MN CONTENT AS A MARKER OF TRANSGRESSIVE EVENTS: AN EXAMPLE OF SOME BALKAN BAUXITES, BABUŠNICA SITE

Original Scientific Paper
DOI: 10.5937/RGD240032S

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Abstract: *Our novel research on Mn content as markers of transgressive events/eustatic changes in marine carbonate environments not only provides a fresh perspective on the development of the Tethyan Ocean and its branches, "Alpine Tethys", as a key area of study in our field, but also offers practical applications. Namely, Mn deposits, often formed in deep to middle-depth marine environments associated with regional extension, are vital in numerous Mesozoic Tethys-related oceans spreading across the Balkans. The Mn role is vital, especially in indicating hitherto undocumented principal stages of eustatic changes essential for following ancient paleooceanic developments. This research significantly deepens our understanding of the Tethys Ocean s.l., particularly the underexplored southern realm of Alpine Tethys (southeastern Serbia). It contributes to the broader paleoceanography and tectonics, with potential implications for future studies and applications in field mapping.*

Key words: MN DEPOSITS, BAUXITE, ALPINE TETHYS, PALEOCEANOGRAPHY, TECTONICS

INTRODUCTION

The primary source of Mn in ancient oceans is mid-oceanic hydrothermal activity attached to the pelagic realm of these now-closed oceans [4]. Such markers (i.e., the content of Mn) can provide essential data on the evolution of ancient oceanic realms, such as very high-water columns traced from deep-water sediments (e.g., pelagic limestones). The study compares Mn values with transgressive events succeeding unconformities and hiatuses for the first time. One unconformity marker is karst-type bauxites [2]. As a chemical deposit, bauxite represents Aluminum's primary ore and is associated with long-term interruptions of sedimentary cycles. Once combined with the values of Mn, it can provide the precise age of either the maximum water column (high-system stand) or the transgressive cycle deposited over an unconformity. Namely, Mn deposits are often formed in deep to middle-depth marine environments associated with regional extension. These are stages where mid-oceanic hydrothermal activity is the source of manganese in the deep-water basins. The long-term variations of the manganese curve, regardless of hydrothermal activity, are correlative with second-order sea-level changes. Once Mn content is logged in the sediments, the main transgressive phases show an increase in manganese, whereas the regressive phases follow the decreasing trend. Importantly, our research has shown that when coupled with bauxites, markers of unconformity events, Mn content can indicate the transgressive event. Such a combination can provide valuable data for deciphering polystage deformations embedded into Carpathian-Balkans and Dinaride-Hellenides.

REGIONAL GEOLOGICAL SETTING

The area of Carpathian-Balkans and Dinaride-Hellenides represents a remnant of the Alpine orogenic event, which culminated in the Late Cretaceous—Paleogene [15, 25, 21]. The polyphase tectonic evolution involved the Getic–Supragetic basement and Mesozoic assembly (nappes), the Severin and Arjana Mesozoic cover nappes, and the Danubian basement and its Mesozoic cover nappes [13].

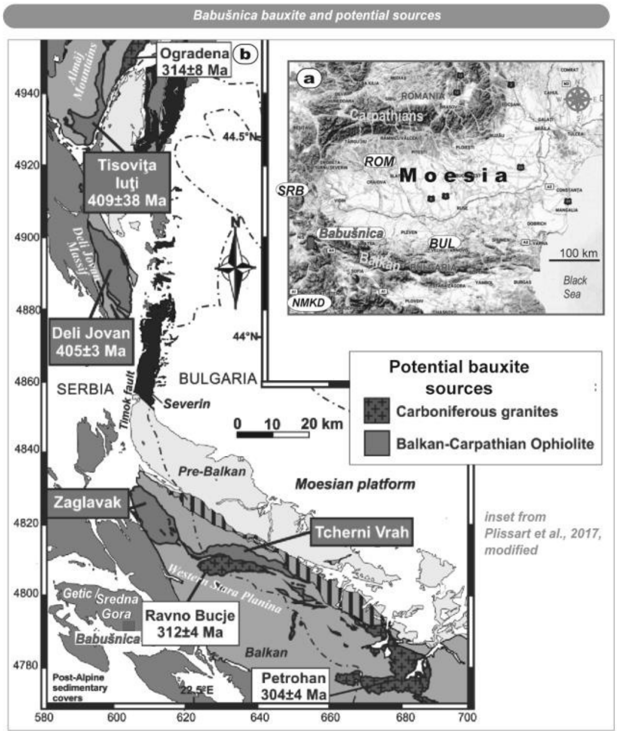

Figure 1, a. Position of the investigated Babušnica bauxite bearing site. b. The main magmatic bodies within the Getic/Sredna Gora unit surround the Babušnica bauxite as potential bauxite sources [*modified* by 24].

