RawMaterials

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RARE EARTH ELEMENTS IN BAUXITES OF MONTENEGRO

Dr Slobodan Radusinović, Grad. Eng. of Geology
Research Associate at the University of Montenegro
e-mail: radusinovic.s@geozavod.co.me

Geological Survey of Montenegro
Krusevac bb, 81000 Podgorica, Crna Gora
www.geozavod.co.me, e-mail:geozavod@t-com.me

ZAVOD ZA GEOLOŠKA ISTRAŽIVANJA CRNE GORE
Geological Survey of Montenegro

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ZAVOD ZA GEOLOŠKA
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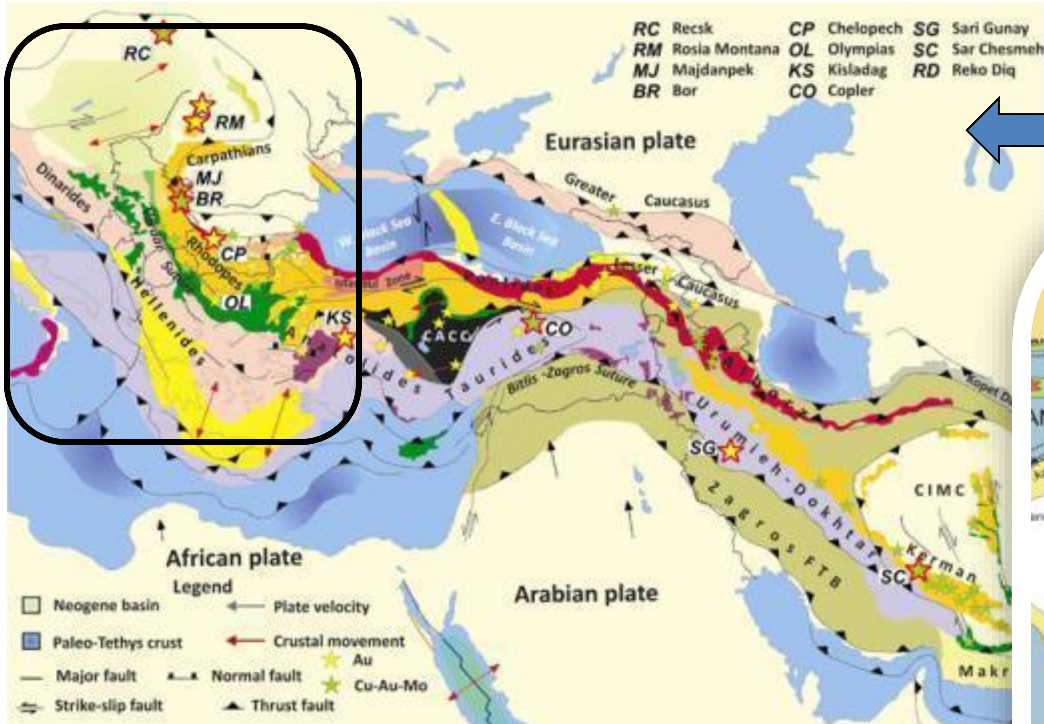
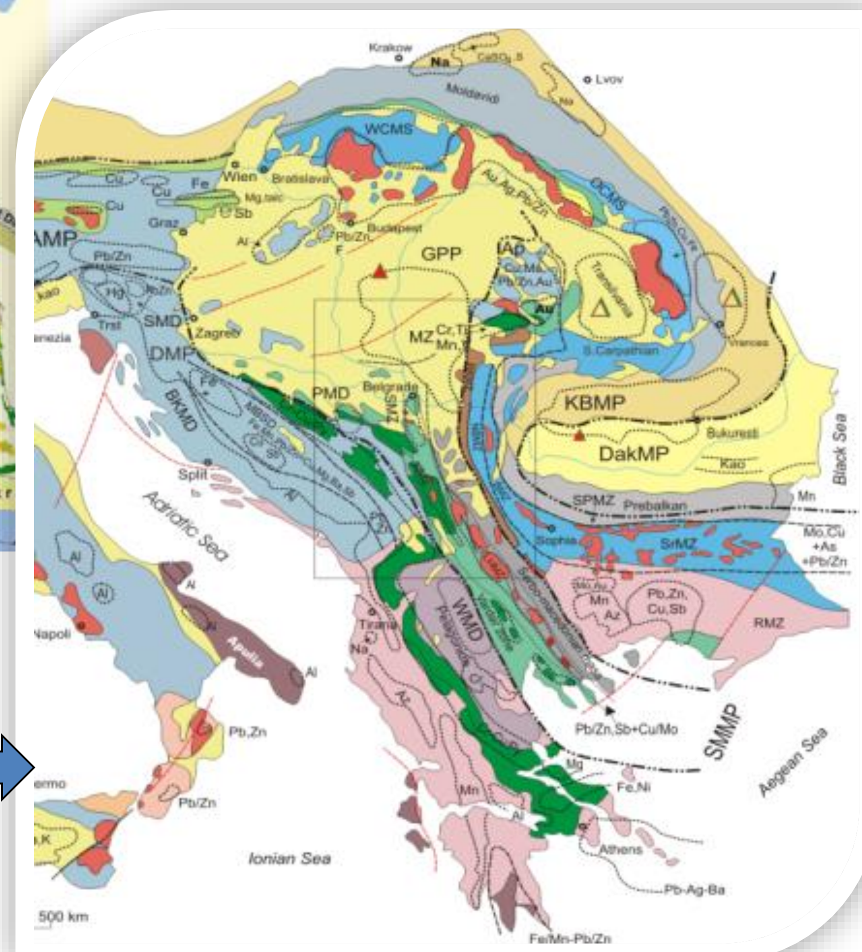
Geological Survey of Montenegro

Introduction



Tethyan Eurasian Metallogenetic Belt

ABCD: Alpine-Balkan-Carpathian-Dinaric metallogenic and geodynamic provinces



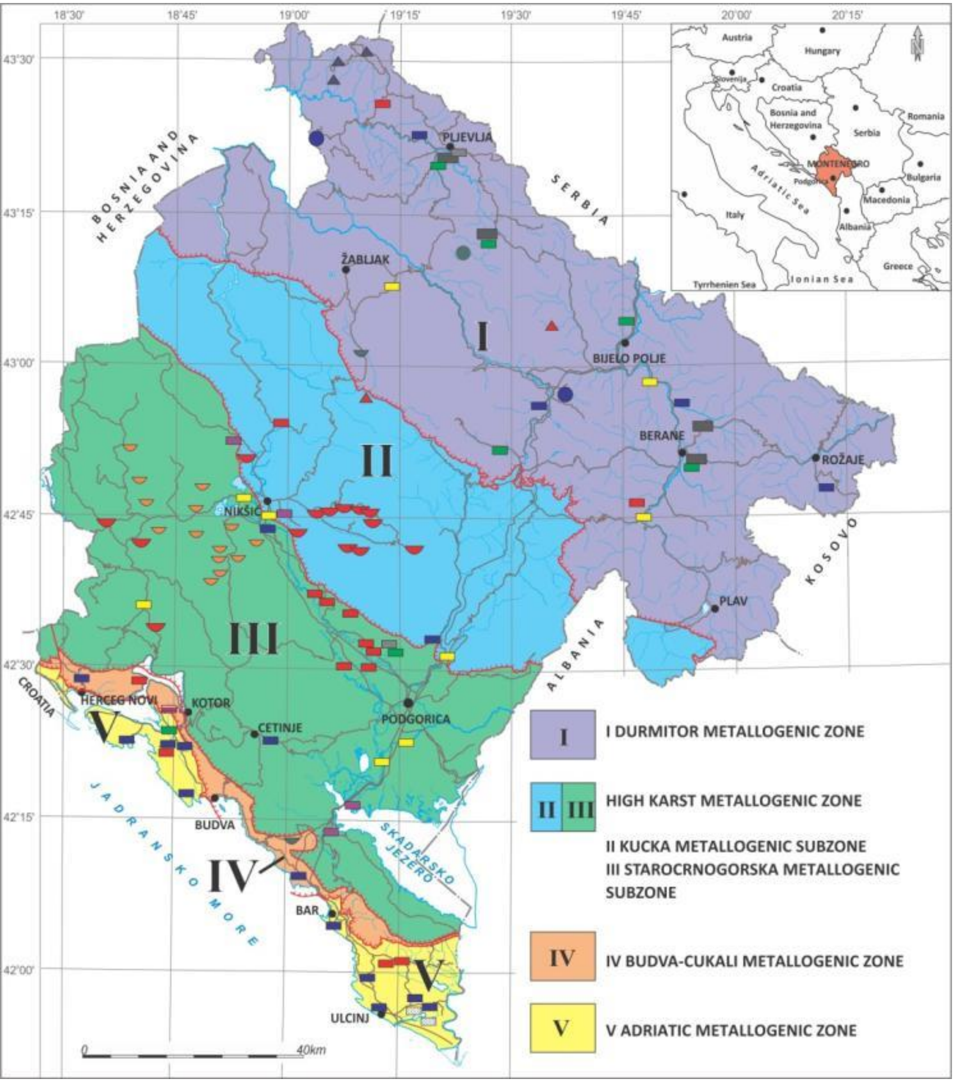
Sector of NE Mediterranean

Metallogenic units of Montenegro are part of regional metallogenic units

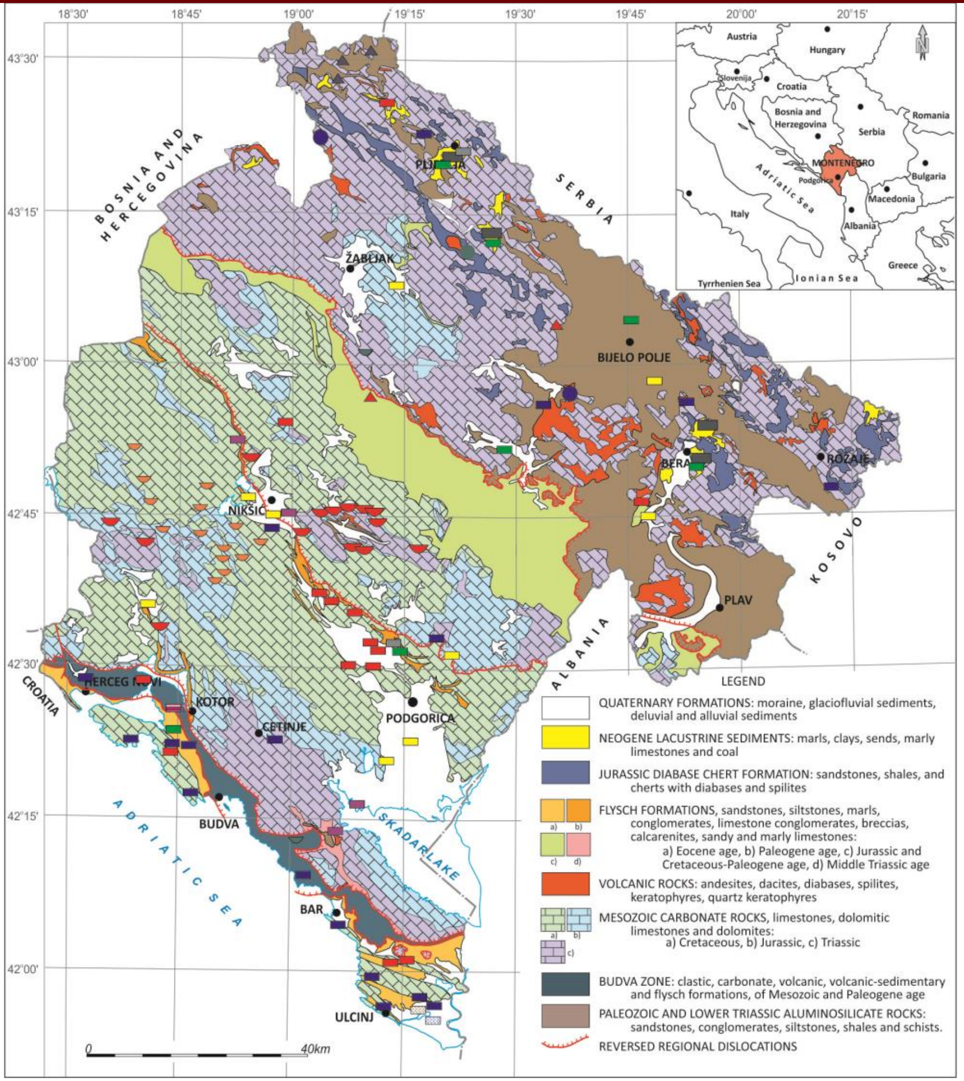
Maps - Jelenković R., et al.: Strategic mineral resources of Serbia and legislation, MINATURA2020, Beograd, 2016

Introduction

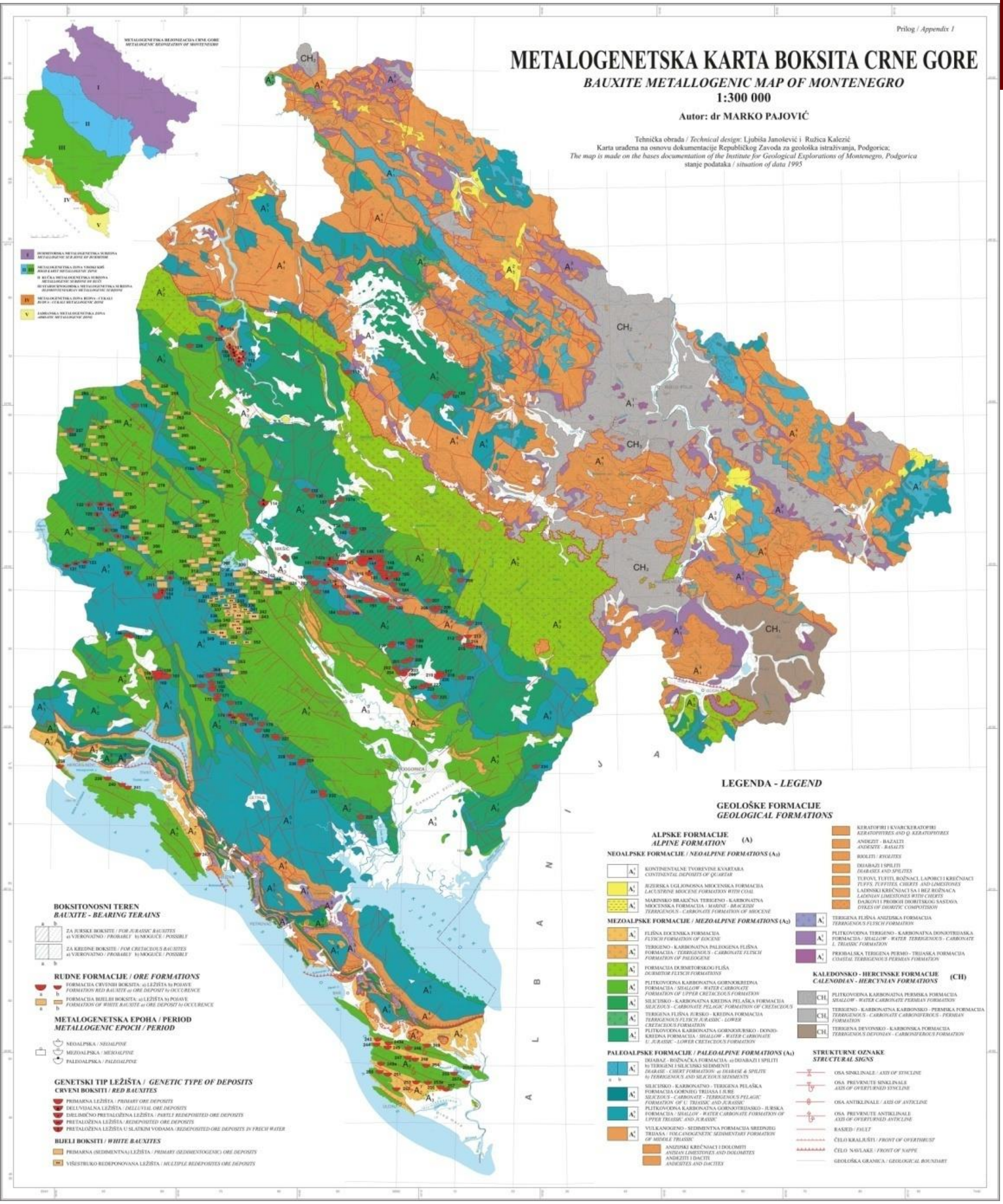
Pajović and Radusinović (2010): Mineralal resources of Montenegro; Montenegro in XXI century in the era of competitiveness MASA, modified



