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# REE's in early Cretaceous bauxites of the Villány Mountains, South Hungary

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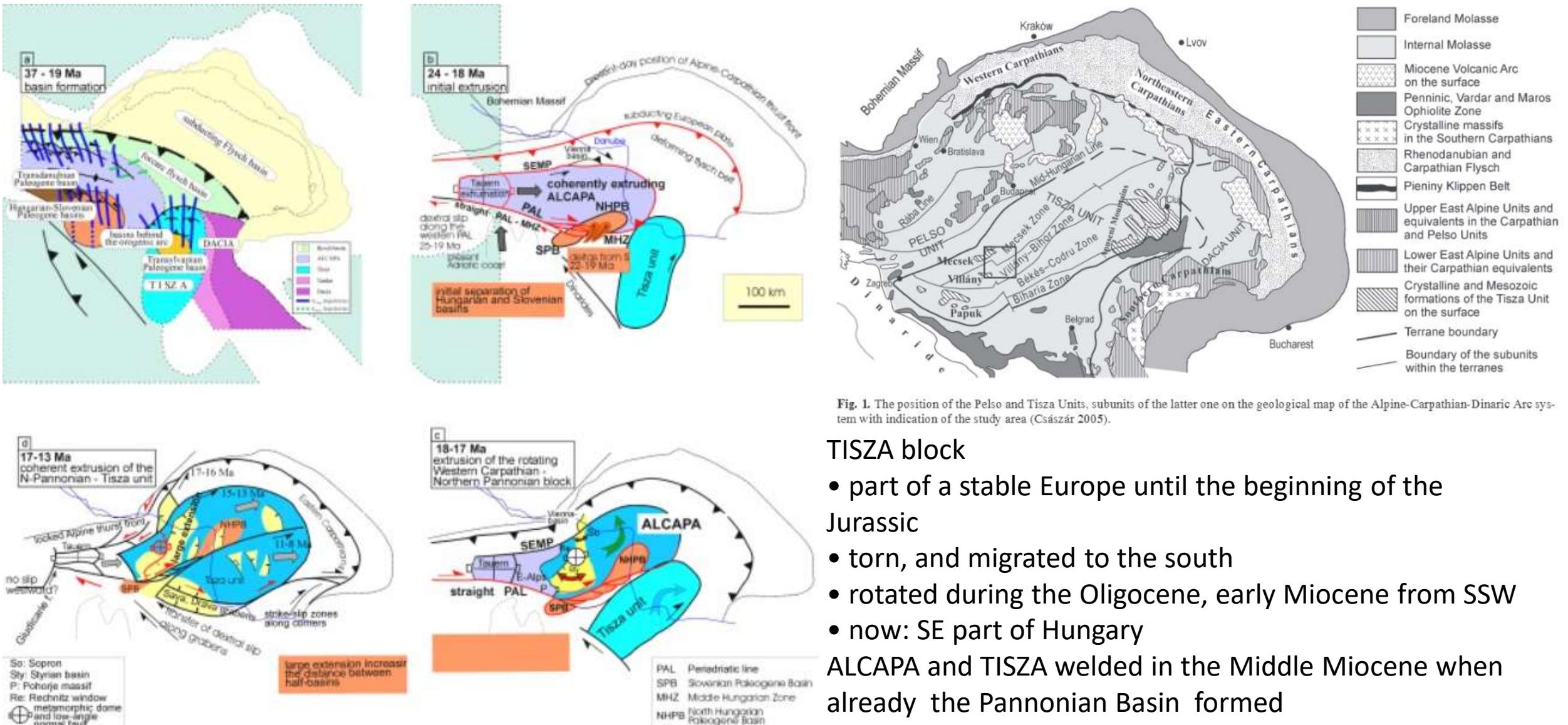
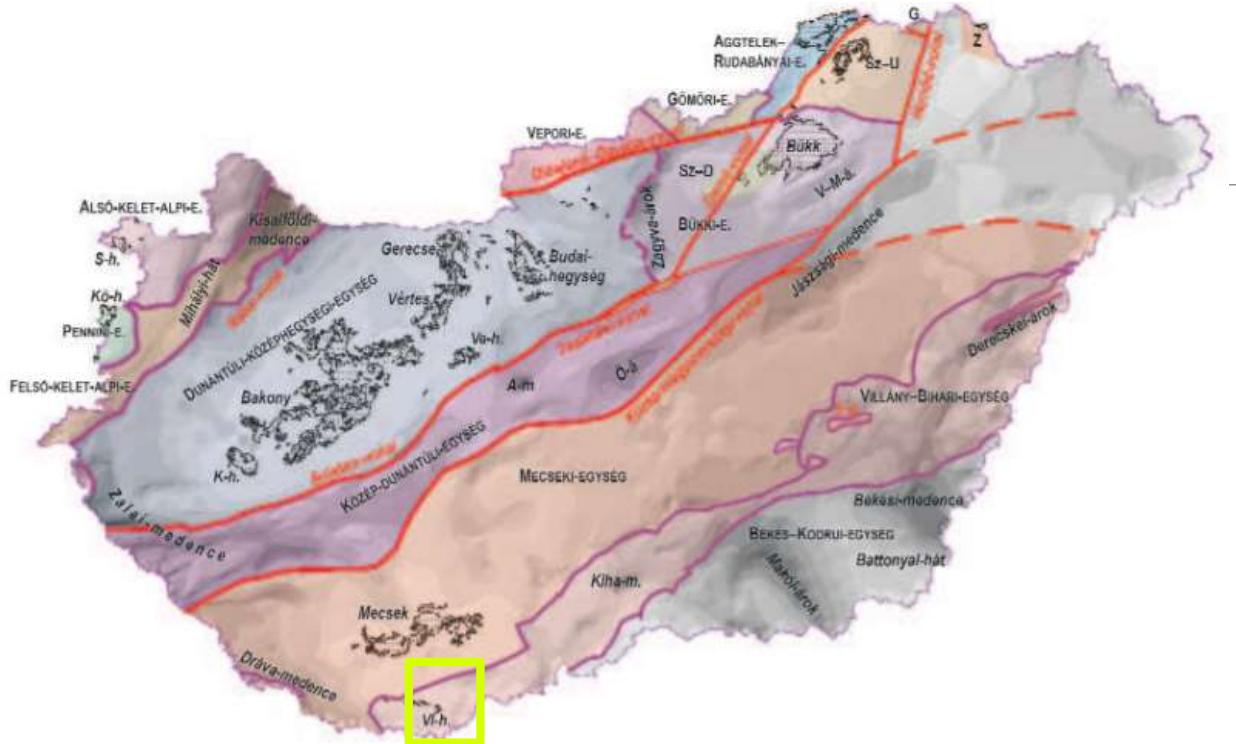


Fig. 1. The position of the Pelso and Tisza Units, subunits of the latter one on the geological map of the Alpine-Carpathian-Dinaric Arc system with indication of the study area (Császár 2005).

## TISZA block

- part of a stable Europe until the beginning of the Jurassic
  - torn, and migrated to the south
  - rotated during the Oligocene, early Miocene from SSW
  - now: SE part of Hungary
- ALCAPA and TISZA welded in the Middle Miocene when already the Pannonian Basin formed

# Paleogeography



- TISZA mega-unit consists of three structural units (Mecsek, Villány-Bihar and Békés). Up to the middle Triassic they had a similar structural evolution.
- However, from the middle Anisian on differences between them began to increase because of the intensification of plate tectonic movements (opening of the Pennine Ocean). This was essential in the development of the Upper Triassic, Jurassic, and Cretaceous strata

