

CARNIAN BAUXITES AT MULJAVA IN CENTRAL SLOVENIA

KARNIJSKI BOKSITI NA OBMOČJU MULJAVE V OSREDNJI SLOVENIJI

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We have investigated the composition of Muljava Carnian bauxites. In the Muljava area in Central Slovenia bauxites of the Karst type have been discovered; these bauxites occur in several 10-m-thick horizon between the underlying Cordevolian and overlying Julian-Tuvallian carbonate rocks. Based on their texture the bauxites are predominantly iron-rich oolitic bauxites. However, they vary considerably in their mineral and chemical compositions in all directions. The main constituent minerals are kaolinite, boehmite, goethite, hematite and quartz. In addition, several particularities of the Muljava bauxite deposits are discussed.

Key-words: Bauxites, composition, textural particularities, EDS, WDS, Carnian, Lower Carniolia, Dinaric Carbonate Platform, Slovenia

Članek obravnava sestavo muljavskih karnijskih boksitov, ki so bili odkriti na območju Muljave v osrednji Sloveniji in so kraškega tipa. Pojavljajo se v več deset metrov debelem horizontu med spodaj ležečimi cordevolskimi in zgoraj ležečimi juljsko-tuvallskimi karbonatnimi kamninami. Po strukturi pripadajo večinoma železnatemu oolitnemu boksitu. Mineralna in kemična sestava boksitov se znatno spreminja v vseh smereh. Glavni minerali v njihovi sestavi so kaolinit, boehmit, getit, hematit in kremen. V članku razpravljamo tudi o nekaterih posebnostih muljavskih boksitov.

Ključne besede: boksiti, sestava, struktura, posebnosti, EDS, WDS, karnij, Dolenjska, Dinarska karbonatna platforma, Slovenija

1 INTRODUCTION

Detailed geological investigations in the framework of the systematic regional field mapping for the Geological Map of Slovenia on a scale of 50,000 have been performed in the Muljava area and its wider surroundings. Between Muljava and the hamlet Vrhe a 1.5-kilometre-wide belt of the relatively heterogeneous Middle and Upper Carnian rocks crops out, being important, primarily, because of the iron-rich bauxites in the lowermost part of the Julian-Tuvallian stratigraphic sequence. The bauxite deposits lie unconformably upon the superficially eroded Cordevolian dolomite and under a 350-m-thick variegated Julian-Tuvallian predominantly carbonate stratigraphic sequence passing gradually upwards into the Upper Triassic Principal Dolomite in the Lofer development¹. A sketch map of the study area is shown in **Figure 1**.

The scope of our work was to explore the Muljava Bauxite Member and to define its lithological, mineralogical and chemical composition, its boundaries, size, stratigraphic position and textural particularities.

Geographically, the investigated area belongs to the Dolenjska District² and from the geological and geotectonic points of view to the Dinaric Carbonate Platform and the Dolenjska-Notranjska Mesozoic Blocks, respectively^{2,5}. The area has been investigated several times²⁻¹⁰.

2 EXPERIMENTAL PROCEDURES

The main geological data presented in this work were obtained during the systematic regional and detailed geological mappings in the field for the Geological Map of Slovenia on a scale of 50,000, executed in this part of

