Professional Development Workshop on

Critical Raw Materials Content in Thermal Waters: Analysis and Assessment

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University of Miskolc, Hungary

Critical element potential of the geothermal project of Szeged

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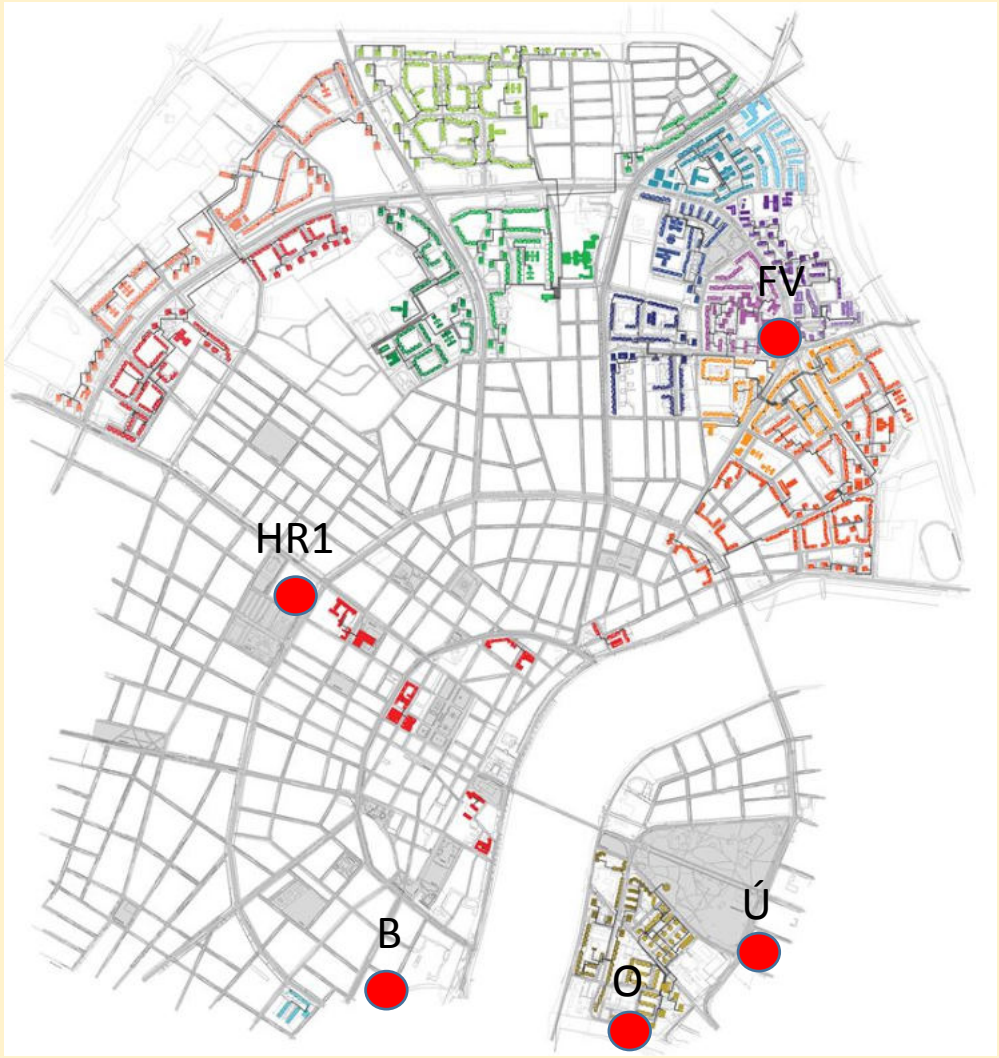
The Szeged geothermal project

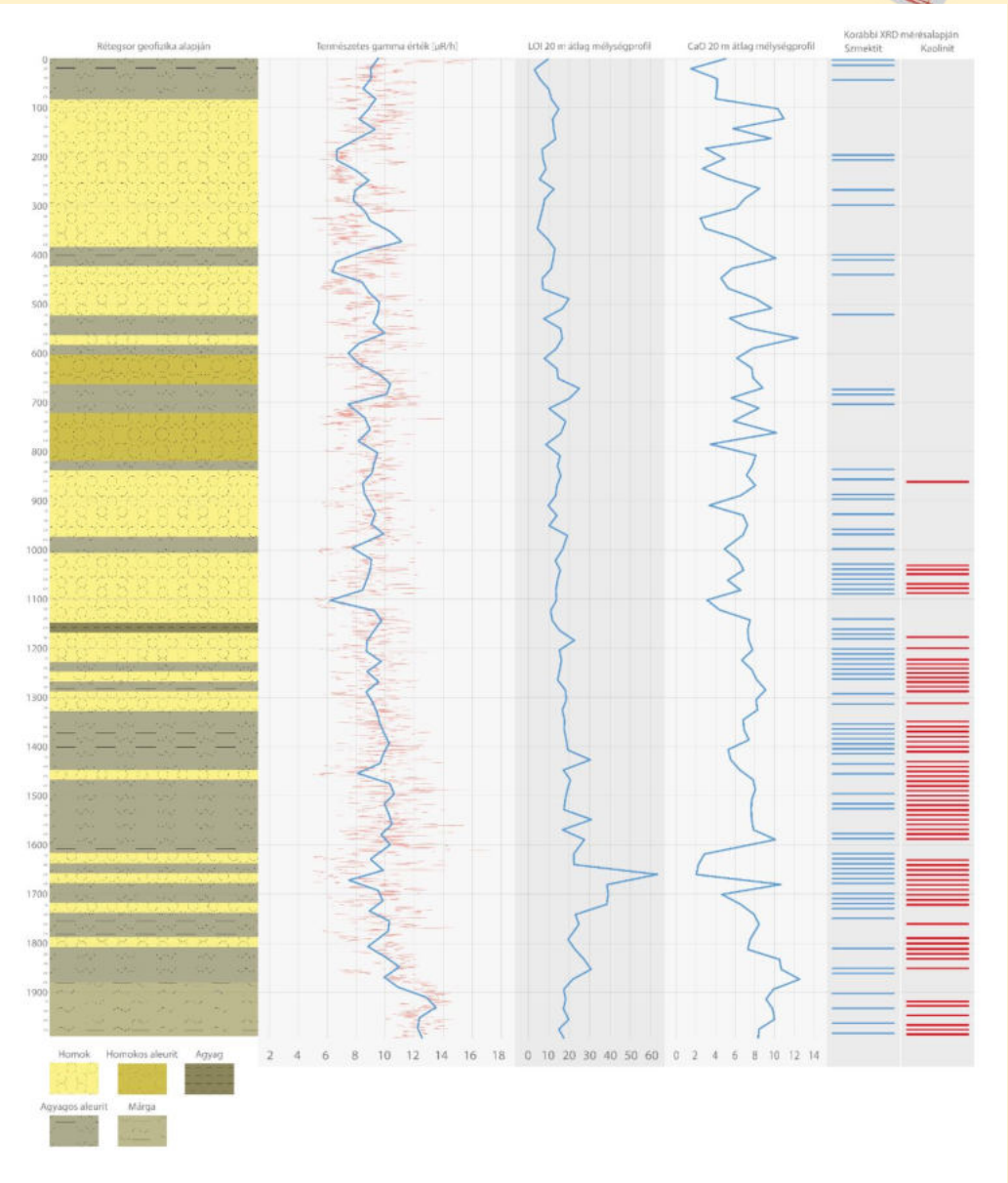
- Second largest geothermal-supplied district heating system in Europe
- 27 500 heated residential units
- 9 geothermal system
- ~50 MW nominal power
- Sold thermal energy: ~ 400 000 GJ
- Retrieved natural gas: ~ 13 000 000 m^3
- Retrieved $CO_{2\ eq}$: ~ 28 000 t

Test wells



The Szeged geothermal project

- Each system has 1 production and 2 reinjection wells
- The depth of the production wells is ~2000 m
- The depth of the reinjection wells is ~1750 m
- The temperature of thermal water on the bottom of the well is 98 °C
- The average water yield of all wells is 60–70 m^3/h
- Total production is 2 700 000 m^3/year



Critical elements of the reservoir – the strategy

Collection of cutting at every 10 m

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Cleaning of the cutting samples

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XRD for the mineralogical composition of the cutting samples

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SEM for mineralogy and microtexture of the samples

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Major and trace element composition of the cutting samples (ICP-MS)

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Multivariate statistical evaluation of the geochemical dataset

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The aim is to understand the major **critical element accumulation processes and horizons**

Composition of the geothermal water

- 5 wells were tested for trace elements
- No water production for years
- Close to equilibrium conditions in the water-rock system
- The concentration of some critical elements
  - B: 5000–12000 mg/l
  - Bi: 20–30 mg/l
  - Ge: 10–15 mg/l
  - Li: 40–70 mg/l
- Significant amount with ~ 3 Ml of annual geothermal water production