Metallogenic reonization map of Montenegro



Lithological map of Montenegro



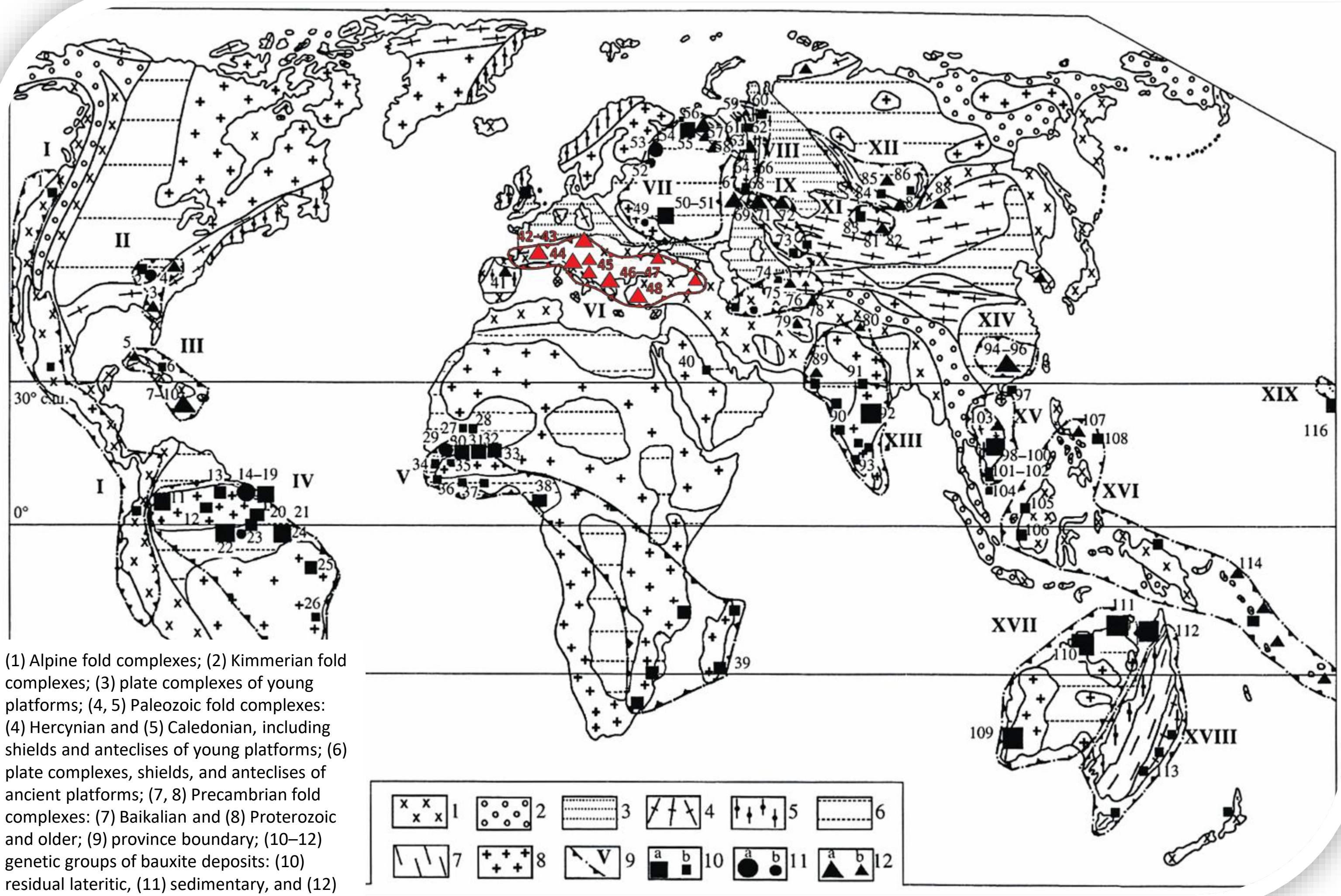
Introduction

- **Deposits and occurrences of karstic bauxites in Montenegro belong to the Dinaridic metallogenic province**
- **Metalogenetic regionalization in Montenegro**
  - **Durmitor metallogenic zone**
  - **Metalogenetic zone of the High Karst**
    - ***Kučka Metalogenetic subzone***
    - ***Starocrnogorska metalogenetic subzone***
  - **Budva –Cukali metalogenetic zone**
  - **Adriatic metalogenetic zone**
- **Karstic bauxites in Montenegro**
  - ***Triassic bauxites - High Karst Zone; Piva, N. Župa***
  - ***Jurassic bauxites - High Karst Zone - Economic importance***
    and rare occurrences in Durmitor metal. unit.
  - ***White Cretaceous bauxites - High Karst Zone;*** *in the area of western Montenegro; 100 deposits and occurrences of white bauxites has been discovered at the area of 1.000 km^2 – Economic importance*
  - ***Bauxites of Paleogene age-*** *a coastal part of Montenegro within the Adriatic zone*
  - ***Bauxites of Neogene age-*** *locality of Bunić, in Nikšićka Župa*

Introduction

Bauxite provinces
Bogatyrev and Zhukov (2009)

- **I** ***East Pacific***
- **II** ***North American***
- **III** ***Caribbean***
- **IV** ***South American***
- **V** ***African province***
- **VI** ***Mediterranean***
- **45, Niksicka Zupa**
- **VII** ***East European***
- **VIII** ***Ural province***
- **IX** ***Kazakh province***
- **X** ***Central Asian***
- **XI** ***Salair province***
- **XII** ***East Siberian***
- **XIII** ***Hindustan***
- **XIV** ***Chinese***
- **XV** ***Indochinese***
- **XVI** ***Indonesian–Philippine province***
- **XVII** ***West Australian province***
- **XVIII** ***East Australian province***
- **XIX** ***Hawaiian province***



(1) Alpine fold complexes; (2) Kimmerian fold complexes; (3) plate complexes of young platforms; (4, 5) Paleozoic fold complexes: (4) Hercynian and (5) Caledonian, including shields and anteclises of young platforms; (6) plate complexes, shields, and anteclises of ancient platforms; (7, 8) Precambrian fold complexes: (7) Baikalian and (8) Proterozoic and older; (9) province boundary; (10–12) genetic groups of bauxite deposits: (10) residual lateritic, (11) sedimentary, and (12) karst; (a) large and medium and (b) small deposits and occurrences.

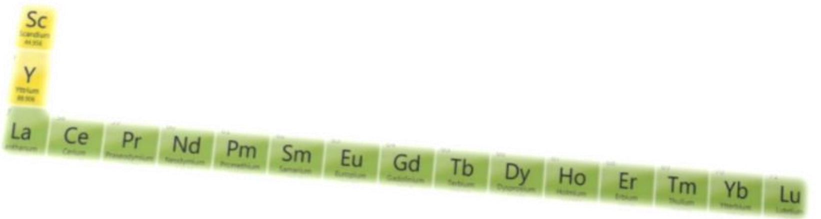
GENERAL CHARACTERISTICS OF KARSTIC BAUXITES

- Bauxites are formed under conditions of humid tropical and subtropical climate; Based on the lithological composition of the underlaying rocks bauxite deposits are classified into two basic groups: lateritic and karstic bauxites.
- In kartsic bauxites, dominate minerals are ***boehmite - AlO (OH)*** and ***diaspore - AlO (OH)***, and in lateritic ***gibbsite - Al $(OH)_3$*** *(Bárdossy, 1981, Bárdossy and Aleva, 1990; MacLean et al., 1997; Mongelli and Acquafredda, 1999; Pajović, 2000; Mameli et al., 2007; Calagari and Abedini, 2007; Bogatyrev and Zhukov, 2009; Deng et al., 2010)*
- Karstic bauxites account for 14% of world's bauxite resources *(Mameli et al., 2007).*
- Jurassic bauxites account for 5% of world's kartsic bauxite resources *(Bárdossy, 1981).*
- Macroelements: **Al**, **Fe**, **Si**, **Ti**, K, Mg, Ca

Distribution of paragenesis of aluminum minerals by the bauxite age (Bárdossy, 1981)

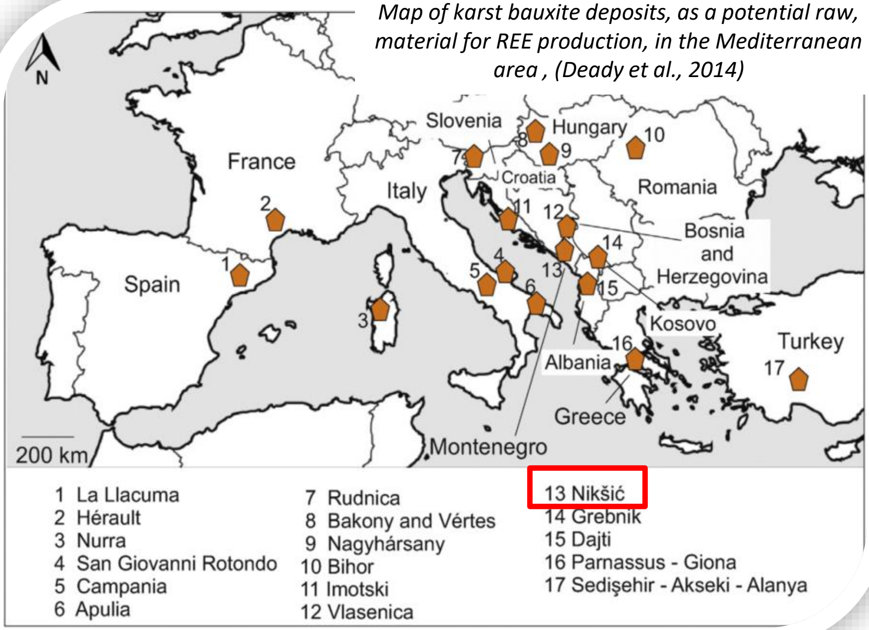
Type of deposit	Paragenesis								
	Gibbsite	Gibbsite-boexmite	Gibbsite-boexmite-diaspore	Gibsbsite-corundum	**Boehmite**	Boehmite-diaspore	Disapore	Diaspore-corundum	Corundum
Quaternary	83	17	-	-	-	-	-	-	-
Pliocene- Miocene	65	34	-	-	1	-	-	-	-
Oligocene	6	17	-	-	6	29	42	-	-
Eocene-Paleocene	29	34	<1	10	21	3	3	-	-
Late Cretaceous	11	9	<1	4	50	13	13	-	-
Early Cretaceous	14	1	2	1	61	9	11	<1	-
Jura (201,6-145,5 millions f year)	**-**	**-**	**-**	**-**	**60**	**37**	**3**	**-**	**-**
Triassic	4	-	1	-	27	41	26	1	10
Perm	-	-	-	-	-	24	54	12	10
Carbon	3	2	-	-	2	27	64	1	<1
Devon	-	-	-	-	18	34	43	3	2
Ordovician	-	-	-	-	-	-	60	40	-
Cambrian	-	-	-	-	-	50	50	-	-

- Microelements: **Li**, **Na**, Rb, Be, Sr, Ba, Ce, Th, U, **Zr**, Hf, **V**, Nb, Ta, Cr, Mo, **Mn**, W, Co, Ni, Cu, Zn, Cd, Pb, Bi, **P**, As, Sb...
- Rare Earth Elements: Scandium, Yttrium + Lanthanides
  Sc, **Y** + **La**, **Ce**, Pr, **Nd**, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu



MICROELEMENTS AND RARE EARTH ELEMENTS IN RED BAUXITES

Map of karst bauxite deposits, as a potential raw, material for REE production, in the Mediterranean area , (Deady et al., 2014)



Characteristics and application:

- *Rare earth elements: Sc, Y i elements La–series*
- *This elements, that is, their ions are characterized by magnetic moment, which in combination with other elements allow the formation of permanent magnets, as well as by ferrimagnetism, which is why they are used to make magnetic semiconductors, etc.*
- *They affect the optical properties of different materials (especially glass, various minerals and synthetic gemstones), as well as their luminescent properties.*
- *They are used to produce thermoelectric materials (for sensors) and thermo-emissive materials (for emission electrodes and electron microscopes).*
- *Neodymium is used to make optically active laser components.*
- *REE metals and their alloys are also used in the manufacture of solar panels, fluorescent lamps, in the production of hybrid cars, laptops, LCD monitors (europium, terbium, cerium, yttrium), smartphones and televisions, and then for electric motors, generators and other components for electric cars...*

(Source: EuroGeoSurveys Mineral Resources Expert Group, 2014)

