Genesis and epigenetic evolution of the Minjera bauxites, Croatia, Istria

Perković, Ivor; Durn, Goran; Matešić, Darko; Vlahović, Igor; Cvetko Tešović, Blanka; Martinuš, Maja

GENESIS AND EPIGENETIC EVOLUTION OF MINJERA BAUXITES, CROATIA, ISTRIA

Ivor Perković[1], Goran Durn[1], Darko Matešić[1], Igor Vlahović[1], Blanka Cvetko Tešović[2], Maja Martinuš[2]

[1] University of Zagreb, Faculty of Science, Department of Geology, Horvatovac 102a, HR- 10000 Zagreb, Croatia

[2] University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, HR-10000 Zagreb, Croatia

This work has been fully supported by Croatian Science Foundation under the project IP-2019-04-8054 – WianLab (Western Istrian Anticline as an Ideal Natural Laboratory for the Study of the Regional Unconformities in Carbonate Rocks).

History of Minjera bauxites

- Minjera bauxites were the first analysed and mined bauxites in the world
- The mining activities begun as early as in the 16^{th} century
- The major mining acitivity happened in the end of the 18^{th} and the beggining of the 19^{th} century
- Used as a ore for the production of alum and green vitriol

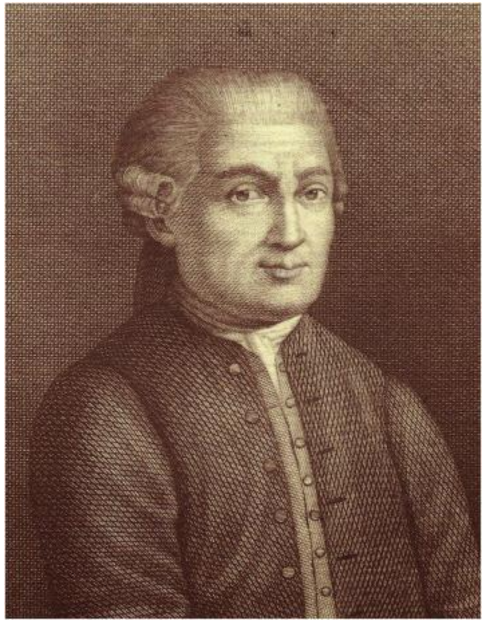

Figure 1. Giovanni Arduino

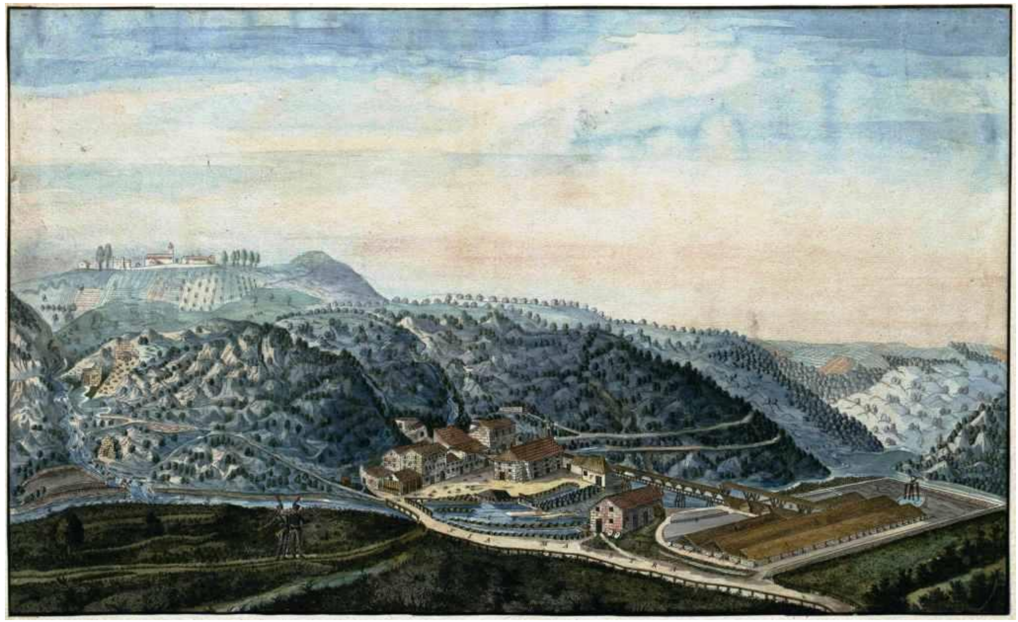

Figure 2. Historic picture of the bauxite processing factory and the Sovinjak area (NEŽIĆ , 2015)