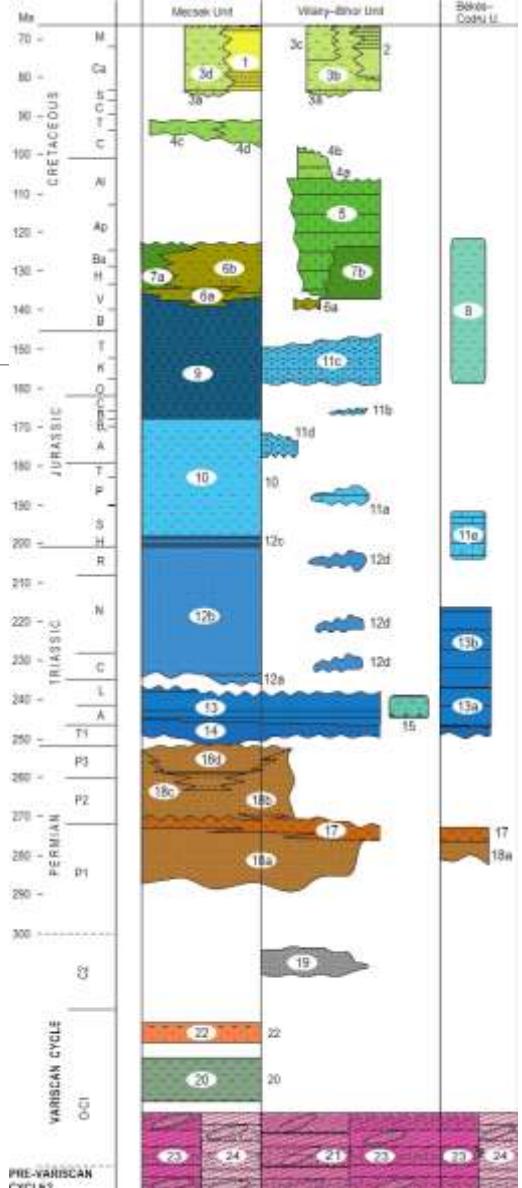
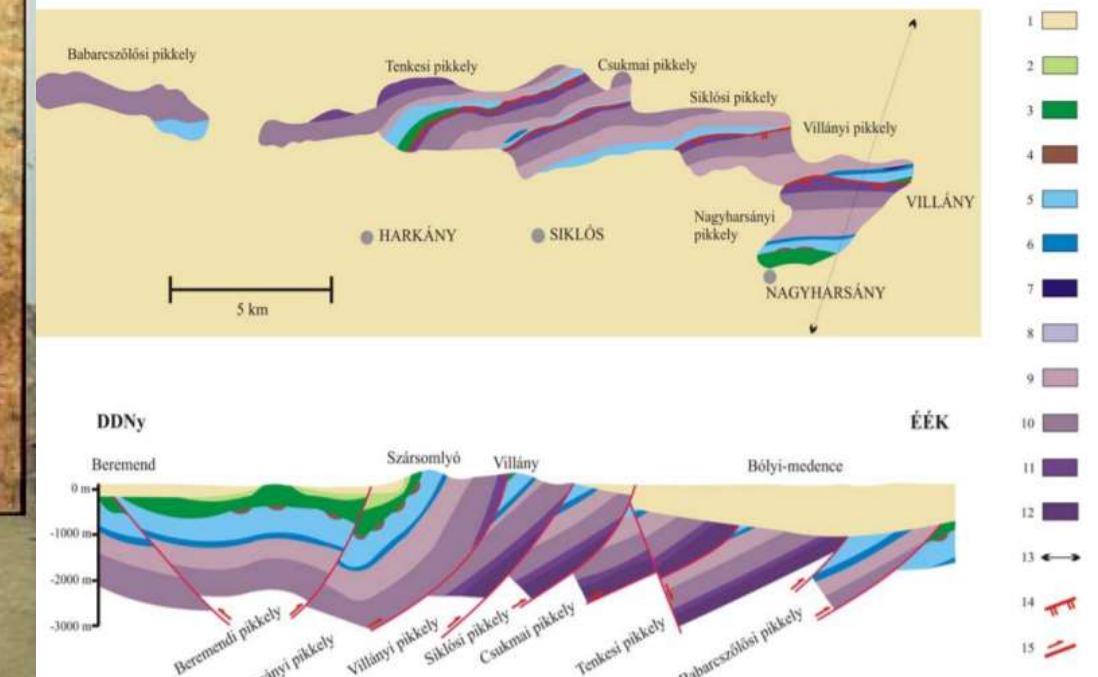


Fig.2 Stratigraphic column of the pre-Cenozoic formations of the Tisza Mega-unit  
 (BARABÁS 1998, BÉRCZI-MAKK 1998, CSÁSZÁR Ed. 1996,  
 FÓZY Ed. 2012, BÉRCZI-MAKK et al. 2004, SZEDERKÉNYI 1998)

# Geology of the Villány Mountains



- Bauxite was deposited in karstic depressions formed on the subaerially exposed surface of the Latest Jurassic earliest Cretaceous limestones (Dudich & Mindszenty 1984).

Fig. 4. The scaly structure of the Villány Mountains (following RAKUSZ & STRAUSZ 1953).  
 Legend: 1. neogeneic sediments; 2. Upper Cretaceous marl; 3. Lower Cretaceous limestone; 4. Lower Cretaceous bauxite; 5. Upper Jurassic limestone; 6. Middle Jurassic ammonite limestone; 7. Lower Jurassic sand limestone; 8. Upper Triassic sandstone; 9. Middle Triassic dolomite; 10. Middle Triassic limestone 11. Middle Triassic variegated dolomite; 12. Middle Triassic clay stone, aleurolite, dolomite; 13. geological section track on the map; 14. scaling limit; 15. shift.

# Mining activities

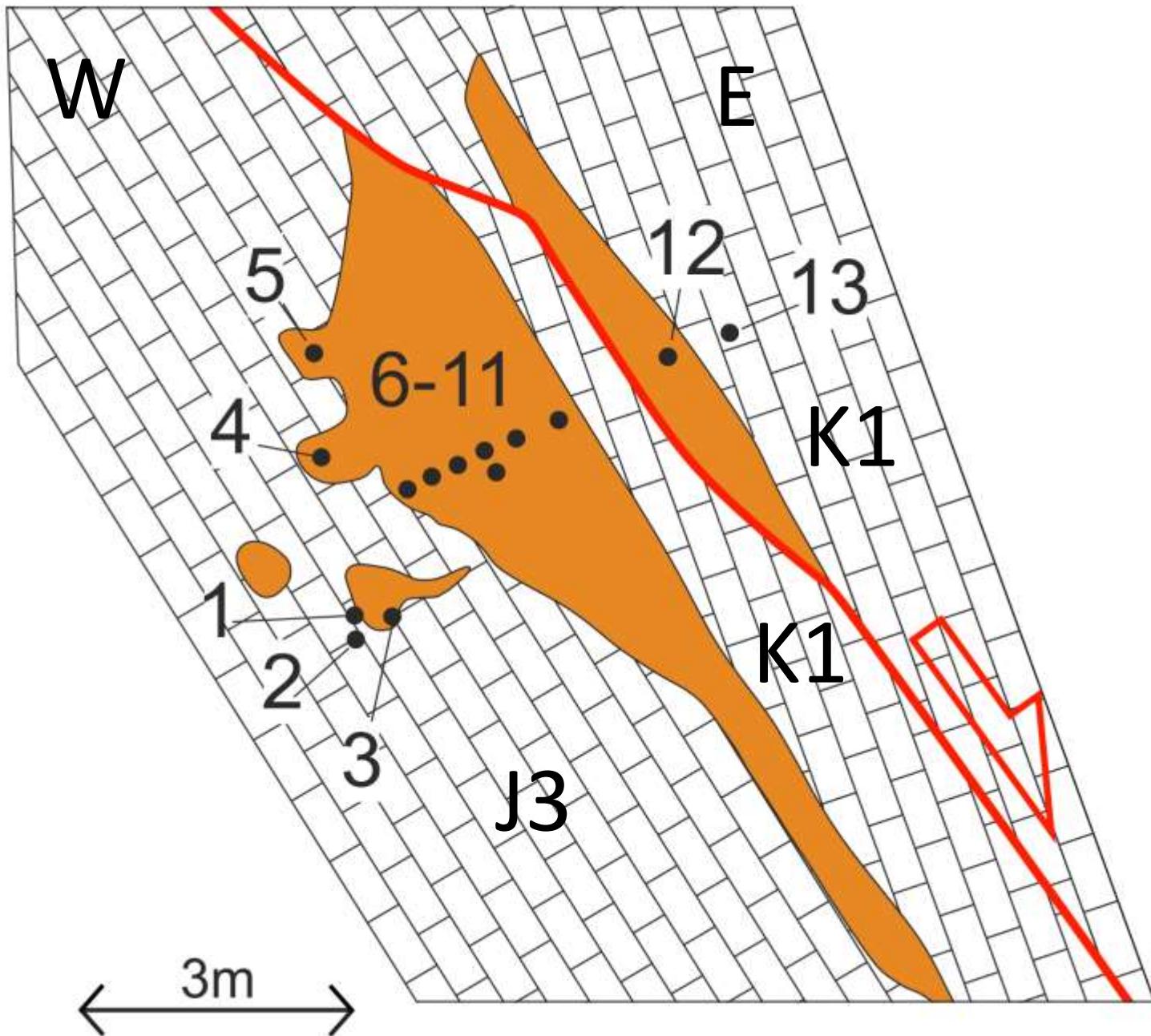
October 2018

- Bauxite exploration in the Villány Mountains was started by Prof. TELELDI ROTH, K. studying the investigation of this contact, between latest Jurassic (Tithonian) and Early Cretaceous (Berriasian to Valanginian) strata.
- Unlike Transylvania, exploitation in Villány was active only for a few years
- 38 Mt was excavated during World War II between 1941 and 1944 and the ore was all exported to Germany
- Accordingly no significant research was done on
- The Nagyharsány Bauxite is one of the least known deposits
- Its bedrock is generally the Upper Jurassic Szársomlyó Limestone and the cover is the Lower Cretaceous Nagyharsány Limestone (both are shallow marine carbonate platform formations)



# Sampling

- Bauxite samples collected in Villány within REEBAUX WP2 activities in 2018 are indicated on the profile
- The bauxite of the lenticular ore bodies often fills also small karstic cavities in the footwall (the Nagyharsány Limestone)
- Between the bauxite-filled Jurassic limestone and its Cretaceous cover there is a very slight but measureable angular unconformity
- In the outcrop where the samples were taken from in 2018, there was a dislocated part of the bauxite lens where sample Nh-12 comes from
- Chemical analysis was performed on 10 samples



