Professional Development Workshop on

Critical Raw Materials Content in Thermal Waters: Analysis and Assessment

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Granite alteration as a source of high lithium content in the South Hungarian formation waters

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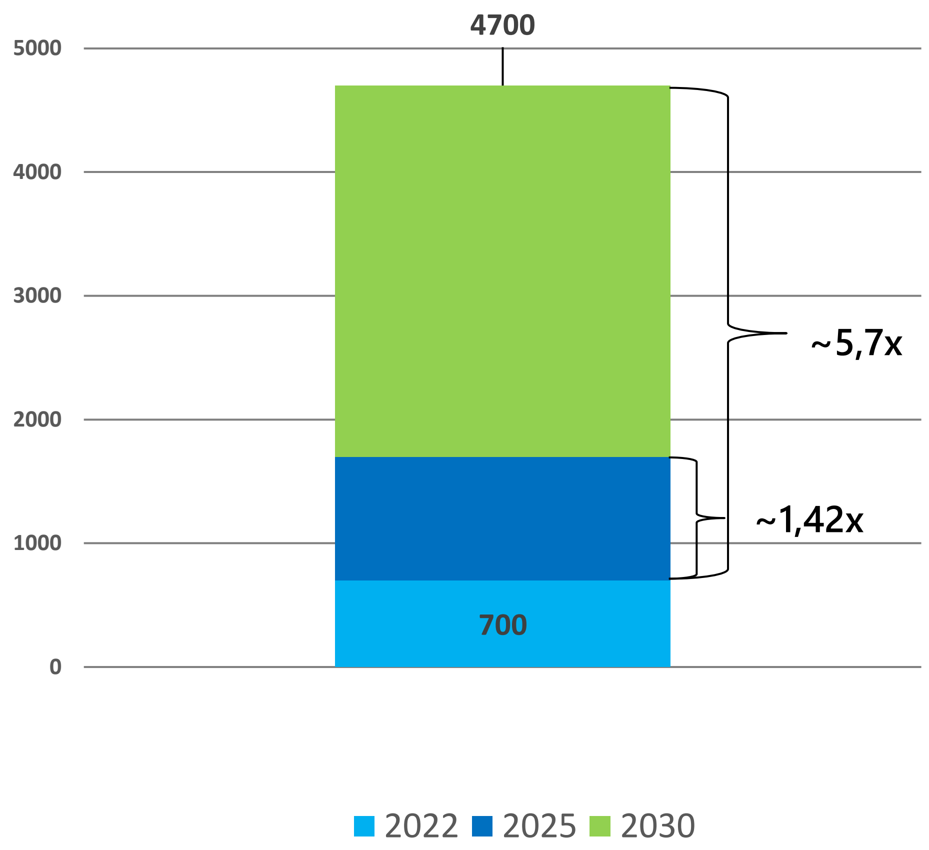
Introduction

Aim of the study

- Lithium is one of the most demanded elements for the battery industry today
- Hungary lacks ores, but we have something else! Countless wells have been deepened in the country because of hydrocarbon and geothermal research
- Elevated concentrations of Li can be detected in the formation waters of the Southern Great Plain. Industrial reports about ~100- 200 mg/l in the formation waters
- **Source?** → Buried granitoid rocks? Which minerals contain the Li?
- What geological processes cause the release of Li?
- Understanding the mechanism → Exploitation opportunities in the future? → *In situ leaching technology (ISL)* or *combination with geothermal water exploitation)*
- An example: Cornish Lithium - Li extraction directly from geothermal waters and hard rocks