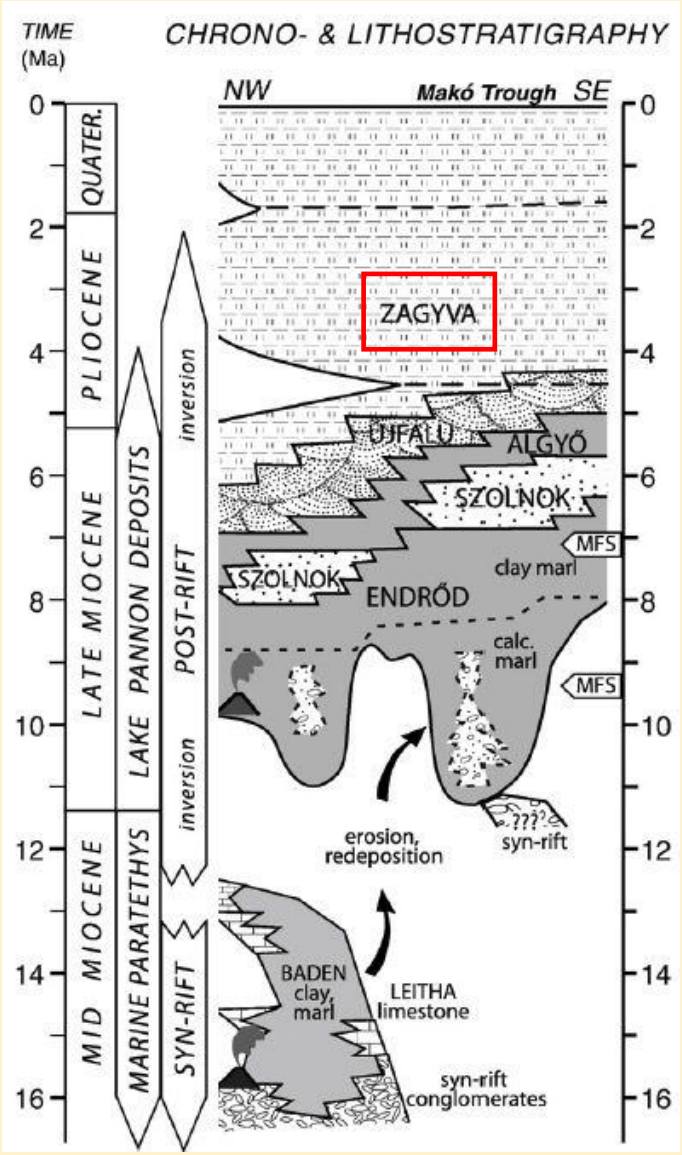
The source rock – Pannonian sedimentary sequences

- During the Late Miocene, the Lake Pannon was slowly filled up by turbidite lobes (Szolnok Formation), slope deposits (Algyő Fm.), and then deltaic lobes (Újfalu Fm.).

- The area became an alluvial plain ca. 5 Ma years ago (Zagyva Formation).

- The typically few metres thick sand beds are intercalated with variegated silty clays of floodplain, marsh and shallow lacustrine origin.

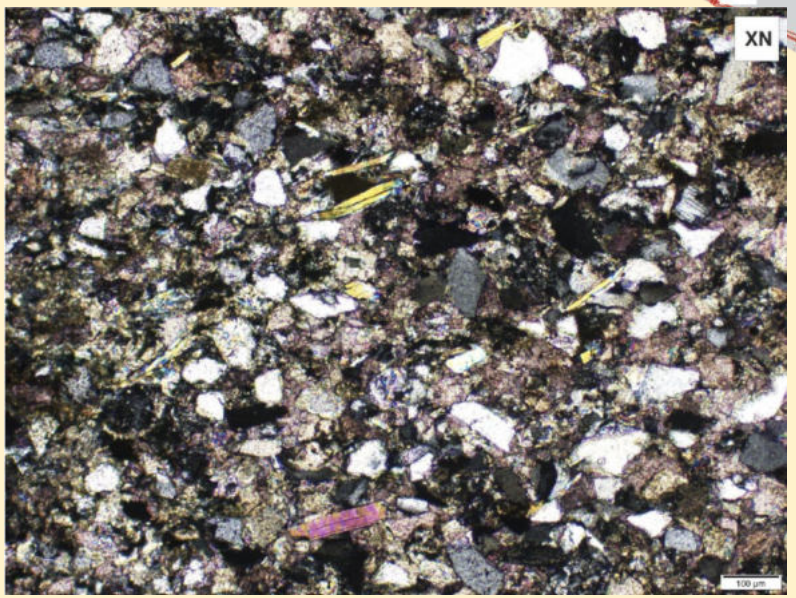
- Coal beds and thick paleosoil horizons with carbonate accumulations frequently occur.

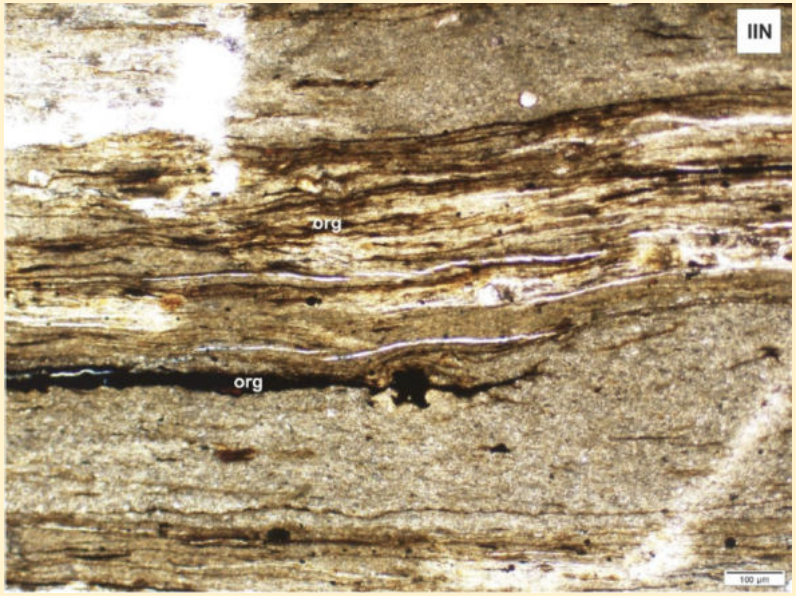


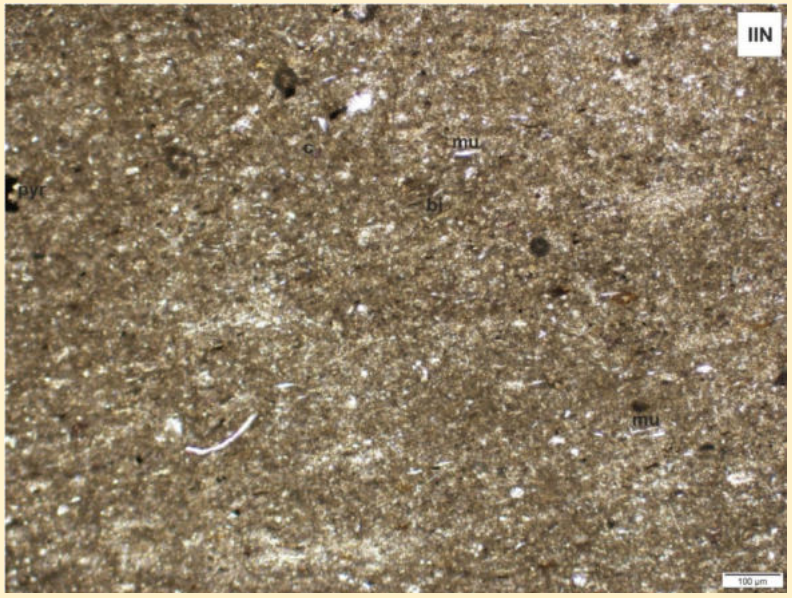
Sztanó et al. 2013

The source rock – Pannonian sedimentary sequences

- The study area can be represented by two major and one minor lithotypes
  - Fine-grained sandstone
  - Calcareous claystone
  - Coaly calcareous siltstone (marl)





