textures were detected [68].

In general, Triassic deposits and occurrences are formed by dark red pisolitic bauxites over which are bright red pisolitic and oolitic bauxites, and gray partially pisolitic bauxite on the top.

In almost all studied Jurassic bauxite deposits, especially the larger ones from the Vojnik-Maganik ore region [75], red pisolitic bauxite was developed at the top of the bauxite deposits, just below the overlying clays that were formed in the first phase of transgression. These deposits are classified into the group of primary deposits with a developed profile [15]. Beneath the pisolitic, red massive ‘granular’ detrital or aphanitic bauxites are most common, usually with tiny oolites and irregular pisolite accumulations—which form the middle part of the bauxite deposits. At the base of the deposit massive bauxites with or without oolites and pisolites can be found. The transitions in texture mentioned above are gradual and irregular. At the contact place with the bedrock limestones, there are so-called ‘bedrock breccias’, while at some localities there are also bedrock clays in which pieces of bedrock limestones can be found.

Cretaceous white bauxites, especially those in the area of Bijele Poljane, are characterised by a very complex geological structure. Lateral and vertical transitions of red bauxites with white bauxites, white and gray bauxite clays and gray pyritic clays.

Paleogene bauxites are characterised by a pisolitic-oolithic, pisolitic and conglomerate structure, gray, yellow and red colour. The characteristic geological sections of the studied bauxite deposits presented in this paper, from different bauxite formations are shown in Figure 5.

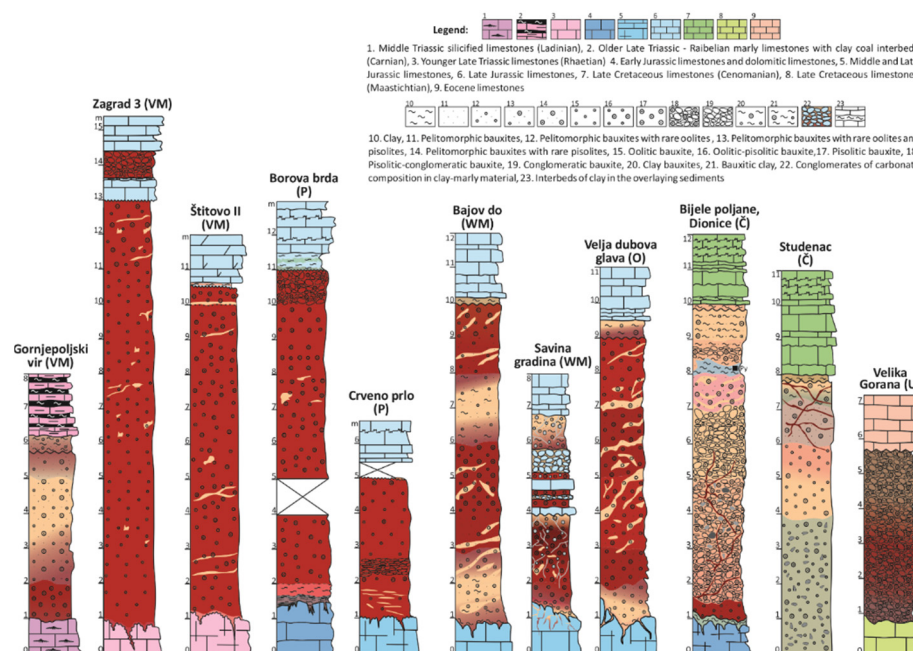


Figure 5. The geological sections of characteristic bauxite deposits/occurrences from different bauxite formations of Montenegro (after Radusinović [5] and REEBAUX project documentation, Radusinović [6]).

4.1. Mineralogy

As it is mentioned above, Montenegrin bauxites have a complex mineralogical composition, which was confirmed in this study as well. The red Triassic bauxites samples of the Gorenjepoljski vir deposits are characterised by the presence of the minerals: kaolinite, böhmite and gibbsite, also goethite, anatase and dolomite, as well as vermiculite in one sample from the middle part of the deposit (Figure 6).

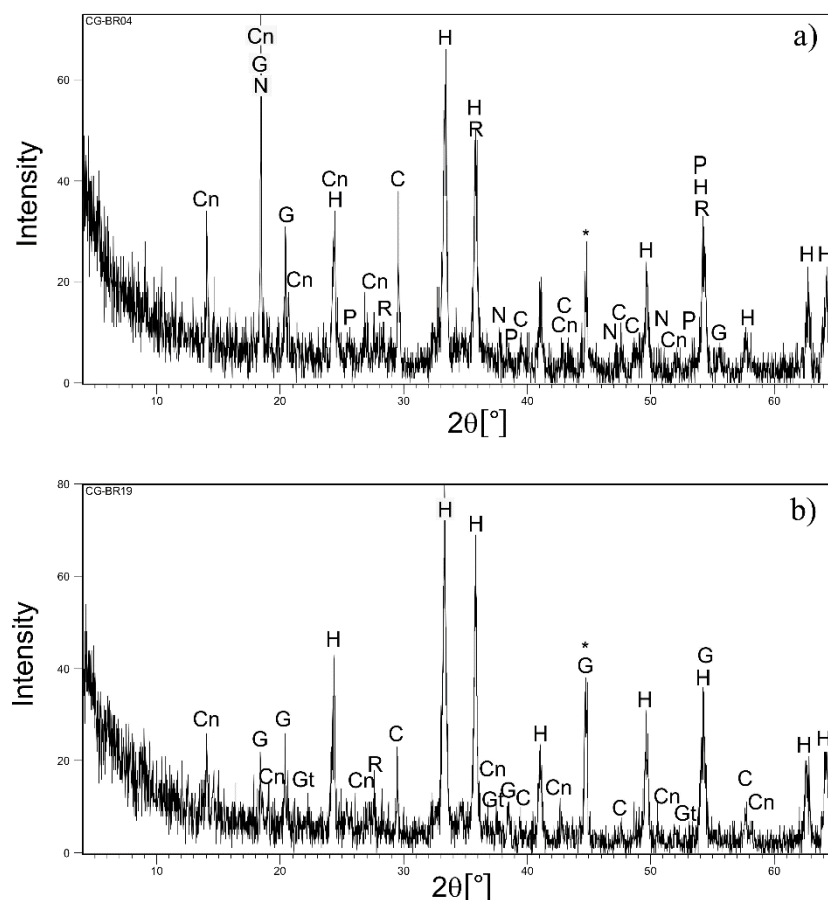


Figure 6. XRD patterns of two typical analysed samples from Gernjepoljski vir deposit: (a) upper part and (b) middle part of deposit (B—böhmite, G—gibbsite, D—dolomite, A—anatase, Gt—goethite, K—kaolinite, V—vermiculite, *—Al-sample holder) (REEBAUX project documentation, Tomašić [6]).

The red Jurassic bauxites of the Vojnik-Maganik and Prekornica ore regions have complex mineral composition as well. The mineral böhmite is the main carrier of aluminium, while gibbsite is the minor Al-carrier. Regarding other major minerals the following are presented: Fe-oxides/hydroxides (hematite and goethite); clay minerals (kaolinite) and titanium minerals (mainly anatase) (Figures 7 and 8).

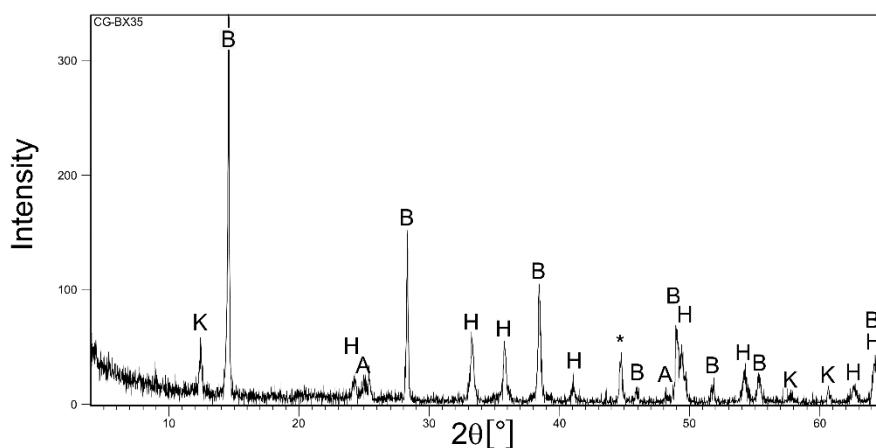


Figure 7. XRD patterns of typical analysed sample from Štitovo II deposit (B—böhmite, A—anatase, H—hematite, K—kaolinite, *—Al-sample holder) (REEBAUX project documentation, Tomašić [6]).

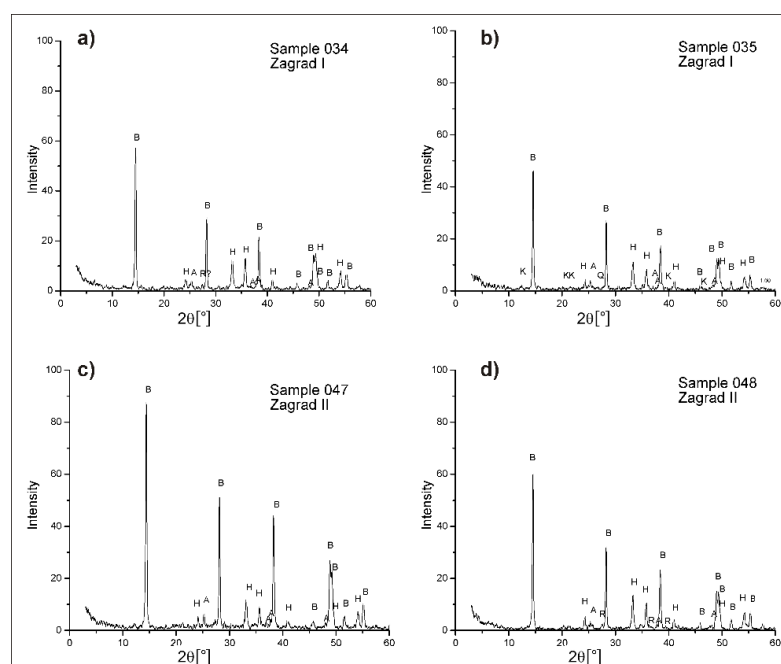


Figure 8. XRD patterns of four typical analysed sample from Zagrad deposit, ore body 3 (B—böhmite; H—hematite; K—kaolinite; A—anatase; R—rutile; Q—quartz) (Radusinović et al. [4]).

The major-, trace- and rare earth element average compositions of the analysed samples are given in Table 4 [5,6].

By using SEM-EDS the following minerals in 34 selected samples from 15 locations (Figures 9–12 [5]), were detected: zircon, ilmenite, magnetite, biotite, K-feldspars, mottramite, REE phosphates-monazite and xenotime as well as REE carbonates-Ce and Nd.