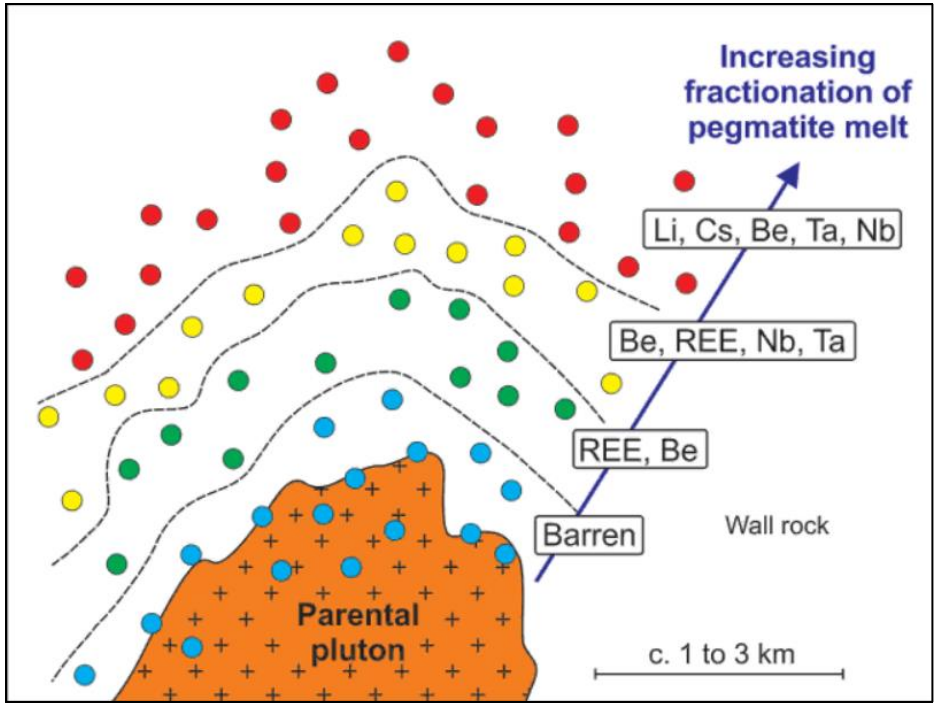
Global Li-ion battery cell demand GWh



Introduction

Lithium-bearing rocks and minerals

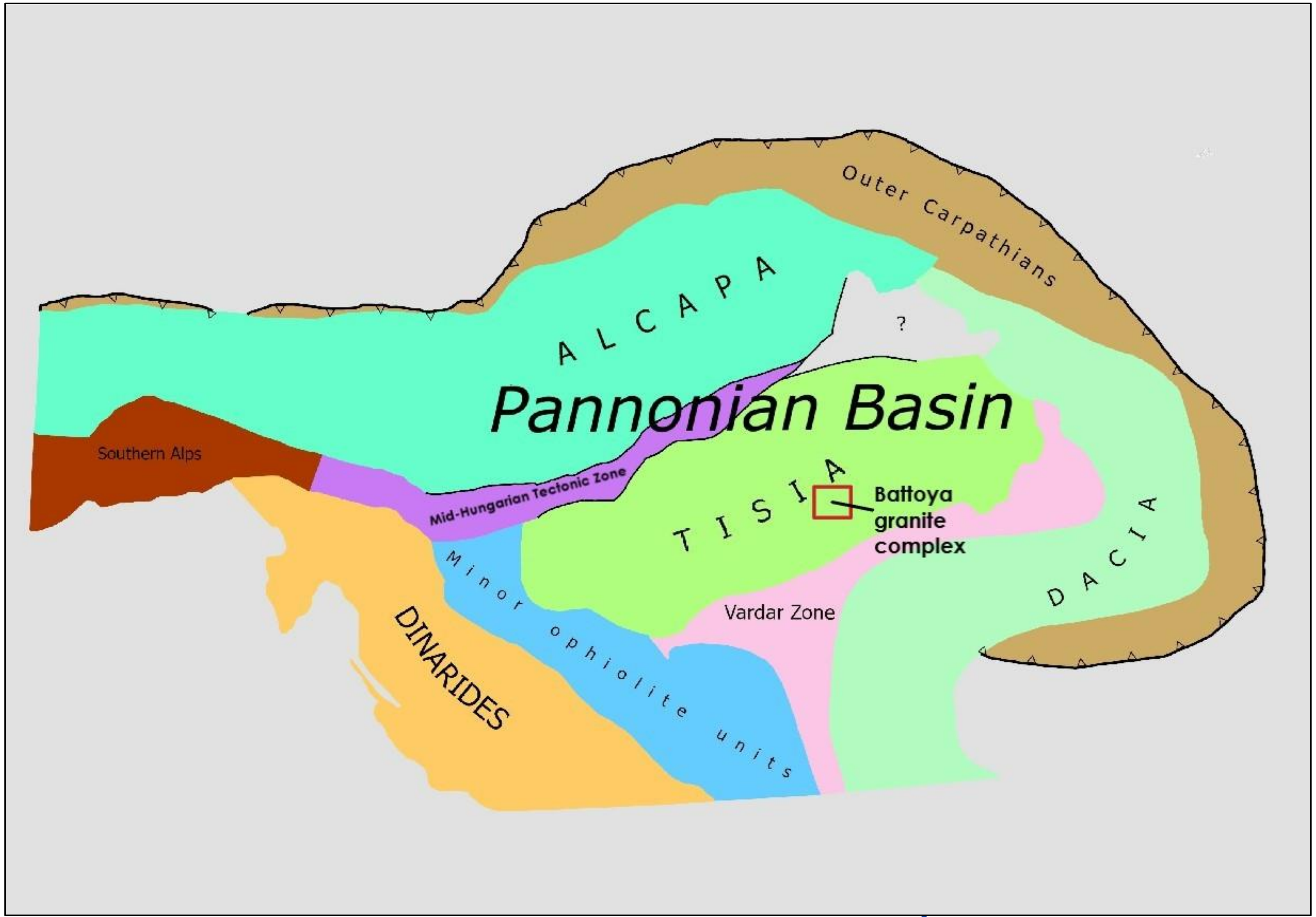
- After brines, the second most important sources of lithium are pegmatites
- Lithium is reasonably incompatible in magmatic systems → rather stays in liquid phase (melt), which means that it is mostly enriched in minerals of the late magmatic and pegmatitic phase → **granites (S-type)** and lithium-cesium-tantalum (LCT) pegmatites
- Post-magmatic processes like hydrothermal alteration are also defining
- In the absence of pegmatitic micas such as zinnwaldite or lepidolite, Li is incorporated into biotite and muscovite → high-volume granitic rocks as a source of Li →
- → → **Battonya granites**



