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Paleoenvironmental and paleoclimatic changes during the deposition of Upper Jurassic bauxites and their immediate cover: Case study of the Rovinj bauxite pit, Istria, Croatia

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Introduction and deposit overview

- The primary objective of this study was the reconstruction of **palaeoclimate** and **paleoenvironmental** conditions during the evolution of the Rovinj deposit (Fig. 1.), based on the collected mineralogical and geochemical data from the bauxite and the overlying clays/marls
- The Rovinj bauxite deposit is a representative locality of the **first unconformity** in the succession of the **Western Istrian anticline**
- The Anticline itself is composed from **four depositional** carbonate-dominated **megasequences**, separated by **four major unconformities** (Velić, 1995; Fig. 2.)
- On other locations, emersion breccias, black pebble breccias, marls, clays, or just a stratigraphic gap represent this unconformity
- This unconformity comprises the environments formed during the Upper Jurassic emersion, which lasted between **3** to **5 Ma**, with Early Kimmeridgian perireefal and sandbar limestones underlying the unconformity, and the Upper Tithonian lagoonal mudstones overlying the unconformity
- The only operating bauxite mine in Croatia is located in the Rovinj, but instead of being used in aluminum production it is being used as a secondary raw material in mineral wool production
- Rovinj deposit is also one of the largest bauxite deposits in Croatia, with the size of the deposit being estimated at 15 Mt
- During the internal transgression which followed the terrestrial phases during which the bauxite had formed, a blue-hole sequence was deposited over the Rovinj bauxite, and is comprised from a cyclical alternation of clays, black-pebble and emersion breccias, together with freshwater and marine limestones

Figure 1. Rovinj bauxite deposit

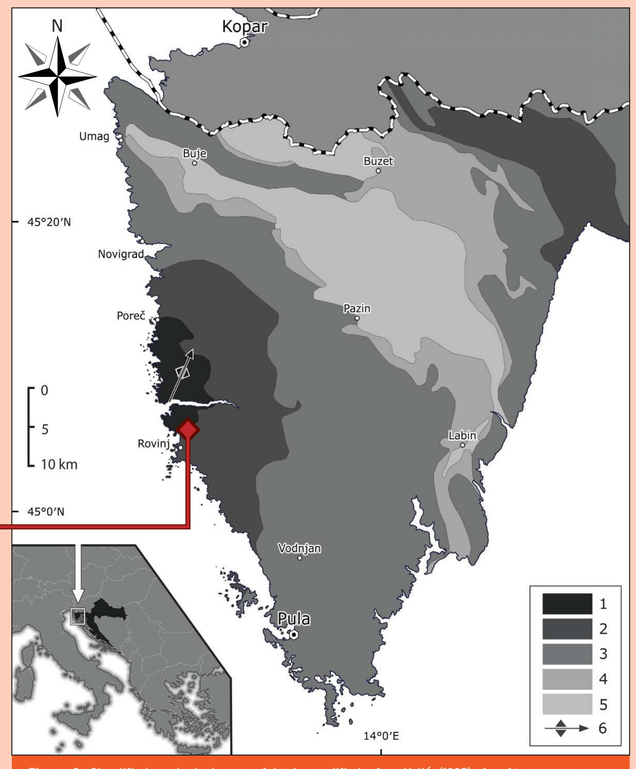


Figure 2. Simplified geological map of Istria modified after Velić (1995). 1 - 1st megasequence (Jurassic), 2 – 2nd megasequence (Lower Cretaceous), 3 - 3rd megasequence (Upper Cretaceous), 4 - 4th megasequence (Lower Eocene), 5 - 4th megasequence (Middle to Upper Eocene), 6 - Western Istrian anticline

Methods

- Samples were collected from the selected profile on the bauxite outcrop
- In this research, data collected from 11 bauxite samples and 7 clays/marls samples is shown
- On bauxite samples, several analytical methods have been performed:
  - **XRPD** on bulk samples
  - **XRF**
  - **ICP-MS**
  - **Petrography**
  - **Micropedology** according to Stoops (2021.)
- On clay samples XRPD of <2 µm fraction was performed together with iron speciation according to the standard chemical protocol described by Poulton and Canfield (2005.)
- Mineralogical composition of bauxite samples and <2 µm fraction from clay/marl samples was determined using Rietveld refiniment in Profex software (Doebelin & Kleeberg, 2015.)
- Clay mineralogy of clay/marl samples was determined from XRPD patterns of non-oriented <2 µm fraction samples which were recorded after air-drying, ethylene-glycol and glycol solvation, dissolution in 1:1 HCl on 60°C as well as heating to 350°C and 600°C