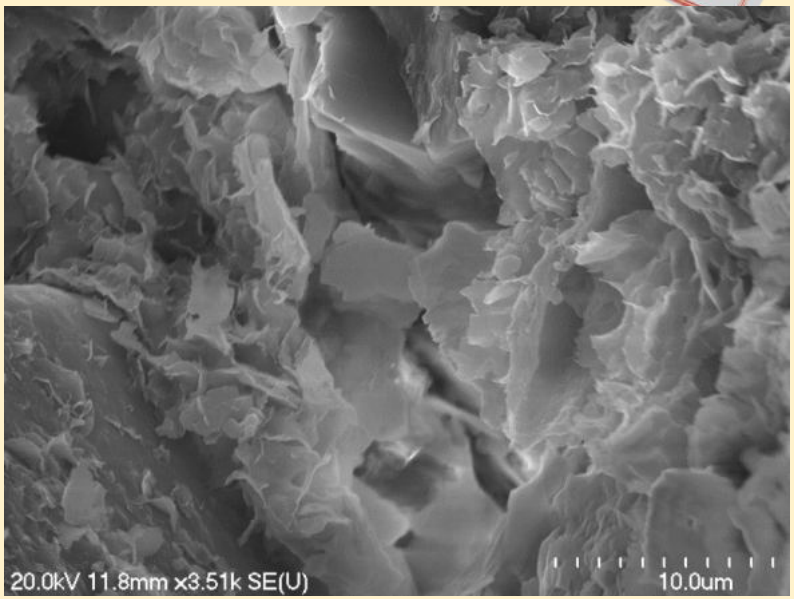


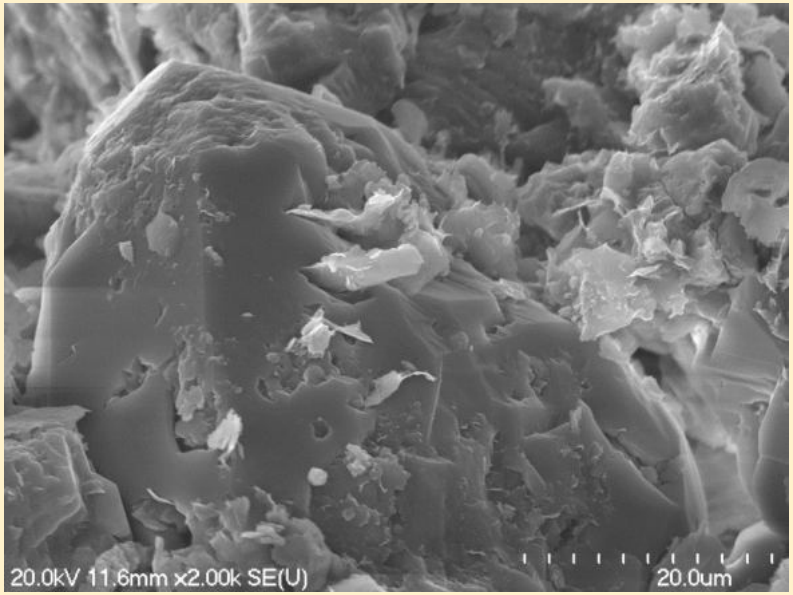
Mineral composition – SEM, XRD

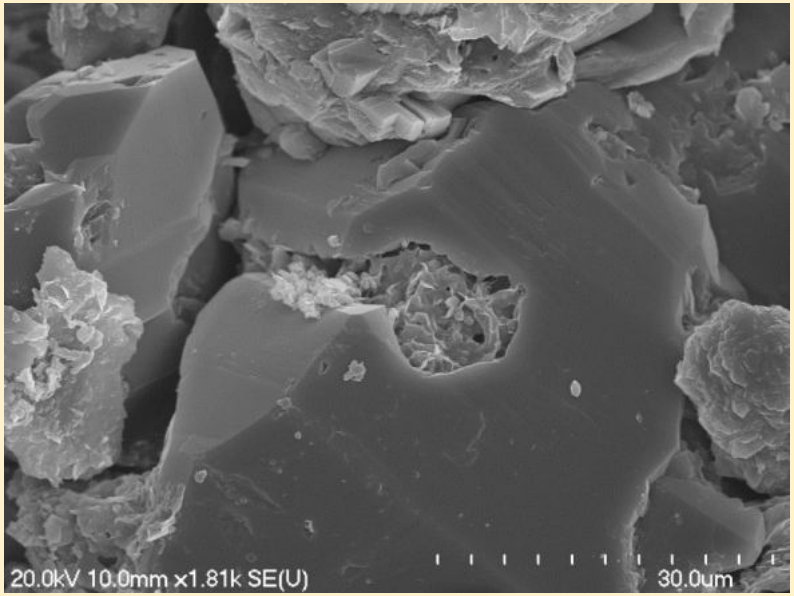
- XRD and SEM measurements prove that the essential clay minerals are smectite and kaolinite

- The sandy layers are dominated by quartz and feldspar.

- Calcite as an important cement phase is typical in both basic lithotypes

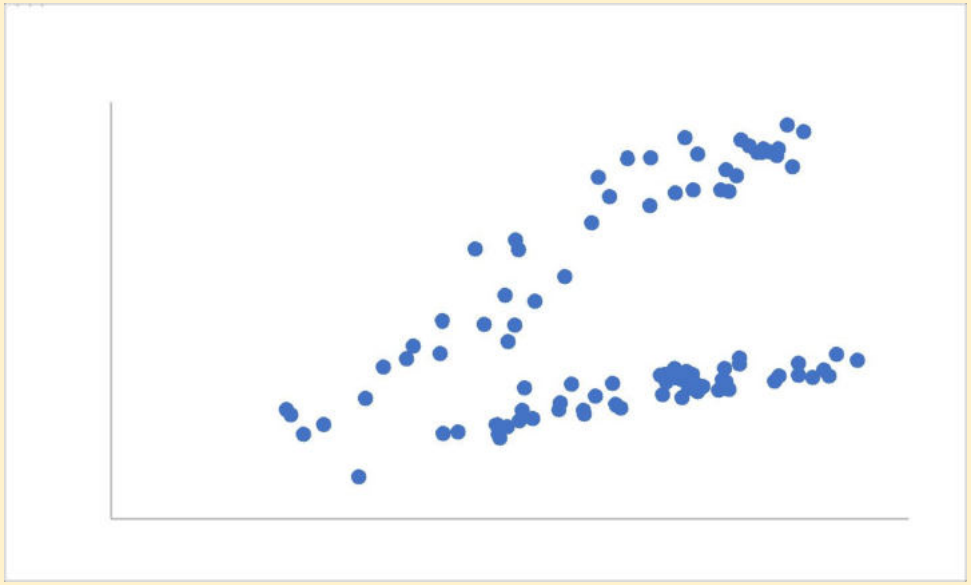


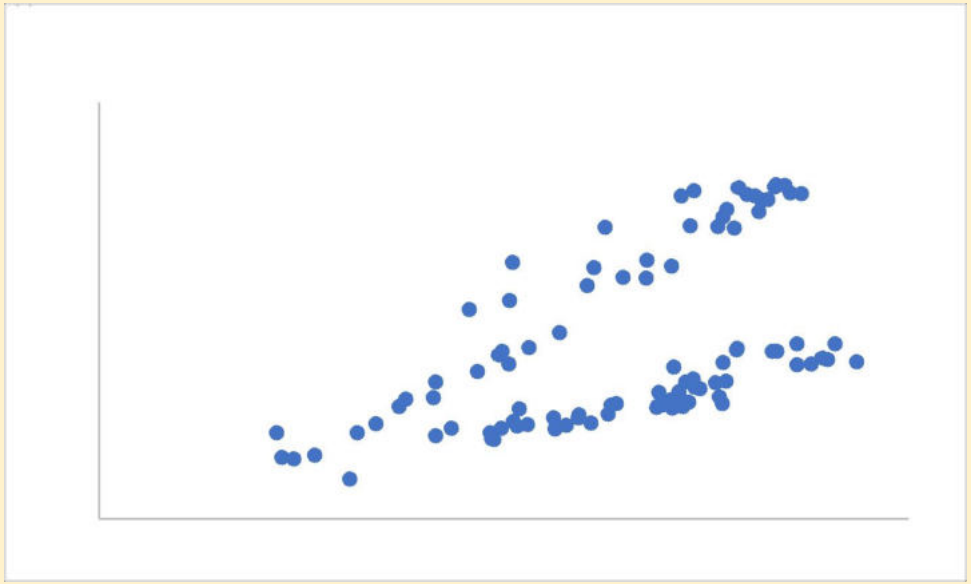




Trace element composition – well W-1

- Most elements show more (usually two) different accumulation trends
- These trends are the most characteristic if plotted with Al_2O_3
- The trends suggest different accumulation mechanisms for trace elements
- Most probably represented by different rock types
- Sandstones
- Claystones/siltstones
- Marls/Carbonate rocks





Statistical evaluation – chemostratigraphy

The wells can be subdivided into sandy and clayey sections using chemical composition

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To do so, Linear Discriminant Analysis (LDA) can be used

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Independent evaluation of geochemical data for the two lithologies

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Principal component analysis (PCA) for major elements to outline major rock-forming processes

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PCA for trace elements to **outline the significant accumulation processes**

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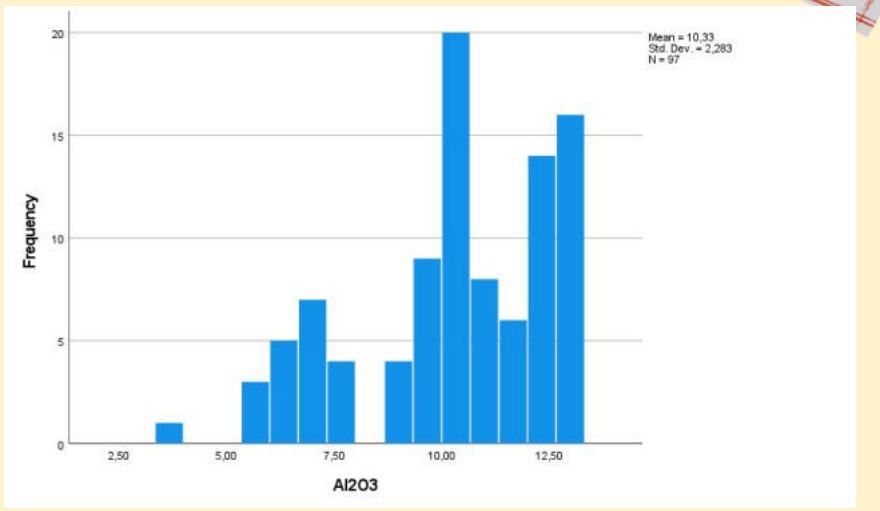
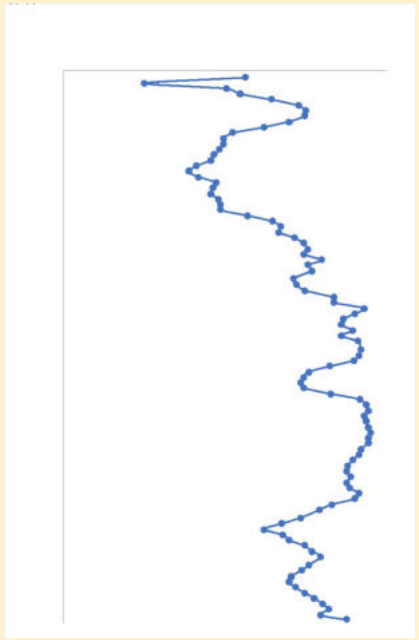
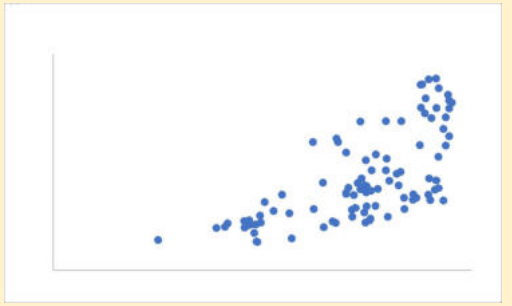
Spatial evaluation along with the studied wells to locate accumulation horizons