# Bauxite Texture

From close to the bedrock-contact

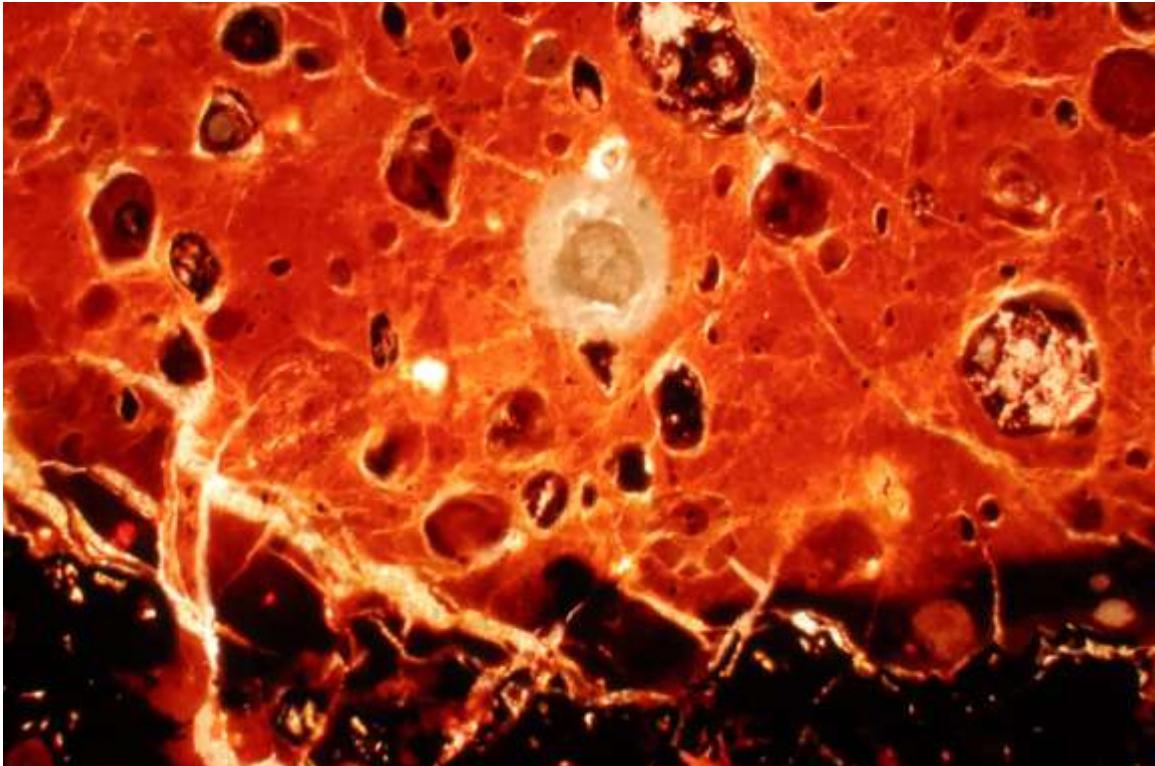


Fig. 7. Thin section of Nh-4: bauxite from paleokarstic cavity with kaolinite veins

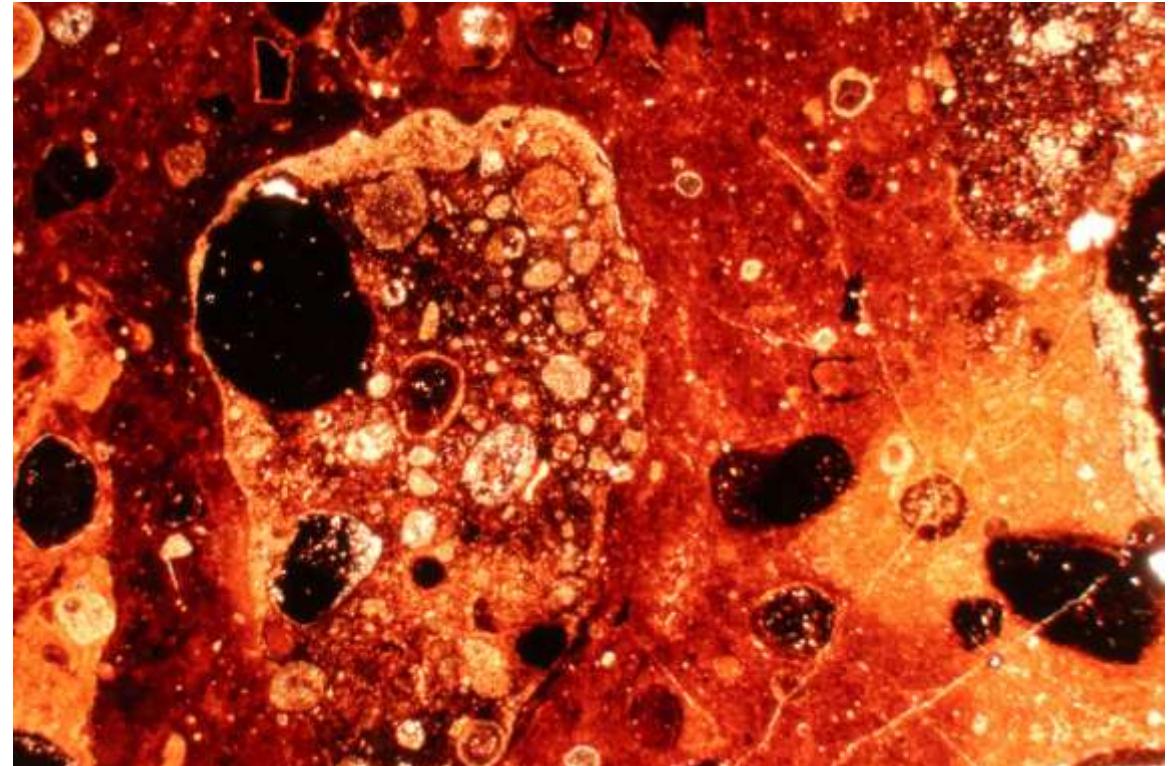


Fig. 8. Thin section of Nh-9: oolithic and pisolithic texture with micro-clastic matrix from the middle of the bauxite lens

# Bauxite texture

From under the cover-beds

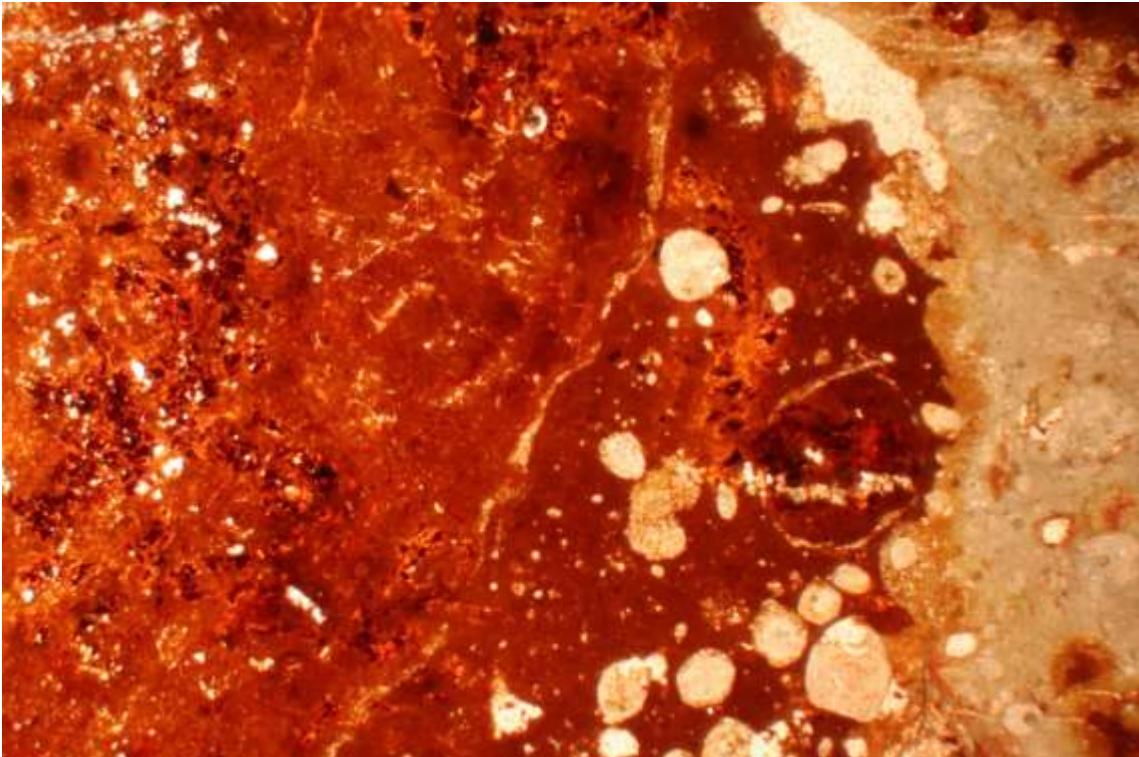


Fig. 9. (Sample: Nh-12) Reddish and pale coloured bauxite.