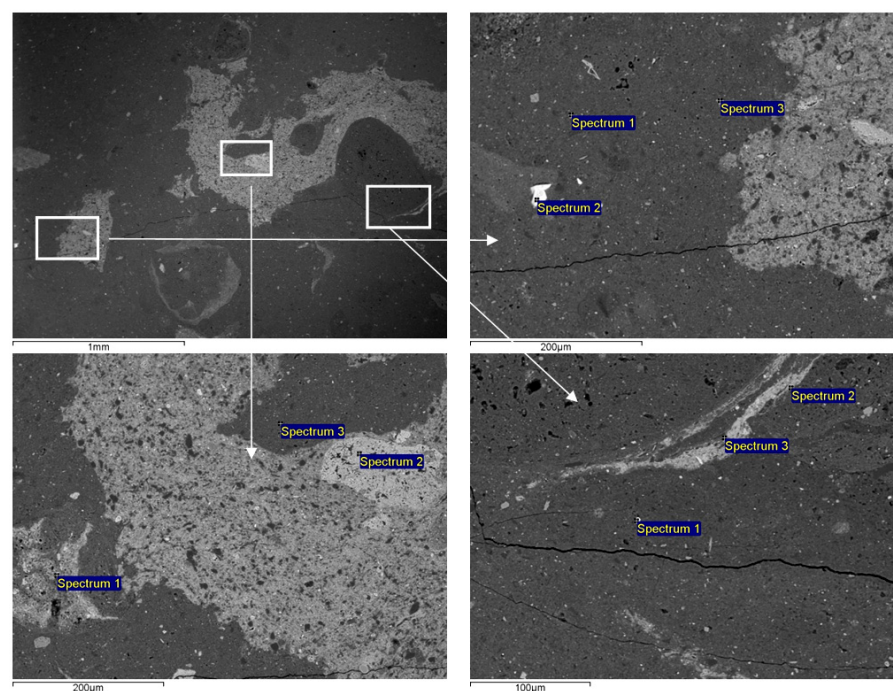


Figure 9. Bauxite deposit Štitovo II. Analysed field 1—sample 099, with details and analysed points. Spectrum 1,2—Zircon; Spectrum 3—Anatase; Spectrum 4—Fe-hydroxides; Spectrum 5—Hematite; Spectrum 6—Al-hydroxides; Spectrum 7—Xenotime; Spectrum 8—Al + Fe-hydroxides; Spectrum 9—Zircon + Al-hydroxides.

Table 4. Major-, trace- and rare earth element average compositions of the analysed samples (Radusinović [5]; REEBAUX [6]).

Bauxite Formations	Triassic					Jurassic							Cretaceous		Paleogene	
Paleorelief age	Middle Triassic		Late Triassic			Liassic		Dogger-Oxfordian					Liassic, Doggerian, Oxfordian, Early Cretaceous		Late Cretaceous	
Bauxite-bearing region/label	PI-II/1	VM-III/1	VM-III/2	VMP-III&IV/1	VM-III/3	P-IV/1	VMP-III&IV/2	P-IV/2	VMP-III&IV/3	VM-III/4	WMO-V&VII/1	WM-V/1	WMC-V&VI/1	WMC-V&VI/2	BK-VIII/1	U-IX/1
<i>Major oxides (wt.%)</i>																
SiO ₂	6.83	30.42	8.82	11.90	14.12	17.40	19.89	16.22	18.04	25.06	13.28	12.00	22.60	23.70	13.07	9.48
Al ₂ O ₃	62.5	43.18	54.10	51.18	50.28	47.65	43.67	47.91	46.48	41.57	40.97	44.16	43.82	42.28	47.37	48.31
Fe ₂ O ₃ (T)	12.85	7.55	19.53	19.44	19.08	18.08	18.20	18.22	18.33	16.73	16.67	22.97	13.32	14.77	19.1	21.49
MgO	0.13	0.24	0.34	0.46	0.35	0.49	0.48	0.97	0.86	0.51	0.46	0.46	0.44	0.39	0.37	0.3
CaO	0.07	0.49	0.33	0.47	1.54	0.15	0.13	0.17	0.15	1.67	7.96	2.36	0.52	0.22	1.11	0.79
Na ₂ O	<0.01	0.03	<0.01	0.05	0.05	0.02	0.07	0.03	0.07	0.09	<0.01	0.03	0.02	0.05	<0.01	<0.01
K ₂ O	0.07	0.14	0.39	0.55	0.52	0.69	0.77	0.66	0.62	0.84	0.27	0.33	0.71	0.47	0.74	0.21
TiO ₂	2.31	1.20	2.63	2.51	1.98	2.21	2.17	2.12	2.03	1.44	1.78	2.01	2.22	2.22	2.77	2.79
P ₂ O ₅	<0.01	0.019	0.049	0.047	0.041	0.045	0.071	0.020	0.028	0.049	0.017	0.02	0.040	0.03	0.060	0.090
MnO	0.07	0.09	0.19	0.17	0.13	0.14	0.13	0.14	0.14	0.08	0.10	0.11	0.01	0.02	0.08	0.09
LOI	14.9	16.40	13.11	12.84	12.97	12.70	12.20	13.10	12.88	13.34	18.19	15.23	15.97	15.54	14.8	15.9
Total	99.73	99.75	99.51	99.61	99.86	99.55	97.78	99.56	99.61	99.86	99.70	99.70	99.67	99.70	99.47	99.45
Total C	0.18	0.19	0.17	0.19		0.13	0.12	0.21	0.18		1.88		0.32		0.41	0.37
Total S	<0.02	<0.02	<0.02	0.026		<0.02	<0.02	<0.02	<0.02		0.03		0.37		0.04	0.08
<i>Trace elements (ppm)</i>																
Ba	20	30	69	79	52	93	106	78	74	87	39	36	63	45	57	54
Be	4	9	6	6	5	8	6	11	6	7	8	5	3	3	9	3
Co	24	17	232	42	42	44	47	31	28	40	33	32	17	12	44	50
Cs	2	1	6	7		11	10	8	9		4	1	3	1	6	4
Cr	123	71	342	334	260	240	240	267	243	222	232	294	341	335	637	835
Ga	71	42	52	48		49	45	53	45		46	44	55	48	40	50
Hf	20	14	15	13	9	13	12	13	11	7	10	7	12	8	14	16
Li					257					485		317		421		
Nb	58	35	55	48	34	45	42	42	37	29	35	36	42	41	90	91
Ni	69	47	258	178	165	169	220	209	237	201	209	239	133	139	289	348
Rb	6	5	32	37	15	61	59	44	43	29	20	5	25	9	33	11
Sc	48	32	58	58	25	59	58	53	52	28	39	46	43	41	28	30
Sn	13	10	14	16	10	14	15	12	13	9	9	11	9	11	9	9
Sr	16	47	97	87	45	116	132	44	48	61	48	56	103	53	142	333
Ta	4	3	4	4	6	3	3	3	3	5	3	2	3	3	4	5
Th	77	56	52	51	24	50	46	49	48	28	39	16	40	15	38	53

Table 4. Cont.

Bauxite Formations	Triassic					Jurassic							Cretaceous		Paleogene	
Paleorelief age	Middle Triassic		Late Triassic			Liassic		Dogger-Oxfordian					Liassic, Doggerian, Oxfordian, Early Cretaceous		Late Cretaceous	
Bauxite-bearing region/label	PI-II/1	VM-III/1	VM-III/2	VMP-III&IV/1	VM-III/3	P-IV/1	VMP-III&IV/2	P-IV/2	VMP-III&IV/3	VM-III/4	WMO-V&VII/1	WM-V/1	WMC-V&VI/1	WMC-V&VI/2	BK-VIII/1	U-IX/1
U	6	6	7	6	6	5	6	5	4	4	6	7	15	14	24	15
V	132	93	300	304	279	236	287	223	247	288	215	312	577	661	652	728
W	7	5	7	7	5	6	6	7	7	5	5	4	5	4	7	6
Zr	750	488	556	476	262	456	421	435	380	194	355	397	431	431	573	618
Y	73	102	128	132	32	114	128	171	161	45	74	65	44	39	44	47
La	54	109	194	199	47	241	283	313	245	71	104	22	57	6	90	108,
Ce	311	313	351	365	100	384	355	365	343	111	187	52	124	20	164	226
Pr	10	25	38	39		38	38.23	42	33		19	6	11	2	16	20
Nd	35	97	139	142		137	136	157	123		69	22	36	7	55	67
Sm	8	19	27	26		25	24	26	21		13	5	7	2	10	11
Eu	2	3	6	5		6	5	6	5		3	1	1	0.4	2	2
Gd	9	18	24	25		26	25	27	22		12	4	7	1	8	9
Tb	2	3	4	4		4	4	4	4		2	1	1	0.3	1	2
Dy	12	17	22	23		22	23	26	23		13	5	8	2	8	9
Ho	3	3	5	5		4	5	6	5		3	1	2	0.5	2	2
Er	10	10	13	14		13	14	17	16		8	3	5	2	5	6
Tm	2	1	2	2		2	2	2	2		2	1	1	0.3	1	1
Yb	10	9	13	13		12	13	15	15		8	3	5	2	6	6
Lu	2	1	2	2		2	2	2	2		1	1	1	0.3	1	1
ΣREE	542	732	966	995		1030	1057	1179	1019		516		309		415	516
ΣLREE	420	567	754	776		831	841	908	769		394		236		338	434
ΣHREE	122	165	212	219		199	216	271	250		122		73		77	82
ΣLREE/ΣHREE	3.45	3.43	3.56	3.55		4.17	3.89	3.35	3.07		3.24		3.24		4.39	5.33

ΣLREE = ΣREE (La – Eu) and ΣHREE = ΣREE (Gd – Lu + Y).

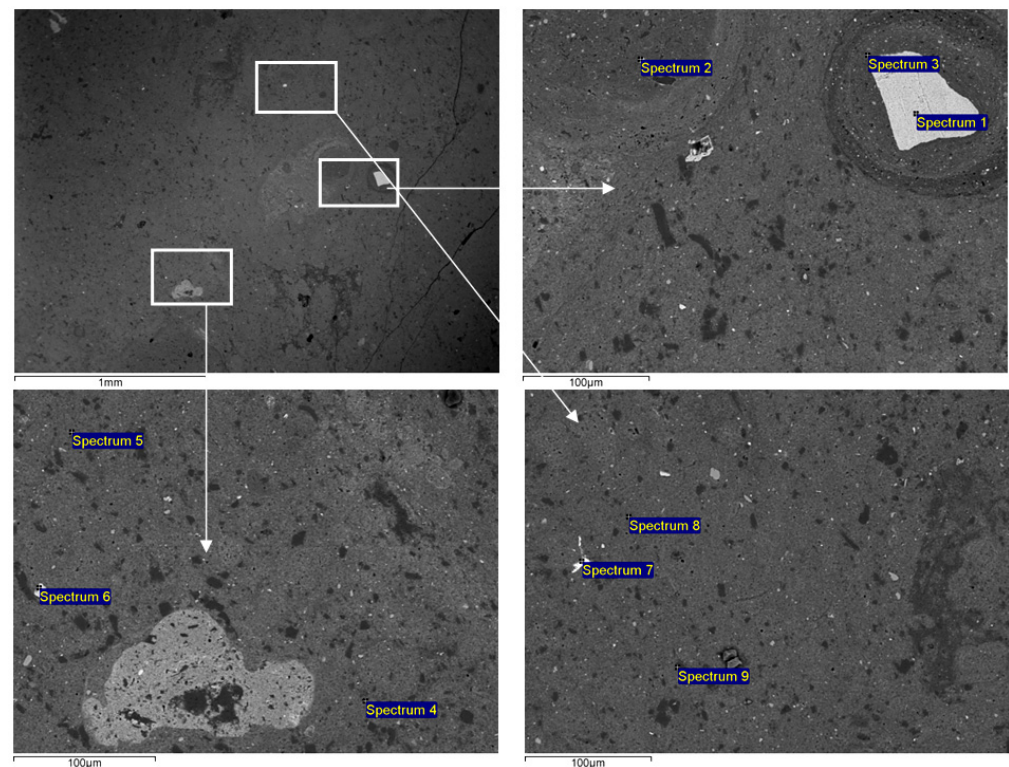


Figure 10. Bauxite deposit Borova brda. Analysed field 1—sample 180, with details and analysed points. Spectrum 1, 4, 6—Hematite; Spectrum 2, 5; Spectrum 3, 7, 8—Monazite; Al + Fe-hydroxides; REE—carbonate; Spectrum 7–8—Monazite; Spectrum 9—Clay + Fe-hydroxides.