Scientific aspect

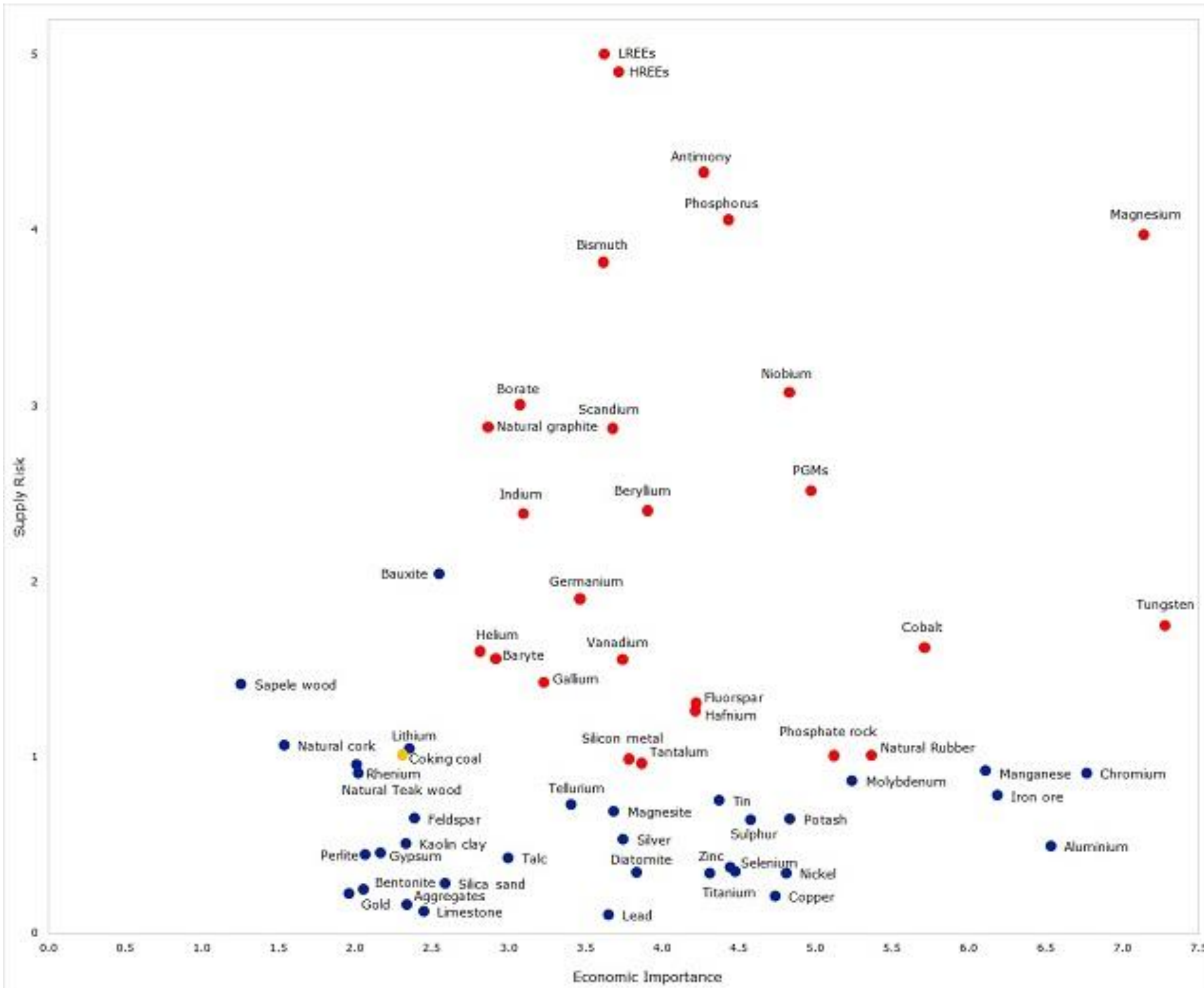
- *Determination of metallogenic characteristics*
- *Determination of the possible origin of the parent material*
- *Study of concentrations, vertical distribution and fractionation of REE´s and other microelements in the process of bauxitazion of parent material*
- *Determination of the geochemical connection of individual elements and groups of elements*
- *Determination of the reached degree of the diagenesis of the parent material*

Economic aspect

- *Bauxite - a potential mineral resource for obtaining the rare earth elements*
- *World demand for rare earth elements has been on the rise for years*
- *Problems in supplying the world's high-tech industry, where the rare earth elements have wide application*

More than half of the world's production of rare earth elements comes from Bajan Obo mine in China

Critical minerals and mineral raw materials



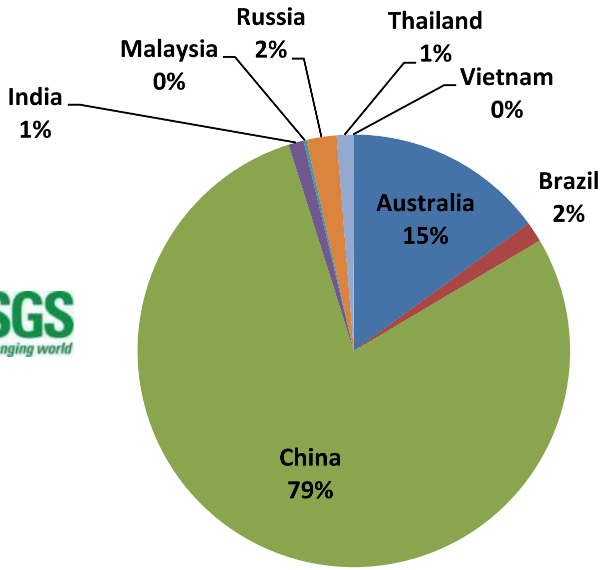
Mineral resources judged as critical by the EU are marked with red

Supply risk indicators compared to indicators of economic importance of mineral resources

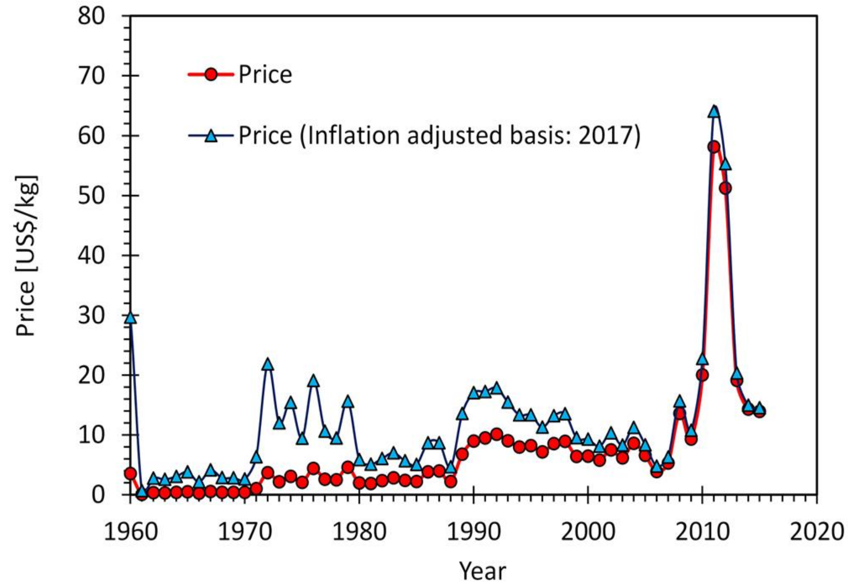
(according to: Study on the review of the list of Critical Raw Materials - Criticality Assessments; Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs Raw Materials; Publications Office of the European Union, 2017 ISBN 978-92-79-47937-3)

Rare earth elements (REE) production and application

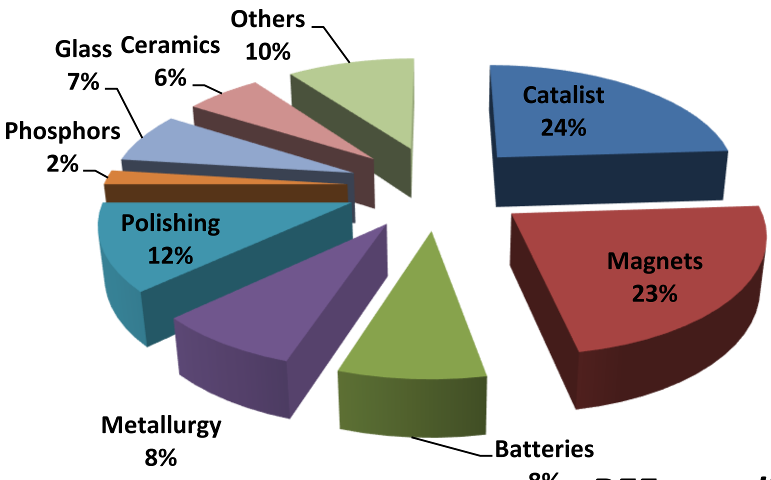
Total production of REE 2017. – 133.000 t



REE prices – historical overview



A. H. Tkaczyk et al. 2018. J. Phys. D: Appl. Phys. 51 203001

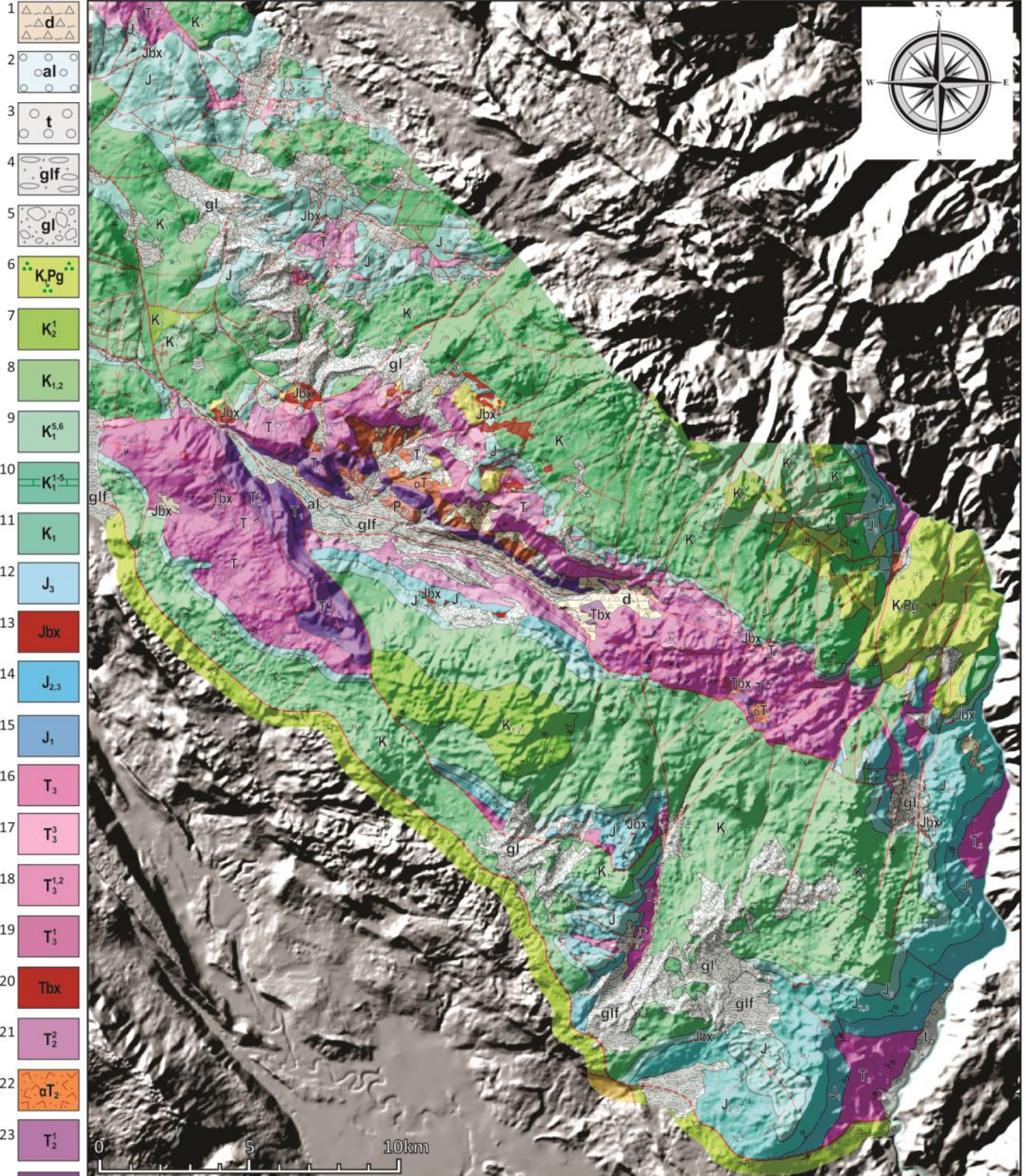


REE - application

Data: N. Tomašić, 9th ESEE Dialogue Conference, Podgorica, Montenegro, November 2018.

HISTORY OF RESEARCH AND STUDYING OF KARSTIC BAUXITES IN MONTENEGRO

- **History of research**
  - *In the last decades of the XIX and the beginning of the XX century: Kovalevski, 1838 - 1878; Boue 1837-1840; Tietze, 1881-1884; Baldacci, 1886-1889; Hassert, 1893-1901; Cvijic, 1897-1913; De Regny, 1901-1905; Kormos and Jekelius, 1917; Koch, 1933; Simic, 1934; Besic, 1933-1937; Pavic, 1939 (according to: Kalezic and Gomilanovic, 2004).*
  - Bešić (1953); Pavić (1956, 1963), Burić (1966); Grubić (1963,1975, 1999); Maksimović (1968, 1976, 1982, 1998 i dr.); Vukotić and Dragović (1981, 1982 et al.); Cicmil (1984); Dragović (1988, 2007); Pajović (2000, 2009); Pajović et al. (2004, 2005, 2017); Pajović and Radusinović (2010, 2012,2015); Radusinović (2017) et al.
  - Basic geological map of SFRJ, 1:100.000, for the territory of Montenegro (16 sheets)
  - Study of the bauxites in Montenegro – Fund documentation/projects, reports, elaborates (Pavić, Bešić, Kalezić, Rašović, Ivanović, Dragović, Đokić, Pljevaljčić, Pajović, Radusinović et al.)
  - MPK of the bauxite-bearing region of Western Montenegro, 1:50.000 (Rašović, Pljevaljčić et al.)
  - ***MPK of the bauxite-bearing region Vojnik-Maganik, 1:50.000 (Pajović et al.)***
  - ***Research of REE´s in the bauxites of ore regions Vojnik-Maganik and Prekornica (Radusinović et al.)***
- **Applied methods of explorations**
  - 1946 -1960. – prospective geological explorations
  - 1960 -1990. - detailed explorations of the bauxites, Bauxites mines– Nikšić (4.800 exploratory drills, cca 400.000 m‘)
  - geophysical exploration
  - chemical, mineralogical and geochemical studies of bauxite (numerous different test methods)



1. Deluvijum, 2. Aluvijum, 3. Terasni sedimenti, 4. Glaciofluvijalni sedimenti, 5. Morene, 6. Durmitorski fliš: laporci, alevroliti, pješčari, konglomerati; karbonatne breče i brečokonglomerati, 7. Slojeviti i bankoviti sprudni i subsprudni krečnjaci, 8. Slojeviti, bankoviti i masivni krečnjaci i dolomitični krečnjaci, 9. Slojeviti krečnjaci sa *Salpigoporella dinarica* i uslojeni krečnjaci sa foraminiferama, 10. Slojeviti, bankoviti i masivni krečnjaci sa algama i foraminiferama, bituminozni krečnjaci i sprudni i subsprudni krečnjaci sa koralima i hidrozoama, 11. Slojeviti i bankoviti krečnjaci, dolomitični krečnjaci i dolomiti, 12. Krečnjaci i dolomiti sa harofitama, *Pianella grudii, Clypeina jurassica* i tintininama, 13. Formacija crvenih jurskih boksita, 14. Slojeviti i bankoviti biomikriti, ooidno-onkoidni krečnjaci i dolomitični krečnjaci, 15. Slojeviti i bankoviti krečnjaci sa amonitima litiotisima, dolomitični krečnjaci I dolomiti, 16. Uslojeni dolomiti, krečnjaci sa megalodonima i dolomitske breče, 17. Bankoviti krečnjaci sa megalodonima i dolomitske breče, 18. Lofer formacija gornjeg trijasa, 19. Rabelj formacija: gline laporci, alevroliti, pješčari i krečnjaci, 20. Formacija crvenih trijaskih boksita, 21. Ladinski sedimenti: Sprudni krečnjaci ladinika; Tufovi i tufiti sa rožnacima; 22. Andeziti i piroklastiti srednjeg trijasa; 23. Bankoviti i masivni krečnjaci i dolomiti; Anizijski fliš; Hanbuloški krečnjaci, 24. Sajski klastiti i kampilski slojevi: škriljci, pješčari, laporci i krečnjaci; Škriljci, alevroliti, pješčari i bituminozni krečnjaci, 26. Crveni boksiti: a) izdanak rudnog tijela, b) tragovi boksita duž eroziono-diskordantne granice, 27. Projekcija utvrđenog rudnog tijela crvenog boksita, 28. Jalovište

Red jurassic bauxites of Vojnik-Maganik and Prekornica mining areas

- The largest and highest quality deposits of red bauxite in Montenegro are located in Vojnik-Maganik and Prekornica regions.