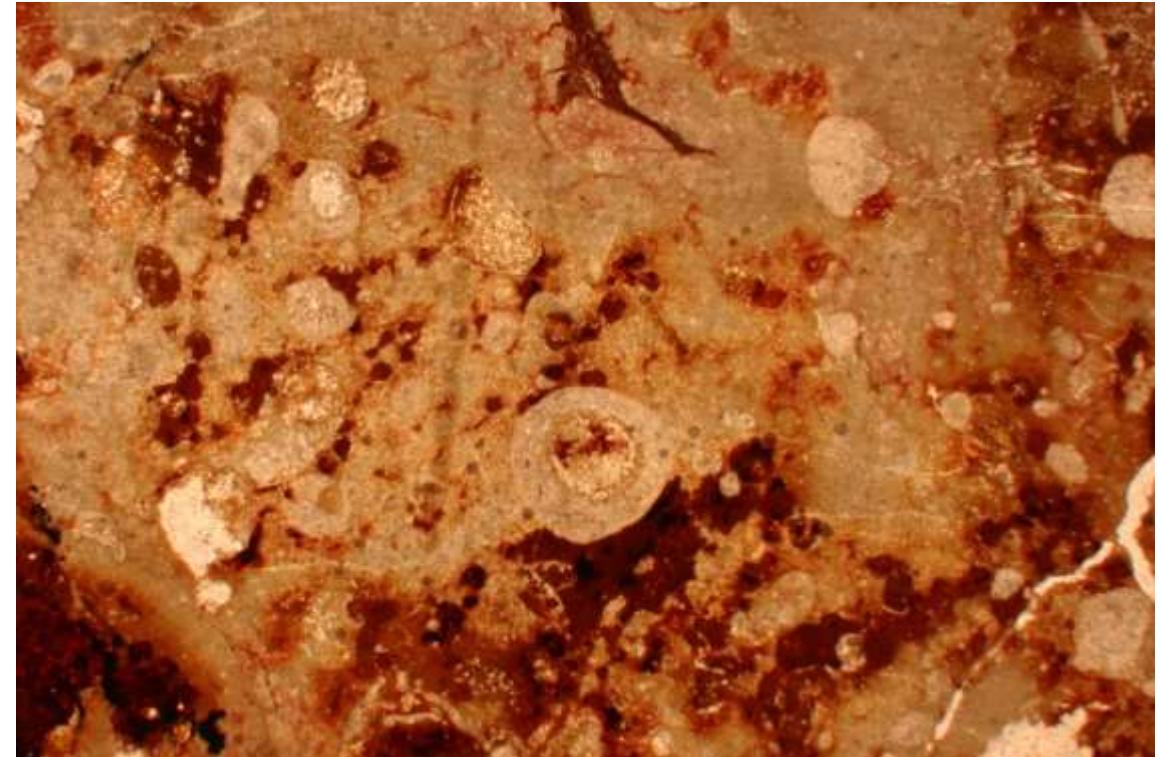


Fig. 10. Pale coloured bauxite with siderite pseudomorphs directly under the covering limestone

# Bauxite texture

From under the cover-beds

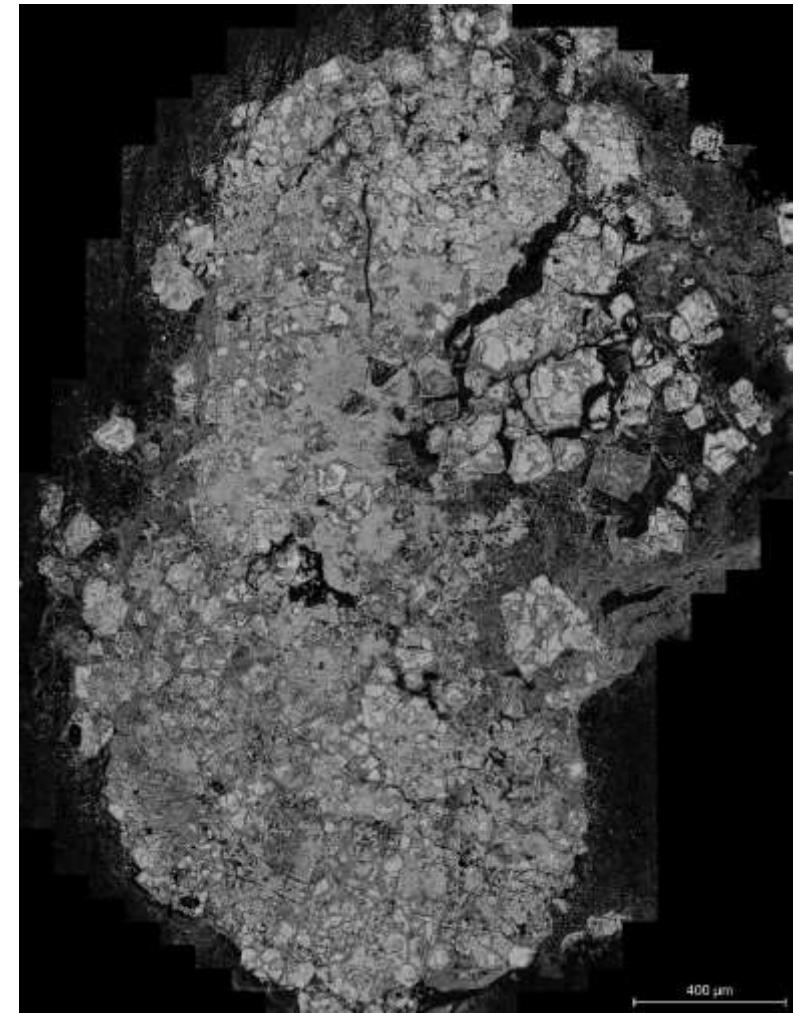
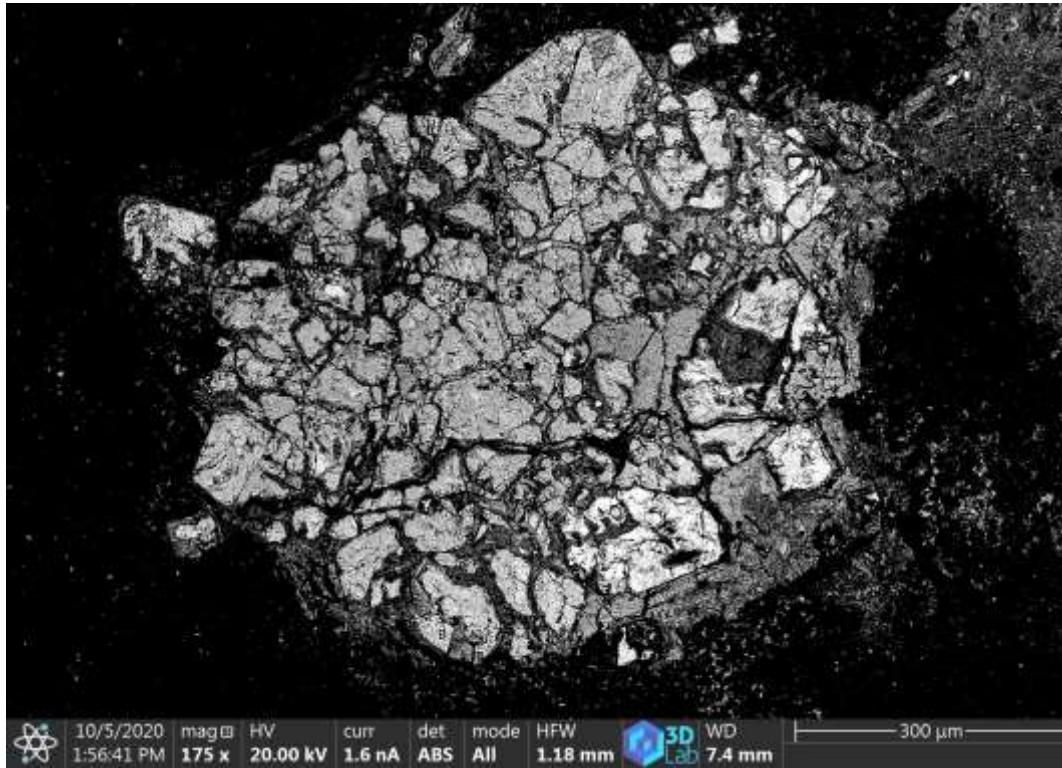


Fig. 11. BSE image of Fe-oxide pseudomorphs after siderite. Siderite suggest low-salinity pore-waters (fresh water) during deposition of the cover-beds. Oxidation of siderite is considered as a late epigenetic process

# Mineral phases identified

- XRD analyses show that major Al-phases are bohmite and diaspore accompanied by minor amounts of gibbsite
- Accessory minerals are haematite, goethite, kaolinite, anatase, rutile, zircon, chamosite.
- The presence of diaspore, chamosite, böhmite and haematite suggest changing the redox conditions during deposition and early diagenesis
- Detrital REE-minerals identified are monazite and xenotime
- Florencite and vein-filling bastnäsite are important REE-bearing autogenic minerals