Geological setting

- These bauxites formed during the third unconformity, which separates the 3rd and 4th megasequence in the depositional succession of Istria
- This unconformity lasted between **25** and **40 Ma**
- Formation of bauxites, palaeosols and calcretes
- In the area of Sovinjak, the bedrock of this unconformity is composed from Rudist limestones and the cover from Liburnian beds and Foraminiferal Limestones
- The Minjera bauxites are always overlain with Liburnian beds

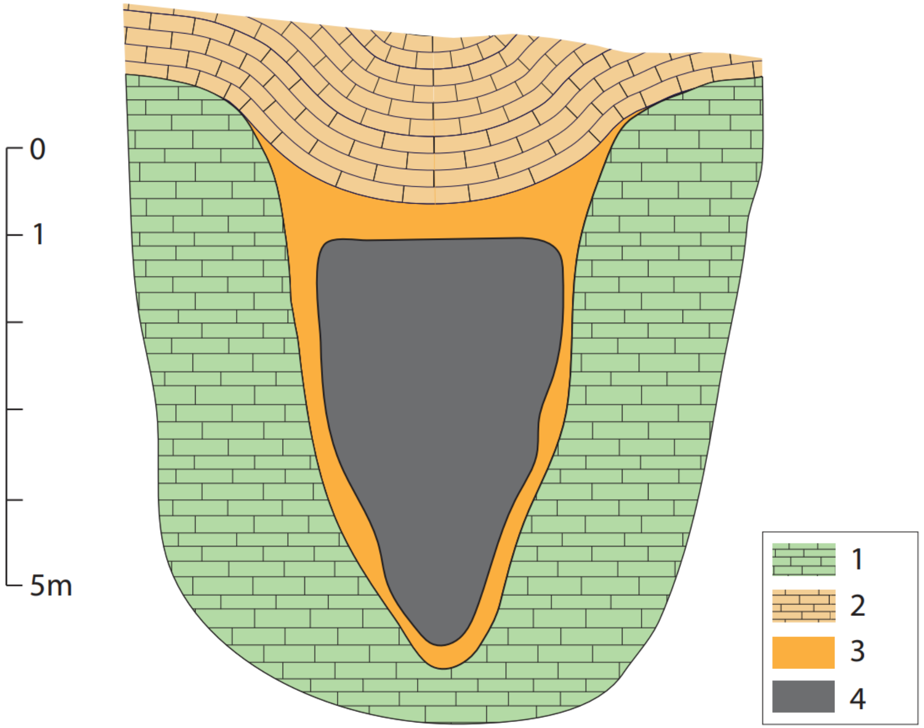

Figure 4. schematic cross-section of typical grey bauxite from Minjera, modified after ŠINKOVEC et al (1994); 1 - Upper Cretaceous limestones, Kozina beds: Palaeocene to Lower Eocene, 3 - Yellowish to red bauxite, 4 - pyritized grey bauxite

Methods

- 19 grey bauxite samples from two deposits and 1 red bauxite sample from the tailing heap were collected
- Petrography
- XRPD
  - Bulk samples – Rietveld refinement in Profex software (Doebelin and Kleeberg 2015)
- XRF and ICP-MS