from: https://www.greenpeg.eu/pegmatites.html

Study area

- The **Battonya Complex** is located in southeast Hungary and belongs structurally to the Békés-Codru Unit of the Tisza Unit
- **Battonya-Pusztaföldvár Ridge**
  - situated between the Makó Trough and Békés Basin
  - highest point about 1 km depth and than sinking toward the northeast
  - Covered with kilometres thick Tertiary and Quaternary sediments
- Various rock types, including **Variscan granites**, crystalline schists, amphibolites, gneisses, and migmatites



Geological background

Battonya granites

- Formed 340-360 Ma ago during the Variscan Period
- **Mineral composition:** quartz, orthoclase, microcline, albite-oligoclase, biotite, and primary and secondary muscovite, as well as apatite, zircon, monazite, and titanite
- Two main rock types → quartz-monzodiorite and granodiorite-granite. The latter is on the focus for this study
- Various degrees of hydrothermal alteration and autometasomatism
- Occurence of chlorite sericite, epidote, and limonite suggests alteration

Rock-types	Colour	Mineralogy	Al-saturation	Geochemical classification	Alteration
Quartz monzodiorite	greenish grey	Amph-Bt without primary Ms Mc and Qz uncommon	metaluminous - marginally peraluminous	I-type	Pl sericitisation Bt chloritisation
Two-mica granodiorite – granite	grey	Bt-Ms, Ms alone or subordinary Mc megacrystal Qz prevalent	peraluminous	S-type	Plg sericitisation Bt chloritisation

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Samples

- Limited availability of drill cores from the research area
- Various degree of alteration based on macroscopic observation
- 9 representative samples were chosen: **8 granites (S1-S3; S5-S9)** and **1 pegmatite (S4)**. S1 was the least altered and so on..
- Key features: weathered, dusty feldspars → sericitisation chlorite → substitution of biotites via chloritisation
- Can alteration affect the lithium content of rocks?

S1

S3

S5

S9

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Methods

Laser-induced breakdown spectroscopy (LIBS)

- Generally lithium is detected by LA-ICP-MS and ion microprobe
- **LIBS** - Provides information from a larger volume and can be applied effectively to lighter elements. Minimal sample preparation required. At least thick section should be used → Polished samples were suitable for measurement
- The Li concentration of individual rock-forming minerals by LIBS: **biotite** (Bt), **chlorite** (Chl), **muscovite** (Ms), **feldspar** (Fsp) and **quartz** (Qz)
- Parameters: beam diameter of 40 µm; total of **274 points** were analysed - 20 **Bt**, 78 **Ms**, 34 **Chl**, 68 **Fsp** and 74 **Qz**; 10 repetitions in one spot
- NIST 610, NIST 612, and NIST 614 glass and the **JF-1 feldspar** and **CRPG Biotite Mica-Fe** standards were used for quantitative calibration
- The lower detection limit was approximately 1 ppm of Li