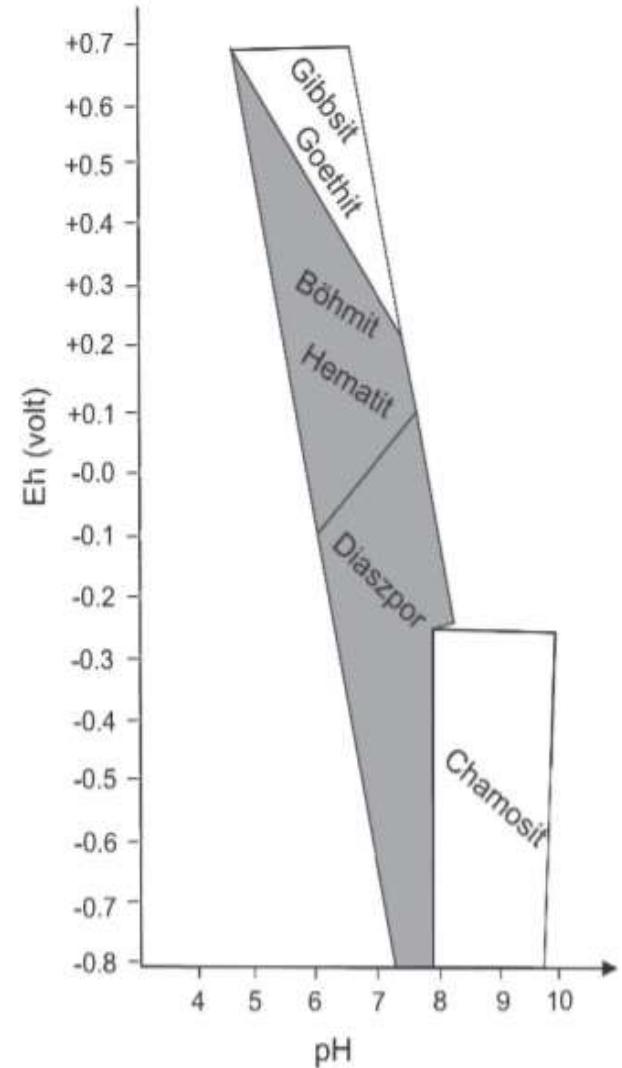


Fig.8. Stability range of main minerals of bauxites as a function of Eh and pH (KÖMLÖSSY 1970, ZARAVANDI et al. 2012).

# Major elements

- On Aleva's triangular diagram the Nagyharsány bauxite plots as „ferritic bauxite” or kaolinitic bauxite/bauxitic kaolin (exception Nh-8 sample).
- Kaolinitic bauxite comes from the small paleokarstic cavities

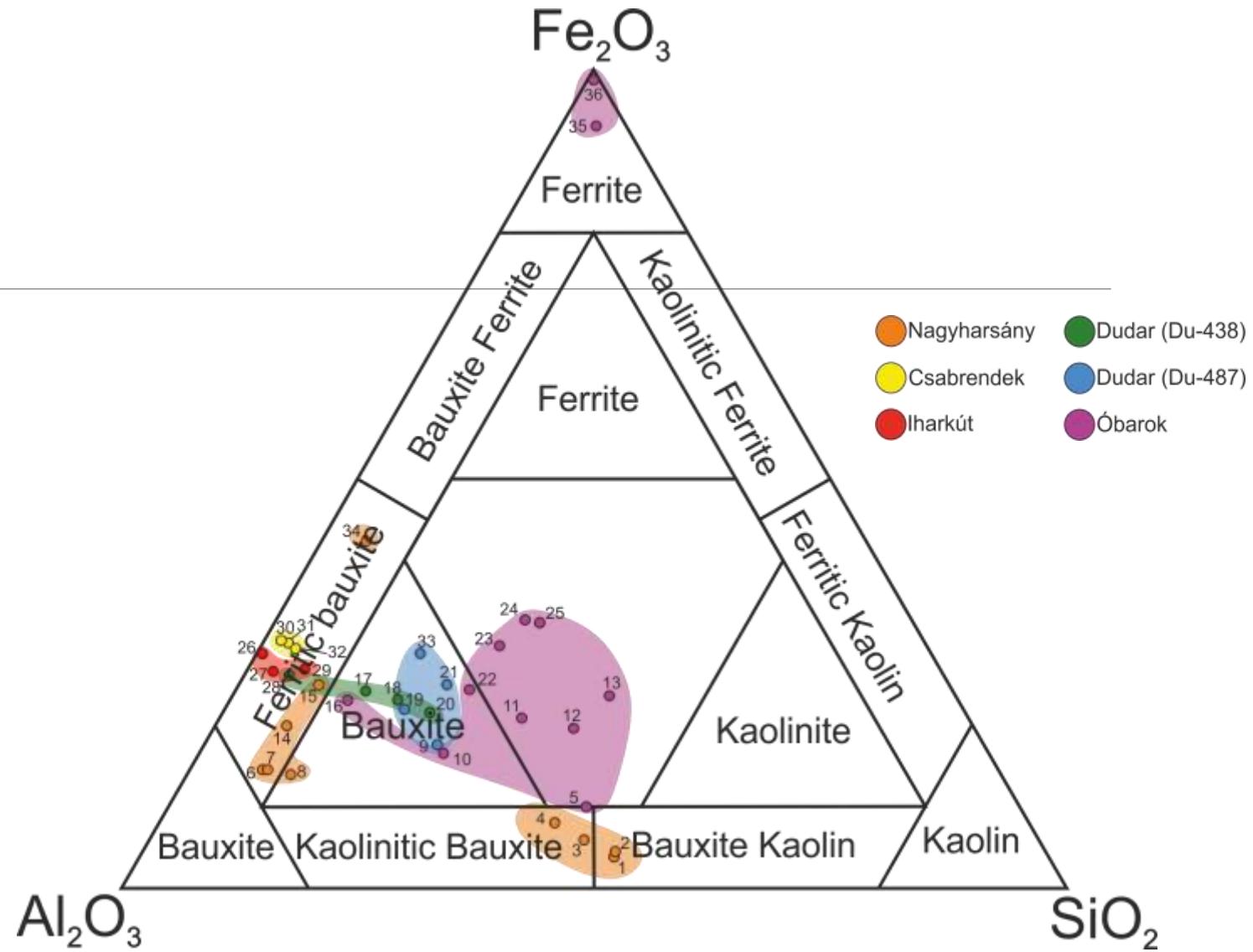
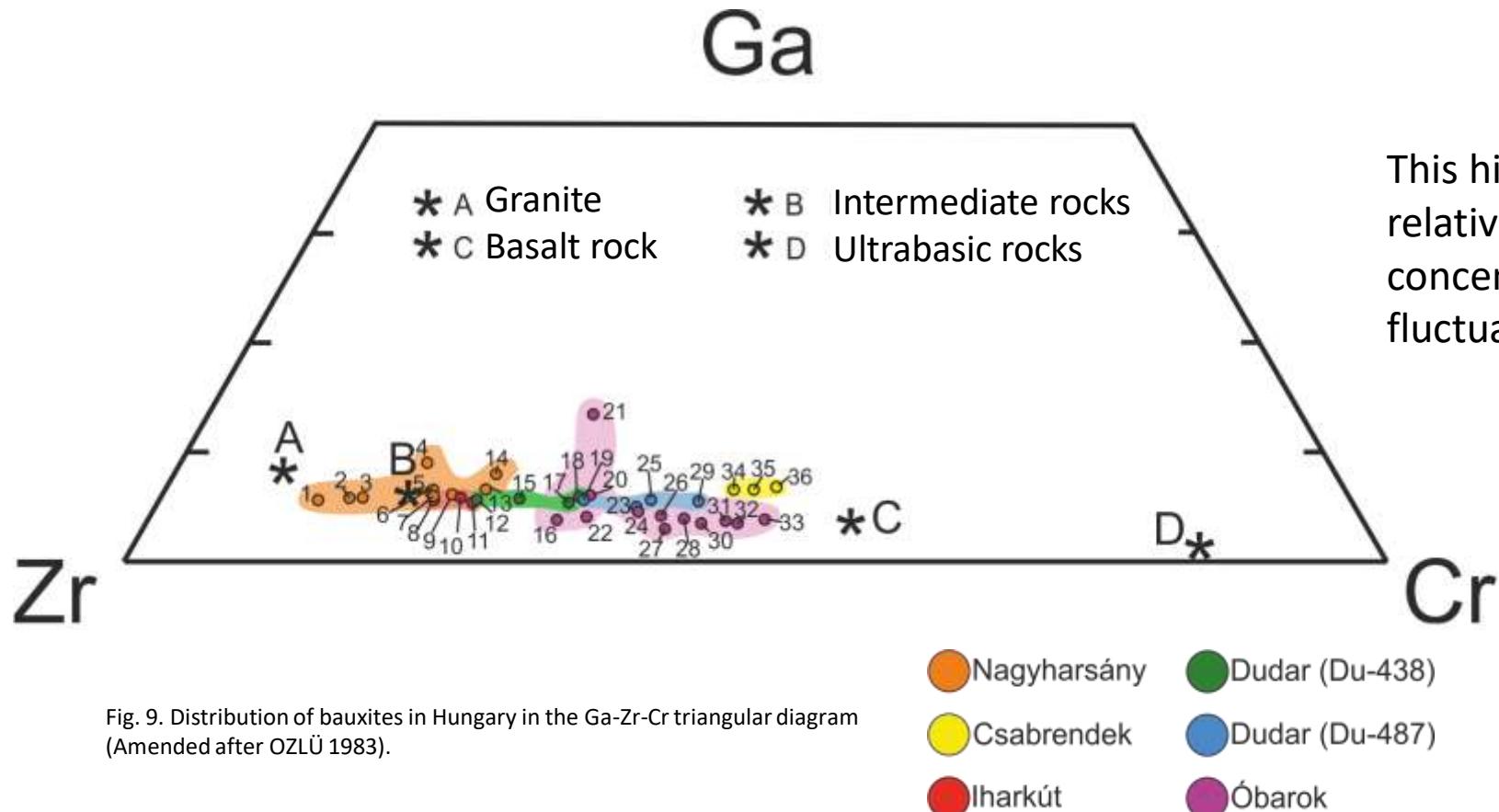


Fig.8. Distribution of bauxites in Hungary  
Fe<sub>2</sub>O<sub>3</sub> - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> in triangular diagram  
(Amended after ALEVA 1994).