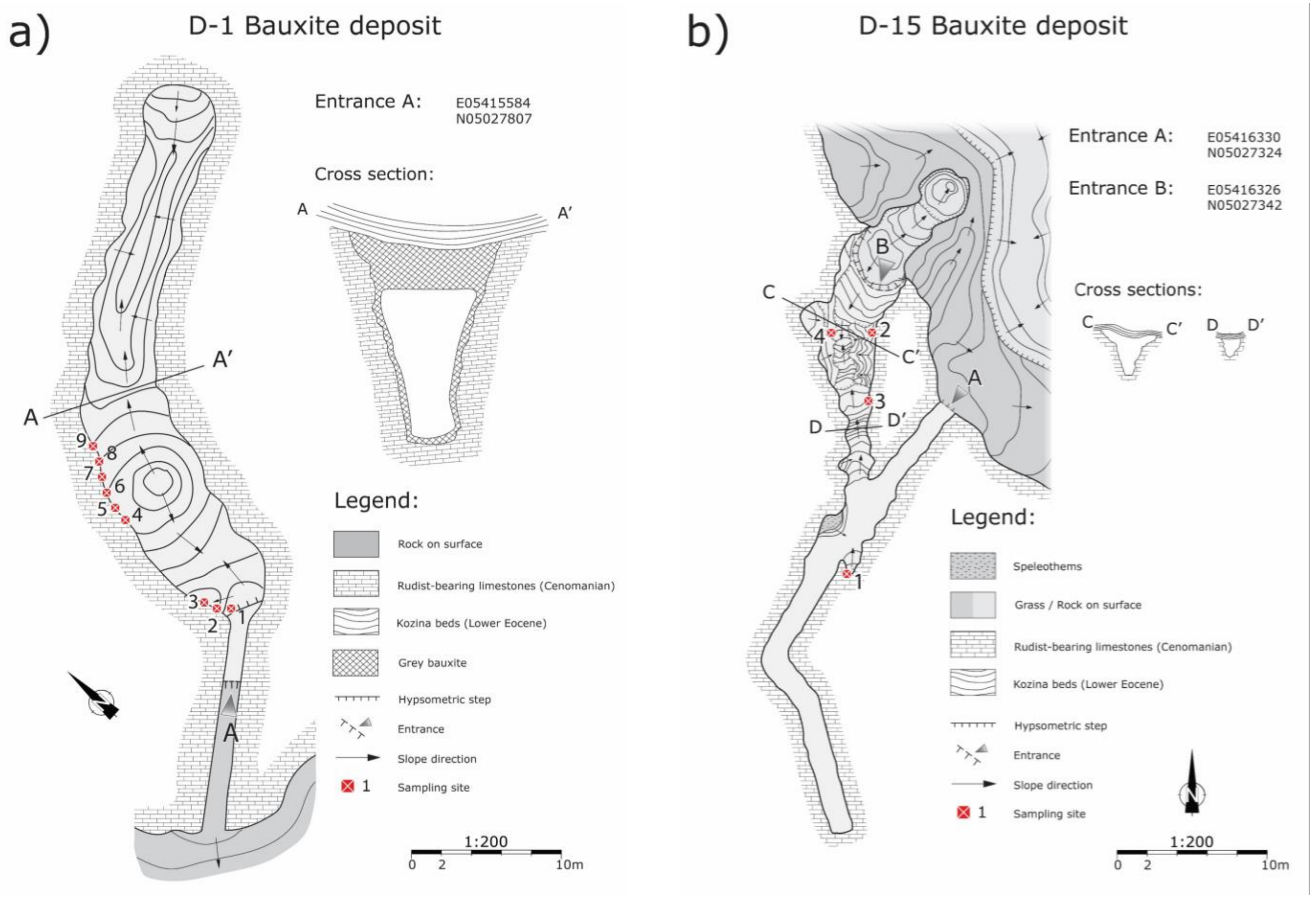

Figure 5. Plans of studied Minjera bauxite deposits and sampling sites within them. a) – plan of the D-15 bauxite deposit, b) – plan of the D-1 bauxite deposit

Results: Fieldwork

- Two types of morphologies were observed in the filed, the **canyon-type** and **sinkhole-type** morphology
- Two main types of bauxite: **grey bauxite** and **pyritised bauxite**
- Pyrite is usually present in veins and bands