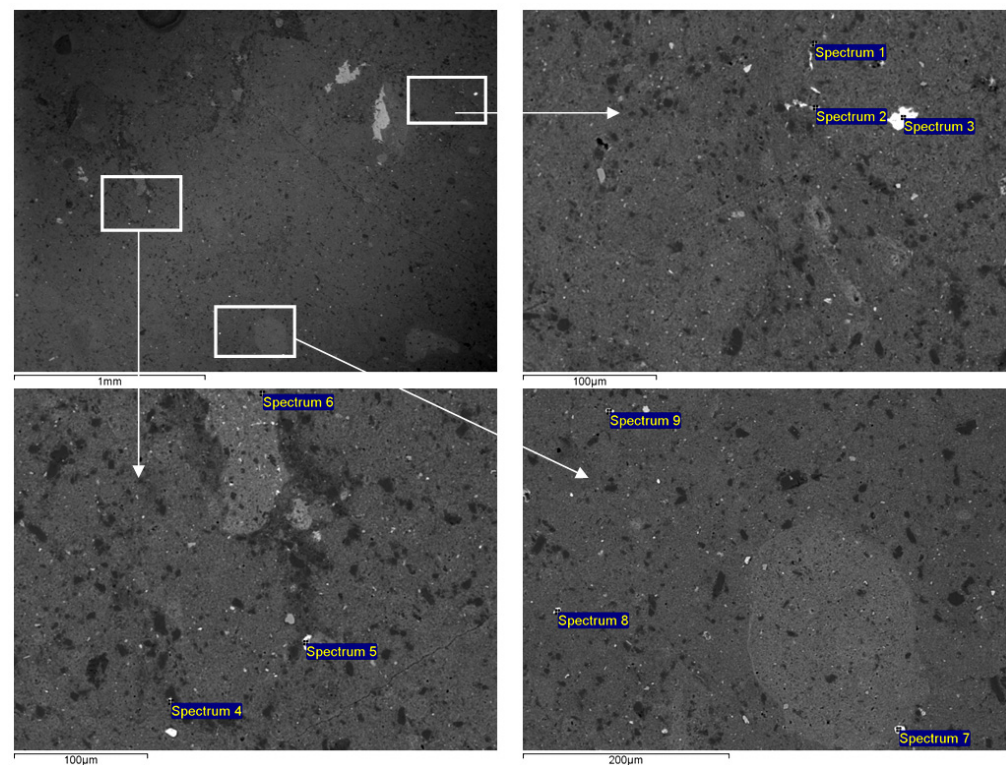


Figure 11. Bauxite deposit Borova brda. Analysed field 3—sample 180, with details and analysed points. Spectrum 1–6—REE-carbonate; Spectrum 7–8—Monazite; Spectrum 9—Xenotime.

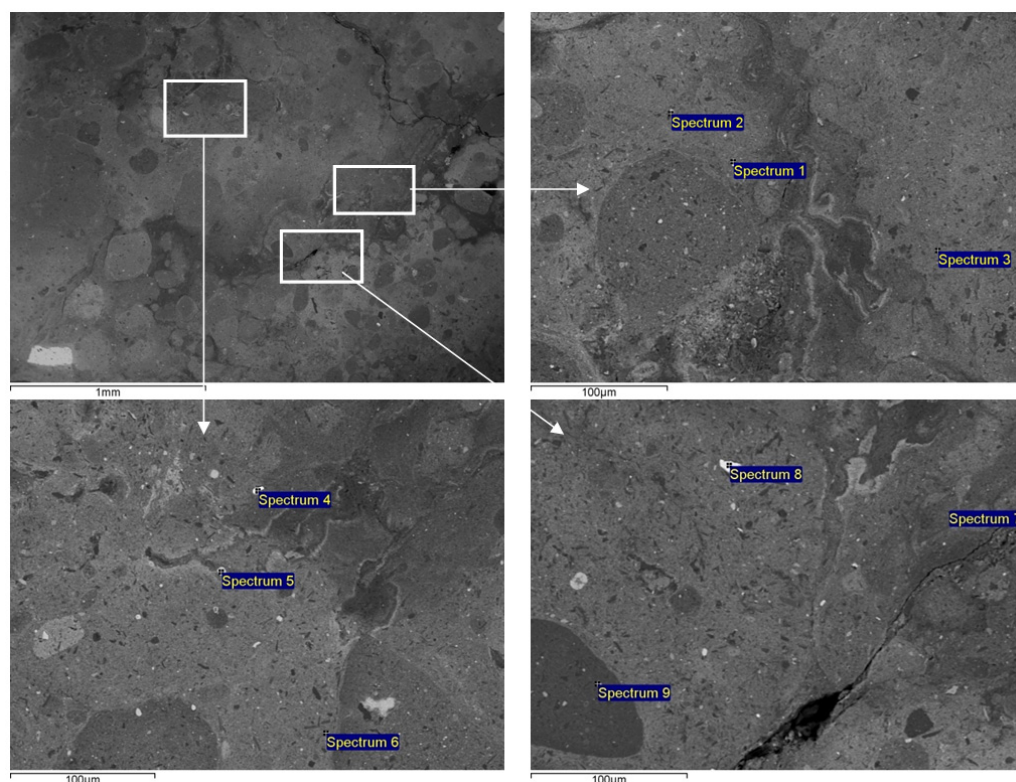


Figure 12. Bauxite occurrence Crvena glavica. Analysed field 3—sample 243, with details and analysed points. Spectrum 1—Xenotime; Spectrum 2, 5—Hematite + Al-hidroksid; Spectrum 3—Clay + Fe-hydroxides; Spectrum 4—Monazite; Spectrum 6–9—Zircon.

It is important to emphasise that among the detected phases, the major REE-carriers are phosphates, as indicated by the very strong positive correlation between REEs, P and Sr.

The presence of residual and authigenic monazite and xenotime clearly indicates that the first REE minerals originate from primary sources, while additional are formed in the first phases of bauxitisation, in oxidation conditions [4,5,77]. SEM-EDS analyses of minerals can be found in Tables 5–8 [5].

Table 5. Results of chemical analysis of points (sample 099, Figure 9).

Element (wt.%)	Spec.1	Spec.2	Spec.3	Spec.4	Spec.5	Spec.6	Spec.7	Spec.8	Spec.9
O	39.1	37.4	50.1	41.4	43.4	55.0	38.3	42.5	52.0
Al	2.0		2.8	3.3	3.7	32.2		11.7	6.6
Si	11.8	12.6	0.4	0.6	0.9	2.3	1.1	1.1	7.4
P				0.3			15.3		
Ti	0.2		35.9	1.0	1.0	1.0		1.5	0.7
Fe	1.6	0.7	10.8	53.4	50.9	9.5	1.0	43.2	6.2
Ca									0.2
Co							0.8		
Y							34.3		
Gd							2.9		
Dy							4.6		
Yb							1.9		
Zr	45.2	48.0							26.9
Hf		1.3							
Total	100.0	100.0	100.0	100.0	100.0	100.0	100	100.0	100.0

Table 6. Results of chemical analysis of points (sample 180, Figure 10).

Element (wt.%)	Spec.1	Spec.2	Spec.3	Spec.4	Spec.5	Spec.6	Spec.7	Spec.8	Spec.9
O	37.7	42.4	40.4	39.8	48.4	44.0	33.9	43.3	40.5
Mg				0.7		1.3			
Al	4.1	10.2	9.4	3.7	28.6	1.2	7.1	11.9	11.7
Si	0.2	0.5			0.7		1.2		4.9
P			10.5		0.3		6.3	9.4	
Ti	0.9	1.5		1.7	1.1	4.5			0.6
Mn		0.3		0.7					0.3
Fe	56.8	44.7	4.2	53.5	20.9	48.9	3.4	5.0	42.1
Ca							2.4	0.2	
Y							2.1		
La			7.8				17.8	6.5	
Ce			19.2					16.1	
Nd			8.6				22.2	7.0	
Th								0.7	
Total	100.0	100.0	100.0	100.0	100.0	100.0	100	100	100.0

Table 7. Results of chemical analysis of points (sample 180, Figure 11).

Element (wt.%)	Spec.1	Spec.2	Spec.3	Spec.4	Spec.5	Spec.6	Spec.7	Spec.8	Spec.9
O	45.3	38.8	34.2	41.1	39.9	45.7	33.5	33.7	35.2
F	4.8	8.0	8.4	6.3	5.4	3.5			
Al	20.3	13.9	3.7	10.2	13.0	16.1			
Si	2.7	0.9	3.0	6.9	3.0	2.4			0.6
P						0.6	14.0	14.8	16.4
Ca	1.2	1.2	2.0	1.9	1.8	0.7	0.4	0.6	
Fe	10.0	7.2	1.0	1.9	7.0	23.3	1.3	1.2	1.4
La	4.4	8.7	13.9	8.7	8.2	3.5	12.8	12.4	
Ce				2.0			27.1	25.6	
Pr				2.5	2.3				
Nd	8.4	13.3	20.1	13.3	13.8	4.3	10.7	11.7	
Sm	1.5	2.6	3.5	2.4	2.8				
Gd		2.9	4.4	2.9	2.9				2.0
Dy									4.6
Er									3.6
Yb									3.3
Y									32.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 8. Results of chemical analysis of points (sample 243, Figure 12).

Element (wt.%)	Spec.1	Spec.2	Spec.3	Spec.4	Spec.5	Spec.6	Spec.7	Spec.8	Spec.9
O	42.1	39.9	47.9	32.7	37.9	46.3	41.3	37.2	47.9
Al		3.5	12.9	0.6	1.0	3.2	1.1		4.1
Si	1.2	1.4	6.1		0.9	10.6	11.9	12.6	10.0
P	15.1			13.6					
K			0.4						
Ti		0.8	0.6		0.6				
Mn					0.3				
Fe	3.0	54.5	32.1	1.4	59.4	3.7	1.0	1.1	1.5
Co	1.2								
Zr						36.2	44.7	47.9	36.5
Hf								1.3	
La				15.1					
Ce				29.8					
Nd				6.8					
Y	31.2								
Gd	6.4								
Total	100	100.0	100.0	100	100.0	100.0	100.0	100.0	100.0

All deposits and occurrences of red Jurassic bauxites from the ore regions of Western Montenegro and Orjen and Čevo were formed on the carbonate paleorelief of the Middle Jurassic-Oxfordian age. They are often characterised by the presence of redeposited bauxites, especially in the upper parts of the deposits. The presence of the following minerals was detected in samples from Bajov do deposits: böhmite, hematite, kaolinite, anatase and goethite (Figure 13a). The following minerals were determined: böhmite, gibbsite, hematite, kaolinite, anatase and rutile (Figure 13b), in white bauxite samples from Bijele poljane deposit - Dionica site, by XRD analyses. Paleogene bauxite occurrence Velika gorana are characterised by the presence of: böhmite, goethite, kaolinite and anatase (Figure 13c).