The Severin nappe complex is exposed only in Romania, where Late Jurassic–Early Cretaceous ophiolites and turbidites are embedded between the Danubian and Getic–Supragetic basement nappes [21]. The Alpine thrusting during the Mid- to Late Cretaceous subduction-collision closed the Alpine Tethys/Severin-Cehlau ocean. In eastern Serbia, however, there are no significant exposures of Mesozoic ophiolites, just older magmatic suites that were likely sources of prolific bauxite sites (Figure 1). The investigated area belongs to the Mesozoic sequence of the Getic unit (Figure 1, red rectangle at the bottom). The Mesozoic succession overlying Paleozoic succession consists of Middle Triassic clastic and carbonate rocks, conglomerates, sandstone, sandy limestone of the Middle Jurassic age, Late Jurassic to Lower Cretaceous limestones, and dolomites. These rocks are overlain by Upper Cretaceous conglomerates, sandstones, marlstones, and claystones, with similar clastic rocks of Oligocene age [29]. Indeed, the Babušnica area is surrounded by a number of magmatic entities that could be a source for the bauxites. The magmatic sources are of

Paleozoic age, thus mainly predating the mid-Mesozoic bauxites (Ogradena, Tisovita Iuti, Deli Jovan, Zaglavak, Tcherni Vrah/Crno vrh, Ravno Bučje, Petrohan, Figure 1).

MINERALOGICAL AND CHEMICAL CHARACTERISTICS OF THE BABUŠNICA BAUXITE

As well-explored Aluminium ores, the origin of bauxite deposits is a well-known process associated with limestones and disrupted sedimentary cycle, humid climate, etc [2]. Bauxites are formed by the weathering of aluminosilicate-rich rocks such as granite, basalt, diabase, andesite, nepheline syenite, marl, tuff, clayey limestone, shale, slate, etc., in tropical and subtropical regions under warm and humid climatic conditions [1]. Major bauxite minerals are: alumina minerals [gibbsite γ-$Al(OH)_3$, boehmite γ-$AlO(OH)$, and diaspore α-$AlO(OH)$], iron minerals [goethite α-$FeO(OH)$ and hematite Fe_2O_3], titanium mineral (anatase, rutile TiO_2) and silicate [kaolinite $Al_4(OH)_8(Si_4O_{10})$].

The bauxite occurrences and deposits in Serbia occur in the Inner Dinarides/Inner Dinaride Ophiolite belt (Poćuta, Tara, Mačkat and Grebnik) and Carpathian-Balkan belt, i.e. Babušnica [28, 29]. Timotijević (2001) states that Babušnica bauxite comprises boehmite, hematite, and kaolinite as major minerals. Minor and/or accessory minerals are limonite, goethite, calcite, quartz, illite, and rutile. The average chemical contents of the major- and trace elements are given in Tables 1 and 2. In addition, elevated content of the Nb, Zr, U, and Th (Table 2) could indicate the acidic and intermediate parental rocks origin of this bauxite [29]. Such an origin is in agreement with the several sources in the wider area (see discussion in the previous Chapter; Figure 1).

Table 1, The average content (in wt. %) of major oxides of the Babušnica bauxite (Radoševac deposit) [29].

Al_2O_3	**SiO_2**	**Fe_2O_3**	**TiO_2**	**CaO**	**LOI**	**Σ^***	**$TiO_2/Al_2O_3^*$**
52.33	9.62	21.43	3.06	0.34	11.88	98.66	0.058

*-calculated in this paper

Table 2, The average content (in ppm) of trace elements of the Babušnica bauxite [29].

Ba	**Be**	**Co**	**Cr**	**Cu**	**Ga**	**K**
49	7	43	257	17	42	900
La	**Mn**	**Mo**	**Nb**	**Ni**	**Pb**	**Sc**
92	2807	3	70	279	54	34
Sr	**Th**	**U**	**V**	**Y**	**Zn**	**Zr**
94	38.7	10.6	487	73	55	879

RESULTS AND DISCUSSION

Several oceanic realms covered this considerably large area during the Jurassic [7, 26, 30]. Despite the ongoing discussions, Dinarides was the place that nested a few oceanic domains (Neotethys Vardar s.s., "Dinaric Tethys" and its southern extension (Budva-Cukali)Pindos ocean. The separate "Alpine Tethys" likely influenced its eastern domain [13, 25, 21]. The Mesozoic development of the Jurassic oceanic crust (for age constraints, see Maffione and van Hinbergen (2018) and compressional tectonism (e.g., Ionescu (1993) have contributed to the development of several bauxite levels that were identified within the Triassic Upper Jurassic-Lower Cretaceous carbonate successions [16,14]. Unlike abundant bauxites in Dinaride-Hellenides e.g. [28, 17, 5, 10], the Carpathian-Balkan Mesozoic oceanic realm has a number of bauxite sites with barely explored evolution and origin of these truncating-type events (Figure 2) [12, 29, 8]. Often these bauxite sites contain terrestrial dinosaur fossils [9]. Opposite to uplift and unconformity as mid-Mesozoic bauxite productive events, Mn values can be used as markers of transgressive events in marine environments [4, 23].