Figure 6. Field photographs of Minjera bauxites a) D-5 bauxite deposit, b) Entrance shaft into the D-7 bauxite pit, c) Lake in the D-3 bauxite deposit, d) Transition from the grey bauxite into the black bauxite and Kozina beds, e) Iron sulphide veins, f) Iron sulphide impregnation

Results: Petrography

- All bauxite types are ooidal, while also containing bauxite pebbles
- Red bauxites shows signs of oxidation-reduction cycles
- Grey and pyritised bauxites contain three different types of iron sulphides
- 1st type replaces the matrix, and is alotriomorphic, 2nd type replaces the ooids and bauxite pebbles and the 3rd type appears in veins
- Diaspore can be seen in veins and in the ooidal cortices, while the other phases are cryptocrystalline

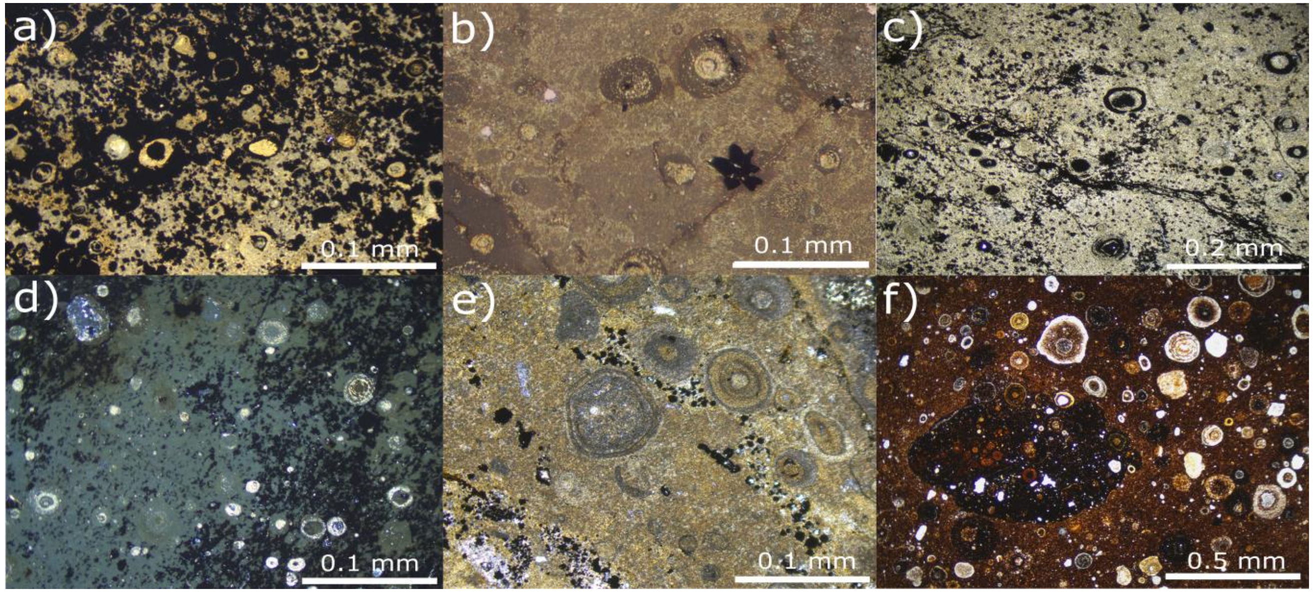

Figure 7. Photomicrographs of different samples from Minjera bauxites. a) – first generation of iron sulphides visible in the bauxite matrix together with iron sulphides replacing the iron oxide rich lamellae in the ooids, D-1 deposit, PPL; b – diasporic ooids and a marcasite rossette, D-15 deposit, PPL; c – iron sulphide framboids in the bauxite matrix and iron sulphide rich lamellae in ooids and veins, D-1 deposit, PPL; d – iron sulphides in the matrix of the bauxite, surrounding the diasporitic ooids, D-1; e – iron sulphide framboids and boehmite ooids in a deferrified bauxite matrix, D-15 deposit, PPL; f – ooids with alternating iron oxide and deferrified lamellae as well as pebbles ofred bauxite (MN-25), PPL.