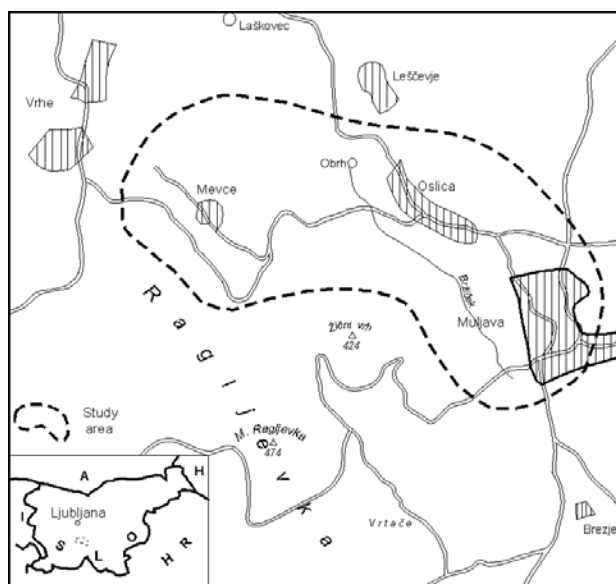


Figure 1: Location sketch map of the investigated area
Slika 1: Lokacijska skica zemljevida področja raziskav

Slovenia by the Geological Survey of Slovenia in the years 2005 to 2007. Detailed stratimetric measurements as well as a sedimentological and facial study of the Carnian sedimentary succession were performed as well. The carbonate rocks are classified according to the practical petrographic classification of limestones¹¹ and the classification of carbonate rocks according to the depositional texture¹². The Muljava bauxite deposits are classified according to Valeton's classification of bauxites^{13,14}.

The microstructure of the bauxites was investigated with field-emission scanning electron microscopy FEG SEM JEOL JSM 6500F operating at a 15-kV accelerating voltage of the primary electron beam. The back-scattered-electron images were taken at 0.1 nA, and on the same spot the X-ray signal was collected from the $Fe_{K\alpha 1}$, $O_{K\alpha 1}$, $Si_{K\alpha 1}$, $Al_{K\alpha 1}$, $Ti_{K\alpha 1}$, $Mn_{K\alpha 1}$ and $K_{K\alpha 1}$ transitions to obtain the energy-dispersive spectroscopy (EDS) X-ray mapping. Some structural details were microchemically analyzed with EDS and the EDS analyses were obtained from larger areas and averaged. The chemical compositions were calculated from the EDS measurements by stoichiometric calculation, considering the analysed element oxygen. The samples for electron microscopy were cut from larger pieces and dry ground up to 2400 SiC grinding paper. Additionally, the quantitative microanalyses were carried out using wavelength-dispersive spectroscopy (WDS) measurements (INCA CRYSTAL 400) in order to clarify the larger oxygen content, as this was expected in bauxite minerals. An accelerating voltage of 20 kV was used and a probe current of 10.24 nA was applied. The standard reference material orthoclase ($KAlSi_3O_8$) was considered to be appropriate for these measurements. The measurements were performed on four different surface features over an area of $100 \mu m \times 80 \mu m$ and on several smaller features with an appropriately smaller site of interest.

3 RESULTS

3.1 Muljava bauxite deposits

The Muljava oolitic bauxites occur in a wide band extending from Muljava to the hamlet Vrhe. The bauxites are trapped in the Cordevolian carbonate rocks as a wide zone of outcrops striking NW-SE and dipping towards the northeast. The Muljava bauxite deposits are built of two varieties: yellow-orange and brown-red bauxites of different chemical and mineral properties. The stratigraphic position of the Muljava Bauxite is shown in **Figure 2**.

Underlying carbonate rocks – Footwall

The footwall of the Muljava bauxite deposits is built of light grey, very light grey and occasionally white, massive (prevalent) or bedded, more or less coarse-grained (crystallized, sparitic) dolomite with sections of

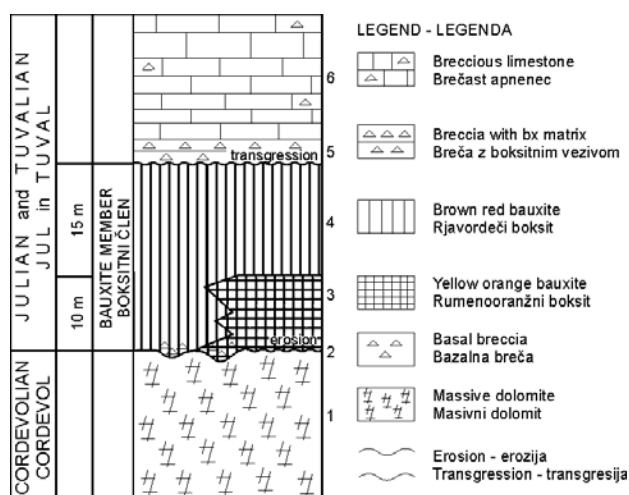


Figure 2: Stratigraphic position of the Muljava Bauxite Member
Slika 2: Stratigrafska lega muljavskega boksitnega člena