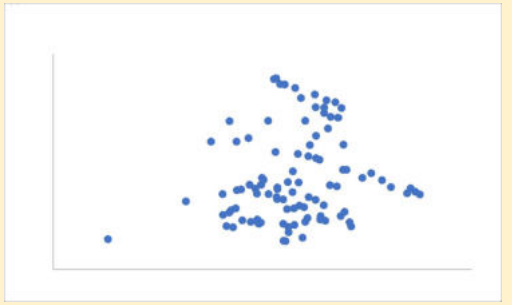
Major elements – consequences on petrography

- The best chemical indicator is the Al-content
- High Al – clayey horizons, low Al – sandy horizons
- The histogram suggests three Modi
- Based on petrology, the sample group with medium Al_2O_3 represent marls
- $Al_2O_{3,}$ along with the well, shows a continuous run
- LDA to distinguish the two basic lithologies (clayey and sandy)
- Carbonate content hardly modifies trace element accumulation

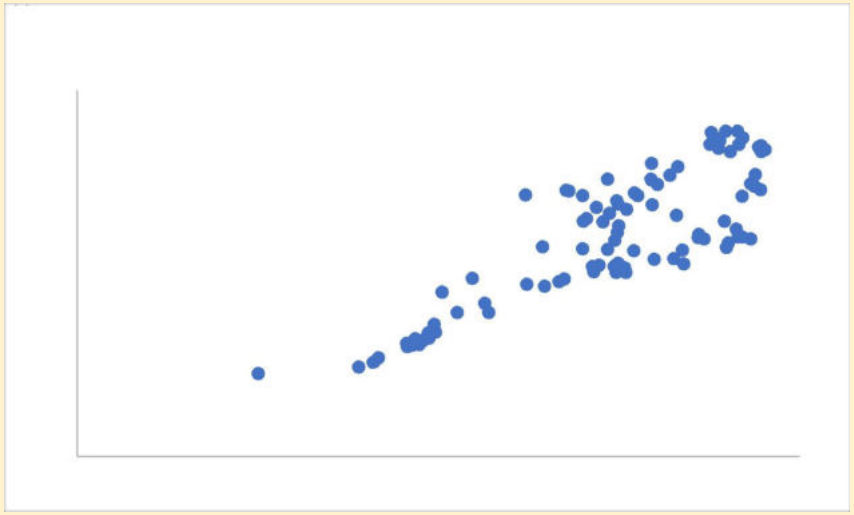


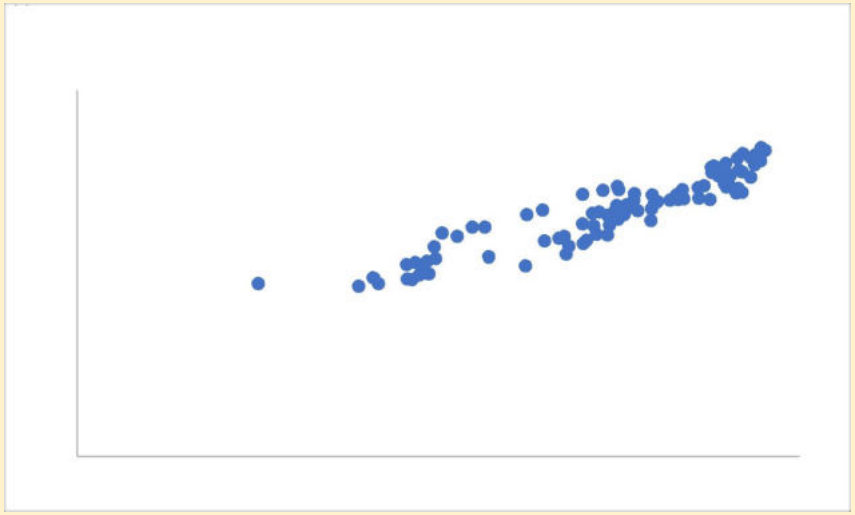


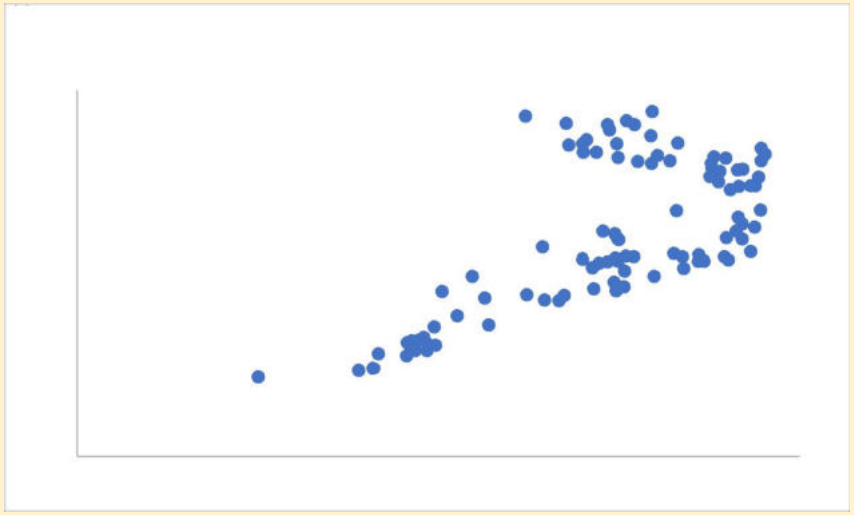


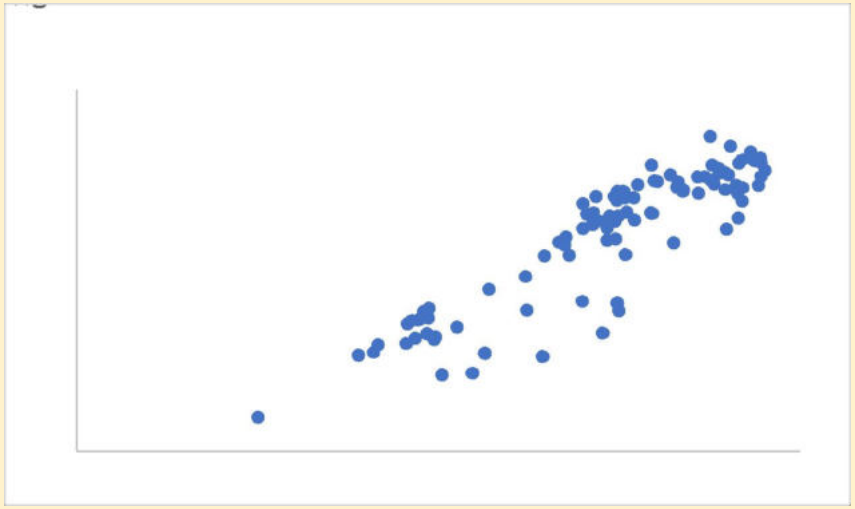


Major element accumulation – Al-dependence (Ti, Fe, Mg, K)