Results: XRPD

- **Two types of bauxites**
  - Grey bauxite – Kaolinite rich
  - Pyritised bauxites – Boehmite and pyrite rich
  - Red bauxite – Boehmite and haematite rich

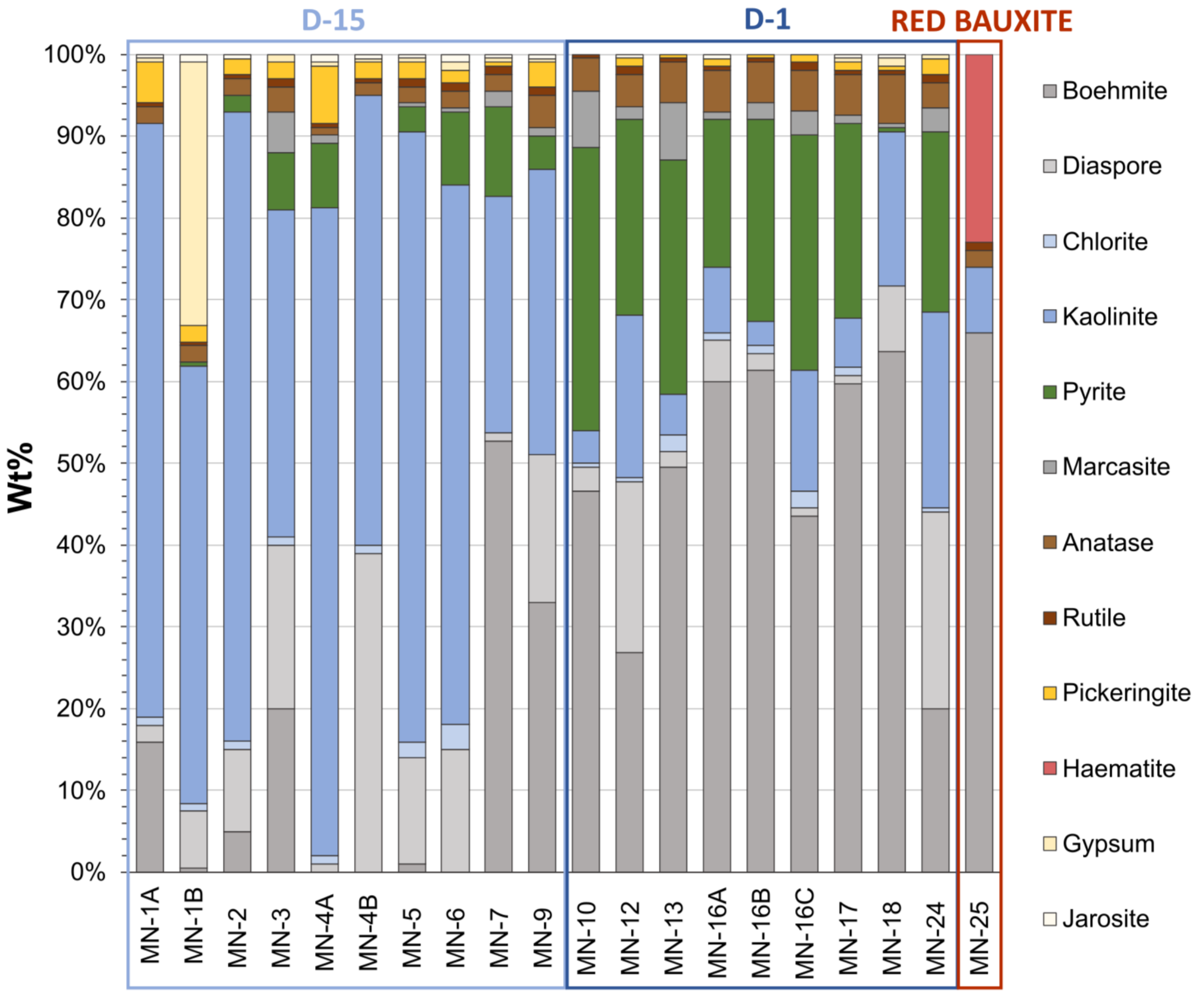

Figure 8. Plot displaying the mineralogical composition of analysed samples

Results: XRF & ICP-MS

- Concentrations of major oxides indicates diffrences between D-1 and D-15 deposits
- D-15 deposit is richer in LILE and bases **– lower leaching**
- D-1 deposit is richer in chalcophile and siderophile elements – **more iron sulphides**
- Both deposits display a slight negative cerium anomaly – **marine influence**