green algae Dasycladacea, mostly of the genus *Diplopore* and species *Diplopore annulata* Schafhäütl, which occurs in Slovenia in the Cordevolian beds. The upper surface of the Lower Carnian beds is karstified and due to karstification it is fairly irregular. The coarse-grained Cordevolian dolomite originated during the late diagenetic processes from the biostromal, inrasparitic and inrasparuditic *Diplopore* limestones. Intensified epirogenetic movements at the end of the Cordevolian epoch contributed to the shallowing of the sea. Afterwards, Cordevolian carbonate rocks were in spots exposed to karstification, erosion and weathering. These conditions enabled the origin of terra rossa and bauxites, which are, however, in the main part of eolian origin.

Muljava Bauxite Member

The lowermost and basal rock unit in the Carnian (Julian and Tuvalian) Oslica stratigraphic sequence is represented by a 25-m-thick bauxite horizon, the Muljava Bauxite Member respectively, consisting of three parts: 1) the basal calcareous breccia, 2) the yellowish orange oolitic bauxite, and 3) the brown-red iron oolitic bauxite.

Basal calcareous breccia occurs in the form of lenses close above the dolomite paleorelief. The basal breccia consists of angular fragments of light grey coarse-grained Cordevolian dolomite bound with calcitic cement and a limonitic matrix. The thickness of the basal breccia does not exceed one metre.

Yellowish orange bauxites form the up to 10-m-thick lower part of the Muljava bauxites. The upper boundary of these bauxites is flat, and the lower one, representing the contour of the terrain, is fairly irregular and causes a minor variability in the thickness of the bauxite. The yellow-orange bauxites include varieties of yellow, yellowish orange, brownish orange and light brown colour. There are also samples of a gentle rose colour.

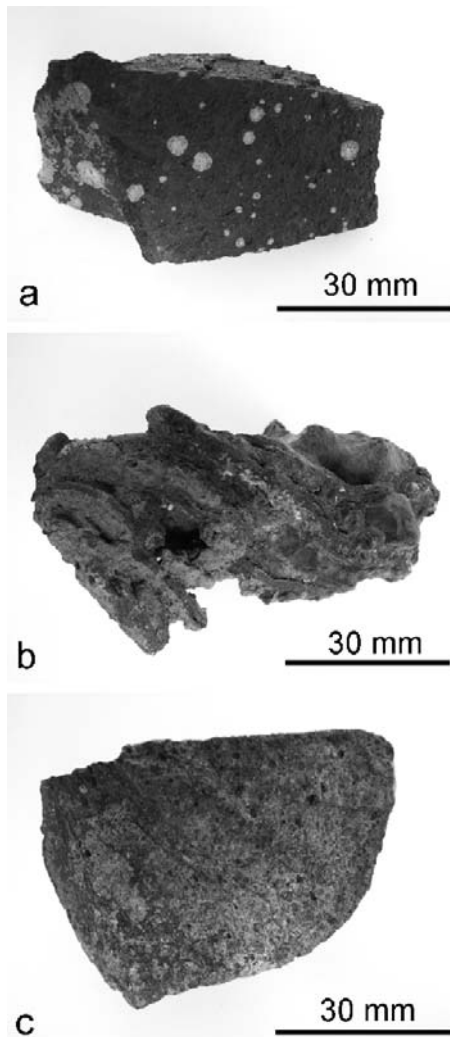


Figure 3: Macrograph of bauxite mineral (a) Muljava 3 (b) Muljava 6 and (c) Muljava 8