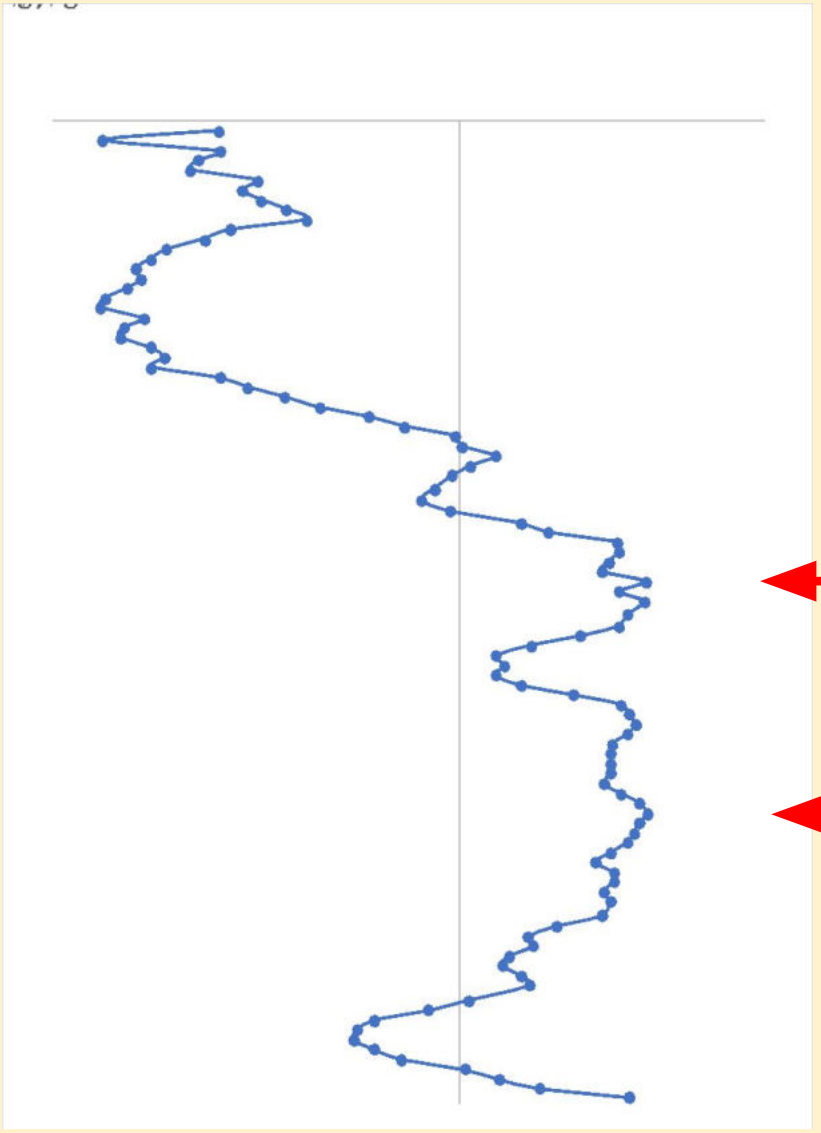






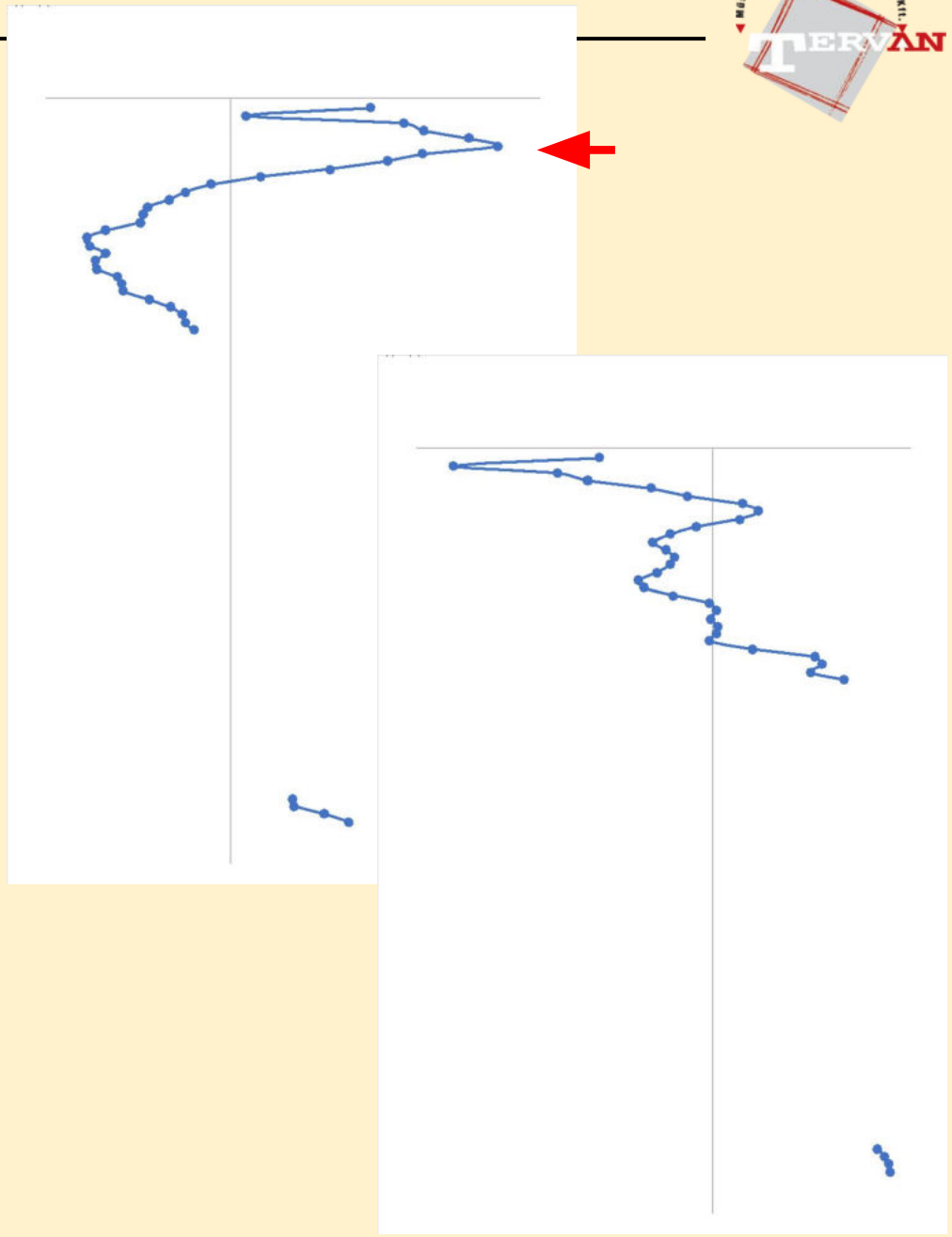
Major elements – consequences on petrography

- For LDA sections with Al_2O_3 < 7% are sands
- Those with Al_2O_3 > 12% are clays
- The others are classified based on the discriminant function
- $D = 2.3Al_2O_3 + 6.2MgO + 1.3Fe_2O_3 -4.6K_2O – 2.6CaO$
- Clayey horizons are defined by
  - increase of smectite-type clays (Al, Mg) and limonite (Fe)
  - decrease of K-feldspar (K)
  - decrease of calcite (Ca)
- Continuous change from clays towards more sandy layers



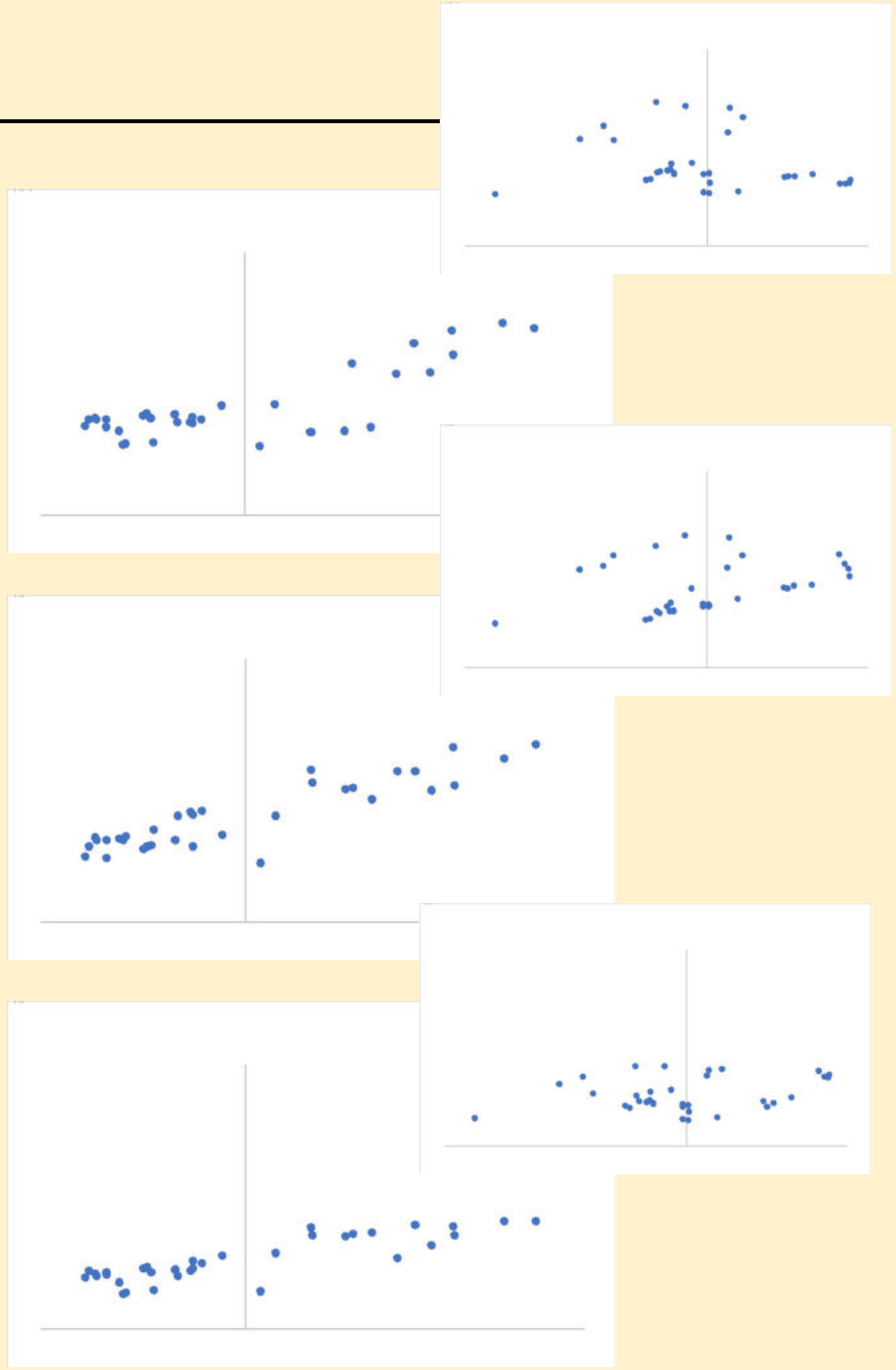
The sandy horizons – major elements

- PCA results in two principal components
- PC1_1: Ti, Al, Fe, Mn, Na, K, P
- PC1_2: Ca, Mg
- PC1_1 represents the immature siliciclastic sandy sediments
- PC1_2 is for the role of carbonates in the sandstones
- Likely calcite-cemented sandstone horizons become recognisable
- Clue for trace element accumulation tendencies in the sandy horizons