- Enriched in HREE and LREE, while showing a depletion in MREE
- Red bauxite is enriched in MREE and exhibits no cerium anomaly
- Dissolution of iron and managanese oxides – **mobilization of MREE**

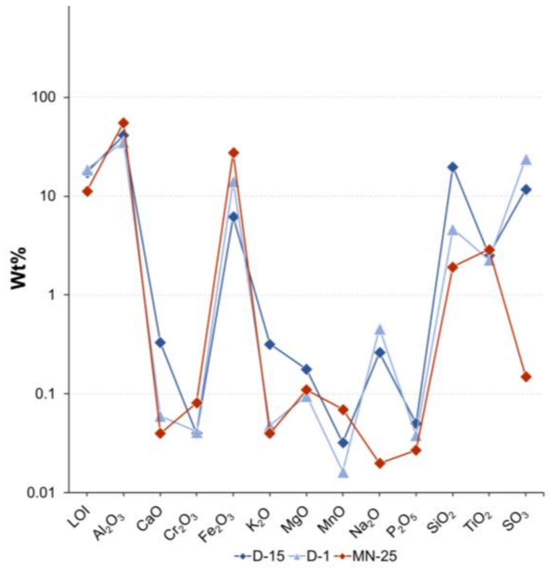

Figure 9. plot displaying the average major oxide composition of the samples from D-15 and D-1 deposits, together with values obtained from the red bauxite sample

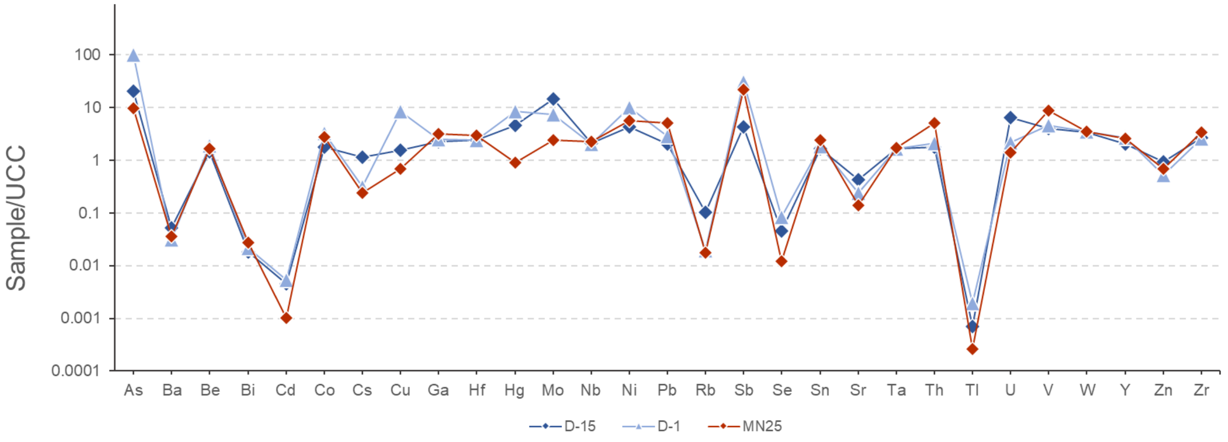

Figure 10. plot displaying the average trace element composition of the samples from D-15 and D-1 deposit, together with values obtained from the red bauxite sample