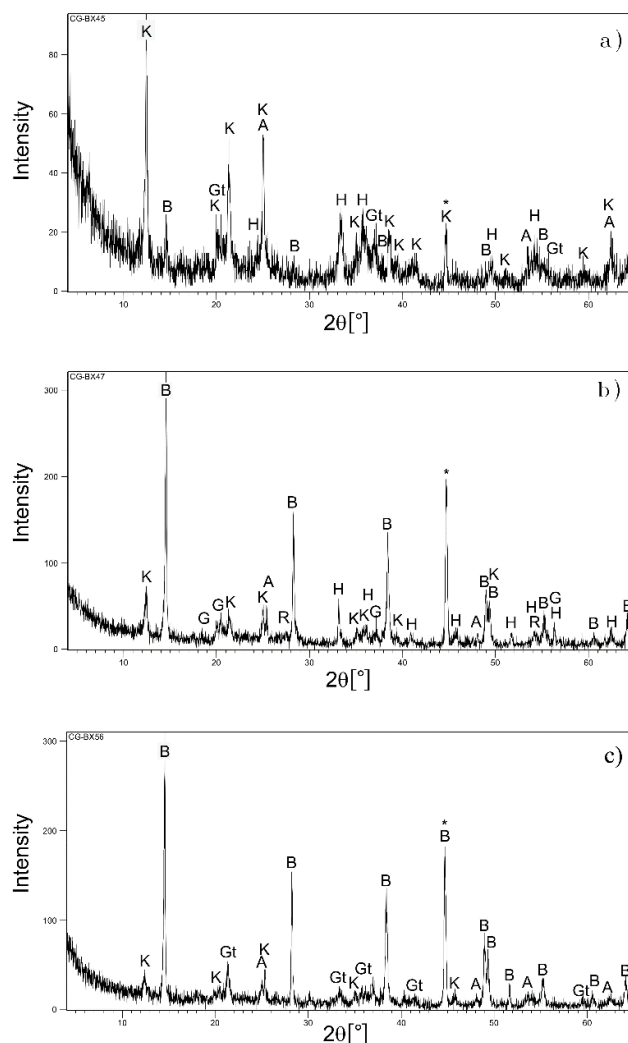


Figure 13. XRD patterns of typical analysed sample from bauxite deposits and occurrences: Bajov do (a), Bijele poljane (b) and Velika Gorana (c). (B—böhmite, G—gibbsite, A—anatase, H—hematite, Gt—goethite, K—kaolinite, R—rutile, *—Al-sample holder) (REEBAUX project documentation, Tomašić [6]).

4.2. Major Elements Geochemistry

Bauxites of Triassic age were studied at two localities: occurrence Rudinice in Piva and the Gornjepoljskivir deposit, which belongs to the bauxite-bearing region of Vojnik-Maganik. According to the results of the composite sample formed from six individual bauxite samples from the occurrence of Rudinice, it can be seen that these bauxites are characterised by high Al_2O_3 (62.5%), low Fe_2O_3 content (12.85%), relatively low SiO_2 content (6.83%) and TiO_2 (2.31%) (Table 4). On the contrary, the bauxites of the Gornjepoljski vir deposit contain low contents of Al_2O_3 (43.18%) and Fe_2O_3 (7.55%), a high average content

of SiO_2 (30.42%) and relatively low content of TiO_2 (1.20%). MgO , Na_2O , K_2O , MnO and P_2O_5 contents are very low and significantly higher in the bauxites of the Gornjepoljski vir deposit.

According to the analysis of statistical parameters of the analysed oxides in bauxites of the ore regions Vojnik-Maganik and Prekornica (Tables 4 and 9 VMP-III&IV/1), it can be seen that in bauxites formed on the Late Triassic underlying bed, the SiO_2 range in individual samples is from 1% to 27.44%, with an average content of 11.9%; while on the Early Jurassic underlying bed, the range is from 11.61% to 27.44%, with a average content of 19.89%; and at Middle Jurassic-Oxfordian range is 11.90% to 27.13%, with an average content of 18.04%. Regarding the bauxite formed on Late Triassic, Al_2O_3 has an average content of 51.18% and a range from 33.5–69.73%; on Early Jurassic average 43.67% and range 36.9–52.44%; at Middle Jurassic average 46.48% and range 41.59–50.26%. Fe_2O_3 contents in bauxites formed on the Late Triassic are in average 19.44%, with a range from 2.56% to 26.15%; on Early Jurassic average 18.20% and range 9.36–21.91%; at Middle Jurassic-Oxfordian average 18.33% and range 10.84–24.11%.

Triassic bauxites have the highest Al_2O_3 average content and the lowest SiO_2 . The Fe_2O_3 content is uniform and averagely slightly higher in bauxites from the upper parts of the primary bauxites geological sections. Samples from the middle and upper parts, compared to samples from the lower parts of bauxite ore bodies have elevated SiO_2 contents and slightly lower Al_2O_3 contents.

TiO_2 shows a uniform presence in the tested samples, averagely 2.36% in the range from 1.53% to 3.50%.

The CaO content in individual samples of these bauxites is characterised by a range from 0.03% to 11.14%. Bauxites formed on the Late Triassic carbonate sediments have elevated contents of CaO , especially those from the middle and upper parts of ore bodies. MgO is characterised by a range from 0.07% to 2.05% in all individual samples. The increased content of MgO in bauxites from Middle Jurassic-Oxford paleorelief (0.86%) in comparison to other bauxites is clearly expressed. Elevated contents of Na_2O and especially K_2O in individual samples are characteristic of bauxites from the Early Jurassic and Middle Jurassic-Oxfordian paleorelief. K_2O shows on average higher contents at higher upper parts of ore bodies in all bauxite formations.

The P_2O_5 content varies in a wide range from 0.01% to 0.53%. Regarding bauxite deposits and occurrences formed on the Late Triassic (95 samples above the detection limit) the range is from 0.01% to 0.53% and the average content 0.047%; while on the Early Jurassic (33 samples) the range is from 0.01 to 0.71% and the average content is 0.071%. In Middle Jurassic–Oxfordian bauxites, contents of P_2O_5 are detected in individual samples (10 samples) ranging from 0.01% to 0.05%, with an average of 0.028%. P_2O_5 shows the highest contents in bauxites from the lower part of bauxite bodies from the Early Jurassic (0.156%) and Late Triassic paleorelief (0.085%).

The average LOI, in bauxites from all three underlying beds and from different parts of the ore bodies, is uniform. The sulphur content in 96% of the samples was below the detection limit of 0.02%. Slightly higher content of C is shown by bauxites from the lower part of deposits formed on the Middle Jurassic-Oxfordian paleorelief and the middle and upper parts of ore bodies formed on the Late Triassic and Middle Jurassic-Oxfordian.

The contents of the main oxides from the detailed database of the REE VMP project, correspond to the exploration results of the most significant and largest deposits and characteristic bauxite occurrences of Montenegro, from the REEBAUX project (VM-III/2, P-IV/1 and P-IV/2). Slightly higher on average Al_2O_3 content and slightly lower on average SiO_2 content are shown by samples from the REEBAUX project database, when it comes to bauxites formed on the underlying beds of all three ages. It should be noted that the samples from the Zagrad and Biočki stan deposits originate from underground mines and bauxites from these parts of the deposit were tested for the first time. Furthermore, the results of chemical and geochemical explorations of bauxite obtained through the project MPM VM (VM-III/3, VM-III/4) are in accordance with the presented data.

Table 9. Statistical parameters of geochemical analyses of major oxides in Jurassic bauxites of the Vojnik-Maganik and Prekornica ore regions (after Radusinović [5]).

Paleorelief Age	Statistical Parameters		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃	LOI	TOT/C	TOT/S
			%	%	%	%	%	%	%	%	%	%	%	%	%	%
Late Triassic (<i>n</i> = 160)	Minimum	Min	1.00	33.50	2.56	0.07	0.03	0.01	0.01	1.68	0.010	0.02	0.026	11.3	0.06	0.02
	Maximum	Max	27.44	69.73	26.15	2.05	11.14	0.08	2.02	3.50	0.530	1.64	0.096	20.2	2.37	0.03
	Arithmetic mean	$\bar{x}$	11.90	51.18	19.44	0.46	0.47	0.05	0.55	2.51	0.047	0.17	0.049	12.84	0.19	0.026
	Standard deviation	σ	6.54	5.78	3.14	0.28	1.43	0.02	0.42	0.36	0.09	0.19	0.02	1.06	0.29	0.01
	Coefficient of variation	Cv	0.55	0.11	0.16	0.61	3.02	0.43	0.77	0.14	1.92	1.07	0.31	0.08	1.56	0.21
Liassic (<i>n</i> = 51)	Minimum	Min	11.61	36.90	9.36	0.15	0.07	0.04	0.24	1.53	0.010	0.03	0.023	11.8	0.05	0.02
	Maximum	Max	30.17	52.44	21.91	0.81	0.43	0.09	1.88	2.66	0.710	0.96	0.043	14.5	0.42	
	Arithmetic mean	$\bar{x}$	19.89	43.67	18.20	0.48	0.13	0.07	0.77	2.17	0.071	0.13	0.035	12.20	0.12	
	Standard deviation	σ	4.17	6.55	3.26	0.13	0.07	0.02	0.29	0.34	0.16	0.05	0.01	1.71	0.06	
	Coefficient of variation	Cv	0.21	0.15	0.18	0.27	0.56	0.22	0.38	0.16	2.29	0.38	0.16	0.14	0.54	
Dogger-Oxfordian (<i>n</i> = 41)	Minimum	Min	11.90	41.59	10.84	0.46	0.08	0.05	0.13	1.62	0.010	0.07	0.030	11.6	0.07	0.02
	Maximum	Max	24.13	50.26	24.11	1.36	0.24	0.10	1.30	2.24	0.050	0.19	0.048	15.10	0.42	
	Arithmetic mean	$\bar{x}$	18.04	46.48	18.33	0.86	0.15	0.07	0.62	2.03	0.028	0.14	0.036	12.88	0.18	
	Standard deviation	σ	2.33	1.85	2.25	0.23	0.05	0.01	0.33	0.13	0.01	0.03	0.00	0.62	0.09	
	Coefficient of variation	Cv	0.13	0.04	0.12	0.27	0.32	0.19	0.53	0.06	0.44	0.20	0.11	0.05	0.51	

n—Total number of samples.

Deposits and occurrences of red Jurassic bauxites in the bauxite-bearing regions of Western Montenegro and Orjen (REEBAUX, WMO-V&VII/1) which are formed on the Middle Jurassic-Oxfordian age paleorelief, are characterised by a high average SiO_2 content (13.28%), low Al_2O_3 content (40.97%), slightly lower content of Fe_2O_3 (16.67%) and TiO_2 (1.78%) and extremely high average content of CaO (7.96%). It was previously emphasised that these bauxites are characterised by redeposition, which may explain the high CaO contents. It should be considered, compared to the results of the MPM WM project that sampling was performed by different methods, so it is not surprising that the average CaO content and the slightly higher Al_2O_3 content are significantly lower (Table 4).

Cretaceous white bauxites, due to their genetic specificities, show an elevated average content of SiO_2 (22.60%) and lower content of Fe_2O_3 (13.32%) in comparison to red Jurassic bauxites of bauxite-bearing regions of Western Montenegro and Čevo (Tables 2 and 4—REEBAUX, WMC-V&IV/1). The average contents of Al_2O_3 (43.82%), TiO_2 (2.22%), as well as CaO , MgO , Na_2O , K_2O , MnO and P_2O_5 , mainly correspond to the earlier data, as well as to MPM WM project data (Table 4—WMC-V&IV/2).

Paleogene bauxites in Boka Kotorska and Ulcinj regions showed relatively uniform average contents of SiO_2 (13.07% and 9.48%), Al_2O_3 (47.37% and 48.31%), Fe_2O_3 (19.10% and 21.49%) and TiO_2 (2.77% and 2.79%). The first have slightly more CaO (1.1%) and K_2O (0.74%) on average. The average contents of other oxides were uniform: MgO , MnO and P_2O_5 , while Na_2O remained below the detection limit (0.01%).

Based on the mineralogical classification [81], the Triassic bauxites of Piva (Rudinice), as well as the bauxites of a number of Jurassic deposits formed on the paleorelief of the Late Triassic age, are classified as ferritic bauxites. The Triassic bauxites of Gornjepoljski vir and the Cretaceous bauxites of Međeđe deposit belong to the group of kaolinitic bauxites. All other bauxites from the Jurassic, Cretaceous and Paleogene deposits belong to the bauxite group. All Jurassic formations formed on the paleorelief of different ages, as well as the Cretaceous and Paleogene bauxite formations are classified in the bauxite group (Figure 14).