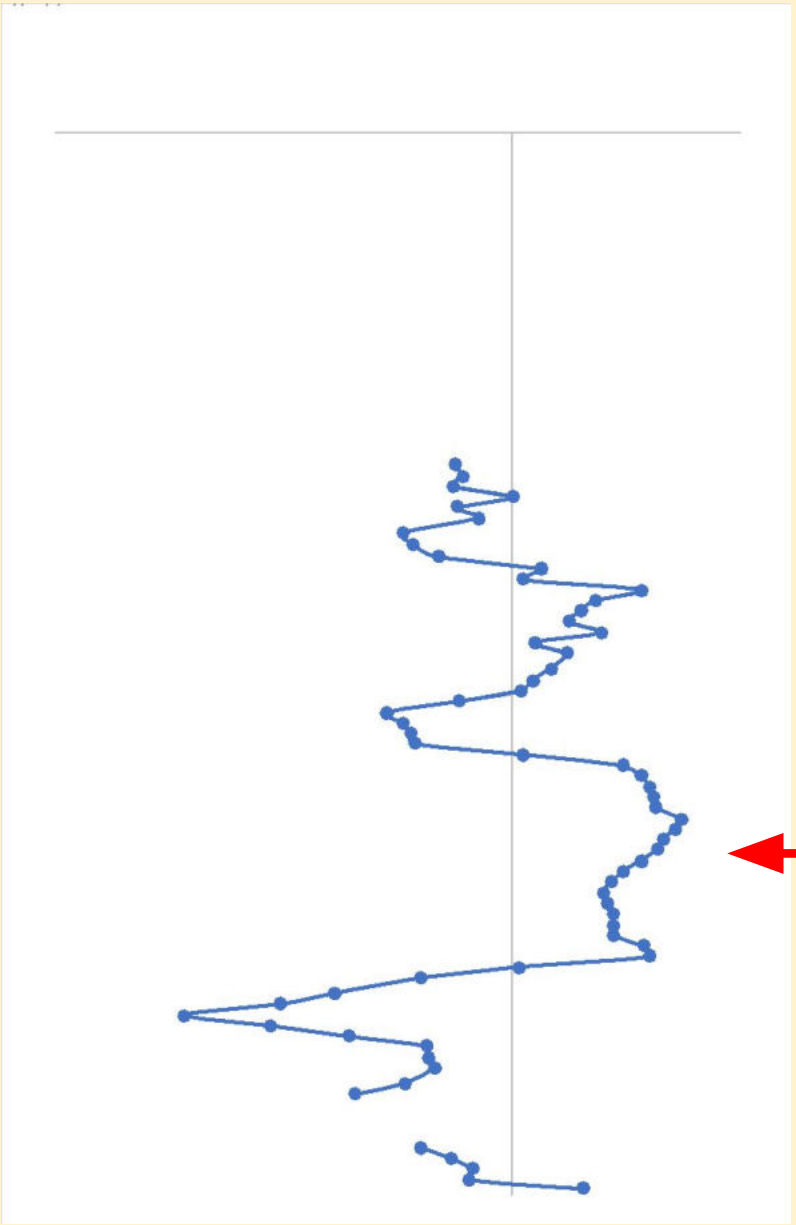
Trace element behaviour in the sandy horizons

- Most lithophile elements (e.g. Zr, Li, REE) increase significantly with the PC1_1 variable.
- The less mature the sandstone is (more Al, K, Ti, Fe, etc.), the more trace elements it may contain, probably as accessory phases.
- The value of the PC1_2 variable is independent of the trace element concentrations.
- Carbonate content has no significant effect on critical element accumulation of the sandstones.



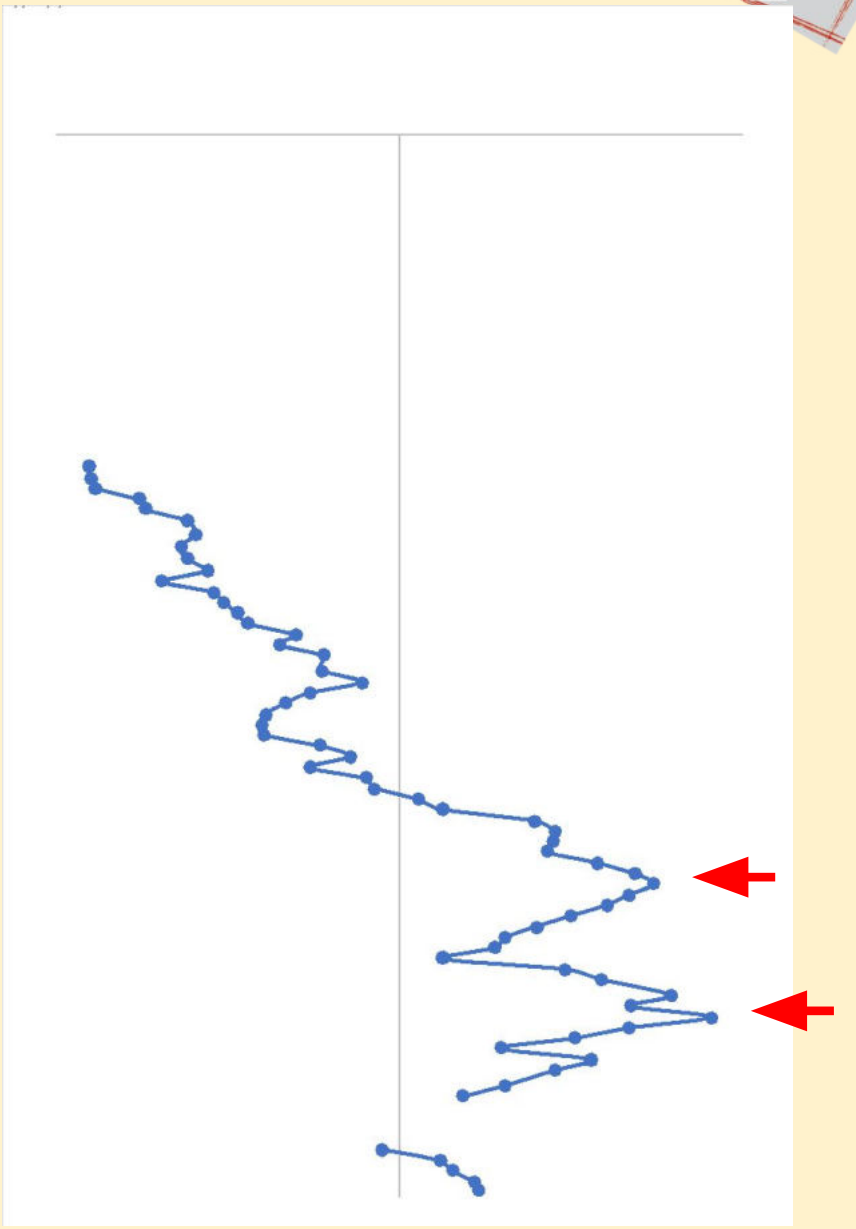
The clayey horizons – major elements, mineralogy

- PCA of the clayey horizons resulted in three PCs
- PC2_1 concludes CaO, MnO and P2O5
- Most probably, PC2_1 represents the combined role of the carbonate content and the organic material (marls)
- PC2_2 concludes Al_2O_3, MgO and K_2O
- Role of smectite-type clay mineral
- PC2_3 concludes Fe_2O_3 and TiO_2
- PC2_3 represents the role of the Fe-oxide and Fe-hydroxide minerals



The clayey horizons – major elements, mineralogy

- Vertical variation of the three PCs points to the
  - marly sections (PC2_1)
  - the smectite-dominated horizons (PC2_2)
  - the sections of Fe-mineral accumulation (PC2_3)
- Variation is continuous in all cases
- Smectite dominates the clayey sediments in the 1200–1600 m depth interval.
- The role of the Fe-minerals increases downwards with two maxima at 1400 m and 1600 m



Trace element behaviour in the clayey horizons

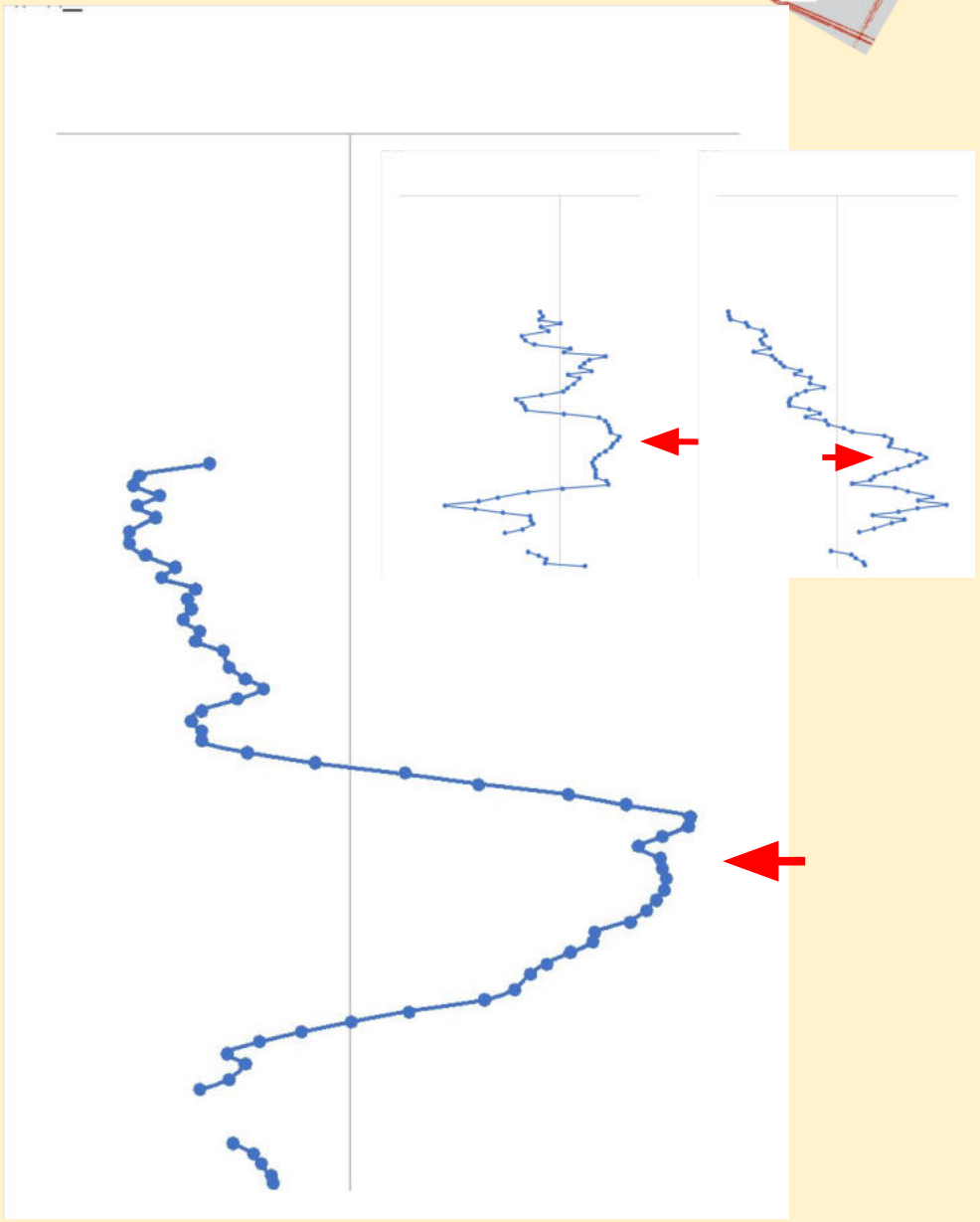
- PCA for trace elements in the clayey horizons points to the significant accumulation processes