Slika 3: Makroposnetek boksitnega minerala (a) Muljava 3 (b) Muljava 6 in (c) Muljava 8

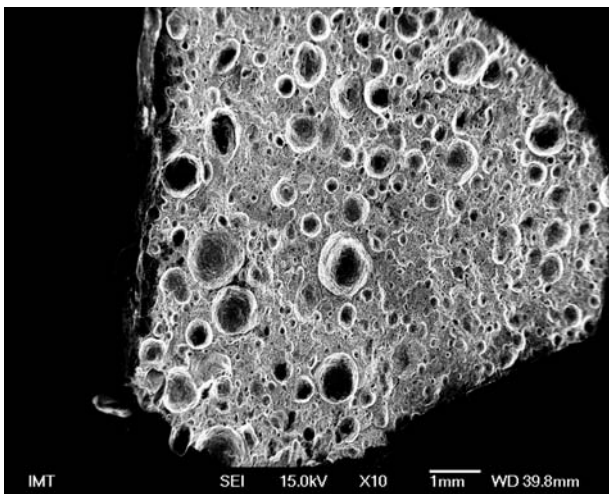


Figure 4: Electron micrograph (secondary-electron image) of Muljava 3 sample – fracture surface

Slika 4: Elektronska slika (slika sekundarnih elektronov) vzorca Muljava 3 – prelomna površina

The yellow-orange bauxites are massive and have the pelitic as well as the oolitic texture. The oolitic texture is not quite homogeneous, because ooids are not as numerous as in the overlying brown-red bauxites.

Brown-red bauxites are of reddish brown, brick-red, brownish red and dark red colour varieties, and mostly oolitic and pisolitic bauxites lying in the up to 15-m-thick upper part of the Muljava Bauxite Member. The bauxites are relatively homogeneous and very compact, and without stratified structures. Pisolites and the pisolitic texture are much less frequent than ooids and the oolitic texture. Pisolites form dark red grains in the bauxite of various sizes, from several millimetres to one centimetre and a half. Their arrangement can be different, but chiefly they are randomly scattered in the bauxite mass. Pisolites are of a homogeneous structure or concentrically layered with an increasing content of iron towards the centre of the pisolites.

Source material and the origin of bauxites

The Muljava brown-red oolitic bauxites were formed during weathering of the coarse-grained (“saharoid”) poorly bound predominantly massive Lower Carnian (Cordevolian) dolomite and in the eolian way. On the basis of reference data and our investigations it is not possible to estimate the part of autochthonous bauxite material and the rate of matter brought by winds.

Our investigations indicate that Triassic yellow-orange bauxite deposits in the Muljava area consist of clay, bauxitic clays and clayey bauxites. Their source is considered to be the weathered material of adjacent brown-red iron-rich oolitic bauxites. In some places the

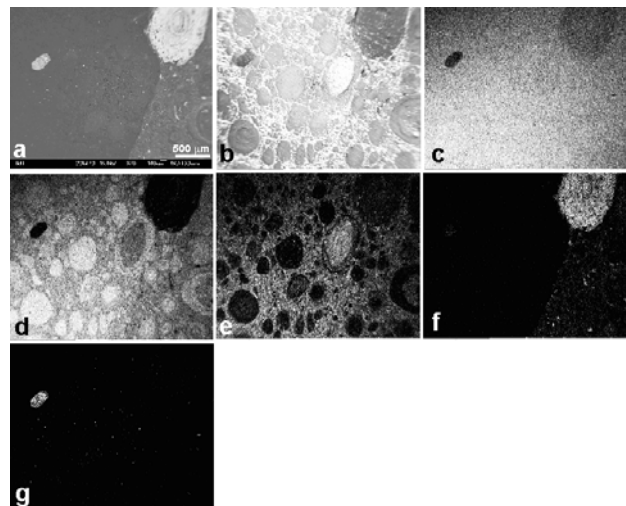


Figure 5: EDS X-ray mapping of Muljava 3 grinded sample (a) backscattered-electron image, (b) secondary-electron image and corresponding X-ray images (c) O $K_{\alpha 1}$ (d) Al $K_{\alpha 1}$ (e) Si $K_{\alpha 1}$ (f) Fe $K_{\alpha 1}$ (g) Ti $K_{\alpha 1}$