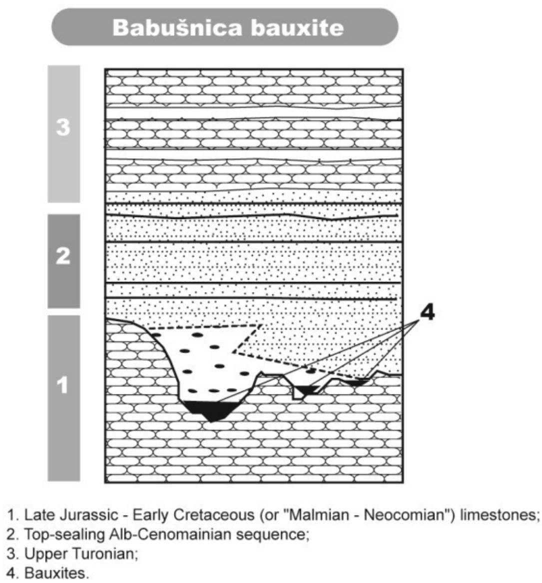

Figure 2, Schematic stratigraphic column of the Babušnica bauxites [*modified after* 29].

Several bauxite sites expose elevated Mn contents, such as Babušnica and Mačkat (eastern and western Serbia, respectively; Table 3), while the slightly elevated Mn contents have Nikšić and Vlasenica (Montenegro and B&H, respectively; Table 3). Nikšić and Vlasenica have similar values despite being slightly outside or at the margins of Jurassic ophiolite belts. However, the site with the highest Mn content is the opposite Carpathian-Balkan Alpine Tethys, observed within the Babušnica site.

Babušnica bauxite lying in Late Jurassic – Early Cretaceous limestones, or "Malm – Necomian" sequence (Figure 2) [29].

Table 3, The average content (in ppm) of Mn in various bauxite locations [6, 29 *and references therein* 10].

Bauxite locations	Poćuta	Tara	Mačkat	Grebnik	Babušnica	Vlasenica	Jajce	Nikšić
Mn	425	311	1985	673	2807	1100	200	1200

Such a higher value suggests a significant increase in eustatic sea level or highstand occurred after the mid-Mesozoic uplift and erosion episode as indicated by Corbin et al., 2000 [4]. Dating of detrital mica from the Cretaceous Sinaia flysch of Alpine Tethys/Severin-Cehlau Ocean, besides dominant Variscan ages (329±3 and 288±4 Ma), also record subordinate Early Jurassic (185±4 and 183±3 Ma), and Late Jurassic/Early Cretaceous (149±3 and 140±3 Ma) ages [21]. The latter age shows that the Late Jurassic/Early Cretaceous was the time of the formation of ductile shear zones, which were likely contributing to the regional exposure of the area. The latest Jurassic uplift, however, was the major event recorded across the entire area of Carpathian-Balkans and Dinaride-Hellenides [3, 22, 27, 19].

The suitable paleogeomorphologic karst-type conditions and subaerial exposure allowed favorable bauxite-forming conditions, particularly as a number of potential basic- and acidic to intermediate-type sources, which were present in wider region (i.e., Tisovita Iuti, Deli Jovan, Zaglavak, Tcherni Vrah/Crno vrh, Ravno Bučje, Petrohan; Figure 1). The elevated presence of Mn shows that protracted subaerial and paleokarstification stage which lasted until Albian [29], was succeeded by the major transgression in Albian [18]. Such a transgression event is documented across the entire Neotethys, inclusive of the south Tethyan extension and successor highstand mid-late Albian marls [e.g. 18, 20, 11].

SUMMARY AND CONCLUSIONS

The results of our study on Mn contents within the mid-Mesozoic bauxites reveal that areas had different paleoceanic histories, or ancient sea levels that were in very high sea-level stages during the middle Mesozoic. By comparing the age of Babušnica bauxite, which is mainly nested in the Jurassic-Cretaceous limestones, the results show the presence of large unconformity lasting until the "Middle Cretaceous" (Albian). The source of Mn is correlative with Jurassic rift-drift and associated hydrothermal activity in Alpine Tethys. The remote hydrothermal activity in the Romanian segment, Severin ophiolites, likely produced large amounts of Mn at the Babušnica site. The hydrothermal activity could be connected to Severin ophiolite, comprised of Jurassic rift and ophiolite successions. The precise connection between the two remote segments of Alpine Tethys could be in Aptian, as the incipient and development stage of northern Sinaia Flysch is consistent with the Late Jurassic to Aptian age. In other words, unconformity lasted from Barremian to Albian; however, Mn was likely transported by the Aptian transgressional event recorded in the southern realm (Babušnica site, conglomerates, various clastics; Figure 2, central part).

ACKNOWLEDGMENT

This work was partially financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-66/2024-03/200026).

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