Rovinj bauxite profile

Figure 3. Rovinj bauxite profile

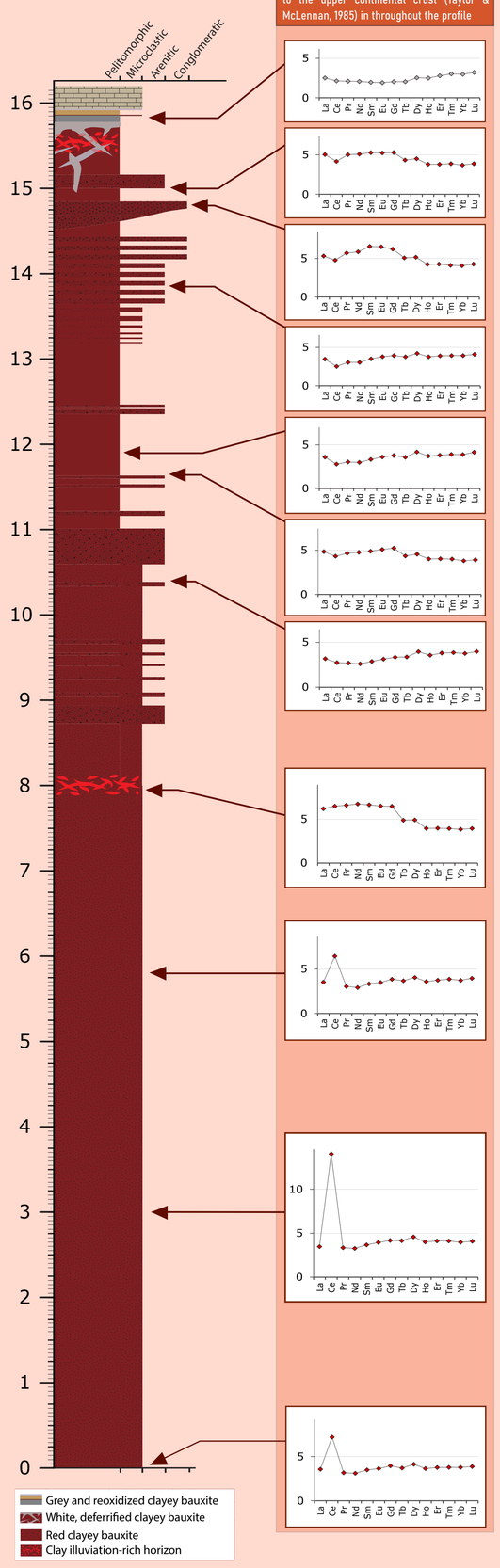


Figure 4. Lanthanide (REE) values normalized to the upper continental crust (Taylor & McLennan, 1985) in throughout the profile