Slika 5: Rentgenska EDS ploskovna porazdelitev elementov brušenega vzorca Muljava 3 (a) slika odbitih elektronov, (b) slika sekundarnih elektronov in pripadajoče rentgenske slike (c) O $K_{\alpha 1}$ (d) Al $K_{\alpha 1}$ (e) Si $K_{\alpha 1}$ (f) Fe $K_{\alpha 1}$ (g) Ti $K_{\alpha 1}$

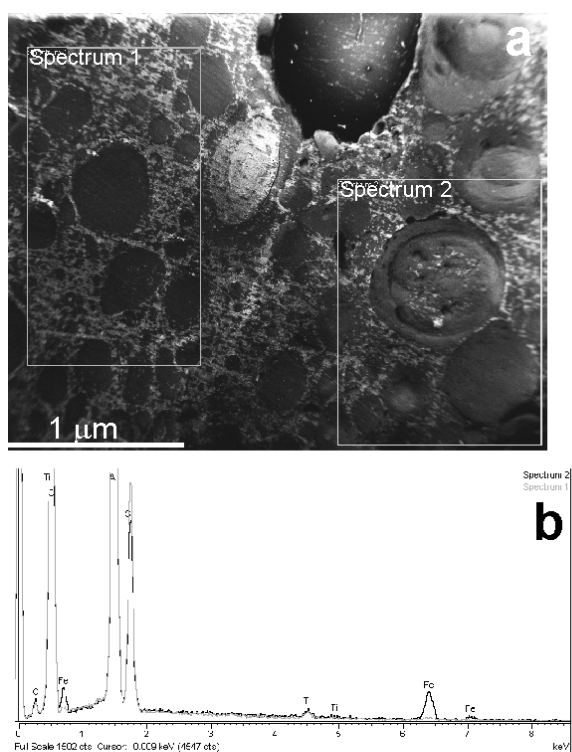


Figure 6: (a) Electron micrograph (secondary-electron image) of Muljava 3 ground surface with marked areas of EDS analysis, (b) EDS spectra, (c) chemical composition of both analyses in mole fractions (%)

Slika 6: (a) Elektronski posnetek (slika sekundarnih elektronov) brušenega vzorca Muljava 3 z označenimi področji, kjer je bila narejena EDS analiza, (b) EDS spektra, (c) kemična sestava obeh analiz je navedena v molskih deležih (%)

brown-red oolitic bauxites were decomposed, eroded, transported and accumulated (trapped) in adjacent depressions and consolidated into a fairly compact yellow-orange bauxite ore. Occasionally, individual broken layers and irregular patches of brown-red oolitic bauxites are preserved in the yellow-orange oolitic bauxites. Accordingly, the yellow-orange oolitic bauxites are resedimented brown-red oolitic bauxites.

Overlying sediments – Hanging wall

The described Muljava Bauxite Member is progressively overlain by an about 350-m-thick fairly heterogeneous and gray-coloured sedimentary succession composed of various limestones, dolomites, calcareous breccias, marlstones, and subordinately variegated clastic rocks, that starts with basal calcareous breča with a bauxitic matrix.