# Source rock ?



This high variability is due to the relatively constant Cr and Ga concentrations, while the Zr content fluctuates considerably

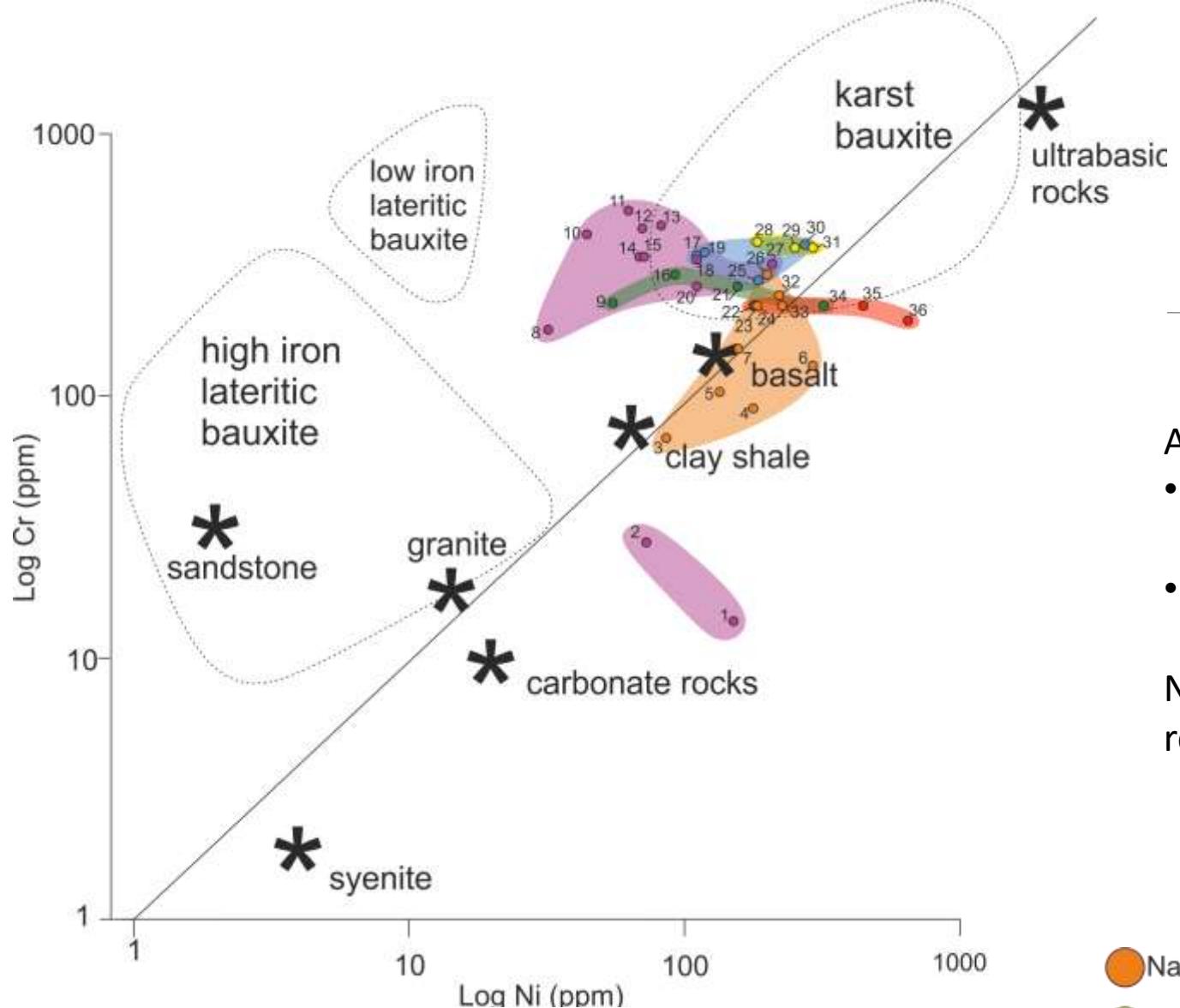


Fig. 10. Bauxites in Hungary  
 Diagram of Ni-Cr concentration in light of the composition of potential source rocks (\*)  
 (As amended by SCHROLL & SAUER after 1968)

# Source rock ?

## Assumptions

- Diabase-like volcanics known from the Mecsek Mts (also belonging to Tisia)
- alkali (phonolitic) volcanism

Ni/Cr ratios in bauxite do not necessarily reflect the protolith of the bauxite!

- |               |                  |
|---------------|------------------|
| ● Nagyharsány | ● Dadar (Du-438) |
| ● Csabrendek  | ● Dadar (Du-487) |
| ● Iharkút     | ● Óbarok         |

# Distribution of major-and trace elements and REE's in the vertical profile sampled in 2018 at Nagyharsány

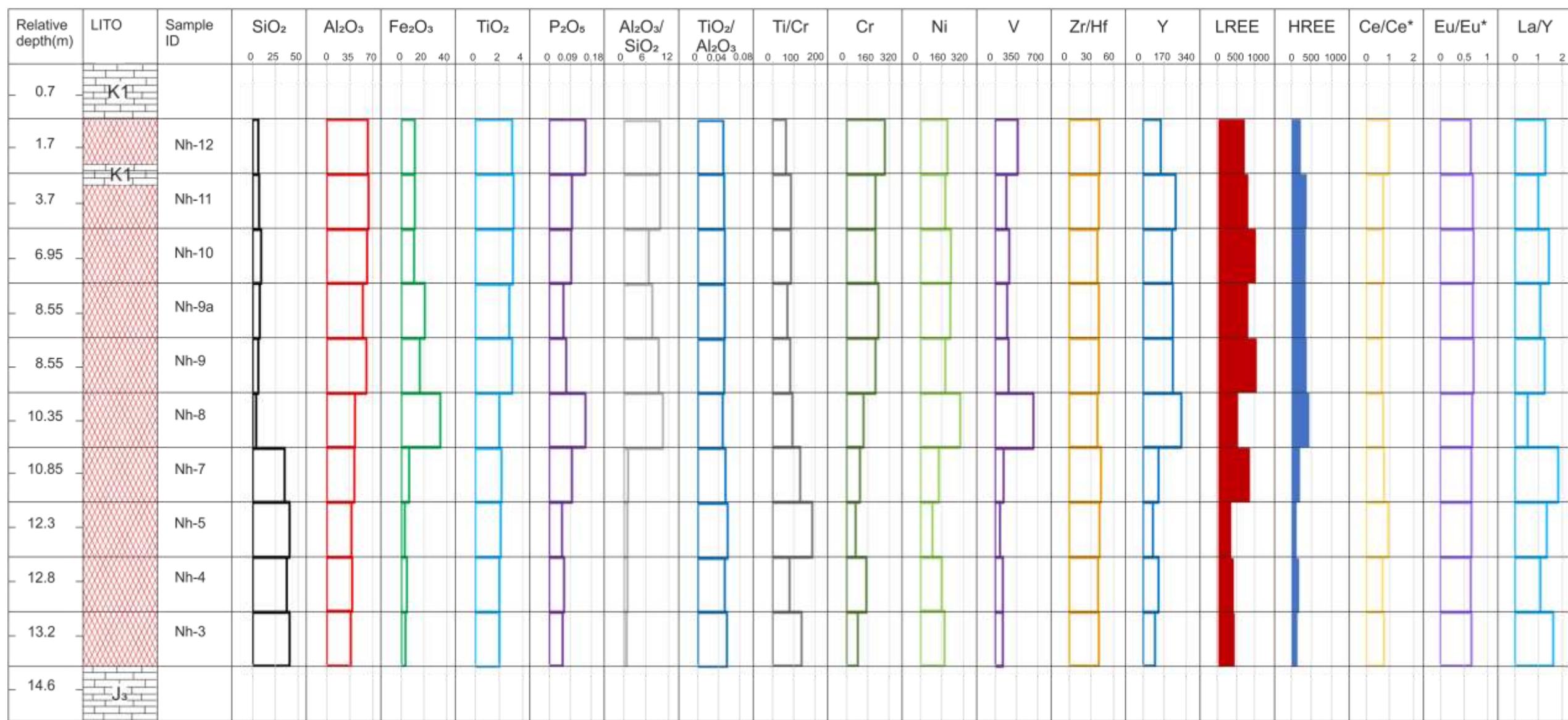


Table1.. Distribution of the major oxides and some trace and REE elements of the Nagyharsany bauxite deposit