Figure 5. Major oxide and lanthanide values (REE) throughout the studied profile

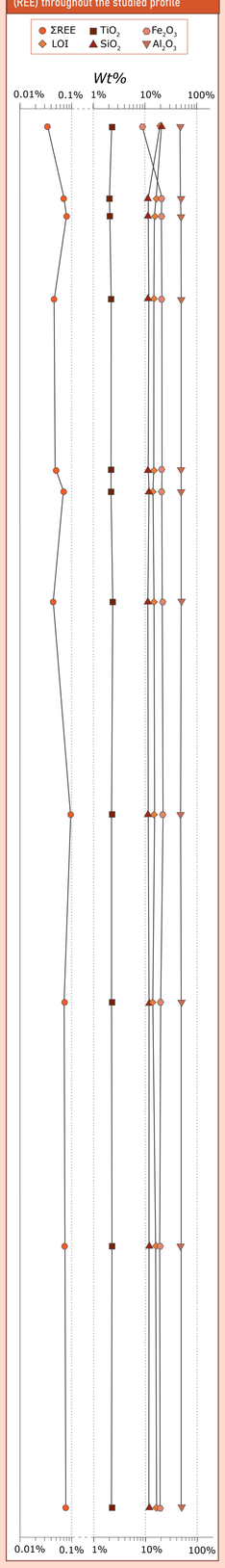


Figure 6. Variations of different elemental ratios along the profile

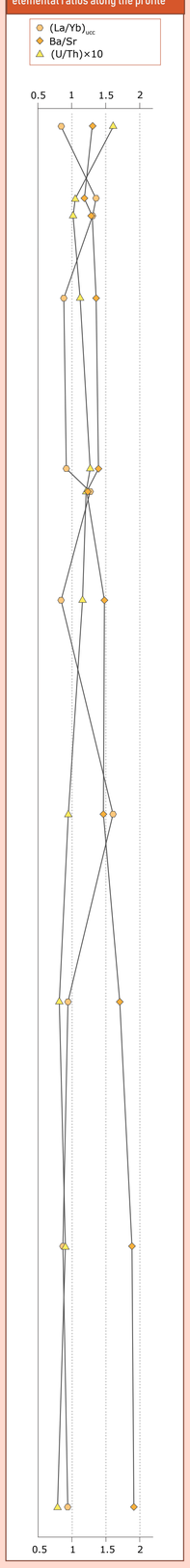
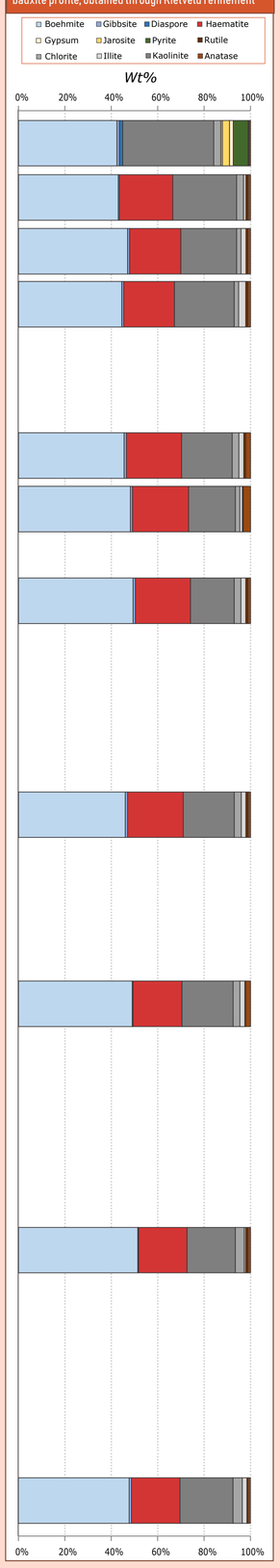


Figure 7. Mineralogical composition throughout the bauxite profile, obtained through Rietveld refinement



Bauxite cover succession

Figure 8. bauxite cover succession

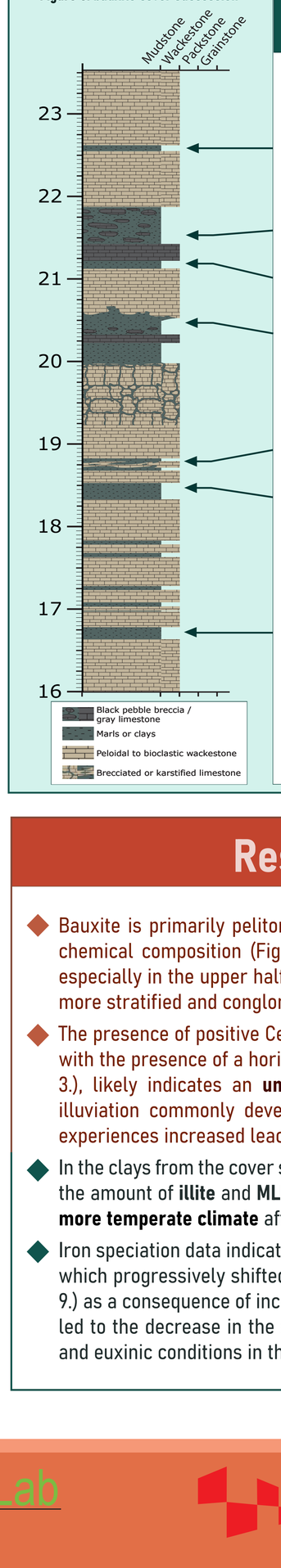


Figure 9. Mineralogical composition of the clays/marls, overlying the bauxite, obtained through Rietveld refinement on XRPD patterns recorded on unoriented <2 µm samples