- PC3_1 concludes PC2_2 (smectite), PC2_3 (Fe-hydroxides), as well as the lithophile (Ba, Be, REE, Ga, Ge, Hf, Li, Nb, Sc, Sn, Th, U, Y, Zr) and the siderophile elements (Co, Cr, Ni)

- The essential critical elements, like Li, Sc and the REEs, relate smectite and the Fe-hydroxides (limonite)

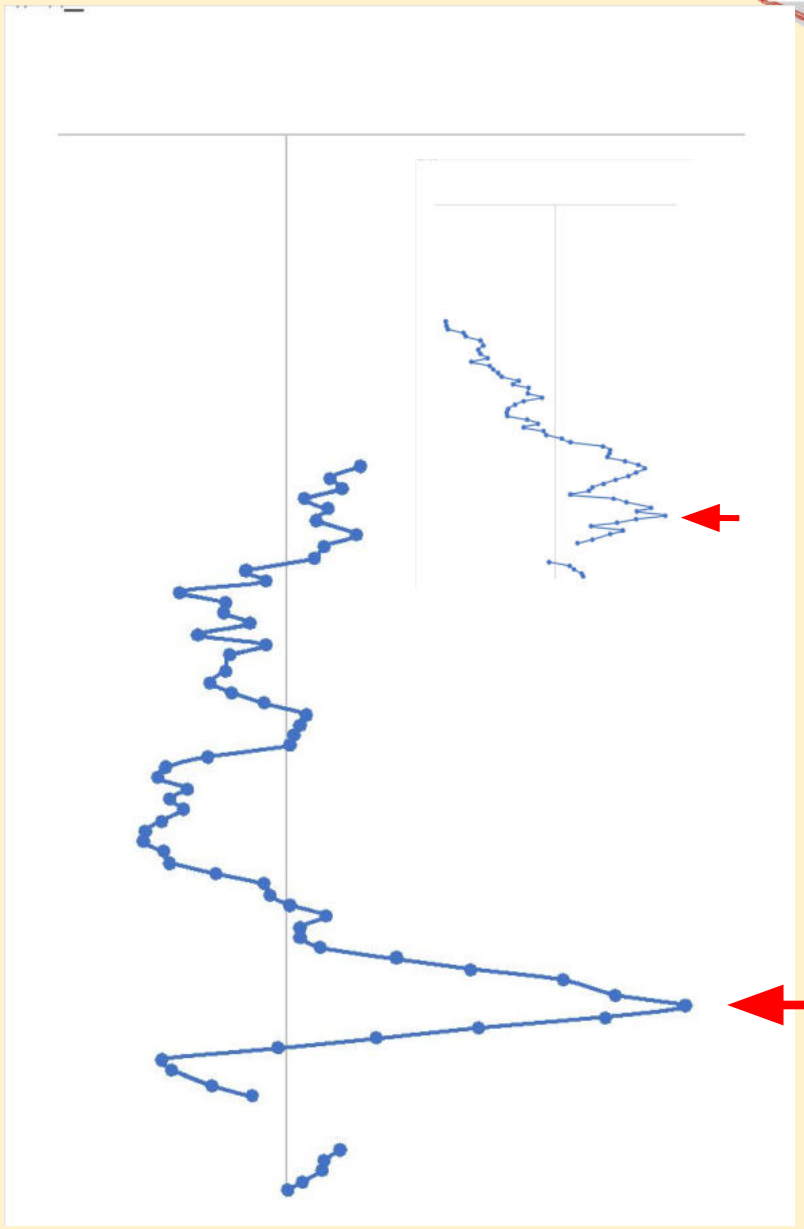
- PC3_2 concludes the chalcophile elements (As, Cu, Hg, Mo) and S.

- PC3_2 is independent of the significant major element PCs



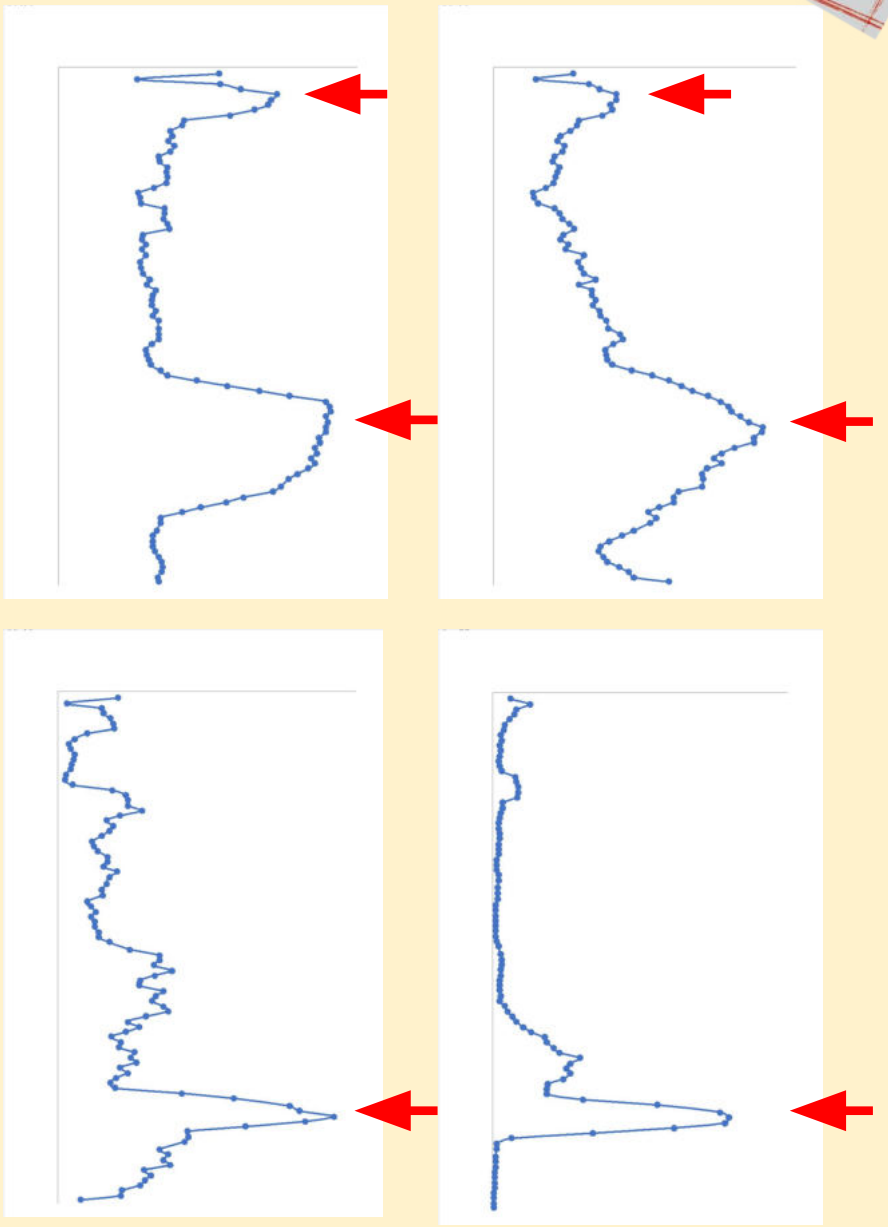
Trace element behaviour in the clayey horizons

- PC3_1 shows a significant peak between 1200 and 1600 m
- This is the interval where the role of smectite-type clay minerals dominate
- The interval fits with the upper peak of Fe-hydroxides as well.
- PC3_2 shows increase at ~1600 m
- Here sulphide minerals tend to accumulate
- The section fits well with the lower peak of the Fe-phases



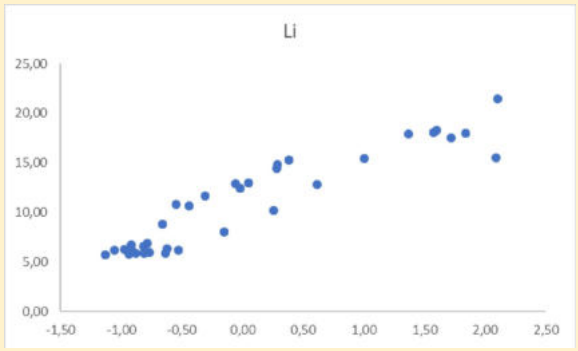
The main accumulation horizons in well W-1