UNDERLYING (footwall) CARBONATE SEDIMENTS:

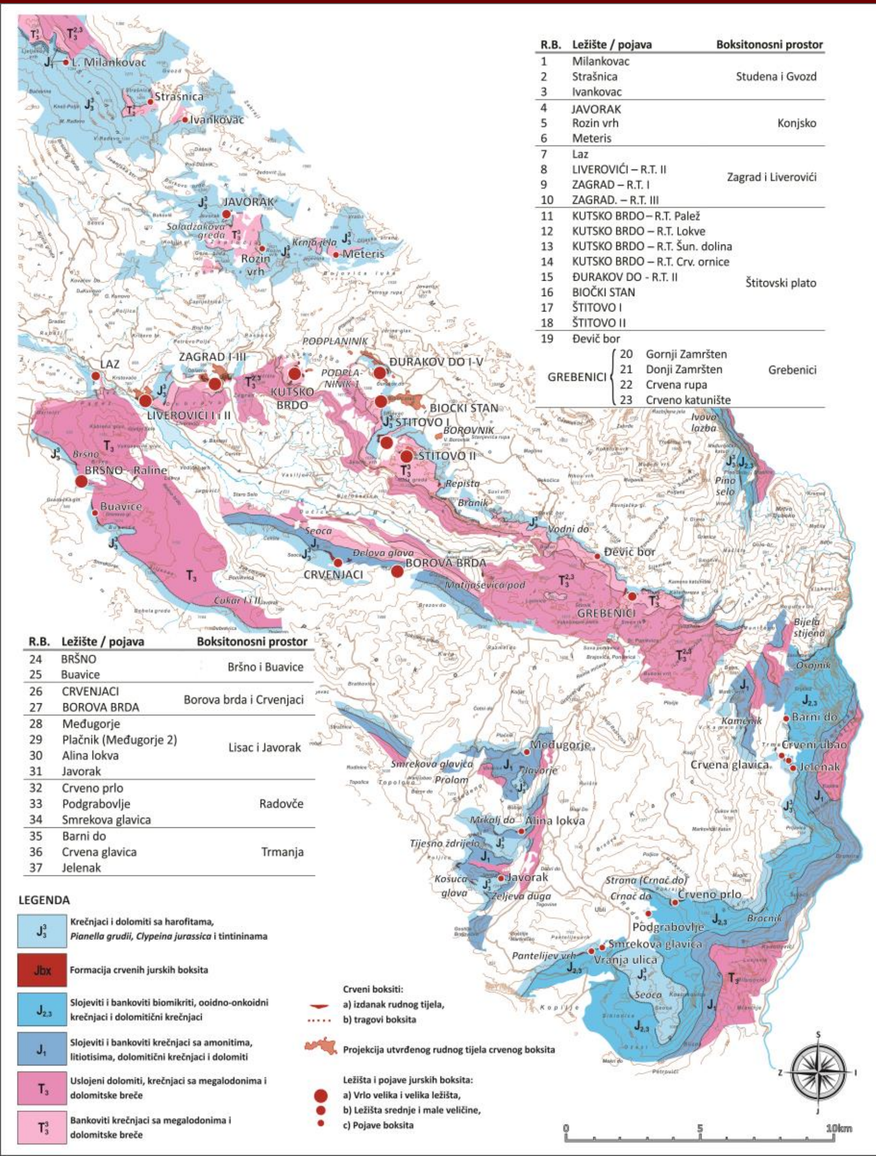
- ***Limestones with Megalodons and dolomitic breccias of Late Triassic age (T_3^3)***
- ***Carbonate sediments of Early Jurassic age (J_1)***
- ***Carbonate sediments of Middle and Late Jurassic age ($J_{2,3}$)***

- ***Jurassic red bauxites (Jbx)***

OVERLYING (hanging wall) CARBONATE SEDIMENTS:

- ***Carbonate sediments of Late Jurassic age (J_3)***

SAMPLES AND ANALYTICAL METHODS

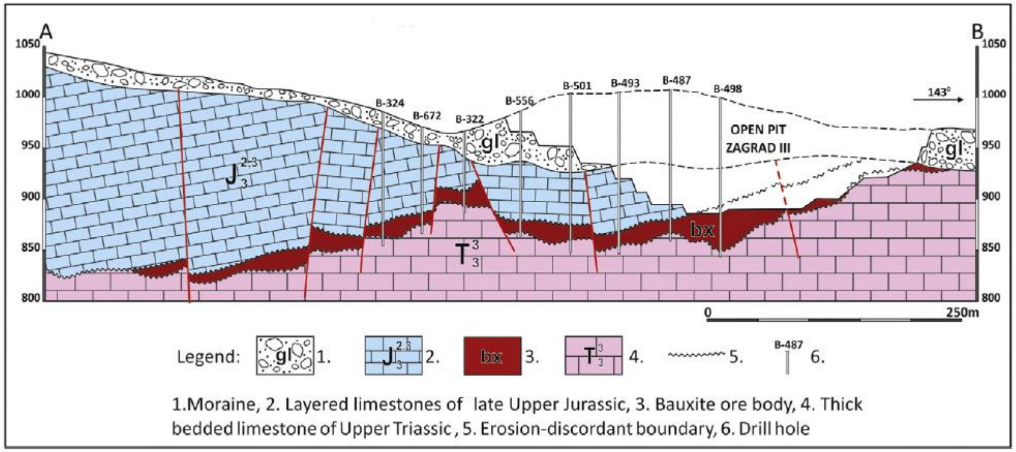


- **Applied methods**:
  - Recording of detailed geological profiles of bauxite bodies at the 37 locality, 47 profiles in total.
  - Sampling by unique principle.
  - Formation of individual samples for geochemical analyzes
  - After the geochemical analyzes were performed, samples were selected for mineralogical testing.

  - Geochemical testing **(ICP-AES/MS)** – 252 samples (11 oxides, 17 microelements i 16 rare earth elements)
  - By using univariate statistical methods, for all oxides / trace elements, was calculated: **x_{min}, x_{max}, $\ddot{x}$, σ i Cv**:
    - For the total population
    - By stratigraphic affiliation of underlying rocks(three classes)
    - By genetic affiliation (two classes)
    - By position in the profile (three classes)
    - By structural type (five classes)

  - Mineralogical testing **(XRD)** - 64 selected samples of bauxites from 15 locations.
  - Mineralogical testing **(SEM-EDS)** - 34 selected samples from 15 locations.

SAMPLES AND ANALYTICAL METHODS



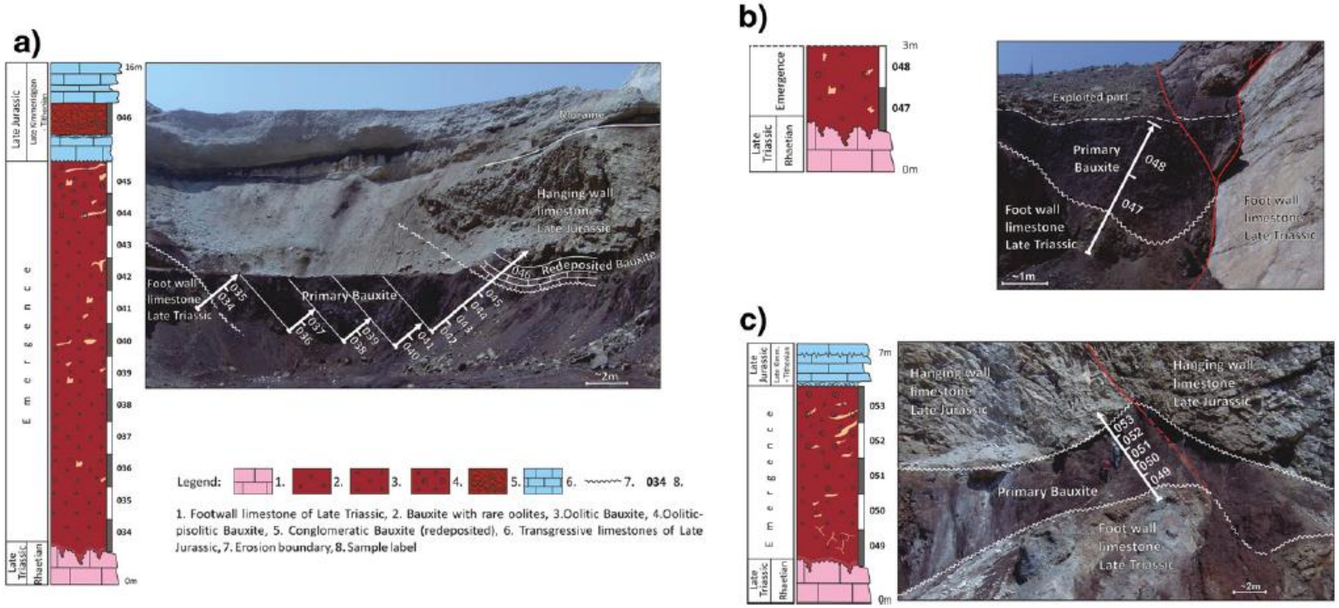


Fig. 3. Field photographs illustrating the palaeocarst terrain, ore body features and overburden of the Zagrad bauxite deposit, ore body 3 in the geological section I (a); the geological section II (b); the geological section III (c).

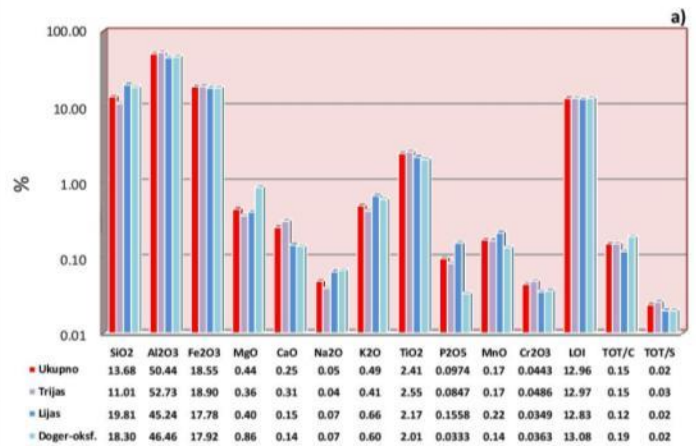
RESULTS AND DISCUSSION

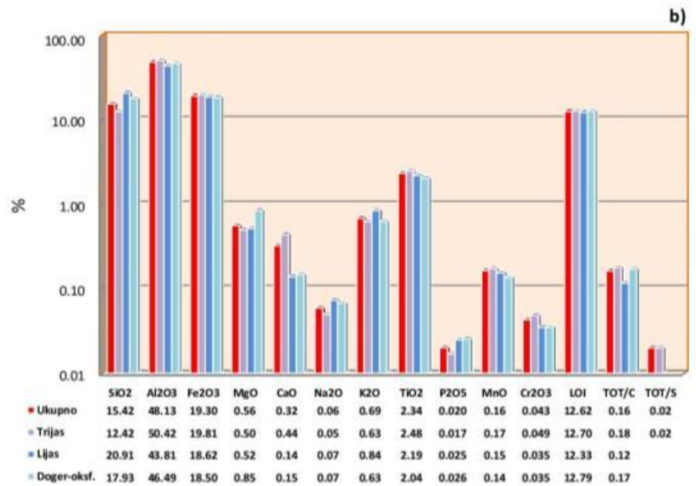
- Many studies have shown that bauxites are enriched with trace elements (Ga, Ti, Cr, Zr, V, etc.) as well as rare earth elements (Rare Earth Elements - REE).
- In particular, karstic bauxites are richer with rare earth elements in comparison to lateritic bauxites *(Mameli et al., 2007; Hanilçi, 2013 et al)*
- Geochemical and mineralogical studies of microelements and REEs in karst bauxite deposits in Montenegro and the Mediterranean show that REEs are extremely mobile during the process of bauxitization of parent material *(Maksimović and Roaldset, 1976; Maksimović and Pantó, 1991, etc.).*
- REEs in bauxites are bound to different groups of minerals *(Maksimovic et al., 1998; Mameli et al., 2007, etc.),* primarily with the ***bastnasite group*** as the most represented autogenic REE minerals.
- ***REE phosphates*** such as monacite– (Nd), monacite– (La) and neodymium-rich goyazite are less represented.