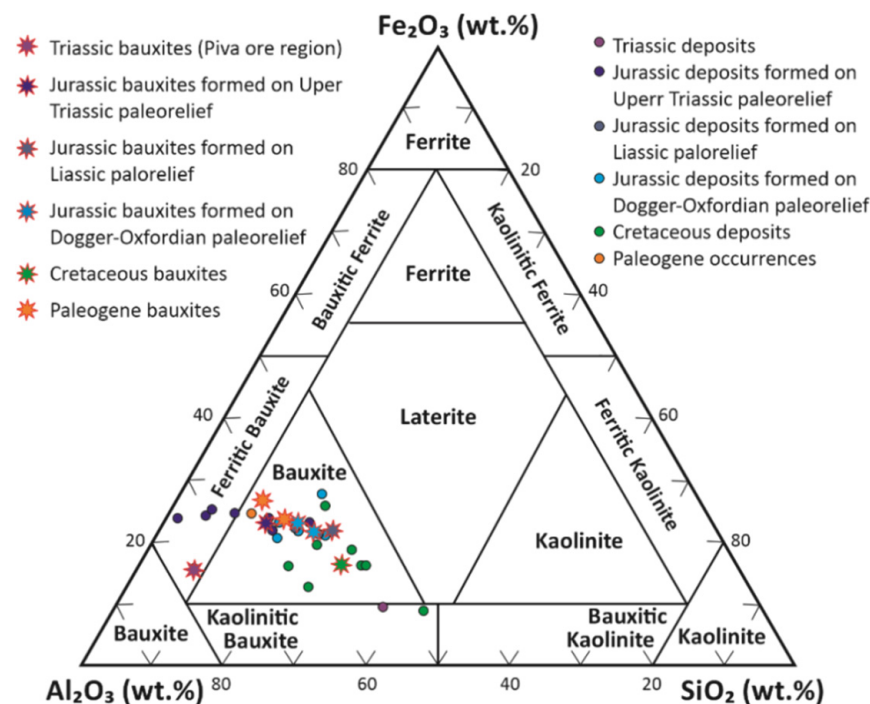


Figure 14. Triangular diagram of SiO_2 - Al_2O_3 - Fe_2O_3 of the bauxite formations and deposits, after Aleva [81].

The enriched Fe_2O_3 contents in some deposits are due to the presence of iron minerals like hematite, which is most likely formed under suitable Eh-pH conditions during bauxitisation processes. It should be emphasised that white Cretaceous bauxites, as well as deposits and occurrences formed on the younger underlying beds of the Late Jurassic and Early Cretaceous age are generally less enriched in Fe_2O_3 .

4.3. Trace Elements Geochemistry

Some trace elements such as Sc, Li, Cr, Zr, Nb, V and Ni occur in considerable amounts in the bauxitic deposits of Montenegro (Table 4). For example, Triassic bauxites contain on average 749.6 and 488.45 ppm Zr, Jurassic from different ore regions and from paleorelief of different ages from 354.59 to 475.71 ppm, Cretaceous 431.1 ppm, while Paleogene contains 573 and 558.1 ppm Zr. Interesting are the data on Ni content, whose average content in Triassic bauxites is only 69 and 47.38 ppm, in Jurassic bauxites formed on the paleorelief of the Late Triassic age 178.43 ppm, Early Jurassic age, 219.91 ppm and Middle Jurassic-Oxfordian age 237.32 ppm and 209.13 ppm. Paleogene bauxites averagely contain the most of Ni, 289 those from the Boka Kotorska region, and 348 ppm from Ulcinj region. From these data, it is clear that the Ni content increases from older to younger bauxites, which was previously determined by studying bauxites from the Triassic to the Eocene age in Yugoslavia and Greece [50]. The situation is similar to the average contents of Cr, which is present in the Triassic bauxites with 71 and 123 ppm, in the Jurassic from 232 to 334 ppm, in the Cretaceous 341 ppm, while in the Paleogene it reaches a high 637 and 835 ppm. Similar to Cr, the most of V has averagely in Paleogene bauxites 652 and 728 ppm in the bauxites of Boka Kotorska and Ulcinj, also in the Cretaceous 576 ppm, Jurassic from 215.16 to 303.62 ppm, and the least in Triassic bauxites, only 93.12 ppm in Gornjepoljski vir, and 132 ppm as was detected in Rudinice in Piva.

Jurassic bauxites from the Vojnik-Maganik and Prekornica ore regions were studied in the most detail [5]. In these bauxites Zr was detected in individual samples ranging from 328.7 to 641 ppm. In bauxites formed on the Late Triassic, Zr has an average content of 475.71 ppm, on the Early Jurassic 420.62 ppm and on the Middle Jurassic-Oxfordian 397.56 ppm (Table 10). Ni is determined in all individual samples in the range of 51 to 678 ppm. Bauxites formed on the Late Triassic paleorelief have a range from 51 to 456 ppm, on the Early Jurassic a range is from 144 to 678 ppm, and on the Middle Jurassic-Oxford from 152 to 307 ppm. Bauxites formed on the Late Triassic have a range of V content from 177 to 850 ppm and an average content higher than average—303.62 ppm, on the Early Jurassic a range from 204 to 466 ppm, a average content of 286.6 ppm, and on the Middle Jurassic-Oxford from 179 to 346 ppm, average content 246.68 ppm.

The average Nb contents in the studied bauxite formations are relatively uniform, with the exception of Paleogene bauxites from Boka Kotorska and Ulcinj bauxite-bearing regions, which contain more Nb—89.8 ppm and 91.4 ppm, respectively. However, Sr is characterised by an uneven distribution. Triassic bauxites averagely contain Sr at least, 16.4 and 47.11 ppm, Jurassic bauxites formed on the Middle Jurassic Oxford underlying bed 48.31 and 48.43 ppm, on the Late Triassic 87.30 ppm, and those formed on the underlying bed of the Early Jurassic age significantly more than 131.83 ppm. Paleogene bauxites are the most enriched in Sr, especially those from the Ulcinj region with an average of 332.5 ppm. When it comes to Sc, the average contents of this economically valuable element are relatively uniform in bauxites of different formations from 28 ppm in Paleogene bauxites of Boka Kotorska region up to 58.41 ppm in Jurassic bauxites of the Vojnik-Maganik and Prekornica ore regions formed on the carbonate underlying bed of Late Triassic age.

Table 10. Statistical parameters of geochemical analyses of trace elements in Jurassic bauxites of the Vojnik-Maganik and Prekornica ore regions (after Radusinović [5]).

Paleorelief Age	Statistical Parameters		Rb	Cs	Be	Sr	Ba	Th	U	Zr	Hf	V	Nb	Ta	W	Co	Ni	Ga	Sn
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Late Triassic (<i>n</i> = 160)	Minimum	Min	0.4	0.1	2	39.1	17	29.1	3.1	328.7	9.3	177	31.2	2.3	4.3	11.9	51	29.2	7
	Maximum	Max	142.7	20.8	15	774	190	70.0	18.1	641.4	17.7	850	68.5	5.0	9.7	402.2	456	57.8	43
	Arithmetic mean	$\bar{x}$	36.60	7.33	5.63	87.30	79.24	50.93	6.03	475.71	13.45	303.62	48.07	3.65	6.53	41.63	178.43	47.88	15.61
	Standard deviation	σ	34.38	5.31	2.67	87.94	47.39	7.21	2.01	61.55	1.60	84.06	6.10	0.47	0.90	43.43	71.24	4.14	5.05
	Coefficient of variation	Cv	0.94	0.72	0.47	1.01	0.60	0.14	0.33	0.13	0.12	0.28	0.13	0.13	0.14	1.04	0.40	0.09	0.32
Liassic (<i>n</i> = 51)	Minimum	Min	10.6	1.8	2	37.6	52	38.6	3.0	335.0	9.2	204	34.6	2.6	4.6	18.9	144	34.8	9
	Maximum	Max	127.4	19.5	15	1406.6	204	65.9	24.3	497.6	13.6	466	51.9	4.0	9.8	539.3	678	54.4	37
	Arithmetic mean	$\bar{x}$	58.94	10.43	5.50	131.83	106.15	46.35	5.80	420.62	11.65	286.60	41.96	3.13	5.76	46.94	219.91	45.34	15.20
	Standard deviation	σ	24.21	3.31	2.92	246.90	33.04	8.17	3.38	71.92	1.90	70.16	6.89	0.51	1.14	74.46	86.17	7.52	5.65
	Coefficient of variation	Cv	0.41	0.32	0.53	1.87	0.31	0.18	0.58	0.17	0.16	0.24	0.16	0.16	0.20	1.59	0.39	0.17	0.37
Dogger-Oxfordian (<i>n</i> = 41)	Minimum	Min	8.5	2.4	2	27.7	27	38.6	3.3	331.3	10.2	179	32.7	2.6	5.0	15.0	152	40.1	8
	Maximum	Max	87.7	16.3	13	85.8	145	59.8	7.9	417.8	11.8	346	39.5	3.8	9.9	78.5	307	51.4	24
	Arithmetic mean	$\bar{x}$	42.57	9.21	6.24	48.31	74.35	48.17	4.22	379.56	11.09	246.68	36.65	3.06	6.65	28.34	237.32	45.45	12.57
	Standard deviation	σ	24.01	4.38	2.35	16.39	32.58	5.04	0.89	16.05	0.43	48.07	1.94	0.28	1.02	11.26	37.23	2.39	3.78
	Coefficient of variation	Cv	0.56	0.48	0.38	0.34	0.44	0.10	0.21	0.04	0.04	0.19	0.05	0.09	0.15	0.40	0.16	0.05	0.30

n—Total number of samples.

In the Jurassic bauxites of the Vojnik-Maganik and Prekornica ore regions, Nb was determined in individual samples ranging from 31.2 to 65.5 ppm (Table 9). The lowest and highest individual values belong to bauxite samples from the Late Triassic underlying bed, which have an average content of 48.7 ppm. The average in bauxites formed on Early Jurassic is 41.96 ppm, and on Middle Jurassic-Oxfordian the average value is 36.65 ppm. These bauxites are characterised by elevated contents of Sr compared to the average, in the ore bodies formed on the Early Jurassic underlying bed. The anomalous Sr contents in the samples stand out, especially from lower, but also the middle part of the Borovabrda deposit.

According to the bauxite explorations during the production of metallogenetic prognostic maps (MPMVM and MPMWM), the average Li content in Jurassic bauxites in the Vojnik-Maganik region formed on the Late Triassic paleorelief is 256.83 ppm, while that formed on the Middle Jurassic-Oxford age paleorelief is significantly higher and is 484.96 ppm. Jurassic bauxites in the region of Čevo and Western Montenegro contain on average 316.76 ppm, while Cretaceous bauxites contain 421.03 ppm Li in average.

4.4. Rare Earth Elements Geochemistry

Bauxite formations in Montenegro have significantly different Σ REE average contents. The highest contents were detected in the Jurassic bauxites of the Vojnik-Maganik and Prekornica ore regions from the Early Jurassic, Middle Jurassic-Oxfordian and Late Triassic underlying bed, and are 1057.11, 1019.43 and 994.92 ppm respectively. The Triassic bauxites of Gornjepoljski vir have an average total content of 732.27 ppm and of Rudinice 541.68 ppm. Jurassic bauxites from the ore regions of Western Montenegro and Orjen have a 515.96 ppm Σ REE content, while Paleogene bauxites from Ulcinj region and Boka Kotorska have average values of 515.76 and 414.7 ppm respectively. The lowest average total content, of 309.15 ppm, was shown by Cretaceous bauxites of the ore regions of Western Montenegro and Čevo (Figure 15, Table 4). Bauxite formations have Σ LREE contents (236.24–840.99 ppm), Σ HREE contents (7291–27,081 ppm) and Σ LREE/ Σ HREE ratios (3.07–5.33) (Table 4).