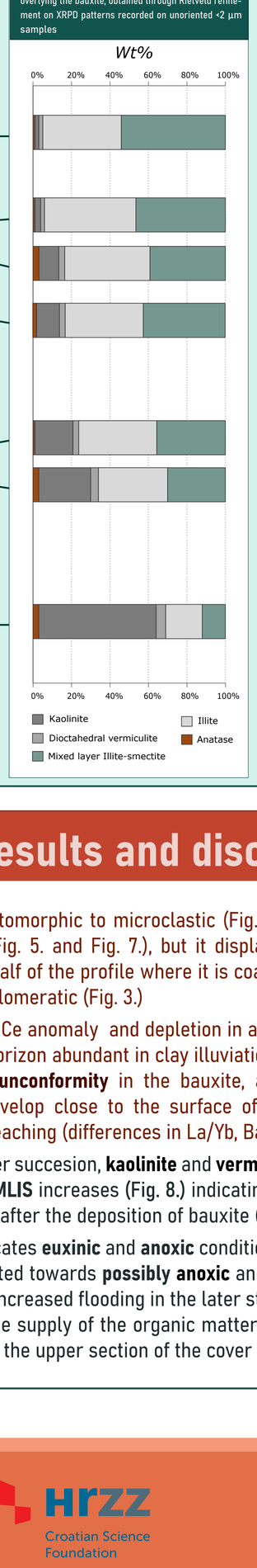
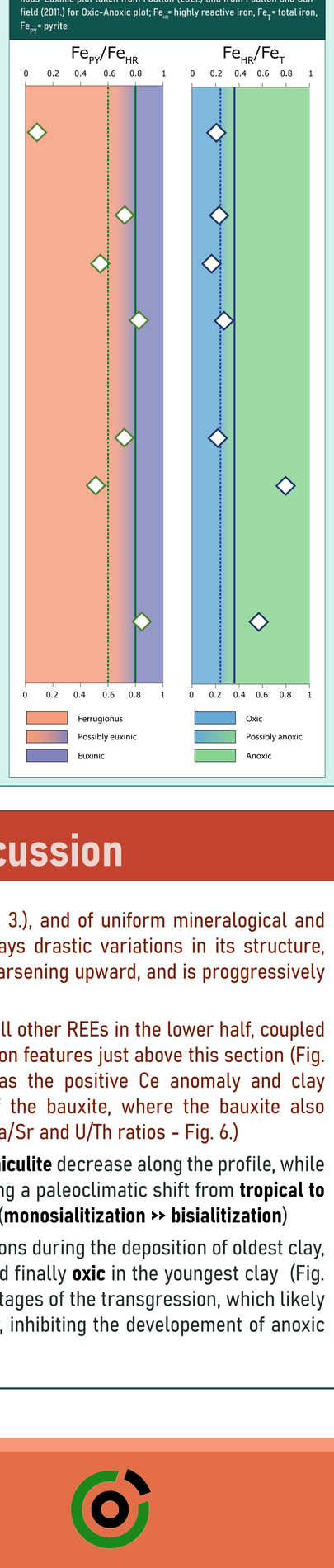


Figure 10. Plotted Iron speciation data with threshold values for Ferrugi-nous-Euxinic plot taken from Poulton (2021.) and from Poulton and Can-field (2011.) for Oxic-Anoxic plot; Fe_{HR}= highly reactive iron, Fe_T= total iron, Fe_{PY}= pyrite



Results and discussion

- Bauxite is primarily pelitomorphic to microclastic (Fig. 3.), and of uniform mineralogical and chemical composition (Fig. 5. and Fig. 7.), but it displays drastic variations in its structure, especially in the upper half of the profile where it is coarsening upward, and is proggressively more stratified and conglomeratic (Fig. 3.)
- The presence of positive Ce anomaly and depletion in all other REEs in the lower half, coupled with the presence of a horizon abundant in clay illuviation features just above this section (Fig. 3.), likely indicates an **unconformity** in the bauxite, as the positive Ce anomaly and clay illuviation commonly develop close to the surface of the bauxite, where the bauxite also experiences increased leaching (differences in La/Yb, Ba/Sr and U/Th ratios - Fig. 6.)
- In the clays from the cover succesion, **kaolinite** and **vermiculite** decrease along the profile, while the amount of **illite** and **MLIS** increases (Fig. 8.) indicating a paleoclimatic shift from **tropical to more temperate climate** after the deposition of bauxite (**monosialitization >> bisialitization**)
- Iron speciation data indicates **euxinic** and **anoxic** conditions during the deposition of oldest clay, which progressively shifted towards **possibly anoxic** and finally **oxic** in the youngest clay (Fig. 9.) as a consequence of increased flooding in the later stages of the transgression, which likely led to the decrease in the supply of the organic matter, inhibiting the developement of anoxic and euxinic conditions in the upper section of the cover

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Acknowledgements:

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