Geochemical testing (ICP-AES/MS)

Results – oxides, C, S

Age of the Underlying rocks	Stat. par.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	G.Ž.	Tot. /C	Tot. /S
		%	%	%	%	%	%	%	%	%	%	%	%	%	%
Bauxites Vojnik–Maganik and Prekornica (total) (n 252)	Min	1.00	33.50	2.56	0.07	0.03	0.01	0.01	1.53	0.010	0.02	0.021	11.3	0.05	0.02
	Max	30.17	69.73	26.15	2.05	11.14	0.10	2.02	3.50	0.710	1.64	0.096	20.2	2.37	0.03
	ẍ	14.79	48.89	19.04	0.52	0.35	0.06	0.62	2.36	0.051	0.17	0.044	12.76	0.17	0.024
	σ	6.70	5.72	2.83	0.28	1.14	0.02	0.39	0.36	0.109	0.17	0.014	0.92	0.24	0.01
	Cv	0.45	0.12	0.15	0.53	3.26	0.38	0.64	0.15	2.131	1.02	0.316	0.07	1.39	0.22
Bauxites at Late Triassic (n 160)	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
	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
	ẍ	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
	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
	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
Bauxites at the Early Jurassic (n 51)	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	
	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	0.02
	ẍ	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	
	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	
	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	
Bauxites at the Middle – Late Jurrasic (n 41)	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	
	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	0.02
	ẍ	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	
	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	
	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	





Histograms of the mean contents of the analyzed oxides, C and S, in the Vojnik – Maganik and Prekornica bauxites, formed on the upper Triassic, Liassic and Dogger-Oxfordian age: lower part of ore bodies (a); middle and upper part ore bodies (b). ICP-EAS and ICP-MS (VMP_04)

Geochemical testing (ICP-AES/MS)

Results – microelements

Age of the Underlying rocks	Stat. Par.	Rb ppm	Cs ppm	Be ppm	Sr ppm	Ba ppm	Th ppm	U ppm	Zr ppm	Hf ppm	V ppm	Nb ppm	Ta ppm	W ppm	Co ppm	Ni ppm	Ga ppm	Sn ppm
Bauxites of the ore region Vojnik–Maganik and Prekornica (total) *(n* = 252)*	Min	0.4	0.1	2	27.7	17	29.1	2.6	328.7	9.2	177	31.2	2.3	4.3	11.9	51	29.2	7
	Max	142.7	20.8	15	1406.6	204	70.0	24.3	641.4	17.7	850	68.5	5.0	9.9	539.3	678	57.8	43
	ẍ	43.16	8.42	5.71	91.32	85.64	49.66	5.70	450.02	12.72	291.52	45.13	3.45	6.40	41.68	197.58	47.11	15.08
	σ	32.39	4.97	2.66	136.59	44.43	6.70	2.33	63.97	1.66	76.96	6.67	0.48	0.95	49.64	73.79	4.02	5.05
	Cv	0.75	0.59	0.47	1.50	0.52	0.14	0.41	0.14	0.13	0.26	0.15	0.14	0.15	1.19	0.37	0.09	0.33
Bauxites at the Late Triassic *(n = 160)*	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
	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
	ẍ	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
	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
	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
Bauxites at the Early Jurassic *(n = 51)*	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
	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
	ẍ	58.94	10.43	5.50	131.8	106.1	46.35	5.80	420.62	11.65	286.60	41.96	3.13	5.76	46.94	219.91	45.34	15.20
	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
	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
Bauxites at the Middle-Late Jurassic *(n = 41)*	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
	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
	ẍ	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
	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
	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

Geochemical testing (ICP-AES/MS)

Results – rare earth elements

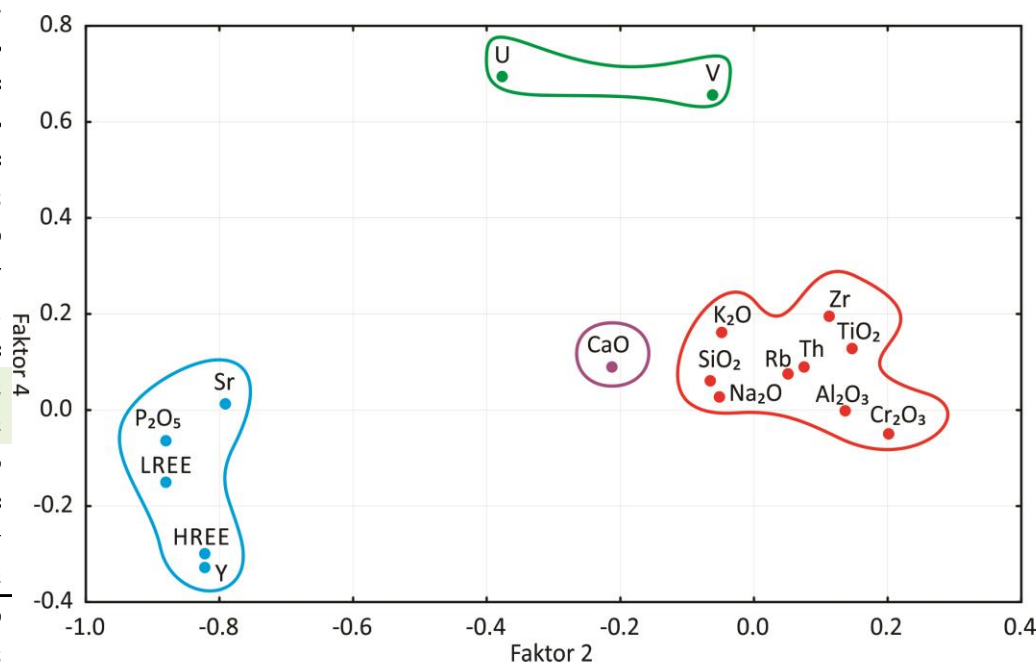
Age of the Underlying rocks	Stat. par.	Sc ppm	Y ppm	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm
Bauxites of the ore region Vojnik–Maganik and Prekornica (total) *(n* = 252)*	Min	38	62.6	87.7	159.5	13.02	44.3	8.36	1.85	8.69	1.65	10.59	2.26	6.58	1.00	6.40	0.98
	Max	159	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
	ẍ	57.45	136.0	225.11	360.31	37.80	138.22	24.84	5.29	24.24	3.86	23.07	4.81	13.98	2.12	13.66	2.09
	σ	10.93	136.88	253.89	107.41	45.80	177.21	31.15	6.56	30.59	4.31	23.45	4.54	12.04	1.69	10.27	1.56
	Cv	0.19	1.01	1.13	0.30	1.21	1.28	1.25	1.24	1.26	1.12	1.02	0.94	0.86	0.80	0.75	0.74
Bauxites at the Late Triassic *(n = 160)*	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
	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
	ẍ	58.41	131.6	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
	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
	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
Bauxites at the Early Jurassic *(n = 51)*	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
	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
	ẍ	58.00	128.3	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
	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
	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
Bauxites at the Middle-Late Jurassic *(n = 41)*	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
	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
	ẍ	51.84	161.1	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
	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
	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

Application of bivariate and multivariate statistical methods

Factor analysis - emphasizes poorly expressed but often significant anomalies of individual elements with the aim of pointing to associations of macro and microelements and rare earth elements.
Factor analysis of data from the VMP_04 basic matrix distinguishes four important factors:

	Factor 1	Factor 2	Factor 3	Factor 4
SiO_2	**−0.85918**	−0.064490	0.247744	0.063657
Al_2O_3	**0.91626**	0.135740	0.210895	−0.003031
Fe_2O_3	0.407608	0.300725	0.325691	−0.309956
MgO	−0.570322	0.138146	0.089036	−0.343542
CaO	−0.247921	−0.213475	**−0.78488**	0.089460
Na_2O	**−0.85670**	−0.053150	0.402944	0.025705
K_2O	**−0.79205**	−0.047118	0.448516	0.159908
TiO2	**0.85145**	0.147833	0.274260	0.130655
P_2O_5	0.272053	**−0.88045**	0.208933	−0.063706
Cr_2O_3	**0.75145**	0.202891	0.008260	−0.048498
Ni	−0.503262	−0.582436	−0.330607	0.243366
Sc	0.631768	−0.517665	0.297193	−0.157918
Ba	**−0.74311**	−0.092551	0.521814	0.238082
Co	−0.090586	−0.557059	−0.488346	0.328440
Rb	**−0.77184**	0.050110	0.460206	0.077717
Sr	0.260625	**−0.79091**	0.223022	0.012271
Th	**0.72270**	0.075801	0.118461	0.089348
U	0.344096	−0.376655	−0.018386	**0.69282**
V	0.255298	−0.060446	0.329790	**0.65453**
Zr	**0.86428**	0.114103	0.269662	0.195389
Y	0.134770	**−0.82197**	0.020032	−0.329168
LREE	0.243852	**−0.88164**	0.174395	−0.149397
HREE	−0.095743	**−0.82250**	0.087299	−0.301023
Expl.Var	8.271714	4.868822	2.522581	1.706650
Prp.Totl	0.359640	0.211688	0.109677	0.074202

- Factor 1: Al_2O_3, TiO_2, Cr_2O_3, Zr, Th, SiO_2, Na_2O, K_2O, Ba, Rb, (+Ni, +Mg);
- Factor 2: P_2O_5, Sr, Y, LREE, HREE, (+Sc, +Co);
- Factor 3: Ca(+Ba) i
- Factor 4: U, V .



Application of bivariate and multivariate statistical methods

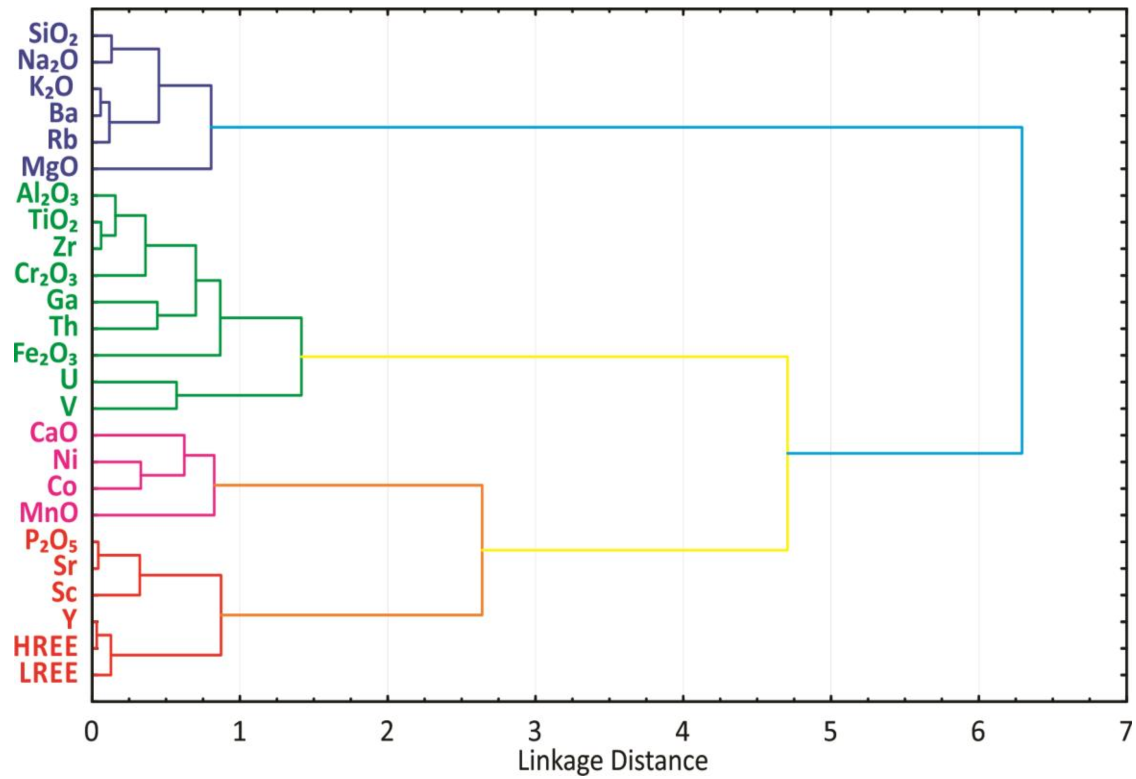
- **Cluster analysis** - the interpretation of geochemical data with the aim of defining **subtle relationships** among variables or patterns. Relationships between variables or patterns are determined by grouping them into groups or clusters based on the similarity of the measured attributes.

  - To the **first group** belongs: P_2O_5, Sr, Sc, Y and REE.
    - Highest correlation has Y and HREE which are further correlated with LREE.
    - High correlation has P_2O_5 and Sr which are correlated with Sc.

- **Second group** is composed of : Mn, Co, Ni, CaO.
  Ni and Co that are best correlated in this group.

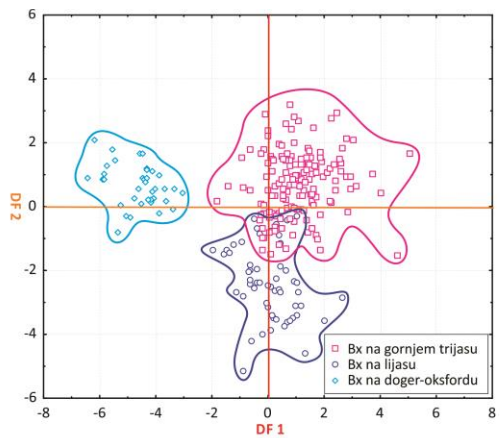
- To the **third group** belongs: TiO_2, Zr, Al_2O_3, Cr, ali i Ga, Th and Fe – elements concentrated in bauxites, as well as U and V.

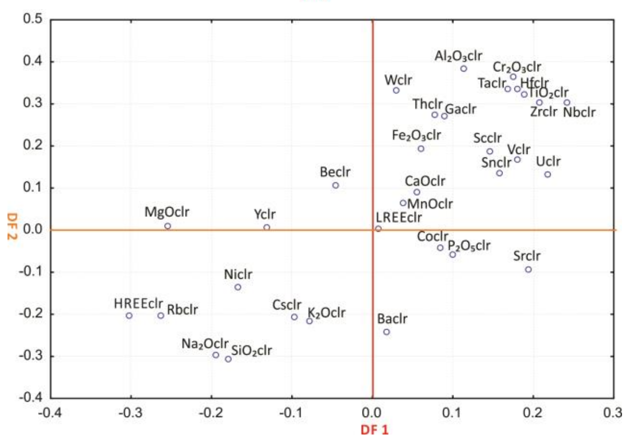
- The **fourth group** is represented by Si, Na, K, B, Rb and Mg elements which are leached in the process of bauxitization of the primary alumosilicate material.



Application of bivariate and multivariate statistical methods

Discriminate Analysis - allows the study of differences between two or more groups of objects based on a number of variables observed simultaneously. The matrices were processed on clr (central log-ratio) transformed geochemical test data, for two databases (VM-02 and VMP-04, STATISTICA 7) for the following geological criteria: age of the underlying carbonate rocks, genetic type, position and structural type. We show two models:





In the first model, based on the VMP_04crl database, the age of the underlying rocks was separated as an independent geological criterion with respect to the measured variables, ie the contents of the tested oxides and trace elements.

DF1's first feature separates bauxite samples from carbonate rocks of Late Triassic and Early Jurassic age from those from Middle-Late Jurassic age: on the left side of the sample diagram are bauxites formed on carbonate rocks of Middle-Late Jurassic age, and also variables SiO_2, Na_2O, K_2O, MgO, Rb and Ni.

We can assume that the parent material from which these bauxites came from, contained magnesium silicate minerals and nickel.

It is also possible that the conditions at later genesis were more reductive, and the material itself points to an origin from the ophiolitic zone.

On the other side of the diagram are bauxites formed on the carbonate rocks of Late Triassic and Early Jurassic age. They are characterized by: Al_2O_3, Cr_2O_3, Fe_2O_3, TiO_2, V and a number of other elements indicating oxidation conditions.

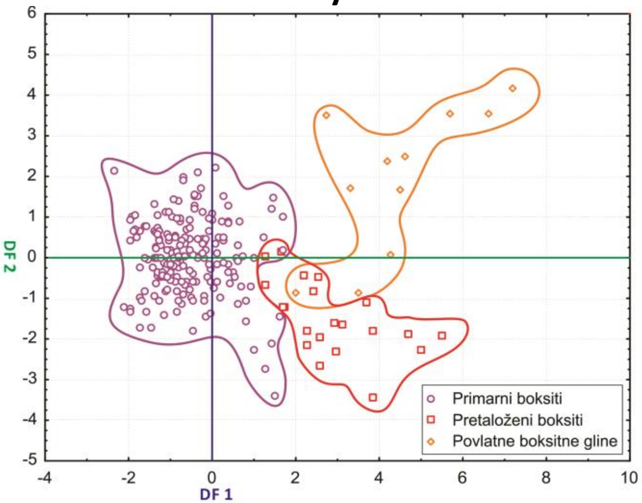
Based on the first discriminant function, we can assume that similar conditions prevailed during the bauxitization process Late Triassic and Early Jurassic age.