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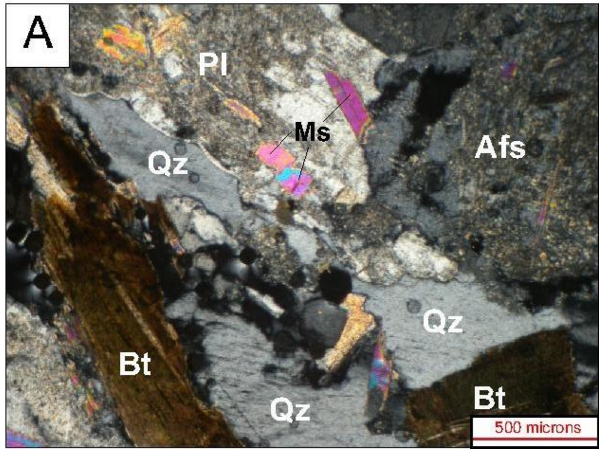
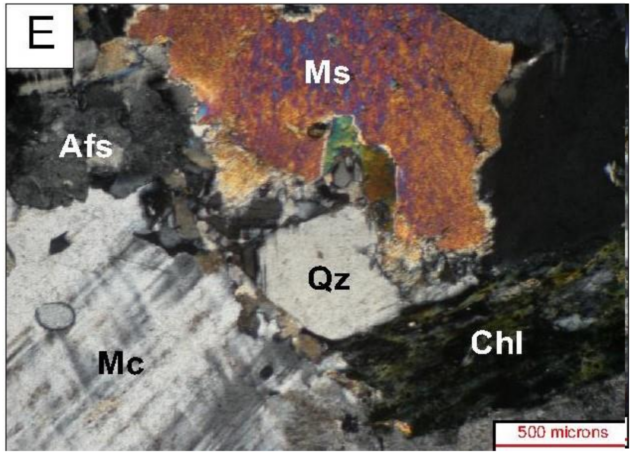
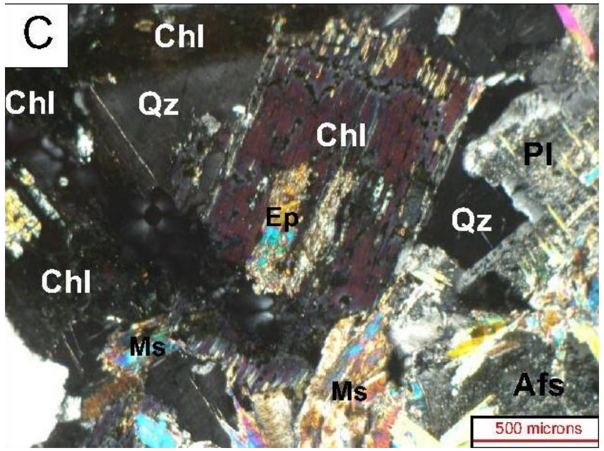
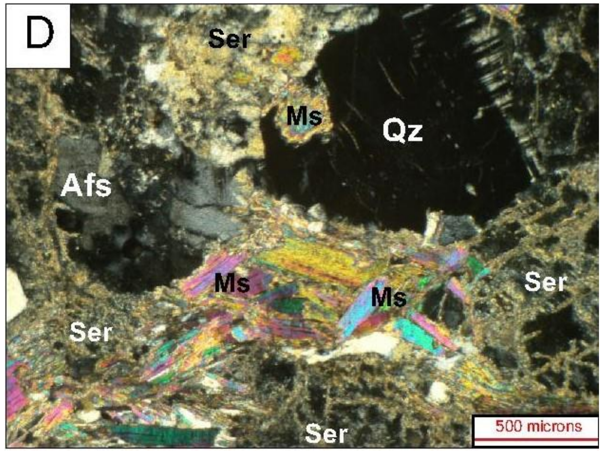
Degree of alteration →