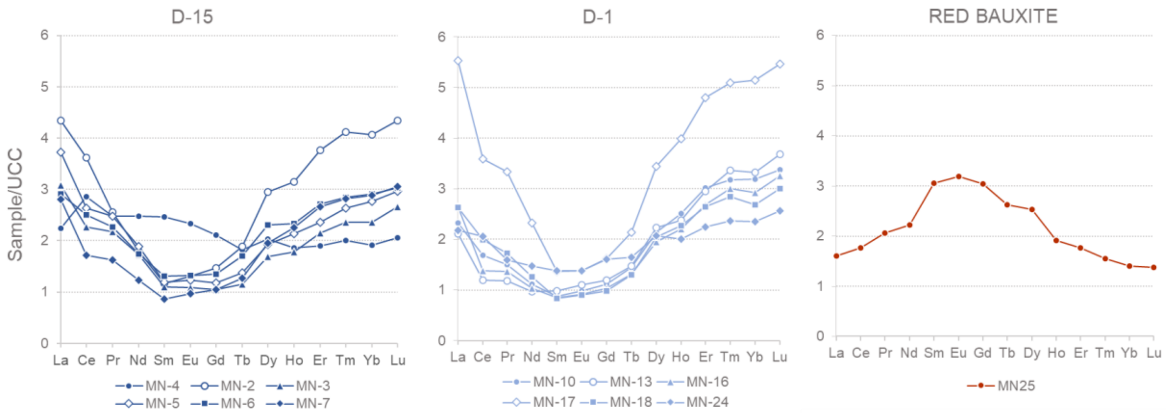

Figure 11. Spider plots displaying the concentrations of rare earth elements normalized to the upper continental crust values (TAYLOR and MACLENNAN 1989) in the analysed bauxite samples

Discussion

- Pyritisation happened after bauxitisation, during the initial stages of the transgression when marshy environments formed over bauxite depressions

- The main source of sulphur was the microbial reduction of marine sulphate – **enrichment in HREE, negative Ce anomaly**

- **Three stages of pyritisation**:

  - **1st stage** – reduction of the poorly crystalline iron oxides of the bauxite matrix, formation of poorly crystalline iron sulphides

  - **2nd stage** – reduction and replacement of iron oxides in ooid cortices and more iron rich bauxite clasts

  - **3rd stage** – compaction and fracturing of the bauxite and crystallisation of pyrite veins

Discussion

- The two studied deposits differ in mineralogy and geochemistry – different bauxite types
- D-15 deposit is less leached compared to the D-1 deposit – kaolinite > boehmite, enriched in LILE and bases
- This is likely a consequence of their different palaeotopographical positions which their different morphology also supports
- Canyon-type – higher paleotopographical position – **increased fluid-flow**
- Sinkhole-type – lower palaeotopographical position – **reduced fluid-flow**

Conclusions

- Different bauxite morphologies in the same bauxite group
- Mineralogical, geochemical differences between the two bauxite deposits
- Differences in palaeotopography
- Marine source of sulphur
- Three stages of pyritisation


Thank you
for your
attention!

Acknowledgement

The work was supported by the Croatian Science Foundation under the project “Western Istrian Anticline as an Ideal Natural Laboratory for the Study of the Regional Unconformities in Carbonate Rocks – WianLab” (IP-2019-04-8054).

References

- NEŽIĆ, M. (2015): Minjera. Pregled rudarske i prerađivačke djelatnosti podno Sovinjaka, Buzet. Katedra Čakavskog sabora Buzet, 160.
- TAYLOR, S. R., & MCLENNAN, S. M. (1985): The Continental Crust: Its Composition and Evolution. In The Continental Crust: its Composition and Evolution. An Examination of the Geochemical Record Preserved in Sedimentary Rocks. Blackwell, 312.
- ŠINKOVEC, B., SAKAČ, K., & DURN, G. (1994): Pyritized bauxites from Minjera, Istria, Croatia. *Natura Croatica*, *3*(1), 41–65.