# REE contents

Chondrite-normalised diagram:

- Shows an increased amount of LREE
- Samples show negative Ce and Eu anomaly
- Ce anomaly remains also in UCC2 normal diagram

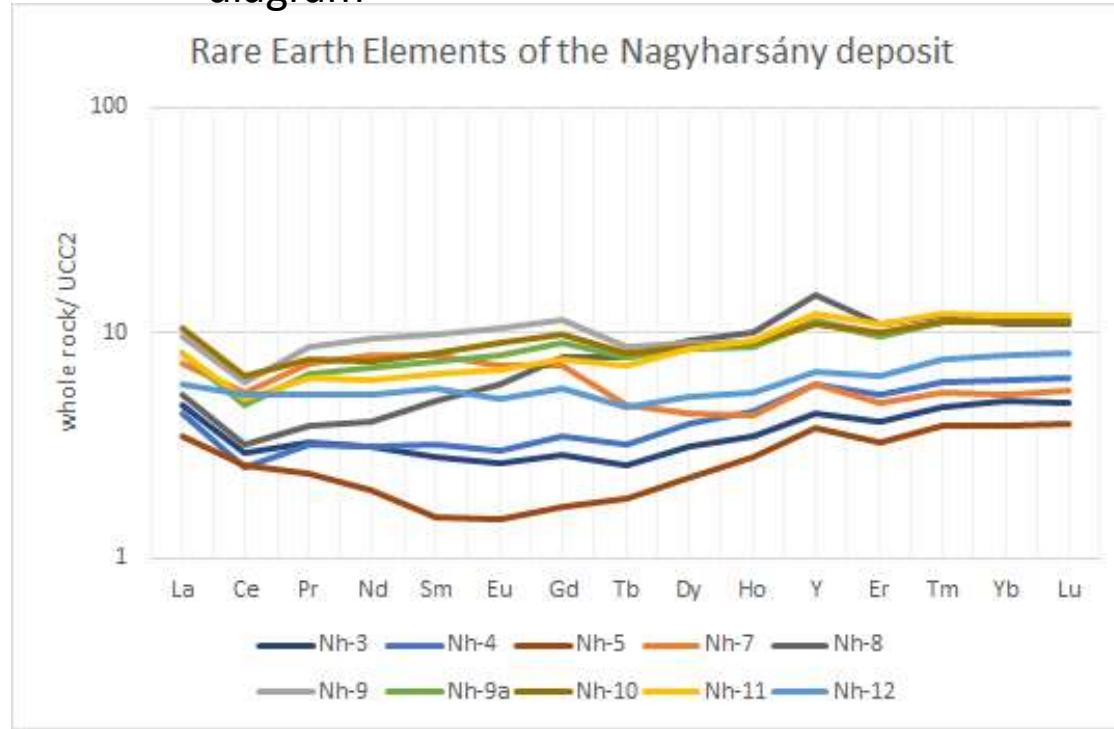


Fig. 12. UCC2 normalised data for REE values

Rare Earth Elements of the Nagyharsány deposit

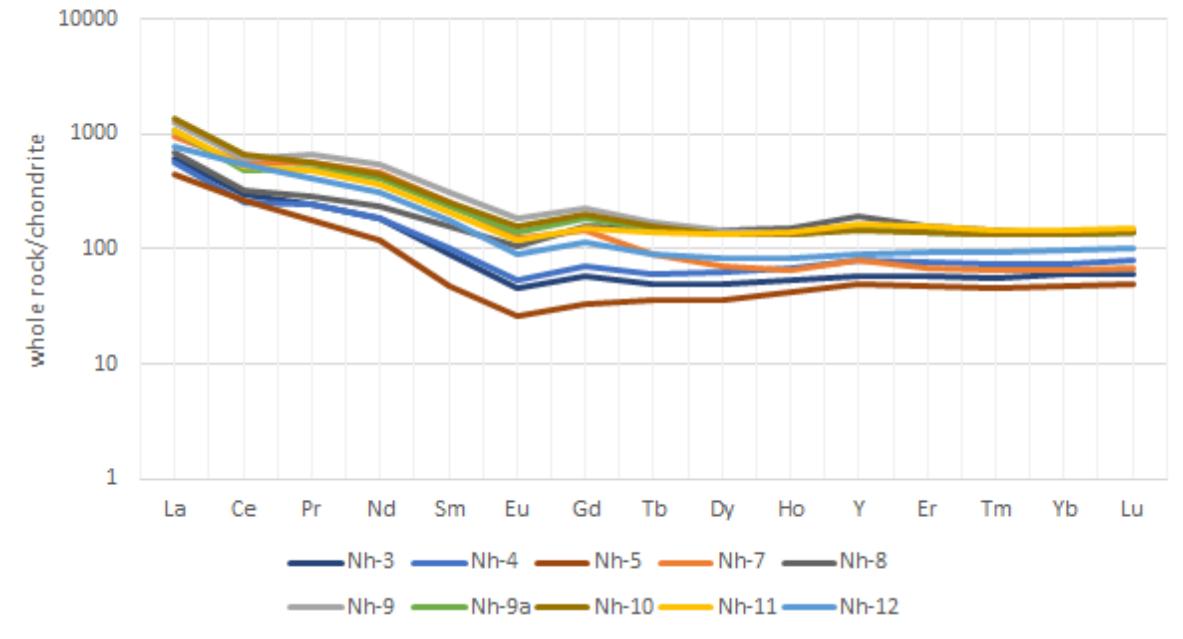


Fig. 11. Chondrite-normalised data for REE values

UCC2-normalized diagram:

- Preserved Ce anomaly
- Significant Yttrium content
- Kaolinitic bauxite shows lower amounts of REE