Group 1	Group 2	Group 3	Group 4
S1, S2	S3, S4	S5, S6	S7, S8, S9
unaltered or weakly chloritised biotite	chloritisation	chloritisation	muscovite-bearing granites
muscovite	residual biotite plates	sericitisation	more extensive sericitisation
feldspars – initial sericitisation	sericitisation	epidote	cracks and veins









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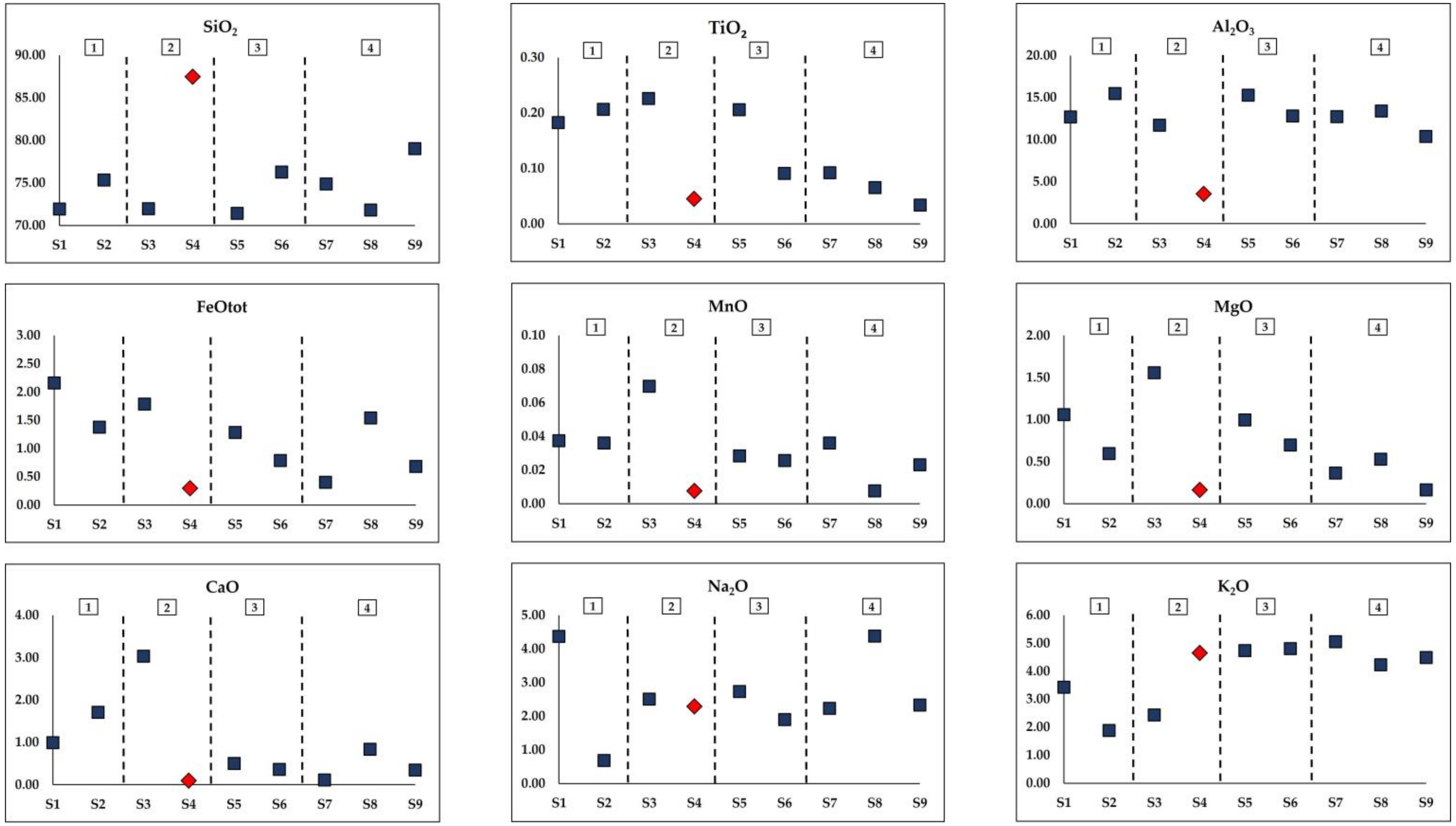
Results

Major element composition of the rock samples

- SiO_2 and Al_2O_3 do not depend on the alteration
- The TiO_2, FeO_{tot}, MnO, and MgO contents decrease along with the alteration trend due to chloritisation and less mafics
- CaO decreased and K_2O increased with intensifying alteration, the Na_2O concentration was independent of the post-magmatic processes
- S4 pegmatite should be treated separately. The major element composition is consistent with the quartz-rich and feldspathic appearance observed visually.