Limestone breccia with a bauxitic matrix. The hanging wall sedimentation starts with transgressive limestone breccia with a bauxitic matrix. On the

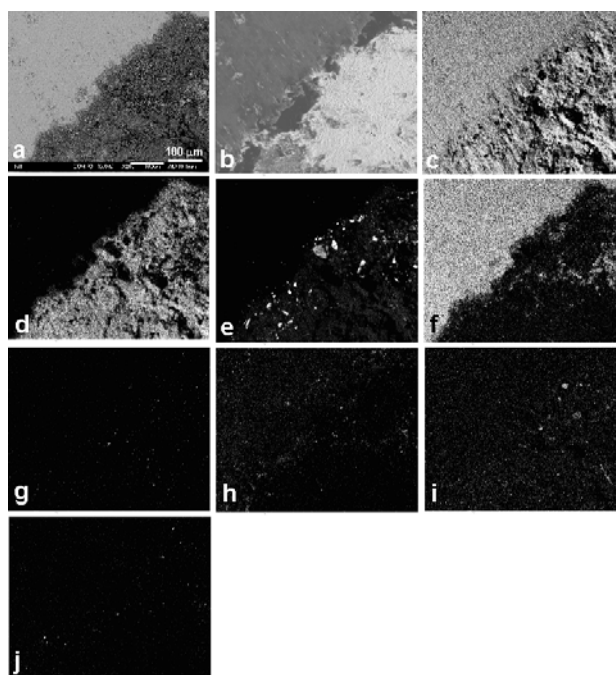


Figure 7: EDS X-ray mapping of Muljava 3 grinded sample (a) backscattered-electron image, (b) secondary-electron image and corresponding X-ray images, (c) O K α 1 (d) Al K α 1 (e) Si K α 1 (f) Fe K α 1 (g) Ti K α 1 (h) Mn K α 1 (i) K K α 1 (j) Ca K α 1

Slika 7: Rentgenska EDS ploskovna porazdelitev elementov brušenega vzorca Muljava 3 (a) slika odbitih elektronov, (b) slika sekundarnih elektronov in pripadajoče rentgenske slike, (c) O K α 1 (d) Al K α 1 (e) Si K α 1 (f) Fe K α 1 (g) Ti K α 1 (h) Mn K α 1 (i) K K α 1 (j) Ca K α 1

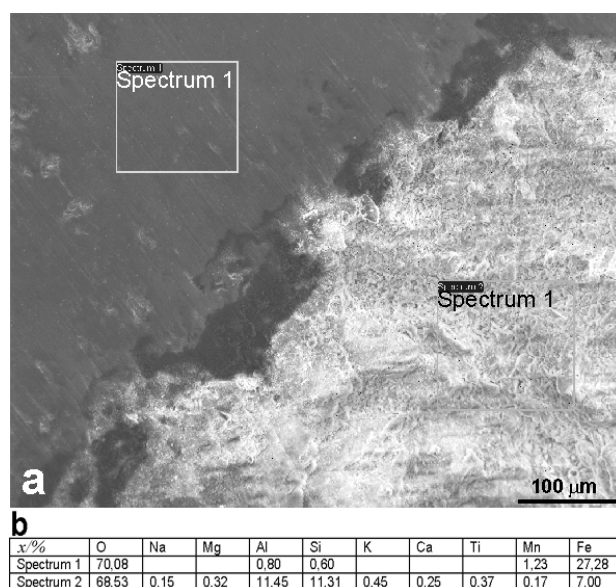


Figure 8: (a) Electron micrograph (secondary-electron image) of Muljava 6 ground surface with marked areas of EDS analysis, (b) chemical composition of both analyses in mole fractions (%)

Slika 8: (a) Elektronski posnetek (slika sekundarnih elektronov) brušenega vzorca Muljava 6 z označenimi mesti, kjer je izvedena EDS analiza, (b) kemična sestava obeh analiz v molskih deležih (%)

boundary between the bauxite horizon and the Julian thick-bedded limestone occurs an about 1-m-thick lenslike bed of brownish grey medium-grained compact limestone breccia bound with a limonitic and bauxitic matrix. It consists of minor and bigger angular fragments, black and grey micritic and rarely sparitic limestones belonging to the lowermost Julian sedimentary succession.