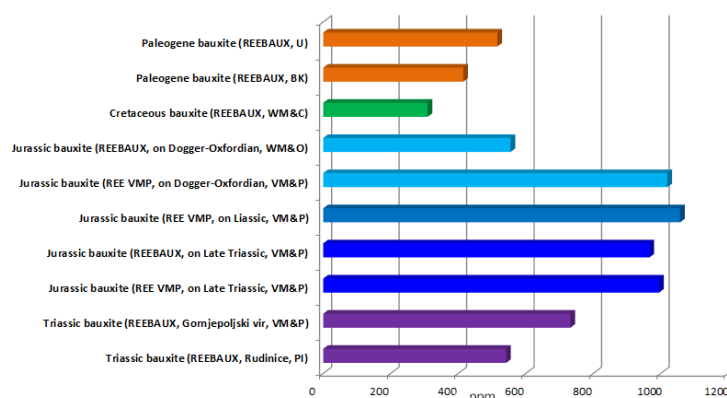


Figure 15. Content of Σ REE in the studied bauxite formations in Montenegro, (after Radusinović [5]; REEBAUX [6]), (ppm).

On average, the highest contents of Σ REE + Sc (more than 1000 ppm) are presented in Biočki stan, Zagrad, Liverovići and Borova brda deposits, as well as the occurrence of Crveno prlo from the bauxite-bearing regions Vojnik-Maganik and Prekornica [6]. Other studied deposits of these regions also have elevated contents, as well as the Velja Dubova glava deposit from Orjen ore region and the Triassic deposit Gornjepoljski vir. The lowest average contents are presented by Cretaceous bauxite deposits and occurrences (all below 400 ppm, except Paklarica) (Figure 16).

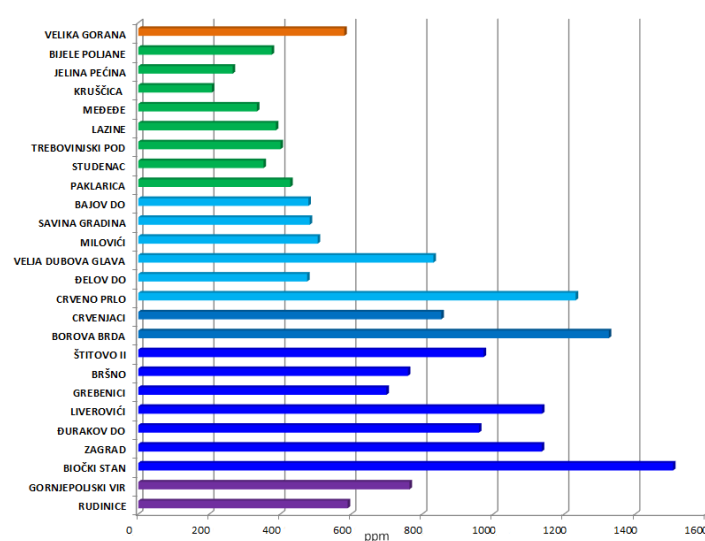


Figure 16. Content of $\Sigma\text{REE} + \text{Sc}$ in the studied deposits and occurrences of different bauxite formations in Montenegro, (after REEBAUX [6]), (ppm).

The average La content in bauxite samples from the Late Triassic underlying bed was 199.49 ppm ranging from 87.7 to 1799.1 ppm; from Early Jurassic 288.89 ppm, range from 111.4 to 1648 ppm and in samples from the Middle Jurassic-Oxfordian underlying bed 244.63 ppm, and range from 136.9 to 570.9 ppm (Table 11).

Exceptionally high La contents in individual samples (>1000 ppm) were found in the lower part of the bauxite geological sections in Liverovići, Zagrad 3 and Borova brda deposits, and elevated (>300 ppm) in Crvene ornice, Biočki stan, Štitovo II, Crveno katunište, Crvenjaci, Alina lokva, Crveno prlo and Smrekova glavica, in other words in all bauxites formed on paleorelief of different age. Elevated contents of La are exclusively characteristic for the lower parts of bauxite bodies formed on the Late Triassic and Early Jurassic, while bauxite from the Middle Jurassic-Oxfordian underlying bed is characterised by a uniform vertical distribution of this element. The Ce content varies from 159.5 to 908.3 ppm, in individual samples. Triassic bauxites are characterised by an average Ce content of 365.01 ppm. More specifically, on the Early Jurassic bauxites 355.26 ppm with a range from 208.3 to 663.9 ppm and on Middle Jurassic-Oxfordian bauxites 342.69 ppm in the range from 168.4 to 598.7 ppm. High contents in individual samples (>500 ppm) were found in Zagrad 1, Liverovići 2, Palež, Lokve, Đurakov do 2, Bršno, Buavice, Borova brda, Međugorje, Alina lokva, Javorak, Crveno prlo, Smrekova glavica and Crvena glavica. It can be stated that the average contents of Ce in bauxites from all three underlying beds and from different parts of the geological sections are uniform. The Pr content in individual samples is in the range from 13 to 421 ppm. The average content in bauxite samples from the Late Triassic paleorelief was 38.51 ppm; from the Early Jurassic 38.23 ppm; and from Middle Jurassic-Oxfordian 33.39 ppm. In the samples from the lower part of bauxite deposits from the Late Triassic geological sections, the average is significantly higher—67 ppm compared to the samples from the middle and upper part—only 24 ppm. The same case for Pr is present with the samples from Early Jurassic underlying bed (65 ppm and 30 ppm), while in the samples from Middle Jurassic-Oxfordian paleorelief, uniform contents of 31 ppm in the lower and 34 ppm in the middle and upper part of the geological sections were observed. Elevated contents in individual samples (>100 ppm) are characteristic mainly for the lower parts of bauxite bodies formed on the Late Triassic and Early Jurassic (Liverovići, Zagrad 3, Biočki stan, Štitovo II and Borova brda), while bauxites from the Middle Jurassic-Oxfordian underlying bed are characterised by mostly uniform Pr contents in all parts of the geological sections, with the highest in the Smrekova glavica occurrence (75 and 83 ppm). The range of Nd content is from 44 to 1797 ppm. The average content in bauxite samples from the Late Triassic paleorelief is 142 ppm, from the Early Jurassic 136 ppm and in the samples from the

Middle Jurassic-Oxfordian paleorelief 123 ppm. Bauxites from the Late Triassic underlying bed from the lower part of the geological sections have an average Nd content of 251 ppm, and from the middle and upper part 88 ppm; bauxites from the Early Jurassic underlying bed 226 and 109 ppm; and from the Middle Jurassic-Oxfordian underlying bed 112 and 127 ppm. Exceptionally high contents in individual samples (>1000 ppm) were found in the lower part of the bauxite geological sections in Zagrad 3, and elevated (>300 ppm) in Liverovići 2, Zagrad 1 and 3, Biočki stan, Štitovo II, Borova brda, Plačnik (Međugorje) and Smrekova glavica. Elevated Nd contents are characteristic exclusively for the lower parts of bauxite bodies formed on the Late Triassic and Early Jurassic, while bauxites from the Middle Jurassic-Oxfordian underlying bed are characterised by a uniform vertical distribution of this element.

The Y content in the individual samples ranged from 62 to 1226 ppm. The average content in the samples from the Triassic underlying bed is 131.62 ppm, in the samples from the Early Jurassic 128.34 ppm, while in the samples of bauxite from Middle Jurassic-Oxfordian it has the highest value and amounts 161.14 ppm. In the samples from the lower part of deposits formed on the Late Triassic carbonate sediments the average Y content is 202 ppm, while from the middle and upper part is 96.5 ppm; from Early Jurassic 177.6 and 116.8 ppm; and from Middle Jurassic-Oxfordian 158.2 and 162.4 ppm. Exceptionally high contents in individual samples (>1200 ppm) were found in the lower part of the geological sections in Zagrad 3, and elevated (>300 ppm) in Borova brda, Biočki stan and Smrekova glavica. It is clear that elevated contents are characteristic of the lower parts of bauxite bodies formed on the Late Triassic and Early Jurassic paleorelief, while bauxites from the Middle Jurassic-Oxfordian underlying bed, are characterised by mostly uniform Y contents, and slightly higher contents in samples from the middle and lower bauxite bodies. Sm, Eu, Gd, Tb, Dy and Ho belong to the yttrium subgroup. High contents in individual samples of all elements characterise the samples from the lower part of the geological sections, especially in Zagrad 3, also in Liverovići 2, Biočki stan, Štitovo II, Borova brda and Smrekova glavica. Therefore, elevated values characterise mainly the lower parts of bauxite bodies formed on the Late Triassic and Early Jurassic paleorelief. However, for bauxites from Middle Jurassic-Oxfordian paleorelief, average higher contents of Sm, Eu, Gd, Tb, Dy and Ho were found in the middle and upper part of the ore bodies and outcrops.

The range of scandium content is from 38 to 159 ppm. The average content in bauxite samples from the Early Triassic underlying bed was 58.41 ppm; from the Early Jurassic 58 ppm; and in the Middle Jurassic-Oxfordian underlying bed samples 51.84 ppm. In the first group of bauxite samples, from the lower part of the geological sections, the average Sc content is 60.6 ppm and from the middle and upper part 57.3 ppm; from Early Jurassic paleorelief 69.4 and 54.9 ppm; and in samples from Middle Jurassic-Oxfordian paleorelief 51.3 and 52.1 ppm. Elevated Sc content in individual samples (>70 ppm) was found in the lower part of the geological sections in bauxites on Late Triassic and Early Jurassic paleorelief, in Zagrad 1, Crveneornice, Biočki stan and especially in Zagrad 3 and Borova brda deposits (>100 ppm). Uniform contents of Sc are shown by bauxites from Middle Jurassic-Oxfordian paleorelief. According to geochemical characteristics Er, Tm, Yb and Lu belong to the Sc subgroup and have elevated contents in the same bauxite samples as Sc. As with the elements from the yttrium subgroup, higher average contents of Er, Tm, Yb and Lu in the middle and upper parts of bauxite bodies formed on Middle Jurassic-Oxfordian paleorelief are characteristic. High contents in individual samples of all elements characterise the samples mainly from the lower part of the geological sections, especially in deposits an occurrences: Zagrad 3 and Borova brda, also in Liverovići 2, Crvene ornice, Biočki stan, Štitovo II and Smrekova glavica.

When the contents of rare earth elements in bauxites of different formations in Montenegro [5,6] and Mesozoic Mediterranean deposits and bauxite formations of: Croatia [23], Turkey [28], Greece [26], Italy [22,37,39], France [82] and Spain [40] are compared, fairly clear uniformity of average REE contents in bauxites of similar or the same age can be observed.

Table 11. Statistical parameters of geochemical analyses of rare earth elements, Y and Sc in Jurassic bauxites of the Vojnik-Maganik and Prekornica ore regions (after Radusinović [5]).

Paleorelief Age	Statistical Parameters		Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Late Triassic (<i>n</i> = 160)	Minimum	Min	38	62.6	87.7	159.5	13.02	44.3	8.36	1.85	8.69	1.65	10.59	2.26	6.58	1.00	6.40	0.98
	Maximum	Max	111	1266.2	1799.1	908.3	421.42	1797.4	327.46	68.08	309.56	40.49	206.26	37.79	105.01	15.30	94.75	14.40
	Arithmetic mean	$\bar{x}$	58.41	131.62	199.49	365.01	38.51	141.94	25.99	5.44	24.49	3.87	22.85	4.68	13.59	2.06	13.35	2.06
	Standard deviation	σ	9.11	165.04	245.96	111.06	53.65	210.22	37.29	7.77	35.82	5.04	27.35	5.30	14.20	2.00	12.14	1.84
	Coefficient of variation	Cv	0.16	1.25	1.23	0.30	1.39	1.48	1.43	1.43	1.46	1.30	1.20	1.13	1.05	0.97	0.91	0.90
Liassic (<i>n</i> = 51)	Minimum	Min	43	77.7	111.4	208.3	16.80	54.4	10.15	2.22	10.30	1.90	12.74	2.87	8.78	1.37	8.99	1.36
	Maximum	Max	159	597.7	1648	663.9	184.52	616.2	101.59	23.92	125.40	22.18	137.93	27.67	70.45	10.03	62.15	9.31
	Arithmetic mean	$\bar{x}$	58.00	128.34	282.89	355.26	38.23	135.55	23.82	5.24	24.54	3.93	23.35	4.80	13.58	2.08	13.46	2.03
	Standard deviation	σ	18.46	77.03	330.47	109.08	34.55	120.16	19.46	4.58	23.31	3.39	18.98	3.64	8.94	1.25	7.68	1.15
	Coefficient of variation	Cv	0.32	0.60	1.17	0.31	0.90	0.89	0.82	0.87	0.95	0.86	0.81	0.76	0.66	0.60	0.57	0.56
Dogger-Oxfordian (<i>n</i> = 41)	Minimum	Min	45	84.3	136.9	168.4	15.67	52.9	9.23	2.19	10.52	2.08	14.83	3.61	11.16	1.64	10.62	1.64
	Maximum	Max	57.00	323.9	570.9	598.7	82.84	329.3	53.20	11.25	53.07	7.29	41.03	8.70	25.38	3.51	21.76	3.18
	Arithmetic mean	$\bar{x}$	51.84	161.14	244.63	342.69	33.39	122.88	20.85	4.55	22.02	3.62	22.97	5.28	15.83	2.36	14.95	2.28
	Standard deviation	σ	3.18	52.60	120.03	111.69	17.57	71.31	11.62	2.47	11.43	1.38	7.04	1.36	3.71	0.49	2.79	0.40
	Coefficient of variation	Cv	0.06	0.33	0.49	0.33	0.53	0.58	0.56	0.54	0.52	0.38	0.31	0.26	0.23	0.21	0.19	0.18

n—Total number of samples.

Significant deviations and variations are observed in Jurassic bauxites formed on carbonates of Early and Late Jurassic age. Based on Figure 17, Greek bauxites formed on the Late Jurassic paleorelief from the Parnassos-Ghiona geotectonic zone show the highest REE average content (about 1280 ppm), followed by the Jurassic bauxites of Montenegro bauxite-bearing regions Vojnik-Maganik and Prekornica (about 1000 ppm), as well as Turkish bauxites from Namtun tectonic unit (about 950 ppm). Slightly lower contents are shown by the Triassic bauxites (from 540 to 740 ppm). The lowest average content was found in Jurassic bauxite of the bauxite-bearing regions of Western Montenegro and Čevo in Montenegro, around 550 ppm, as well as in the Greek bauxites of the Parnassos-Ghiona geotectonic zone formed on the Liassic paleorelief, only around 390 ppm. When it comes to Cretaceous bauxites, the average REE contents in the shown regions are fairly uniform. The highest contents (more than 700 ppm) belong to Italian bauxites from the Caserta district and French bauxites from Provence and Languedoc, while the lowest belong to Montenegrin (about 310 ppm), Greek (about 420 ppm) and Spanish bauxites from the Catalan Coastal Range (about 440 ppm).

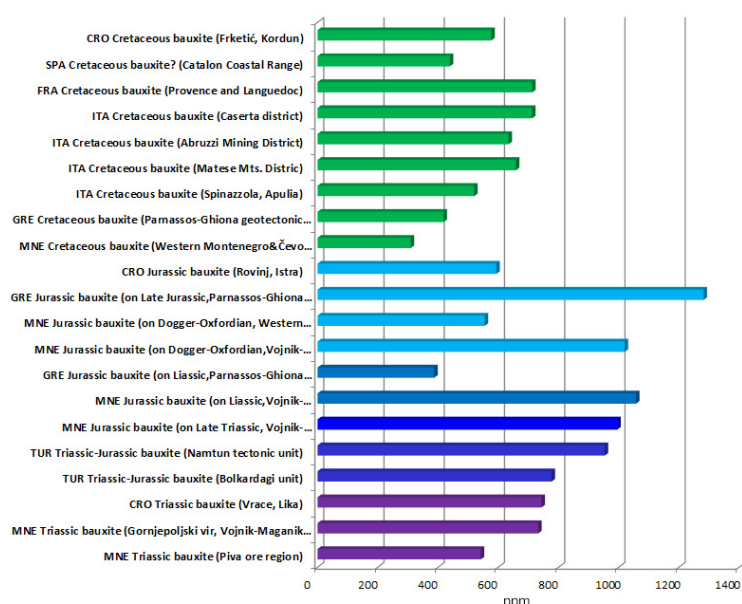


Figure 17. Content comparison of $\Sigma\text{REE} + \text{Sc}$ in the bauxite formations in Montenegro and some Mesozoic Mediterranean bauxite formations, (ppm).

Despite the fact that bauxite formations were studied at an uneven level of exploration and that average values were derived based on analyses of different numbers of samples, according to the average REE contents, it can be concluded that Jurassic bauxite formations have the highest perspective.

4.5. Rare Earth Elements in Bauxite Residue

Aluminium factory—Podgorica (KAP) from the beginning of its operation in 1972, up to the closure of the Alumina Production Factory in 2009, was continuously supplied by the company Bauxite mines—Nikšić (RBN). The Aluminium Factory—Podgorica exclusively used bauxite from Montenegrin deposits for the production of alumina. During this period 20.5 Mt of bauxite was produced of which 16.6 Mt, that is to say, about 81% was delivered to the Aluminium factory—Podgorica, in which factory 6.8 Mt of alumina and 3.1 Mt of aluminium were produced (Figure 18; Data from: RBN database and KAP database).

The total quantities of bauxite residue amount to about 7.5 million tons in basins A and B in the Aluminium Factory Podgorica. The calculation of the average content of main and other oxides, trace elements and rare earth elements of 19 composite samples are given in Table 12.

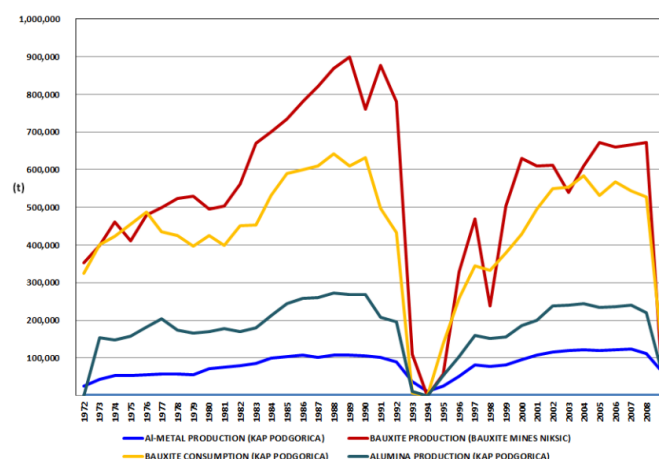


Figure 18. Bauxite production and consumption, alumina and aluminium production in Montenegro, 1972–2009, (t).

Table 12. The average content of major oxides and trace elements in bauxite residue from basins A and B in Aluminium factory—Podgorica (KAP). REEBAUX [6].

BAUXITE RESIDUE (Number of Samples)	Basin A (9)	Basin B (10)	Average
<i>Major oxides (%)</i>			
Al ₂ O ₃	24.44	20.70	22.47
SiO ₂	10.72	11.97	11.37
Fe ₂ O ₃	33.02	34.29	33.68
TiO ₂	4.58	4.64	4.61
CaO	6.03	6.92	6.50
LOI	13.48	13.07	13.26
MgO	0.60	0.63	0.61
Na ₂ O	5.80	6.31	6.07
K ₂ O	0.32	0.35	0.34
P ₂ O ₅	0.09	0.14	0.12
MnO	0.25	0.26	0.25
Cr ₂ O ₃	0.10	0.10	0.10
<i>Trace elements (ppm)</i>			
Ni	238	233	235.37
Ba	76	83	79.32
Be	6	6	5.79
Co	60	59	59.06
Cs	6	6	6.14
Ga	36	24	30.04
Hf	26	28	26.88
Nb	93	94	93.56
Rb	23	27	25.13
Sn	19	21	19.95
Sr	180	189	184.89
Ta	6	7	6.66
Th	88	92	90.03
U	11	11	11.12
V	461	516	490.21
W	8	10	9.27
Zr	959	1000	980.38
Sc	103	107	104.68
Y	173	186	179.51
La	287	318	303.20
Ce	545	569	558.02
Pr	55	61	58.11
Nd	204	225	214.96
Sm	39	42	40.39
Eu	8	9	8.32
Gd	34	38	35.96
Tb	5	6	5.59
Dy	31	34	32.67
Ho	6	7	6.75
Er	19	20	19.89
Tm	3	3	2.95
Yb	19	20	19.78
Lu	3	3	3.02
ΣREE	1535	1646	1593.79

An average content of REE was determined in basin A of red mud in Podgorica with an average of 1535.3 ppm and a range from 1343.76 to 1704.81 ppm, while the average determined content in basin B was 1646.42 ppm, ranging from 1121.61 to 1903.65 ppm in individual samples. On average, the highest contents were detected in drillholes B5 and B6 in basin B [6].

It is clear that there is a change in the geochemical and mineralogical composition in relation to the primary bauxite in the bauxite residue after the alumina production process (Figure 19).

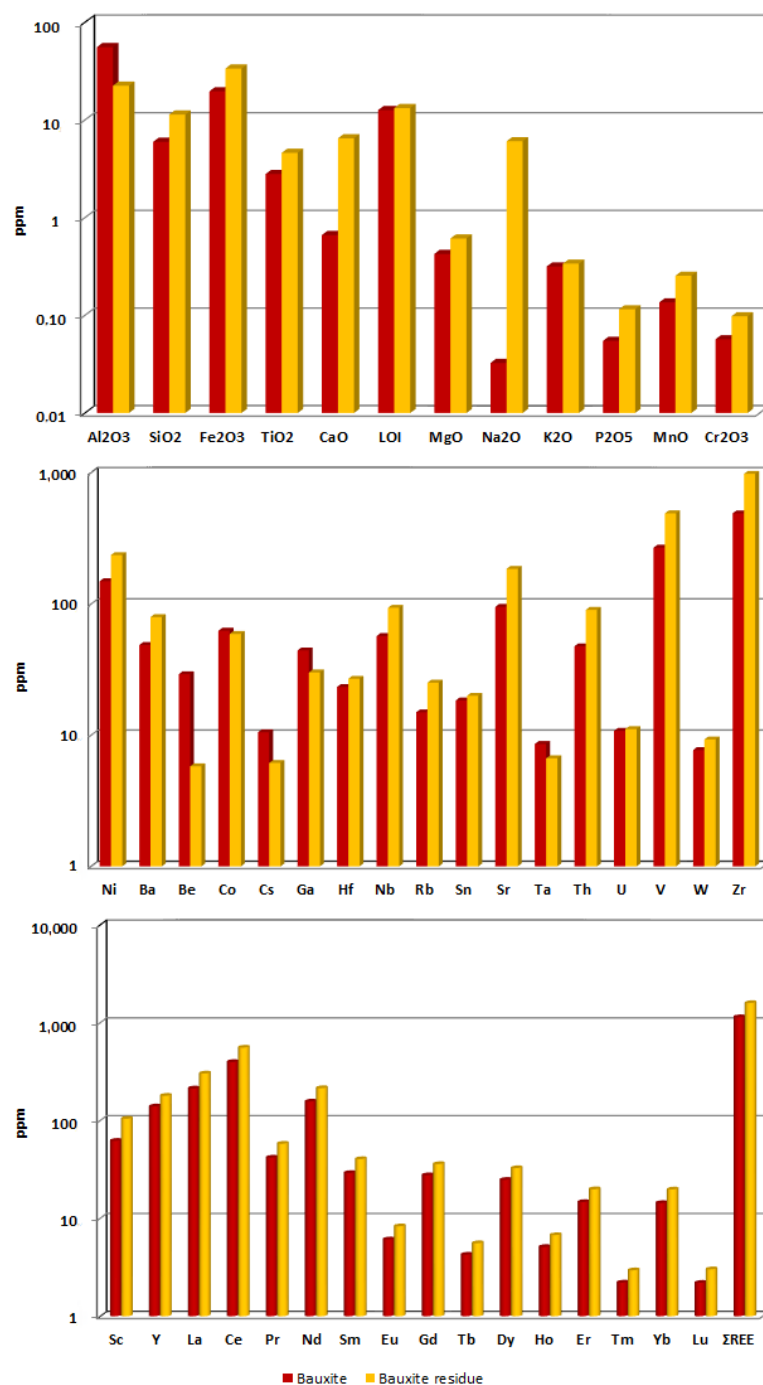


Figure 19. Content comparison of analysed oxides, microelements and rare earth elements in bauxites and bauxite residue. Based on data: (Radusinović [5] and REEBAUX [6]); Bauxite mines—Nikšić and Aluminium factory—Podgorica (KAP).