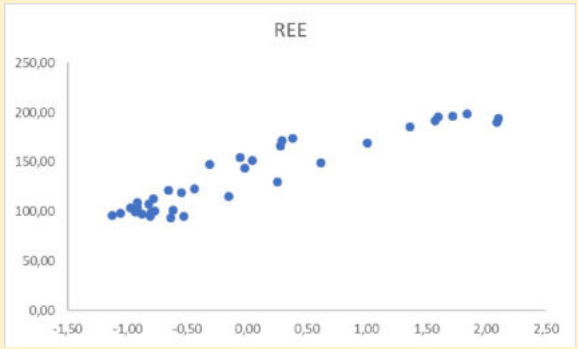
- In well W-1, both sandy and clayey sediments tend to accumulate critical elements
- In the sandy layers, the least mature (low quartz/feldspar ratio) sandstones contain Li, Zr, and REEs in accessory phases
- The main Li, Zr and REE accumulation relates to the section between 1200 and 1600 m, where smectite-type clay minerals dominate
- Calcophile element accumulation is evident in the lower part of the well at ~1600 m

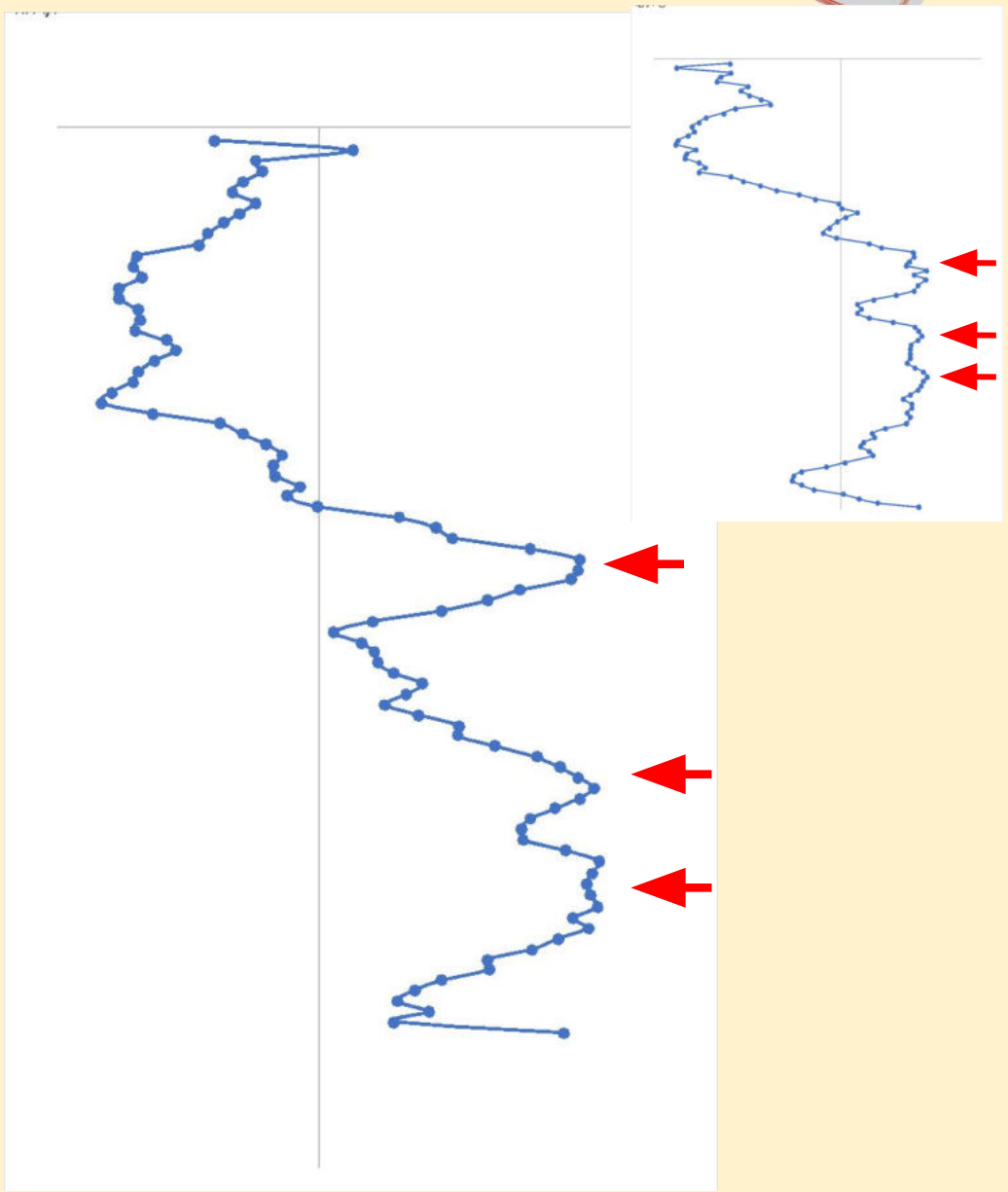


The profile of well W-2 – compared to W-1

- The spatial distribution of sandy and clayey horizons is comparable
- The results of the PCA are the same
- Less mature sandstones accumulate Li, Sc and the REEs

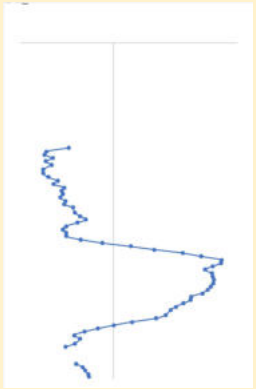


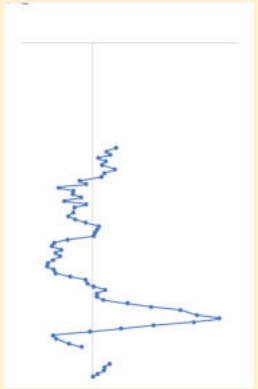


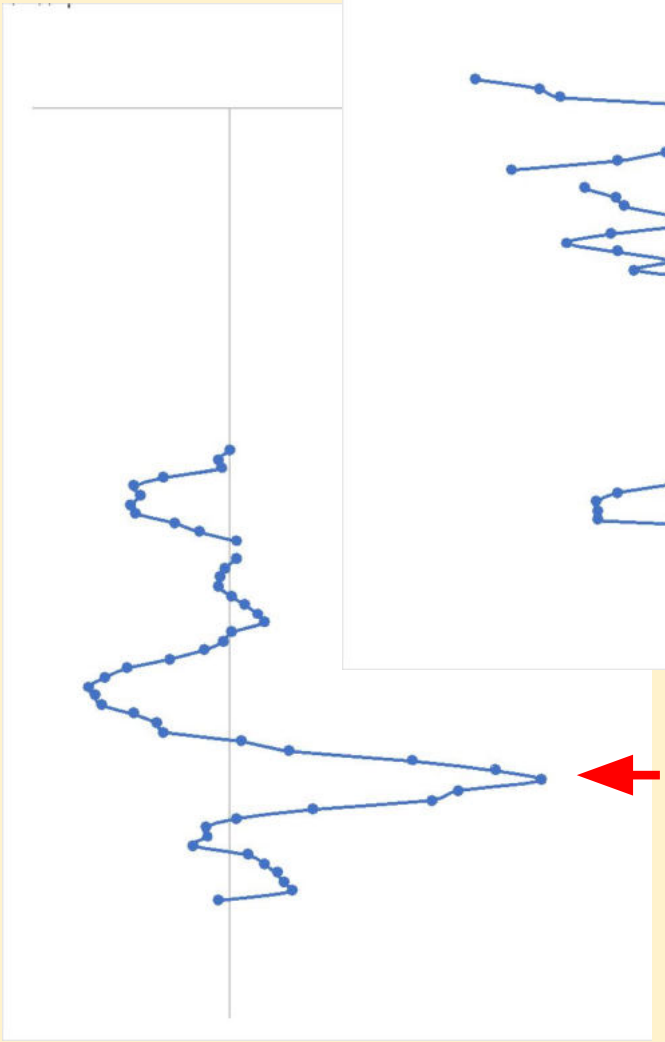


The profile of well W-2 – compared to W-1

- The two major accumulation processes in the clayey horizons relate to
  - Litophile element enrichment in the smectite-dominated claystones
  - Calcophile element accumulation in a well-defined depth section
- The chemostratigraphy, including **trace element accumulation horizons, are comparable in the two wells**







Conclusions

- Altogether 27 geothermal wells penetrated the young sedimentary sequence below Szeged down to 2000 m depth.

- 9 of them are production wells, and 18 are reinjection wells.

- The test measurements resulted in a relatively high concentration of Li (40–70 mg/l).

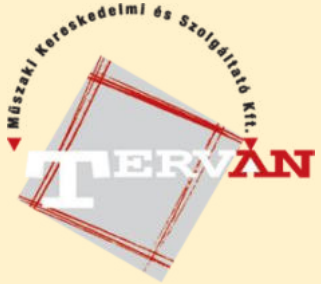
- Two main accumulation horizons are identical in both study wells.

- Immature (low quartz/feldspar) sandy sediments contain critical elements probably in accessory mineral phases (zircon, tourmaline, rutile, apatite, monazite, etc.).

- The most significant accumulation relates to clayey horizons with smectite and limonite dominance. Here most lithophile elements (including Li, Sc and the REEs) accumulate.

- Calcophile elements accumulate in a few tens of metres thick, well-defined intervals.

- Having 3 million of m^3 annual production, the metal content (especially Li) in the Szeged geothermal field has real economic potential (~15 tons of Li a year)



Thanks for your attention!

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(„Fenntartható geotermikus energiatermeléshez kapcsolódó kritikus elem kutatás-módszertani protokollrendszer kidolgozása termálkutak komplex vizsgálata alapján”)