3.2 Microstructural examination

Muljava bauxites 3, 6 and 8 were chosen for detailed structural and microchemical analyses (**Figure 3**). The compositions of all three bauxites are shown in **Table 1**. **Table 2** shows the results of the elemental composition converted to oxides. The Muljava 3 sample was fractured and the fracture surface was investigated (**Figure 4**). Small ooids with sizes from 0.1 mm up to 1 mm form the convex fracture surface topography, while larger pisolites of yellow colour are not distinguished in the secondary-electron mode of imaging. The polished Muljava 3 sample surface was investigated with EDS X-ray mapping (**Figure 5**). The left part of the image represents a larger pisolite of light yellow colour with a lower iron concentration. The EDS analyses of the light yellow and dark red-brown regions are shown in **Figure 6**. The spectra of the respective regions as well as the corresponding chemical compositions are also shown. The amount of oxygen, aluminium and silicon is similar, while in the red-brown region the titanium and iron contents are higher. Also, the additional measurements shown were similar results. EDS X-ray mappings were obtained on a polished surface of the sample Muljava 6 (**Figure 7**). The analysis area was chosen to show both bauxite minerals, dark-brown and yellow in the left-top and in the right-bottom part of the EDS map, respectively. The left-top region is rich in iron and fairly uniform concerning other elements' distribution. On the other hand, the right-bottom region has non-uniformly distributed silicon, iron and potassium. The results of the local areas EDS measurements show a much higher iron content in the dark-brown layer and a higher concentra-

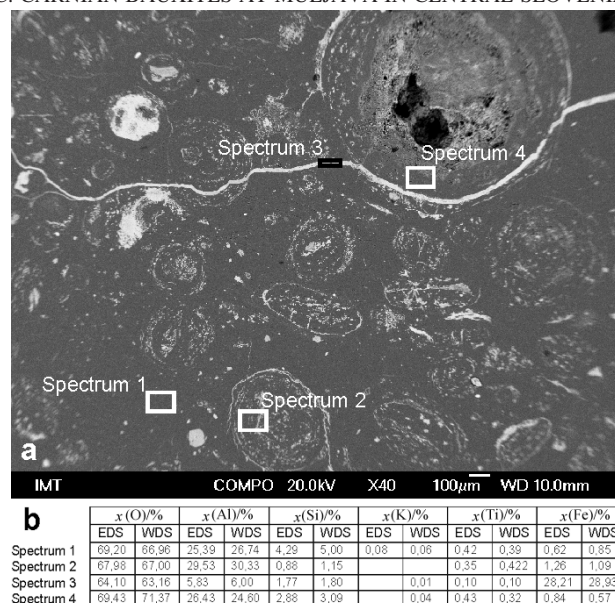


Figure 9: (a) Electron micrograph (secondary-electron image) of Muljava 8 grounded surface with marked areas of EDS and WDS analyses. (b) Chemical composition of four spectra obtained by EDS and WDS in mole fractions (%)

Slika 9: (a) Elektronski posnetek (slika sekundarnih elektronov) brušenega vzorca Muljava 8 z označenimi mesti, kjer je bila izvedena EDS in WDS analiza, (b) kemična sestava v molskih deležih (%), dobljena z EDS- in WDS-analizo

tion of aluminium and silicon in the yellow layer (**Figure 8**). Microchemical analyses using EDS and WDS were performed on exactly the same areas as the sample Muljava 8. The sample seems to be more homogeneous, except for the thin curved iron-rich layer. The results of the oxygen-content measurements obtained with both analyzing techniques are very similar (**Figure 9**). The reliability of the measurements was additionally checked against several standards: $\text{NaAlSi}_3\text{O}_8$ (albite), Al_2O_3 , SiO_2 and CaSiO_3 (wollastonite). With reference to these standards none of the two analytical techniques, WDS or EDS, measures the elemental concentrations in mole fraction with an error greater than 1.5 %. The oxygen concentration in mole fraction measured in all three Muljava samples is approximately 20 % too high to match the data-processing software proposed for the