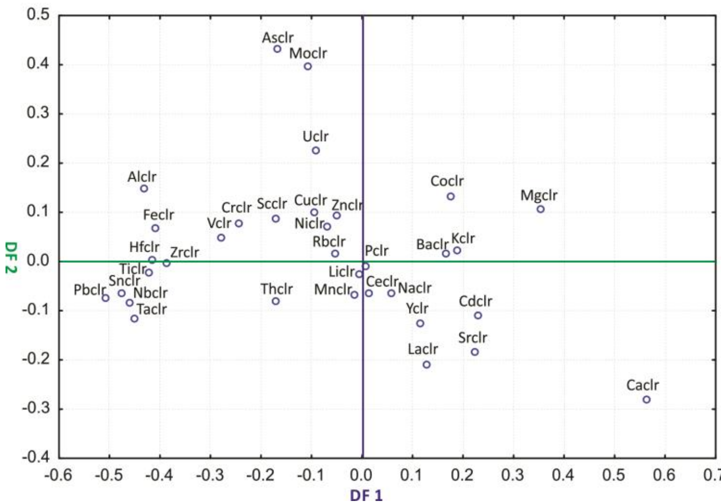
The second discriminant function (DF2) contains residual variability that separates bauxites formed on Late Triassic carbonate rocks from bauxite formed on carbonates of Early Jurassic age.

Bauxites formed on Late Triassic underlying rocks are, in a relative sense, more enriched with the characteristic oxides and elements - Al_2O_3, Cr_2O_3, Fe_2O_3, TiO_2, V, Ga, etc., while they are "absent" in bauxites formed on carbonates of Early Jurassic age.

Application of bivariate and multivariate statistical methods

Discriminant analysis





The second model was made on the basis of the VM_02 database, based on the genetic type as an independent geological criterion in relation to the measured variables, ie the contents of the macro and microelements examined.

The first discriminatory function of DF1 separates samples of primary bauxites from redeposited bauxites and underlying bauxite clays.

On the left side of the sample diagram are the primary bauxites and the variables Al, Fe, Ti, Cr, V, Zr, Hf, Cr, Pb, Nb, Ta, etc., indicating a higher degree of bauxitization of the parent material than the other two groups of samples .

On the right side of the diagram are: Ca, Mg, Na, K, Sr, Ba, etc., which are mostly extracted from primary bauxites.

The second discriminant function (DF2) contains residual variability, which separates redeposited bauxites and the domain of primary deposits from transgressive bauxite clays.

Redeposited bauxites are characterized by the relative "enrichment" of Ca, Na, Sr and Cd, relative to the bauxite clays having "higher" Mg, Co and especially U, Mo and As, indicating reduction conditions in the first stages of transgression.

Mineralogical testing (X-ray diffraction **XRD**)

Results - XRD

- Bauxites of the ore region Vojnik–Maganik and Prekornica are of complex mineralogical composition.
- The main carrier of aluminium in them is the mineral boehmite. Other major minerals are: Fe-oxides/hydroxides (hematite and goethite); clay minerals (kaolinite) and titanium minerals (mainly anatase).
- The following minerals were also detected: phosphates with REE (monazite and xenotime); REE carbonates–Ce and REE carbonates–Nd; ilmenite; magnetite; motramite, biotite; K-feldspar; certain sulphides and silicates. A regular mineral present in the silicate group is zircon.
- The chemical composition of bauxite from the Vojnik–Maganik and Prekornica ore regions is consistent with mineralogical characteristics.
- The studied deposits can be classified into the genetic class of karstic bauxites *(Bárdossy, 1981)*, or the class of so-called primary deposits of karst bauxites *(Pajović, 2000, 2009).*

Results of semi-quantitative analysis of 64 samples of bauxites (mass %)

004-154 bauxites from carbonate rocks of Late Triassic age *(38)*
168-215 bauxites from carbonate rocks of Early Jurassic age *(14)*
216-244 bauxites from carbonate rocks of Middle-Late Jurassic age *(12)*

L.B.	boehmite	hema-tite	anatase	calcite	kaoli-nite	goethite	gibbsite
(004)	27	18	4	–	41	10	–
(006)	29	20	3	–	44	3	–
(008)	44	15	3	2	33	2	–
(029)	52	19	4	–	23	2	–
(030)	61	1	5	–	31	2	–
(032)	67	20	2	–	10	1	–
(034)	68	19	3	–	9	1	–
(035)	70	20	2	–	6	1	–
(040)	77	20	2	–	1	–	–
(045)	77	19	2	–	1	–	–
(046)	77	14	2	2	5	–	–
(047)	83	11	2	–	3	–	–
(048)	74	19	2	–	4	1	–
(049)	64	19	1	13	2	–	–
(051)	73	20	2	–	5	1	–
(053)	79	17	2	–	1	–	–
(070)	87	2	2	–	9	–	–
(073)	66	22	2	–	8	1	–
(074)	71	20	2	–	6	1	–
(075)	71	21	2	–	6	1	–
(076)	69	22	2	–	7	1	–
(081)	59	22	2	–	15	2	–
(084)	59	26	2	–	10	2	–
(086)	73	18	2	–	6	1	–
(088)	68	24	2	–	6	1	–
(095)	70	23	2	–	5	1	–
(099)	69	22	2	–	7	1	–
(103)	54	22	3	–	19	2	–
(107)	51	21	2	–	23	2	–
(130)	51	21	2	–	23	2	–
(132)	59	23	3	–	14	2	–
(134)	60	23	2	–	13	2	–
(135)	46	20	4	–	27	3	–
(143)	54	24	3	–	17	2	–
(150)	49	23	3	–	22	2	–

L.B.	boehmite	hema-tite	anatase	calcite	kaoli-nite	goethite	gibbsite
(151)	55	22	3	–	18	2	–
(153)	54	21	3	–	20	2	–
(154)	54	21	3	–	20	2	–
(168)	50	21	3	–	23	2	–
(174)	48	21	3	–	26	3	–
(177)	47	22	3	–	25	3	–
(179)	60	6	4	–	29	2	–
(180)	57	26	2	–	14	1	–
(184)	52	21	3	–	21	2	–
(187)	52	20	3	–	22	3	–
(188)	36	18	4	–	31	1	10
(191	41	20	3	–	33	3	–
(193)	40	21	3	–	33	2	–
(195)	38	19	3	–	37	3	–
(211)	45	23	3	–	26	2	–
(213)	41	24	4	–	29	2	–
(215)	32	18	4	–	44	2	–
(216)	56	11	4	–	26	3	–
(217)	55	18	3	–	22	2	–
(218)	60	18	3	–	17	2	–
(219)	60	19	3	–	17	2	–
(230)	51	24	2	–	22	2	–
(231)	51	23	2	–	22	2	–
(232)	54	22	2	–	21	2	–
(233)	50	21	3	–	24	2	–
(241)	55	10	4	–	28	2	–
(242)	48	20	3	–	27	2	–
(243)	44	24	3	–	27	3	–
(244)	50	17	4	–	28	2	–

Mineralogical testing (Scanning Electron Microscope with Energy-Dispersive Spectrometer **SEM-EDS**)

Results – SEM-EDS

Mineral composition of tested bauxite samples
determinate by SEM-EDS analysis , *30 samples (17, 7, 6)*

Mark.	A	B	C	D	REE minerals				Silicates			Ilm	Mgt	Mtr	S	X
					Mnz	Kst	REE-C Ce	REE-C Nd	Zrn	Bt	Kfs					
006	●	●	●	●	●				●			●				
030	●		●	●	●				●	●				●		
040	●	●	●	●	●		●		●							
045	●	●	●	●					●							●
046	●	●		●	●	●			●			●			●	
073	●	●			●	●			●			●				
074	●	●		●	●	●	●		●			●	●			
075	●	●	●	●	●	●			●			●				
076	●	●	●	●	●				●			●			●	
088	●	●	●	●	●	●			●			●				
095	●	●		●		●	●		●						●	
099	●	●		●		●			●							
103	●	●	●	●	●	●			●			●				
107	●	●		●	●	●			●		●					
130	●	●	●	●		●			●							
135	●	●	●	●	●	●			●			●				
153	●	●	●	●		●			●			●				
168	●	●	●	●	●	●			●			●			●	
179	●	●	●		●				●							
180	●	●	●		●	●		●	●							
184	●	●	●	●		●			●							
187	●	●	●	●		●			●							
188	●	●	●		●	●			●			●				
215	●	●	●	●					●							
216	●	●	●	●	●	●			●			●				
217	●	●	●		●	●			●			●				
218	●	●	●		●	●			●							
219	●	●	●		●		●		●							
230	●	●	●		●				●				●			
243	●	●	●		●	●			●			●				

- **Minerals of rare earth elements in bauxites*:***
- ***Fluor– carbonate group of REE minerals***
- ***Phosphate group of REE minerals***

A – Al-hydroxides, B – Fe-oxi/hydroxides, C – clay minerals, D – TiO_2 minerals, ***Mnz – monazite, Kst – xenotime, REE-C – REE carbonate minerals****, Zrn – zircon, Bt – biothite, Kfs – K-feldspar, Ilm – ilmenite, Mgt – magnetite, Mtr – mottramite, S – sulfides, X –* unidentified *minerals.*

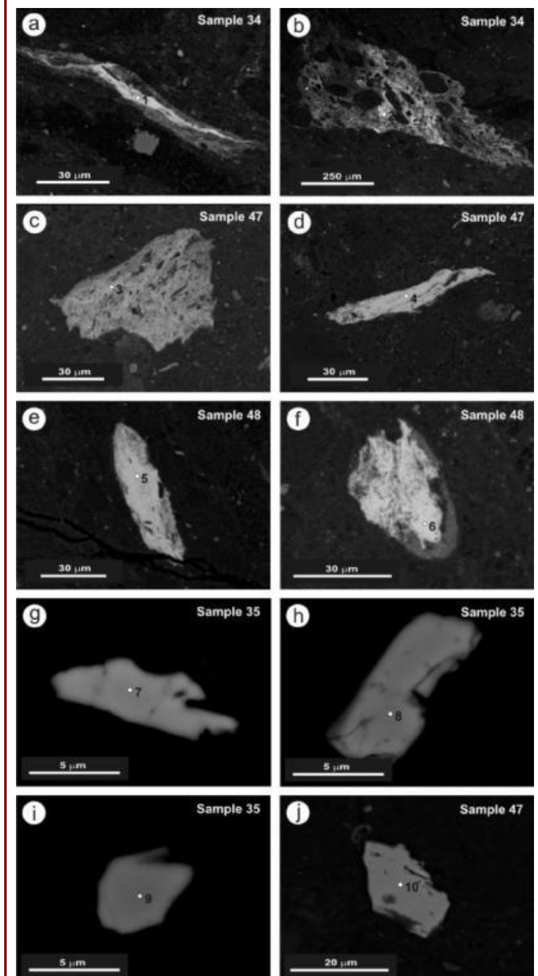
Mineralogical testing (Scanning Electron Microscope with Energy-Dispersive Spectrometer **SEM-EDS**)

Results – SEM-EDS

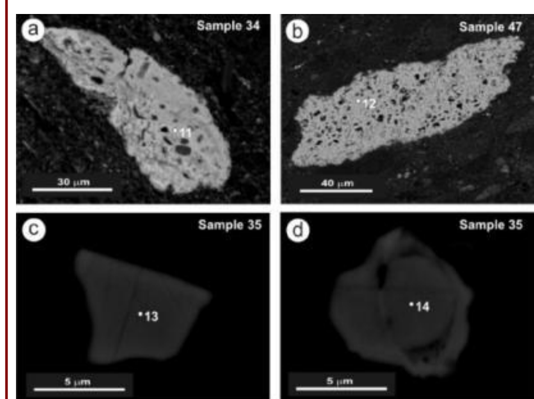
Representative analysis of electronic microprobe of REE minerals from Zagrad deposits *(in mass %, normalized at 100%; empty field– not discovered)*

	Monacite–Nd Authigenic mineral Total number of analysis – 1						Monacite–Ce Residual phase analysis – 4				Xenotime Authigenic mineral Total number of analysis – 3		Xenotime Residual phase Total number of analysis – 3	
Uzo-rak br.	034		047		048		035			047	034	047	035	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Al_2O_3	4.4	4.0	6.2	1.1	1.0	1.2	1.8	0.4	0.4	0.4	2.1	1.7		
SiO_2	2.9	0.9	3.6					0.4			2.7	4.9	1.1	1.7
P_2O_5	28.0	24.7	26.3	29.1	28.5	27.6	29.6	32.3	29.8	30.6	31.9	30.8	37.1	37.8
SO_3	1.7	1.1	1.7	1.4	1.3	1.4								
K_2O			0.5											
CaO	3.4	3.1	3.0	3.4	3.6	3.2		1.1			2.4	1.7		
Sc_2O_3											0.6	0.4		
TiO_2	0.6	0.4					0.4		0.4				0.4	0.3
V_2O_5		0.9									1.5	0.6		
FeO	2.3	10.4	1.6	1.4			2.5	1.9	1.3	0.8	4.3	3.5	2.0	1.9
Y_2O_3											34.9	49.9	41.0	41.6
La_2O_3	8.2	9.0	11.2	14.6	12.7	15.1	16.6	12.3	12.2	16.4				
Ce_2O_3	10.3	7.8	4.8	3.8	4.4	4.0	32.0	26.5	33.4	34.0				
Pr_2O_3	4.5	4.8	5.2	5.8	5.8	6.0	3.4	3.3	3.9	3.7				
Nd_2O_3	20.7	23.1	25.9	28.3	28.9	29.1	11.0	12.0	14.3	10.8	1.6			0.4
Sm_2O_3	5.6	6.4	5.3	6.1	6.4	6.5	1.3	2.5	1.9	2.1	1.2	0.7		0.6
Eu_2O_3					1.5									
Gd_2O_3	4.4	2.8	3.0	3.8	4.2	4.1	0.8	1.6	1.8	1.2	5.5	1.6	2.8	3.1
Dy_2O_3	2.3	0.6	1.7	1.2	1.7	1.8		1.0	0.6		6.1	1.7	5.7	5.1
Er_2O_3											2.8	1.4	4.6	3.5
Yb_2O_3											2.4	1.1	4.6	4.0
ThO_2	0.7						0.6	3.6						
UO_2								1.1					0.7	

Four types of REE phosphate were detected:
1) autigenic monazite – Nd, 2) residual monacite – Ce, 3) autigenic xenotime, and 4) residual xenotime.