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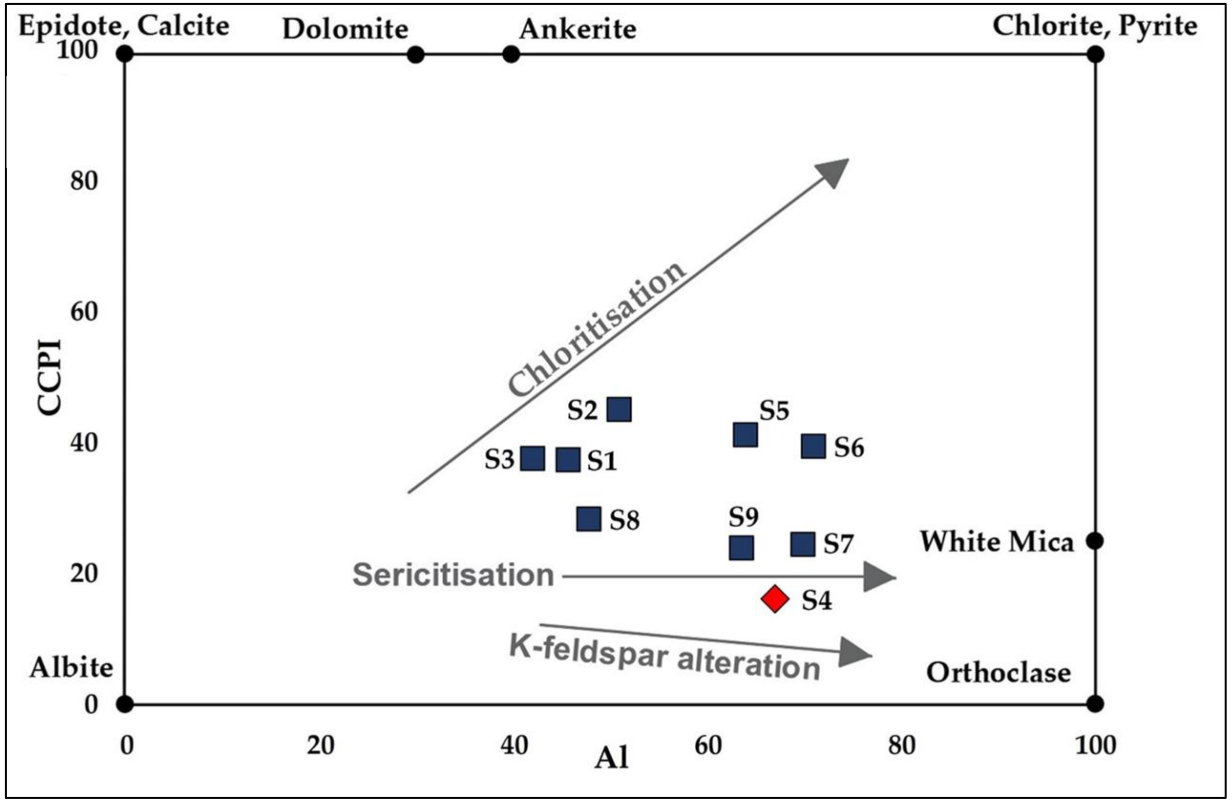
Results