Table 1: Chemical composition of Muljava 3, 6 and 8 bauxite in mole fractions (%)

Tabela 1: Kemična sestava boksitnega vzorca Muljava 3, 6 in 8 v molskih deležih (%)

x/%	O	Mg	Al	Si	K	Ca	Ti	Mn	Fe
Muljava 3	70,82	–	21,44	5,99	–	–	0,27	–	0,21
Muljava 6	68,88	0,12	10,16	4,96	0,16	0,13	0,14	0,19	19,15
Muljava 8	70,07	–	24,15	3,77	–	–	–	–	1,54

Table 2: Chemical composition of of Muljava 3, 6 and 8 bauxite calculated to oxides in mass fractions (%)

Tabela 2: Kemična sestava boksitnega vzorca Muljava 3, 6 in 8 v masnih deležih, preračunano na okside

x/%	Al_2O_3	SiO_2	MnO	TiO_2	MgO	CaO	K_2O	FeO
Muljava 3	68,06	24,05	–	1,60	–	–	–	6,29
Muljava 6	14,07	15,53	4,16	0,54	0,24	0,36	0,38	64,72
Muljava 8	75,73	14,89	–	2,38	–	–	–	7,00

compounds Al_2O_3 , SiO_2 and FeO . Our previous X-ray diffraction (XRD) measurements showed [to be published] that Si and Al create kaolinite rather than quartz and alumina oxide and the Fe might be incorporated into hematite, goethite or limonite. Having this in mind, the calculation is far more correct and only a little excess oxygen is obtained, which can be explained by surface oxygen contamination.

4 CONCLUSIONS

Muljava with the wider surroundings is built of Triassic rocks belonging to three formations: Cordevolian dolomite, Middle and Upper Carnian Oslica Beds as well as Upper Triassic Principal Dolomite.

The bauxite deposits of the considered part of Dolenjska are arranged along the Cordevolian/Julian contact.

The bauxites of Muljava and the wider neighbourhood belong to the Karst or "terra rossa" type of bauxites, being of sedimentary origin. They are denoted as "Muljava Bauxite Member".

The Muljava bauxites lie discordantly upon the Cordevolian dolomite and they are transgressively overlain by a predominantly carbonate Julian-Tuvallian sedimentary succession. The about 25-m-thick Muljava Bauxite Member involves three parts (from bottom to top): 1) basal dolomite breccia, 2) yellow-orange bauxites and 3) brown-red bauxites.

Basal dolomite breccia consists of Cordevolian dolomite fragments bound with calcitic cement and limonitic matrix.

In the lower part of the Muljava Member **yellow-orange bauxites** predominate with pelitic and oolitic textures.

The upper part of the Muljava Member includes **brown-red** fairly commonly silicious and ferrous **bauxites**, which are unsuitable for the production of alumina due to their high contents of iron and silica.

The Muljava brown-red oolitic bauxites originated during weathering of the Lower Carnian (Cordevolian) dolomite and in the eolian way. On the basis of the collected data it is not possible to estimate the part of autochthonous bauxite material and the rate of the

allochthonous substance brought by winds. The yellow-orange bauxites are resedimented brown-red bauxites.

Microchemical analyses performed in a FEG SEM based on the EDS and WDS techniques have shown that Muljava bauxites consist of larger pisolites and small ooids from yellow to a dark red-brown colour, depending on the iron content. A higher iron concentration gives a darker red-brown colour to the bauxite mineral, while areas with less iron usually have higher aluminium and silicon concentrations. Ooids have an onion-like structure, where layers rich in aluminium and silicon follow each other. We also observed ooids consisting mostly of either silicon oxide or aluminium oxide.

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