The content of Al_2O_3 decreases significantly (22.47%), while the contents of SiO_2 , iron oxide and titanium increase significantly. The high average contents of calcium oxide (6.5%) and sodium oxide (6.07%) in the bauxite residue are a consequence of the nature of the alumina production technological process. The increase in average contents in bauxite residue compared to the bauxite is also shown by other tested oxides of chromium, manganese, phosphorus and potassium (from 1.1 to 1.9 times). Trace elements: Be, Cs, Ga, Ta and Co exhibit from 1.1 to 5 times lower contents in bauxite residue compared to bauxite, while all others have higher, especially: Zr (2 times), Sr (1.9 times), V and Th (1.8 times), Rb (1.7), and so on.

According to the presented data, the total average content of rare earth elements (ΣSc , Y, La–Lu) in the bauxite residue in basins A and B is 1.4 times higher than the average content in bauxites. The largest increase in average content is shown by Sc—1.68 times, La and Ce 1.42, that is to say, 1.4 times, while the smallest is by Y, only 1.28 times.

In almost all samples the following minerals have been identified: hematite, gibbsite, calcite, cancrinite, less common but also present are: böhmite, goethite, quartz, rutile, anatase, perovskite, garnet and nordstrandite (Figure 20).

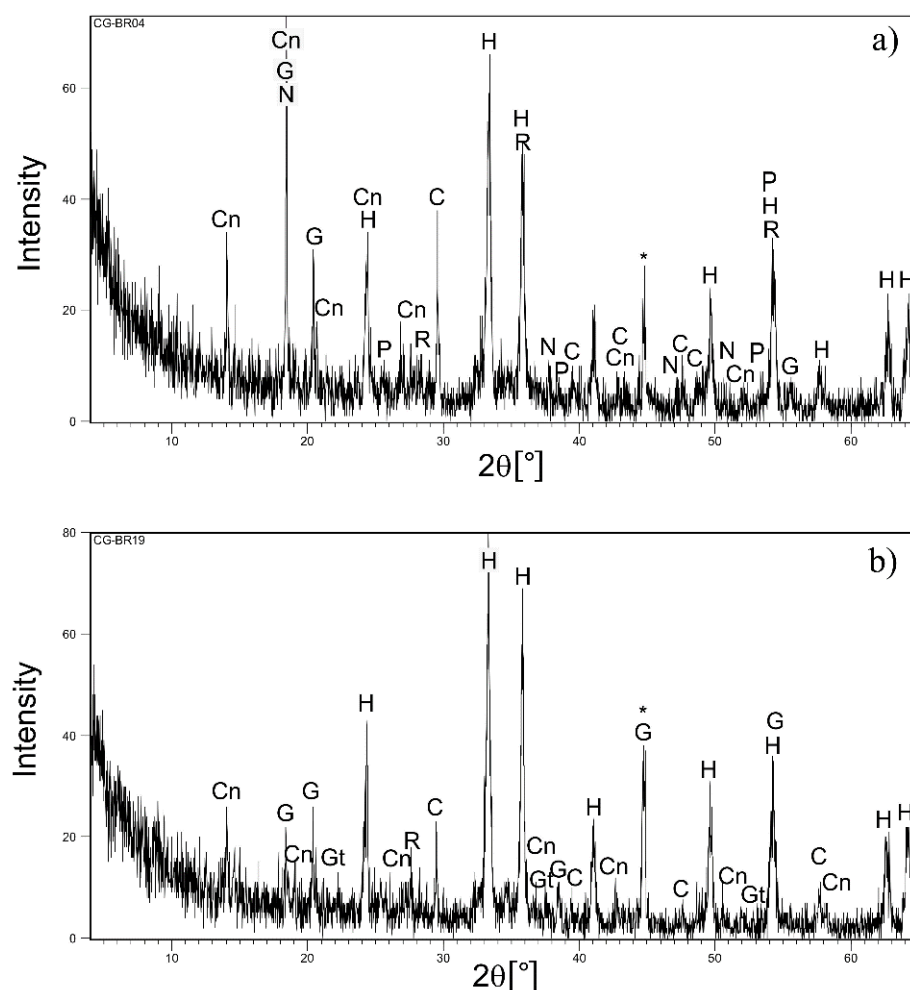


Figure 20. Mineral composition of the red mud samples from the KAP- Podgorica red mud land-fill: Basin A (a), basin B (b). H—hematite, C—calcite, Cn—cancrinite, G—gibbsite, R—rutile, N—nordstrandite, Gt—goethite, P—perovskite, A—anatase, B—böhmite, *—Al-sample holder (REEBAUX project documentation, Tomašić [6]).

Finally, until the completion of more detailed exploration it can be noted that the presented results should be considered as preliminary and indicative.

5. Conclusions

Jurassic bauxites are of the greatest economic importance in Montenegro, especially high-quality deposits of the bauxite-bearing region Vojnik-Maganik, in the wider area of Nikšićka Župa.

The implementation of recent national and international exploration projects has collected new data, especially in the part of geochemical and mineralogical characterisation of bauxites, which complements the previous knowledge about Montenegrin bauxites. This enabled a better assessment of the potentiality of bauxite formations and individual bauxite deposits for REE and associated critical metals.

Mineralogical explorations have confirmed the complexity of the mineral composition of bauxite, when it comes to the main and less represented minerals, as well as accessory minerals. The studied red Triassic bauxites are characterised by the presence of böhmite and gibbsite, followed by hematite, goethite, kaolinite and anatase, as well as vermiculite. The main carrier of aluminium with red bauxite from the Vojnik-Maganik and Prekornica ore regions is the mineral böhmite, partly gibbsite. Regarding other major minerals the following are presented: Fe-oxides/hydroxides (hematite and goethite), clay minerals (kaolinite) and titanium minerals (mainly anatase). In the previously mentioned bauxites, the presence of the following minerals was also detected: zircon, ilmenite, magnetite, biotite, K-feldspars, mottramite, REE phosphates-monazite and xenotime and REE carbonates-Ce and Nd. Studied Cretaceous bauxites are consisted by major minerals: böhmite, gibbsite, hematite, kaolinite, anatase and rutile, while Paleogenic: böhmite, goethite, kaolinite and anatase. The Triassic bauxites of Piva (Rudinice) belong to the ferritic bauxite, as well as the bauxites of a number of Jurassic deposits formed on the paleorelief of the Late Triassic age. The Triassic bauxites of Gornjepoljski vir and the Cretaceous bauxites of Međeđe deposit belong to the group of kaolinite bauxites. All other bauxites from the Jurassic, Cretaceous and Paleogene deposits are classified in the bauxite group.

The content of major oxides in bauxites corresponds to the mineral composition and varies significantly, both in the case of different bauxite formations, and in individual deposits belonging to the same formation, the same or different ore regions. Based on the content of useful and main components, red bauxite which can be used for the production of alumina, are divided as follows: high-quality bauxite with Al_2O_3 content from 55% to 61% and SiO_2 from 0.5% to 6%; low-quality bauxite with Al_2O_3 content from 49% to 55% and SiO_2 from 6% to 15% and poor-quality bauxite with Al_2O_3 content from 43% to 50% and SiO_2 from 15% to 25%.

Due to their genetic specificities and mineral composition, cretaceous white bauxites in the samples from the studied deposits, show a high average content of SiO_2 and lower contents of Fe_2O_3 . These bauxites, that is to say parts of deposits with low Fe_2O_3 content and satisfactory Al_2O_3 and SiO_2 content, were mainly used as raw material for the refractory materials industry.

Bauxite formations in Montenegro have significantly different ΣREE average contents. The highest contents were detected in Jurassic bauxites from the Vojnik-Maganik and Prekornica ore regions from the Early Jurassic, Middle Jurassic-Oxfordian and Late Triassic paleorelief—around 1000 ppm on average, which makes them the most interesting in terms of possible future use for REE extraction. It is important to emphasise that in this sense, low-quality deposits with a high content of SiO_2 are also interesting, from which it is not possible to use bauxite for the production of alumina and aluminium. Jurassic bauxites of these regions are characterised by elevated contents of mainly light lanthanides (LREE), but also Y and Sc. Heavy lanthanides (HREE) are significantly less presented.

Based on preliminary data, at the moment, Jurassic bauxites of the Orjen ore region, which were also formed on underlying bed of the Middle Jurassic-Oxfordian age, can be considered promising, almost like the bauxites of the Vojnik-Maganik and Prekornica ore regions. This cannot be said for the Jurassic bauxites of the Western Montenegro ore region, where REE contents are significantly lower, and for which explanations should be sought through furthermore detailed explorations.

The Cretaceous white bauxites of the exploited deposits are characterised by the lowest average REE contents in comparison to the bauxites of other formations, especially Jurassic, which places them in the group of the least potential in terms of obtaining REE. However, these bauxites are significantly richer in lithium compared to Jurassic, especially those from the largest and highest quality deposits formed on the Late Triassic paleorelief.

Although at this moment we have a small amount of data, we can preliminarily conclude that Triassic bauxites are much less promising in terms of their REE content, but also due to the fact that their proven reserves are small.

Paleogene bauxites, similar to the Triassic ones, cannot have economic significance, because they occur only in the form of occurrences and there are no proven significant amounts of bauxites at any of the investigated locations, although they contain certain contents of REE.

Regarding other critical mineral raw materials (CRM) and other elements, Ti, V, Zr, Nb, Sr and Ga could also be promising in bauxites.

Bauxite residue from Podgorica in decreasing abundance, the following minerals have been identified: hematite, gibbsite, calcite, cancrinite, less frequently but also presented are: böhmite, goethite, quartz, rutile, anatase, perovskite, garnet and nordstrandite.

According to the determined contents of REE and other macro and trace elements in bauxite residue, it can be concluded that this secondary resource is very promising. Compared to the bauxites from which it originates, the contents of individual elements are significantly higher, such as: Zr (2 times), Sr (1.9 times), V (1.8 times), Sc (1.68 times), La (1.42 times), Ce (1.4 times), Y (1.28 times), as well as all other elements from the lanthanide group. In much higher contents in bauxite residue compared to bauxite, Ti, V, Zr, Nb, Sr and other elements, are also present and may be interesting for extraction and exploitation. On the other hand, the contents of Be, Cs, Ga, Ta and Co, in bauxite residue are lower than their contents in bauxites.

Further development of economically and environmentally sustainable technologies for extracting REE from bauxite residue and, why not from bauxite may allow in the future the exploitation of Montenegrin bauxites as sources of CRMs.

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