Alteration - chlorite-carbonate-pyrite index

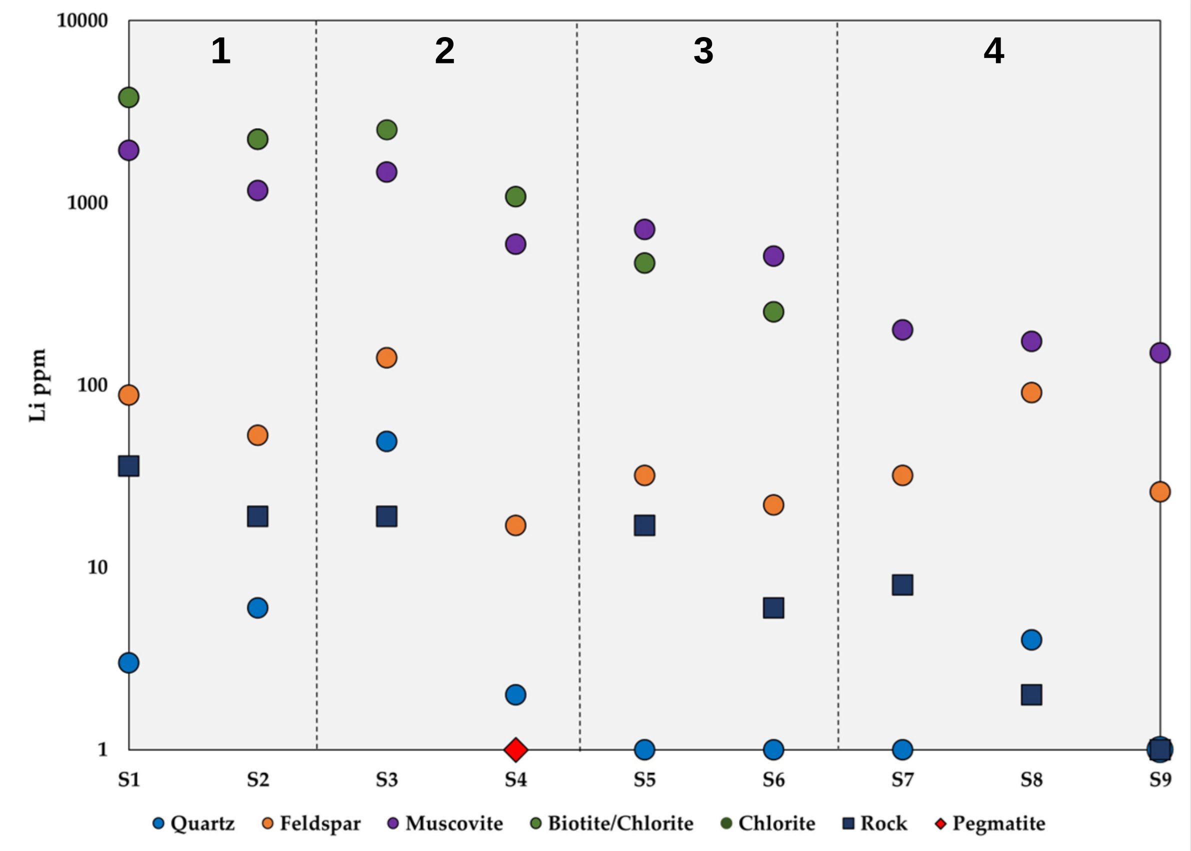
- All samples are placed between the sericitisation and chloritisation alteration trends, but chemically diverse picture
- The alteration features, established both microscopically and chemically, are also visible in the diagram.
- The samples S1–S3 were close to the chloritisation trend
- S5 and S6 rock types more intense chloritisation and sericitisation
- S7–S9 were close to the sericitisation trend, consistent with the microscopic observations.
- Alteration processes were driven by the interaction between the host rocks and the percolating fluids, along with fractures and shear zones which key findings appear in papers by Juhász et al., 2002; Varsányi and Kovacs, 2005; Vass et al., 2018



Results

Lithium content of the rock-forming minerals

- Generally, the intact biotite accumulated Li at the highest concentration
- Based on the alteration mechanisms and trace element measurements Li loss occurs during biotite chloritisation
- Muscovite is the other main lithium-bearing mineral
- If there is less biotite or chlorite in the samples then more Li in muscovite
- Quartz - Li data only from sample S1, S2, S4 and S7 due to low intensity
- No correlation between alteration and lithium content for feldspars and concentration varies in a wide range in the minerals
- **General trend can be observed: Bt > Ms > Chl > Fsp > Qz**