# Secondary Rare Earth Element concentration in the bauxite

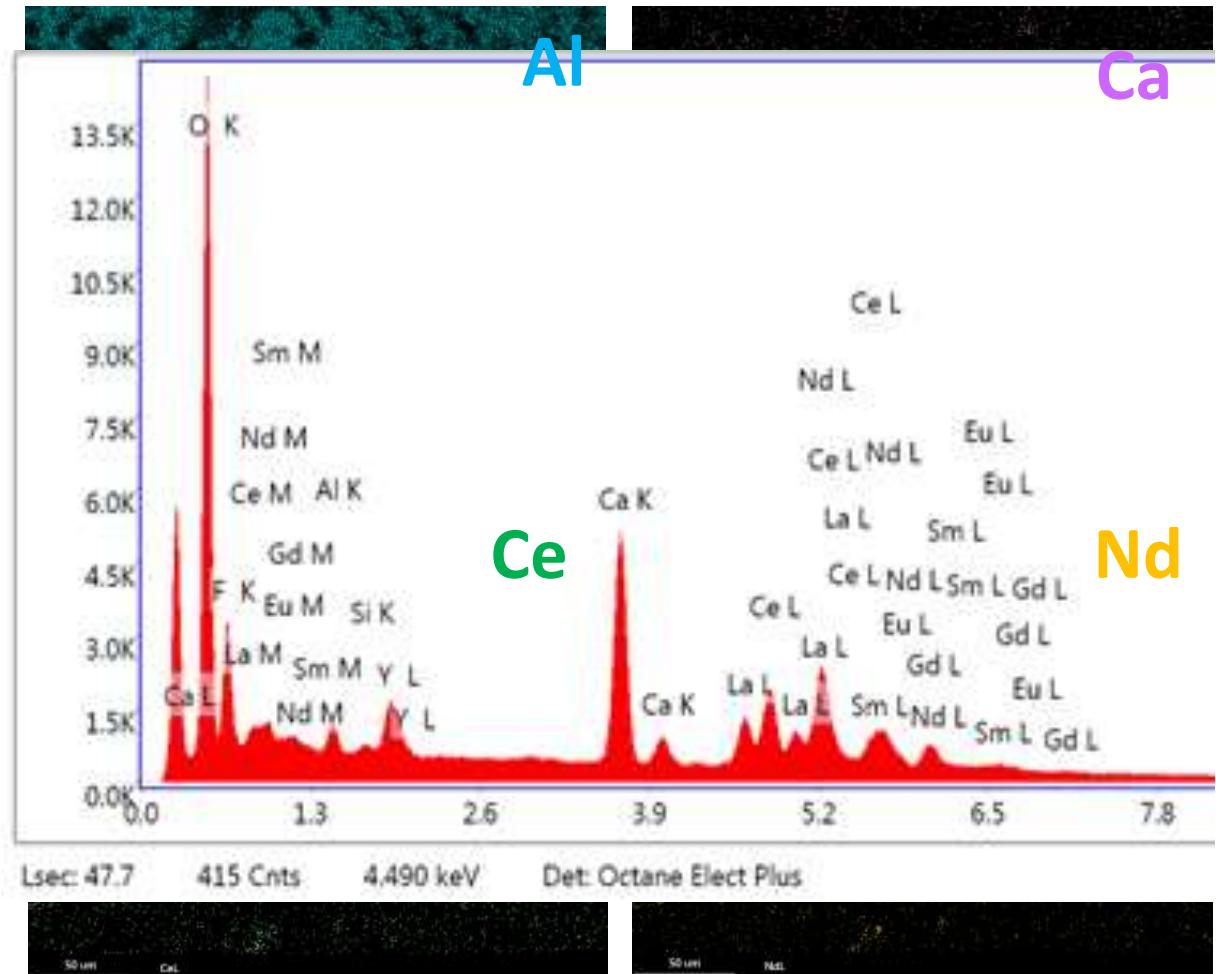
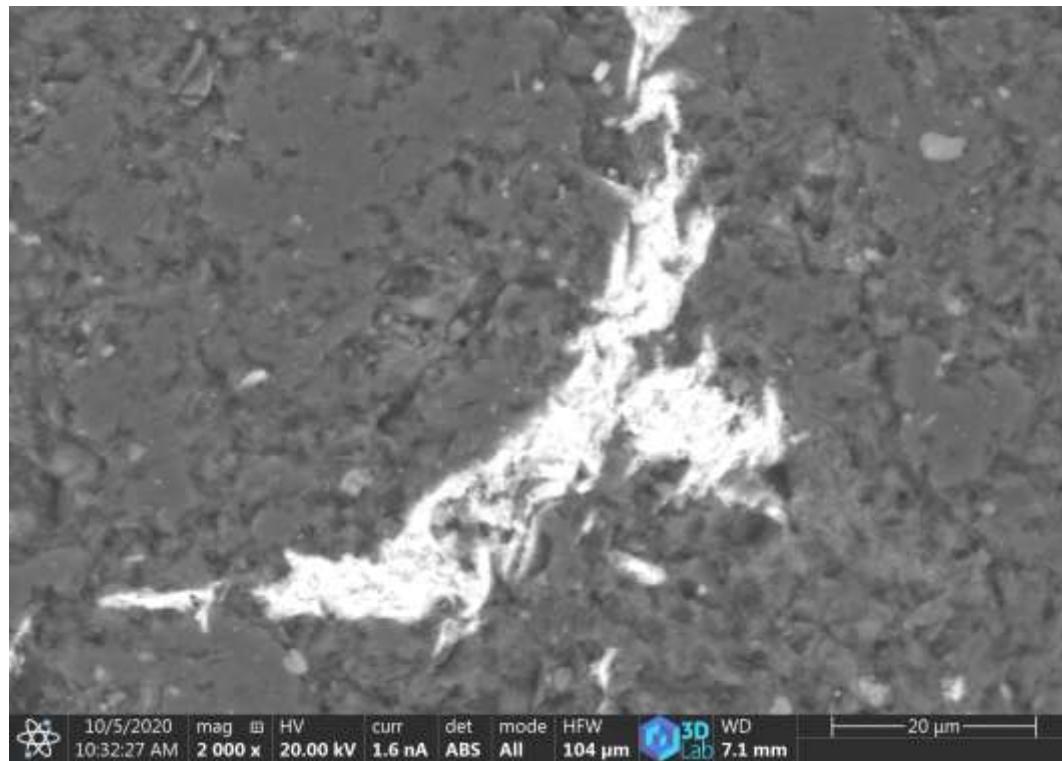


Fig.12: BSE image showing vein-filling, feather-like bastnäsite:

# REE-bearing detrital minerals in the Bauxite

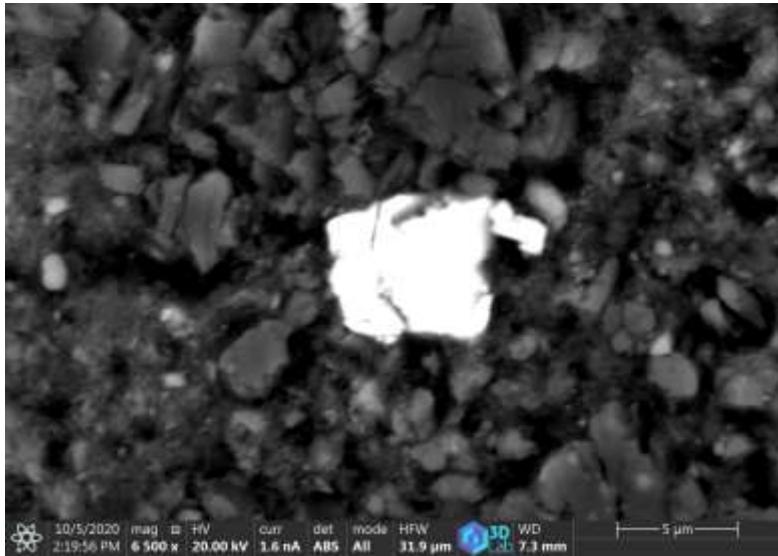


Fig. 13. BSE image of detrital monazite

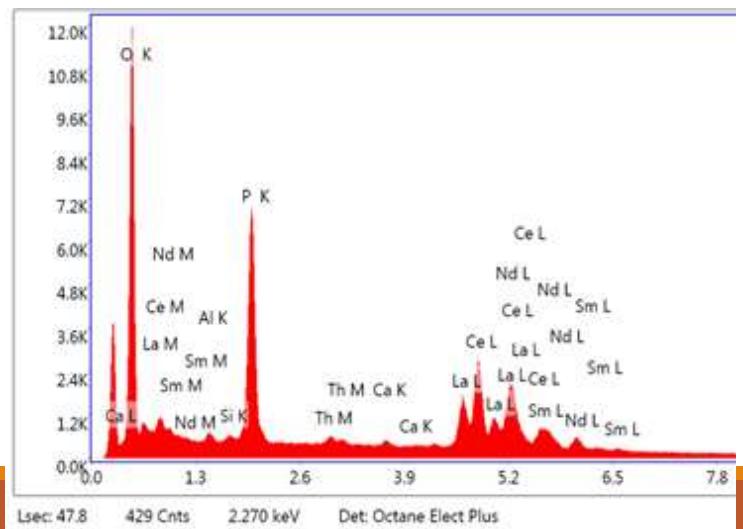
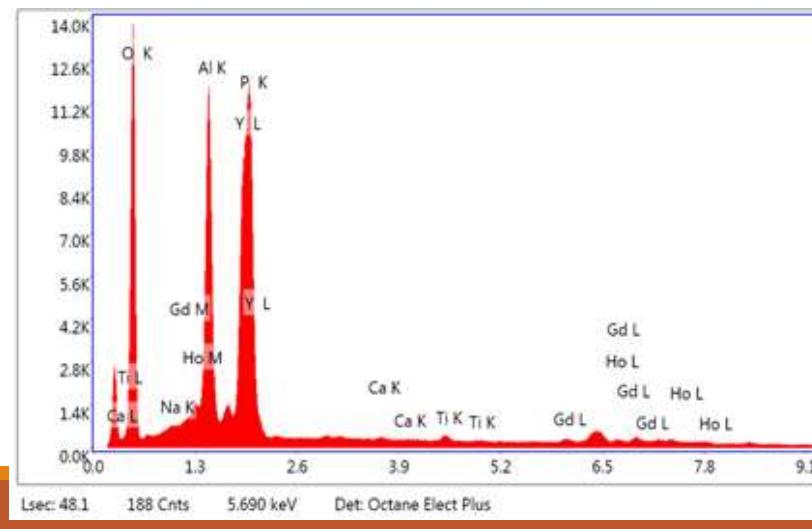


Fig. 14. BSE image of detrital xenotime



# Remaining issues

- Provenance: what is the main source rocks?
- How does the vertical distribution of detrital minerals change?
- What is the age of the source rock?

# Further investigations suggested

- Heavy mineral separation to understand the provenance and the history of bauxites of the Villány Mountains. Previous investigations couldn't give the exact answer what regarding the source of the pre-bauxitic material.
- Age-dating of Zircon grains could help to solve this question and may specify also the age of the bauxite
- Detailed XRD analysis of the clay fraction may give more information about the paleo-drainage

# Summary

- The relatively short apparent stratigraphic gap, morphofacies and lithofacies all point to a close-to-groundwater-table position on a temporarily exposed isolated pelagic platform as the depositional environment of the bauxite.
  - The REE+Y content of the Nagyharsány bauxite are between 463-1426 ppm, based on 10 samples. The low amount of the Eu content come from the source rocks.
  - Significant rare earth mobilization occurred during the diagenesis but rare earths are not enriched in the lower part of the bauxite lens.
  - REE content presumably come from basaltic and alkali volcanism of Mecsek Mts but further investigations can specify the source rock.
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- Acknowledgements to
  - M.Leskó (Miskolc University); S.Józsa and L.Szikszay (ELTE), and to DDCM Co.Ltd Nagyharsány



Thank you for your attention!