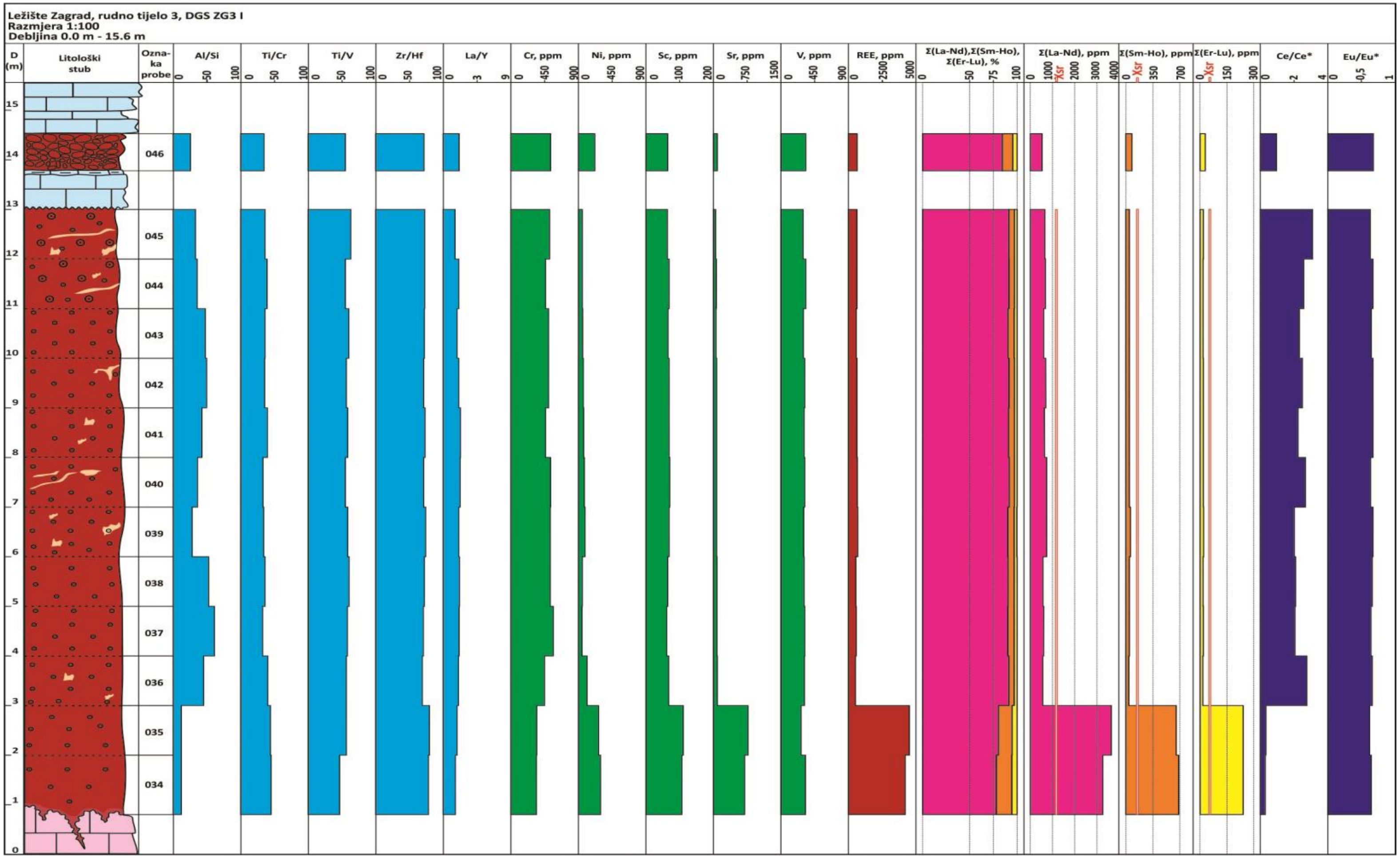
Authigenic monazite-Nd (a–f) and residual monazite-Ce (g–j) in the Zagrad deposit (BSE images). Dots and numbers represent location of electron microprobe analyses



Authigenic (a–b) and residual (c–d) xenotime in the Zagrad deposit (BSE images). Dots and numbers represent locations of electron microprobe analyses

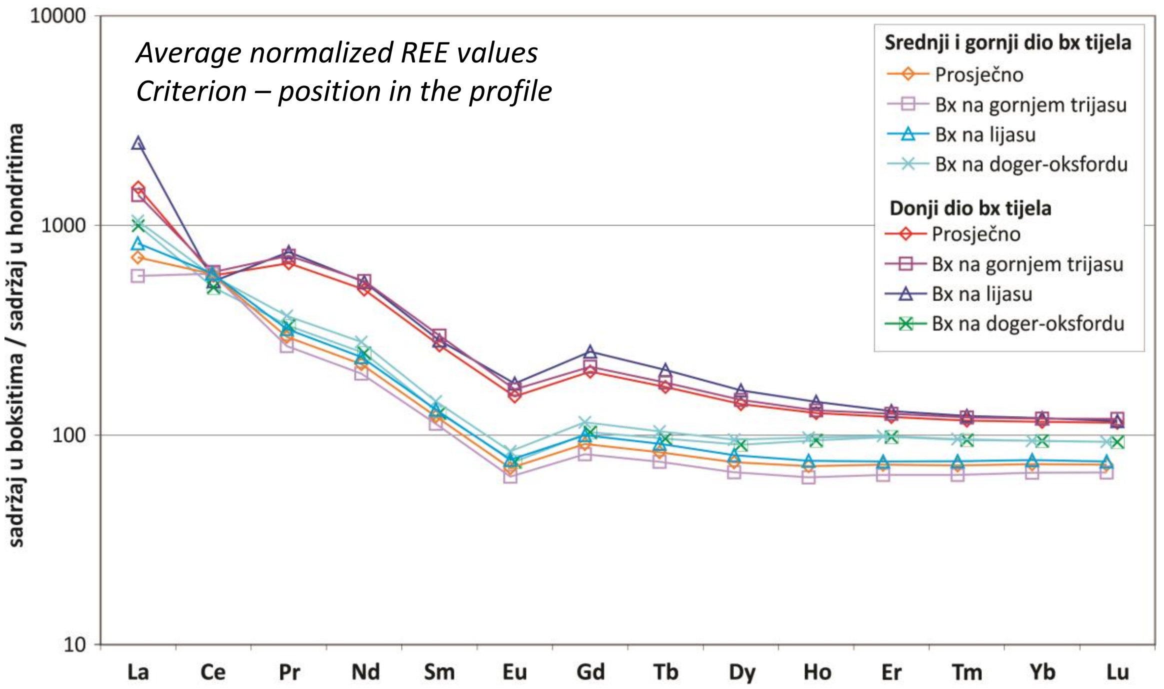
Vertical distribution of REE

- The geochemistry of rare earth elements - REE in the studied karstic bauxites is characterized by a pronounced vertical distribution, that is, enrichment in the lower part of the deposits and occurrences, especially those formed on the carbonate rocks of Late Triassic and Early Jurassic age.



Eu and Ce anomalies

- All samples show a negative **Eu anomaly**, with a relatively small range (Eu / Eu * = 0.60–0.71, average 0.66), as is the case with the karstic bauxites of Turkey (Hanilçi, 2013).
- Values are lower when compared to the Nurra deposit in western Sardinia, (Mameli et al., 2007), or the Apulian karst bauxite (Mongelli et al., 2014).



- **Anomalies of Ce** in the bauxite deposits of the Vojnik – Maganik and Prekornica ore regions show a dual behaviour. In the middle and upper part of deposits, Jurassic bauxites show positive Ce anomalies (range 0.63 to 3.1, average Ce / Ce * = 1.55).

RESULTS AND DISCUSSION

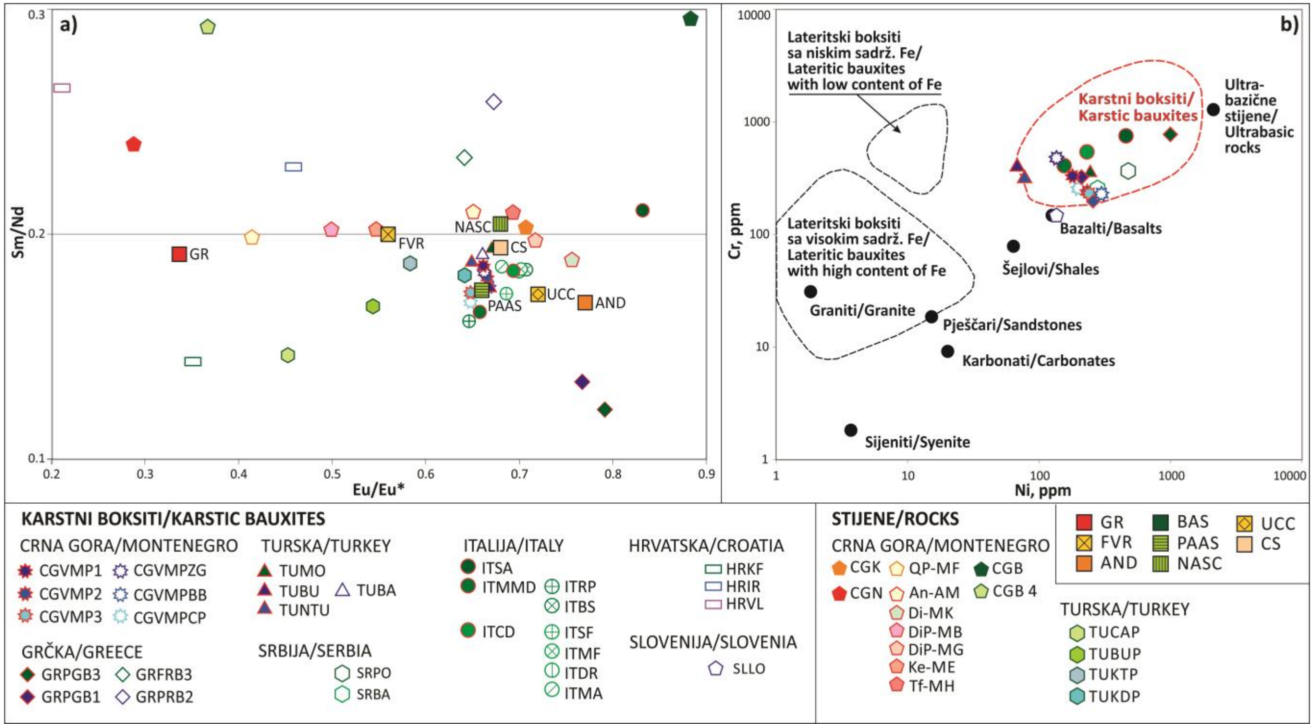
- A total of 62 deposits and occurrences of Jurassic bauxite have been discovered in the Vojnik-Maganik and Prekornica ore regions.
- Mineralogical examination of Jurassic karst red bauxite samples revealed the presence of the following minerals and groups of minerals in the tested bauxites:
  - Al-hydroxides - represented by boehmite and highly subordinate to gibbsite;
  - Fe-oxy/hydroxides - hematite and goethite;
  - Clay minerals - kaolinite;
  - TiO_2 minerals - anatase;
  - Phosphates with REE: monazite and xenotime; REE carbonates – Ce and REE carbonates – Nd;
  - Ilmenite; magnetite; mottramite, biotite; K-feldspar;
  - Certain sulphides and silicates; zircon is a regularly present silicate
- Based on geological conditions, textural, mineralogical and geochemical characteristics of bauxite, studied deposits belongs to the group of primary karstic bauxite deposits.

RESULTS AND DISCUSSION

- By geochemical study of bauxite and statistical data processing, it was found that, in the process of bauxitization of the parent material: Si, Na, K, Ba, Rb i Mg are leached. In the bauxite : Al, Ti, Fe, Zr, Cr, Ga i Th, as well as U and V are accumulated.
- P, Sr, Sc are concentrated in the lower part of bauxite bodies and, with these elements, Y and other rare earth elements.
- The presence of residual and authigenic monacite and xenotime indicates that the first REE minerals originates from primary sources, while the other are formed in the first stages of diagenesis, under oxidizing conditions.
- Analyzed based on the relationships of the characteristic elements used in the literature to determine the origin of the parent material do not give clear results.
- By studying the paleogeographic and paleotectonic processes in the Mediterranean area, and the Dinarides as a segment of Adria, during the Jurassic period, it was concluded that the source material most likely originates from the Ophiolites of the eastern belt of the Western Vardar Ophiolites.

RESULTS AND DISCUSSION

- An analysis regarding ratio of Eu / Eu * and Sm / Nd show that the Jurassic karstic bauxites of Vojnik-Maganik and Prekornica areas are the most similar to the Jurassic bauxite of Turkey and the Cretaceous bauxite of Italy, indicating shales, sandstones and intermediate magmatic rocks, as possible source rocks *(Radusinović, 2017).*
- According to the relation between the content of Ni and Cr, studied bauxites are grouped together with other Jurassic and Cretaceous karstic bauxites of Turkey, Greece, Italy, Serbia and Slovenia indicating that the origin of the alumosilicate material, Jurassic bauxites originate from, is related to the magmatic rocks of the basic composition.



MONTENEGRO: Ore Regions Vojnik–Maganik and Prekornica, *Jurassic bx, average: CGVMP1–deposits on carbonates of Late Triassic age, CGVMP2–deposits on carbonates of Early Jurassic age and CGVMP3–deposits on carbonates of Middle Jurassic-Oxfordian age; Deposits: CGVMPZG–Zagrad 3, CGVMPBB–Borova brda and CGVMPCP– Crveno prlo; CGK–acidic rocks, average, QP-MF–silified-quartz porphyries; CGN–neutral rocks, average, An-AM–andesites Kufin, An-ML–andesites Krnja jela, Di-MK–silified diorites Konjusi, DiP-MB–diorite-porphyries Konjusi, DiP-MG–silified diorite-porphyries Krnja jela, KE-ME–keratophyres Berane, Tf-MH–lithoclastic tuffs Berane; CGB–basic rocks, average, Di-MS–diabases Varine, CGB3–basalts of the northern slope of Moračka kapa;* ***GREECE:*** *GRPGB1–Jurassic bx on Early Jurassic; GRPGB3–Cretaceous bx on Lower Cretaceous, Parnassos-Ghiona geotectonic zone. GRPRB2–Prossorema, Jurassic bx on Early Jurassic; GRFRB3–Frussia, Cretaceous Bx on Lower Cretaceous, Parnassos-Ghiona, Greece, Jurassic bx B2 and Cretaceous bx B3;* ***TURKEY:*** *TUMO average values bx, Mortas district, Cretaceous bx, TUBU–Bolkardaği unit, Jurassic bx: TUNTU–Namtun tectonic unit, Jurassic bx; TUTKDP–Bolkardaği unit, protoliths-Permian shales and recrystallized limestones, TUBUP–Bolkardaği unit, protoliths-Upper Triassic phyllites-shales, recrystallized limestones and dolomites; TUCAP–Camizalani bx zone, protoliths, TUKTP–Karatas deposit, protoliths;* ***ITALY:*** *ITSA–Spinazzola, Apulia, southern Italy, Cretaceous bx. ITMMD–Matese Mts. area, average, South Apennines, Italy, Cretaceous bx: ITRP– Piana Region, Matese Mts. area, ITBS–Bocca del Selva, Matese Mts. area, ITCD–Caserta area, average, South Apennines, Italy, Cretaceous bx: ITSF– San Felice, Caserta area, ITMF– San Felice-Monte Fosco, Caserta area, ITDR–Dragons, Caserta area, ITDR–Maiorano, Caserta area;* ***CROATIA:*** *HRVL–Vrace, Lika, Triassic bx, HRIR–Istra, Rovinj, Jurassic bx, HRKF–Kordun, Frketić, Cretaceous bx;* ***SERBIA:*** *SRPO–Poćuta and SRBA–Babušnica, Cretaceous bx;* ***SLOVENIA:*** *SLLO–Slovenia, Jurassic bx;* ***PAAS****–Post-Archean Australian Shales;* ***NASC****–North American Shales Composite;* ***UCC****–Upper Continental Crust;* ***AND****–Andesite;* ***CS****–Cratonic Sandstones;* ***GR*** *–Granite;* ***BAS****–Basalts;* ***FVR****–Felsic Volcanic Rocks.*

RESULTS AND DISCUSSION

- Paleogeographical and paleotectonic processes in the Mediterranean area during the Jurassic period indicate that the original material most likely originate from the Ophiolitic complex of the Western Vardar Ophiolites, which represent the supra-subduction Ophiolite oceanic type of the island arches, with the intense appearance of effusive volcanism.
- Therefore, it is very likely that volcanic ash and/or material from the decomposition crust of this complex are the parental material from which the Jurassic karstic bauxites in the Dinarides were formed.
- Palogeographical facts support the idea of eolic transport of primary material on the karstic island areas. In conditions of tropical and subtropical climate, occasional and torrential flows, the alumosilicate material was washed and accumulated in formed palokarstic depressions, where its bauxitization was carried out.
- Based on a detailed analysis of the environment of the formation of Jurassic bauxite deposits in Vojnik-Maganik and Prekornica ore regions, as well as on analysis of the geological composition and structure of the brim erosion region, morphological characteristics of the ore bodies, control factors of their position in space and time, as well as texture, mineralogical and geochemical characteristics of bauxites, the previously mentioned deposits can be classified into the genetic class of karstic bauxites, that is to say, the class of the so-called karstic bauxites primary deposits *(Pajović, 2009).*

RESULTS AND DISCUSSION

- Issues regarding the origin of the parent material and how it is transported should be further addressed in order to verify the results achieved.
- Further researches should be directed towards paleogeographic and paleomagnetic studies (new research was launched in 2018 with colleagues from Hungary, Serbia and Austria), mineralogical studies (continued cooperation with colleagues from Serbia), as well as studies of microelements and rare earth elements in magmatic rocks and bauxites in order to contribute to the study of the genesis and complex valorization of karstic bauxites of Montenegro and Dinarides.
- One of the methods is to date zircons as done on samples of Italian karstic bauxites from Caserta province (in early 2019, cooperation with colleagues from Serbia and Germany was initiated).

RARE EARTH ELEMENTS IN SOME MEDITERRANIAN KARSTIC BAUXITES

Mark		Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	ΣREE+Y
	Ore regions Vojnik-Maganik and Prekornica																	
CGVMP1	Jurski bx na G. Trijasu	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	863.30	**994.92**
CGVMP2	Jurski bx na Lijasu	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	928.78	**1057.11**
CGVMP3	Jurski bx na Doger-oksfordu	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	858.29	**1019.43**
	Parnassos-Ghiona geotectonic zone, Grčka, Jurski B1 i B2 i Kredni B3 bx: Deady et al. 2014																	
GRPGB1	**Jurski bx na Donjoj Juri**	**44.40**	**54.50**	**178.00**	**11.50**	**62.33**	**8.40**	**1.95**	**7.20**	**1.10**	**6.90**	**1.40**	**4.10**	**0.50**	**4.30**	**0.70**	**342.88**	**387.28**
GRPGB2	**Jurski bx na Gornjoj Juri**	**159.10**	**258.35**	**427.53**	**42.95**	**149.23**	**57.20**	**12.99**	**61.00**	**8.66**	**46.88**	**9.16**	**23.46**	**3.27**	**19.01**	**2.73**	**1122.42**	**1281.52**
GRPGB3	**Kredni Bx na Donjoj kredi**	**48.30**	**64.80**	**195.00**	**7.85**	**60.39**	**7.36**	**1.87**	**7.10**	**1.82**	**8.20**	**1.90**	**5.44**	**0.99**	**6.14**	**0.94**	**369.80**	**418.10**
	Parnassos-Ghiona , Grčka, Jurski B2 i Kredni B3 bx: Laskou and Economou-Eliopoulos, 2012																	
GRPRB2	Prossorema, Jurski bx na Gornjoj Juri	263.33	295.42	648.86	42.95	220.92	57.20	12.99	61.00	8.66	47.59	9.16	23.46	3.27	19.01	2.73	1453.21	**1716.54**
GRFRB3	Frussia, Kredni Bx na Donjoj kredi	48.25	46.00	258.75	11.25	41.65	9.75	2.08	10.05	1.55	17.18	1.98	6.18	0.98	8.05	1.06	416.48	**464.73**
	Bolkardagi deposits, Karaman,Turska, Trijaski i Jurski bx: Hanilci 2013																	
TUBU	**Bolkardagi unit, Trijasko-Jurski bx**	**87.30**	**176.40**	**253.78**	**34.55**	**124.00**	**21.88**	**4.58**	**20.05**	**3.15**	**18.73**	**3.88**	**11.78**	**1.95**	**12.85**	**1.98**	**689.53**	**776.83**
TUNTU	**Namtun tectonic unit, Trijasko-Jurski bx**	**115.45**	**166.63**	**343.83**	**41.68**	**162.55**	**30.60**	**6.23**	**28.15**	**4.00**	**22.18**	**4.28**	**12.08**	**1.90**	**12.00**	**1.85**	**837.93**	**953.38**
	Istra, Rovinj, Hrvatska, Crnički, 1987																	
HRIR	Istra, Rovinj, , Jurski boksiti	62.62	124.38	193.43	26.86	105.29	24.21	3.26	19.64	3.26	12.24	3.83	6.35	1.10	5.69	1.32	580.13	**593.49**
	Spinazzola, Apulia, Southern Italy, Kredni bx: Mongelli et al., 2014																	
ITSA	**Spinazzola, Apulia, Kredni boksiti**	42.82	91.12	232.35	21.31	71.97	15.15	3.64	11.84	1.92	11.12	2.14	6.05	0.99	6.49	0.94	477.03	**519.85**
ITMMD	**Prosječno Matese Mts. District, Kredni boksiti**	**55.55**	**119.08**	**309.70**	**24.71**	**85.79**	**14.19**	**2.91**	**12.93**	**2.11**	**11.81**	**2.36**	**7.07**	**1.19**	**7.87**	**1.21**	**602.92**	**658.47**
ITCD	**Prosječno Caserta district, Kredni boksiti**	**74.38**	**124.48**	**286.91**	**30.55**	**112.95**	**20.76**	**4.35**	**17.72**	**2.68**	**14.92**	**2.88**	**8.43**	**1.28**	**8.44**	**1.27**	**637.62**	**712.00**
	Kordun, Frketić, Hrvatska. Kredni boksiti Crnički, 1987																	
HRKF	Kordun, Frketić, Hrvatska.,Kredni boksiti	55.00	139.50	190.00	28.00	101.00	14.50	2.05	22.00	2.40	8.40	3.55	3.70	0.74	4.92	0.87	521.63	**576.63**
	Vrace, Lika, Hrvatska. Trijaski boksiti Crnički, 1987																	
HRVL	**Vrace, Lika, Hrvatska. Trijaski boksiti**	**118.92**	**117.28**	**216.77**	**41.23**	**105.54**	**28.00**	**2.56**	**50.23**	**7.55**	**19.92**	**10.08**	**14.08**	**1.55**	**7.54**	**1.97**	**624.31**	**743.23**

ECONOMIC ASPECTS

- The total resources of the red Jurassic karst bauxites in the area of the Vojnik-Maganik and Prekornica ore regions, obtained on the basis of the forecast estimate, are 78 million tons.
- The question is, would it be more useful to use bauxite to produce REE and some other microelements?
- Complex utilization of bauxite deposits in terms of the use of part of deposits for production in the aluminum industry, and parts for the production of rare earth elements, may be a good solution for high quality deposits in the future.
- The fact that Montenegro has limited reserves of high quality bauxite used in the aluminum industry is in favor of justifying further study of the possibility of producing REE from bauxite.
- Most of the reserves proven so far cannot be used for the production of alumina and aluminum.
- If economically interesting concentrations of lanthanides and other trace elements are proven in these low-quality bauxites, the possibility of using them independently of the aluminum industry is created.
- The question of the possibility of extraction of rare earth elements and other microelements from red mad from the Aluminum Plant Podgorica, has also been raised.
- The total quantities of red mud in the A and B basins are cca 7.5 million tonnes and, as such, represent a significant resource.

ECONOMIC ASPECTS

- Red mud (bauxite residue) consists of the undissolved part of bauxite ore.
- Globally, 100 to 120 million t of red mud are produced annually.
- The concentrations of REEs in bauxite residue are approximately twice as high as in bauxites.

Element	Karst Bauxite Greece	Lateritic BauxiteGhana	Bauxite ResidueGreece, AoG
	ICP-MS	INAA	ICP-MS
	(mg/kg)	(mg/kg)	(mg/kg)
La	57 ± 7	19.1 ± 1.3	130 ± 1
Ce	206 ± 8	34 ± 1	480 ± 26
Pr	15 ± 1	n/a	29 ± 2
Nd	53 ± 6	13 ± 1	107 ± 0
Sm	9.8 ± 1.0	2.0 ± 0.2	19.4 ± 0.2
Eu	2.4 ± 0.9	0.8 ± 0.2	4.6 ± 1.1
Gd	10.6 ± 0.6	n/a	22.0 ± 0.3
Tb	2.3 ± 0.5	<0.5	3.3 ± 0.0
Dy	9.8 ± 0.3	n/a	20.1 ± 0.1
Ho	2.1 ± 0.1	n/a	4.1 ± 0.1
Er	7.2 ± 0.8	n/a	13.3 ± 0.3
Tm	<2	n/a	<2
Yb	7.0 ± 0.4	2.5 ± 0.3	13.8 ± 0.3
Lu	<2	0.4 ± 0.0	2.2 ± 0.0
Y	48 ± 2	n/a	108 ± 2
Nb	55 ± 9	n/a	100 ± 1
Th	51 ± 2	22.7 ± 2.3	105 ± 2
ΣLn [1]	382.3		854.4
ΣREE [2]	430.6		962.5

[1] Sum of lanthanides; [2] Sum of lanthanides and yttrium.

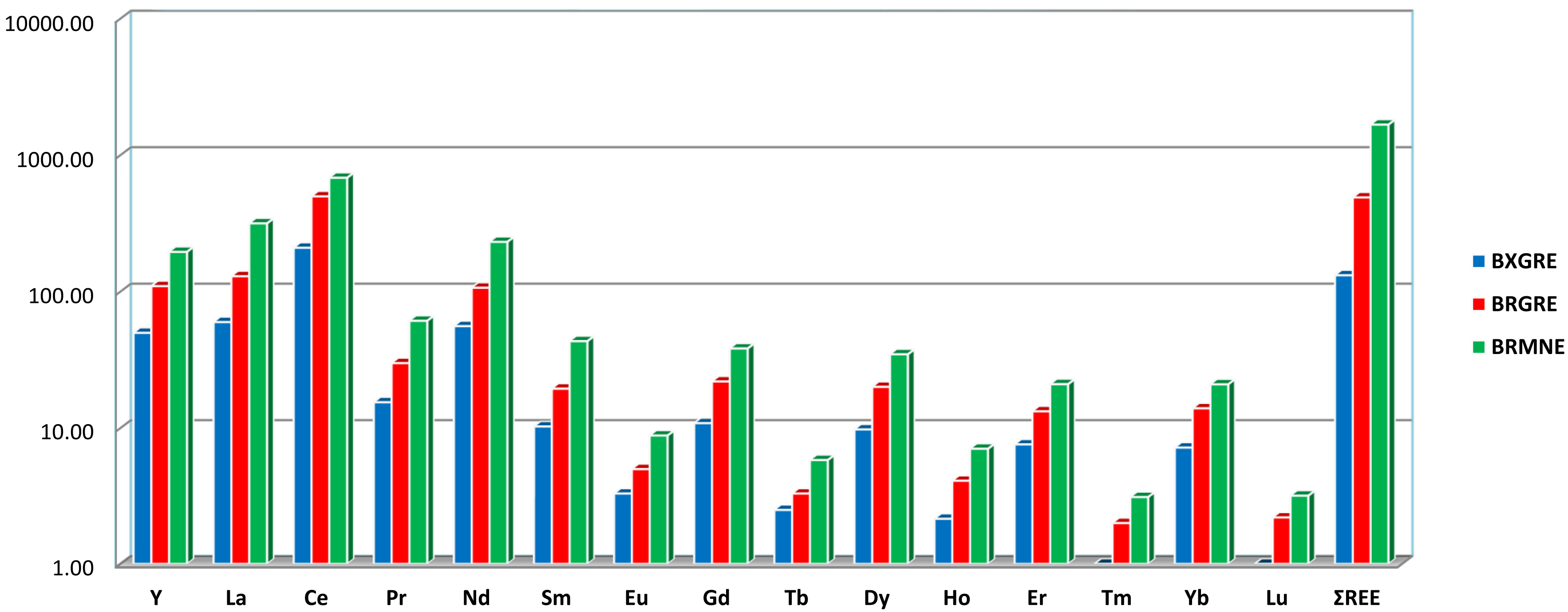
(Vind. J, et al. 2018: Rare Earth Element Phases in Bauxite Residue)

ECONOMIC ASPECTS

- REE concentrations in red mud in pools A and B - Aluminum Plant Podgorica

(Results of pilot sample analyzes, 2019)

Bazen	Sc ppm	Y ppm	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	∑REE+Y+Sc ppm
A	121	207.7	327.1	664.2	58.46	216.4	40.01	8.24	36.43	5.74	34.93	7.28	22.28	3.29	22.26	3.32	1778.64
B	111	184.2	306.9	704.4	64.05	247.4	46.95	9.44	40.39	5.92	34.71	6.84	19.78	2.93	19.7	3.05	1807.66



ECONOMIC ASPECTS

- Existing and new quantities of red mud can be considered as an important resource for the extraction of critical metals such as REE, metals of greater economic importance for Europe such as Ti and V, but also base metals such as Al and Fe.
- The goal of several projects that have been completed or are in the process of being implemented is the development of innovative and sustainable technology for the production of important metals from red mud: ENEXAL, EURARE, REECover, REE4EU, REMAGHIC.
- A project is in implementation phase in Greece to extract scandium from red mud, at the AoG plant in Agios Nikolaos. The project is in the pilot phase. New so-called ionic liquids are being used. This is a research within the Scandium Aluminum Europe - SCALE project. (http://scale-project.eu/objectives/)
- Project **Recovery of Critical Metals from the Bauxite Residues (red mud) of the primary alumina refining industry - Mud2Metal,** deals with all REEs and also envisions the use of ionic liquids or common acids for extraction.

ACKNOWLEDGMENTS

Ministry of Economy of Montenegro

Geological Survey of Montenegro

Uniprom metali d.o.o. Nikšić, Bauxite mines

Colleagues and professors from

Geological Survey of Montenegro

Faculty of mining and geology, Belgrade

Croatian Geological Institute, Zagreb

THANK YOU!!!

ZAVOD ZA GEOLOŠKA ISTRAŽIVANJA CRNE GORE

Geological Survey of Montenegro