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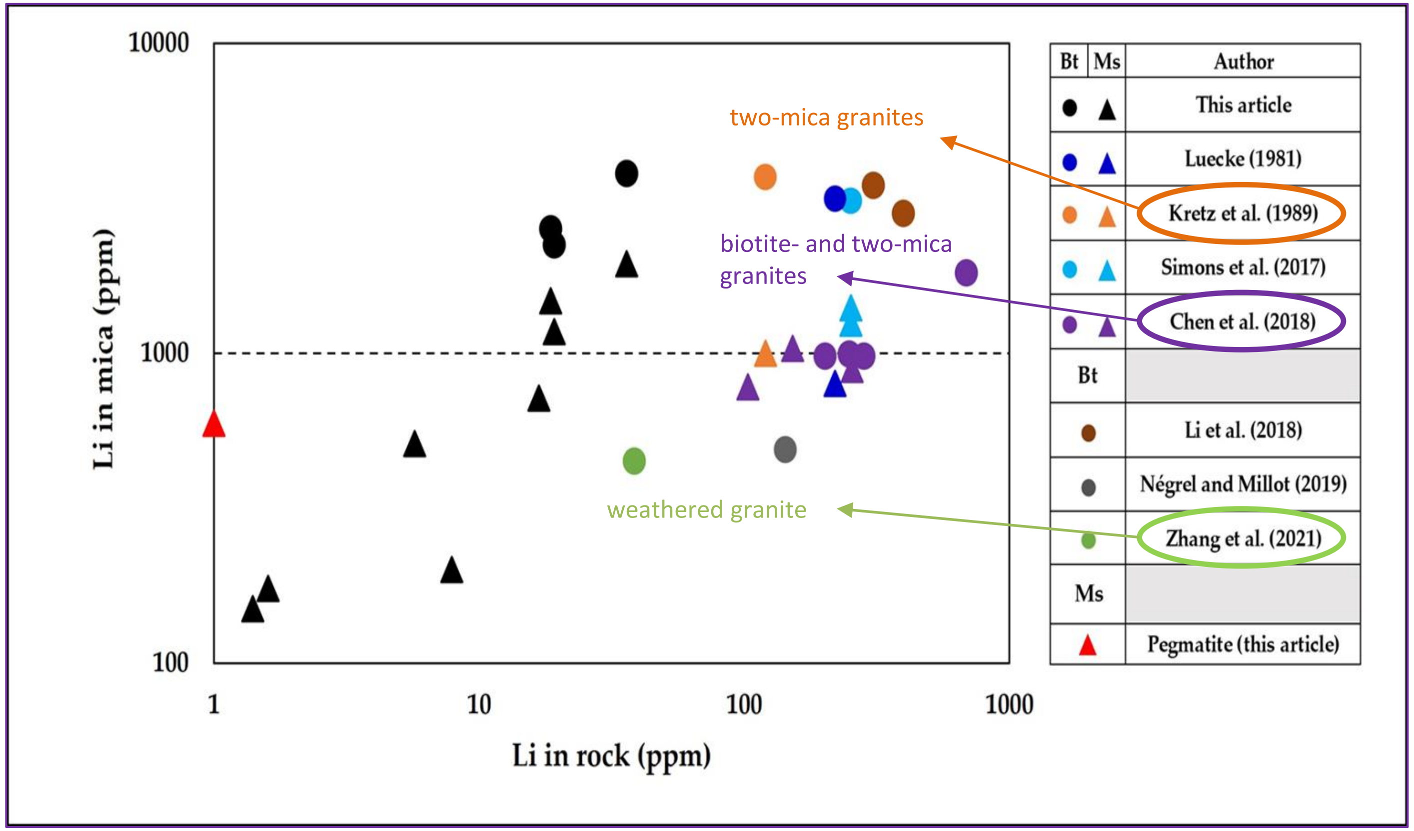
Results

Data comparison

- Similar granites were also found to contain the most lithium in micas
- The measured lithium concentration in micas was in same range as it occurs in the literature
- Low bulk composition because of the relatively low amount of mica and the total absence of Li minerals in the Battonya granites



Conclusions

- Biotite chloritisation and partial sericitisation of feldspar were demonstrated as a potential explanation for the high Li content of the geothermal waters around the Battonya Complex
- The microscopic observations and chemical data revealed that the samples had undergone different degrees of hydrothermal alteration from fresh, nearly intact two-mica granites to granites with chloritisation and sericitisation
- Lithium loss increased with the rate of biotite chloritisation, although chloritized biotite could still trap Li at relatively high concentrations
- The role of sericitisation in lithium loss is not negligible
- Limited amount of biotites means lower bulk Li content in comparison with the literature
- More information is required about spatial position, depth, and thickness of different altered granite types

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CA questions: