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Trace elements in quartz: a tool for sediment provenance

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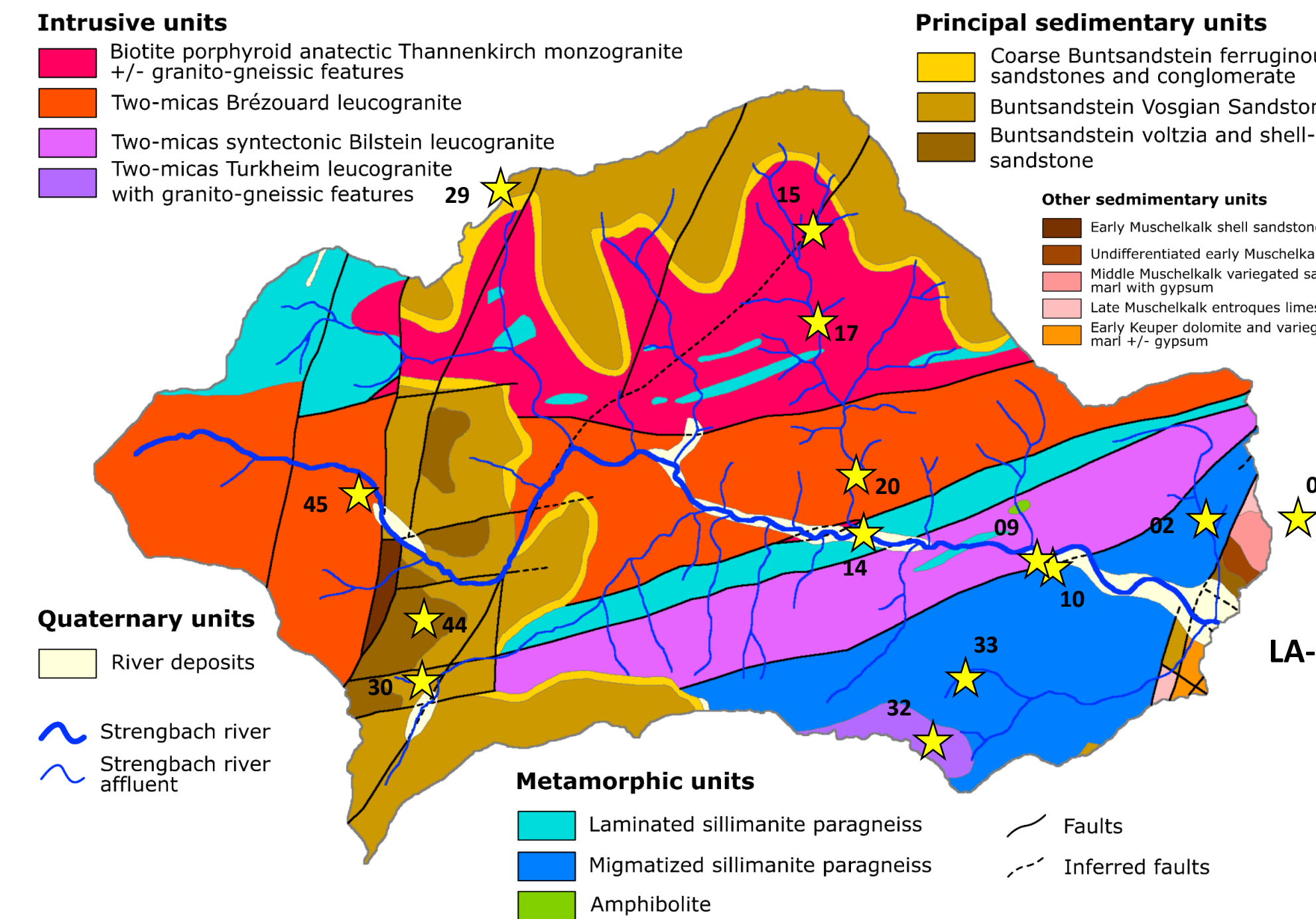
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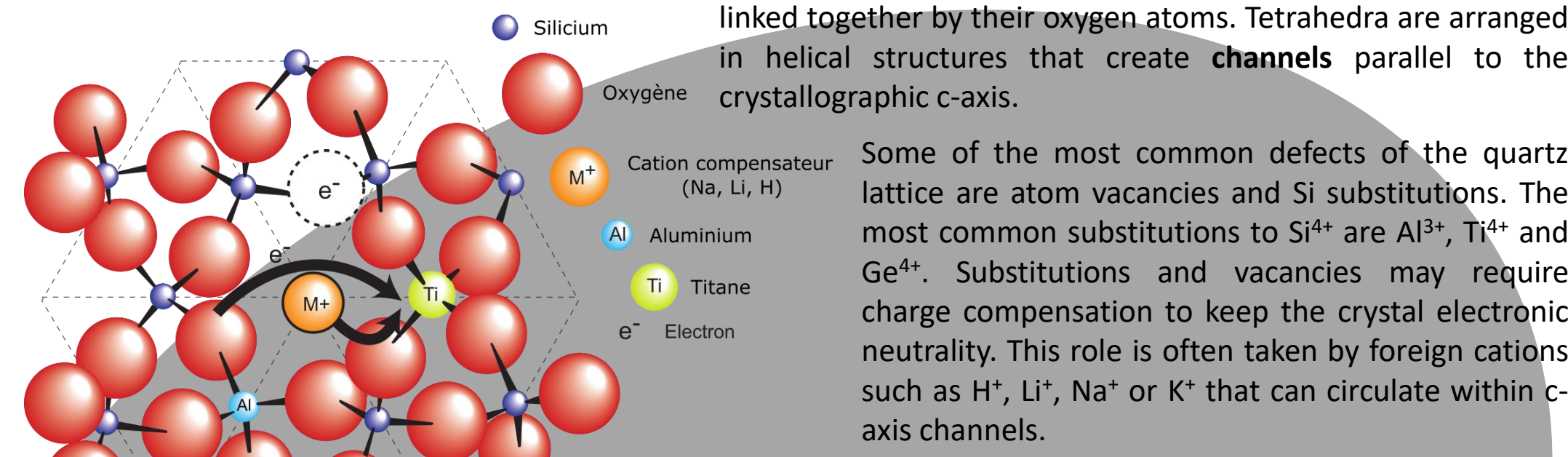
Quartz is ubiquitous within continental crust and can virtually be found within all rock types (plutonic, metamorphic and sedimentary). During erosion, weathering and sedimentation processes, it has a very high preservation potential and is therefore a good candidate to **trace sediment production and transport dynamics**. One of the aims of the Quartz ANR project is to develop a multi-method protocol for quartz characterization that can be used to trace the origin of river sediments.

The Strengbach catchment, selected to develop the method, is relatively small (ca. 40 km²) with a relatively simple lithology. As a first step, **bedrock samples** have been characterized to establish their quartz signature that will be compared in a second step to the quartz signature within river sediments.

The Strengbach river catchment



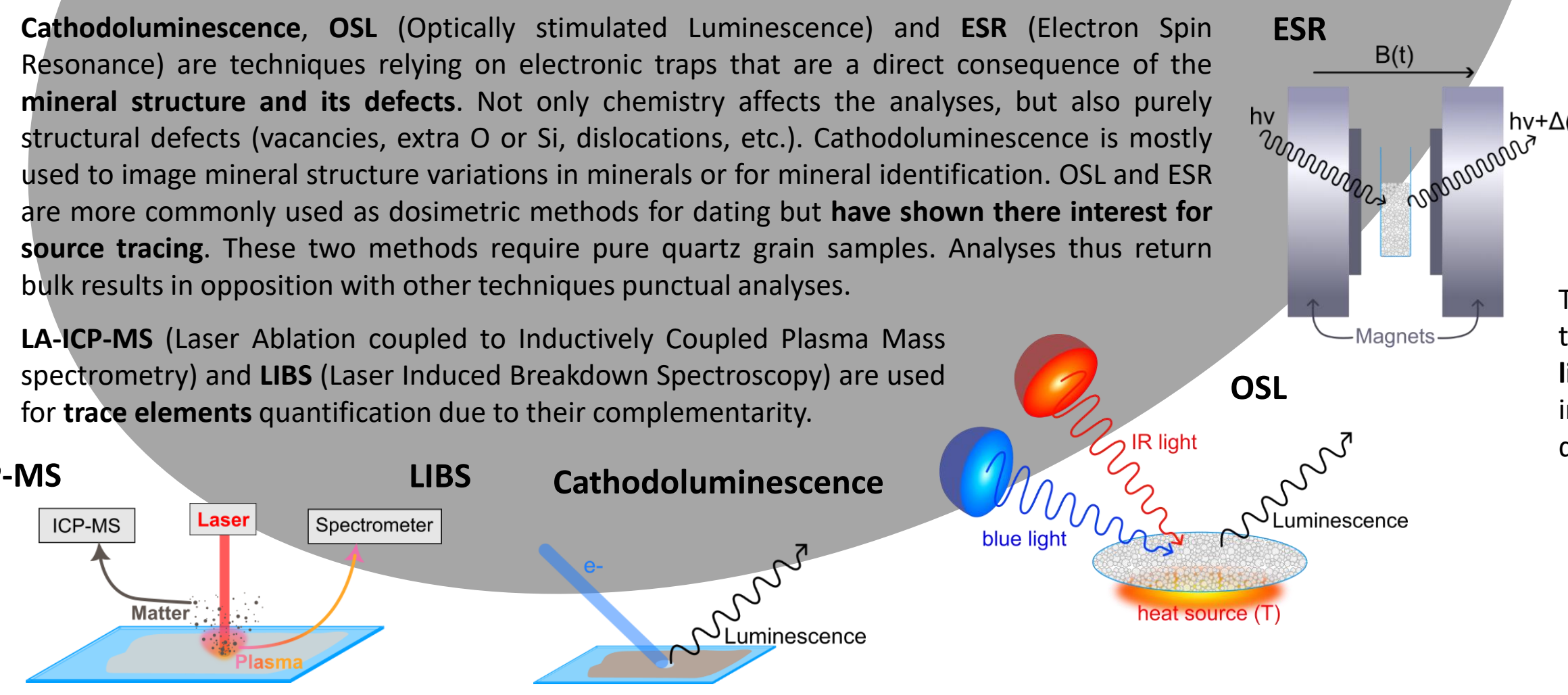
Quartz structure defects



The ideal quartz structure is a network of SiO₄ tetrahedra linked together by their oxygen atoms. Tetrahedra are arranged in helical structures that create channels parallel to the crystallographic c-axis.

Some of the most common defects of the quartz lattice are atom vacancies and Si substitutions. The most common substitutions to Si⁴⁺ are Al³⁺, Ti⁴⁺ and Ge⁴⁺. Substitutions and vacancies may require charge compensation to keep the crystal electronic neutrality. This role is often taken by foreign cations such as H⁺, Li⁺, Na⁺ or K⁺ that can circulate within c-axis channels.

Defects in the quartz structure are intricately linked to quartz conditions and environment of crystallization and consecutive history (recrystallization, metamorphism, alteration, etc.). It implies that, by choosing complementary analytic methods, it is possible to establish a signature common to quartz with a similar history.



Quartz trace elements characterization

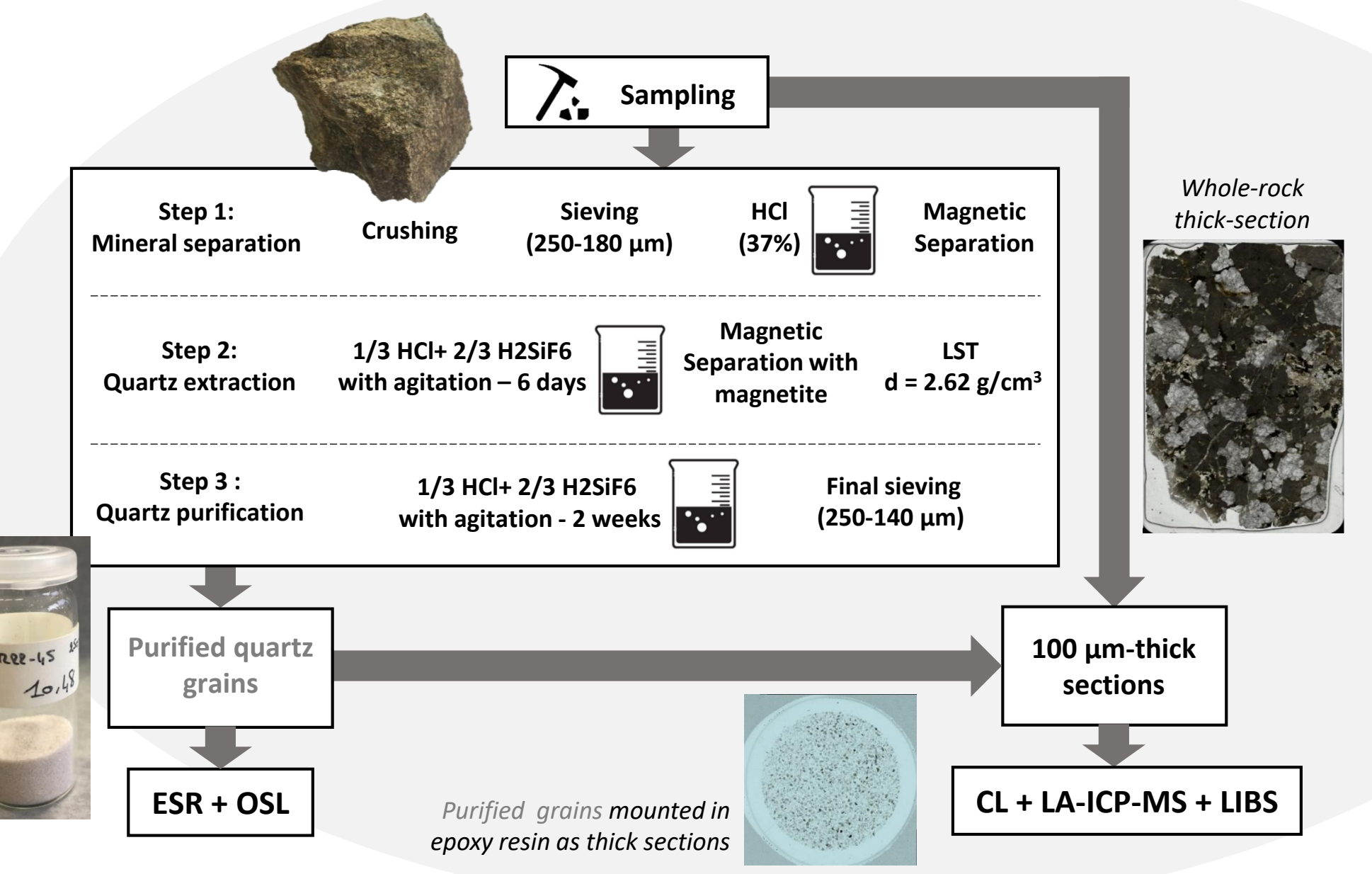
LA-ICP-MS analyses were carried out on an Agilent 8900 triple quadrupole ICP-MS coupled to a Teledyne Excite Excimer 193 nm laser in the BRGM (French survey) laboratories. Quartz being a difficult mineral to analyze with LA-ICP-MS due to its high resistance and its transparency, a particular setup had to be used. During analyses, the laser energy was set to 6 mJ instead of the usual 4 mJ, and analyses were carried out on thick sections (100-150 μm thickness) instead of more common thin sections (30 μm thickness). Spot size used for measurements was 50 μm for whole-rock samples and 35 μm in the case of grain samples.

LIBS imaging analyses were carried out using an ABLATOM microLIBS equipment (ELM-XS-1) allowing microchemical analysis on a macroscopic scale (surface area of several square centimeters).

LIBS imaging instrumentation is based on the generation of a series of plasmas at different positions on the sample following a scan sequence. Each spectrum is then processed to build the corresponding elemental maps. The step size was between 40 et 50 μm for about a millions spectra allowing the analysis to cover the whole surface of the sample. 3 spectrometers were used simultaneously, laying a range for a wide elemental analysis including major, minor elements and even light elements like H and Li.

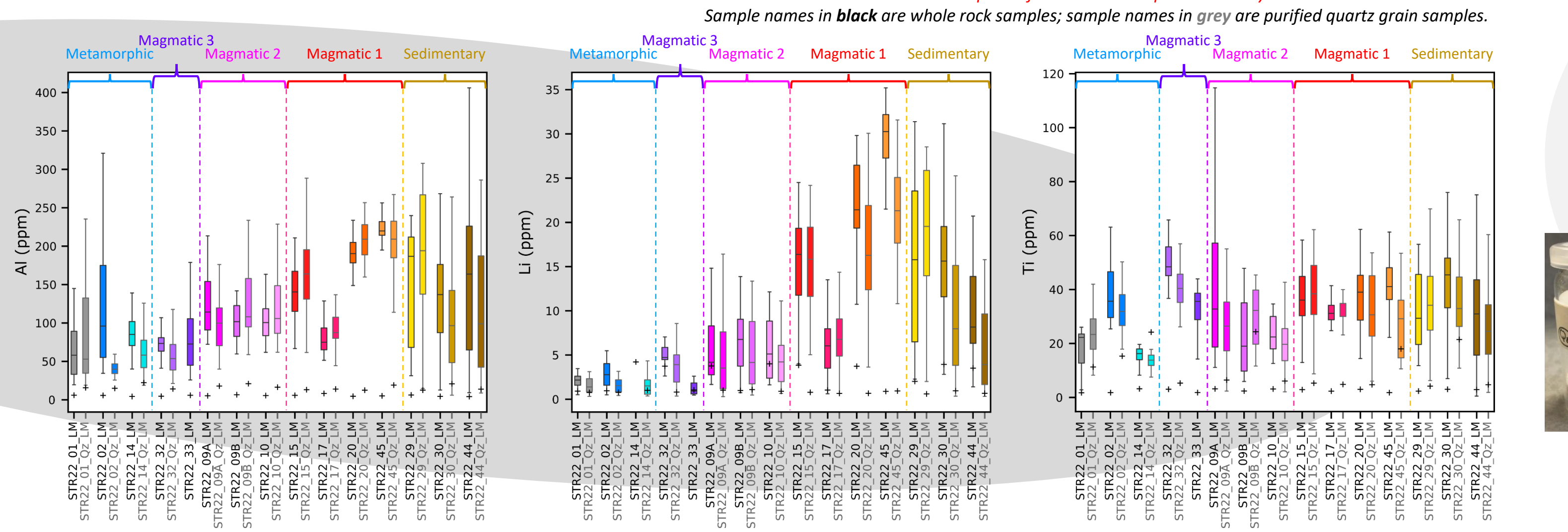
The combination of LA-ICP-MS and LIBS techniques is particularly interesting because both are sensitive to different elements. LA-ICP-MS is particularly good at analyzing heavy elements while LIBS is best for light elements (some of them being difficult or impossible to analyze using ICP-MS). LIBS is also an interesting complement to LA-ICP-MS as it can generate elemental maps much quicker than what can be done with LA-ICP-MS, highlighting areas interesting to further investigate using LA-ICP-MS.

Sample preparation



LA-ICP-MS: Grains vs whole-rock

- LA-ICP-MS analyses carried out in quartz of both whole-rock and purified grains samples
- Analyzed elements: Li, Be, B, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Ge, As, Rb, Sr, Sb, Cs, Pb, Th, U, REE
- Main elements detected: Al, Ti, Li
- No significant effect of quartz purification
- Exception: STR22-02 due to selective quartz type sampling



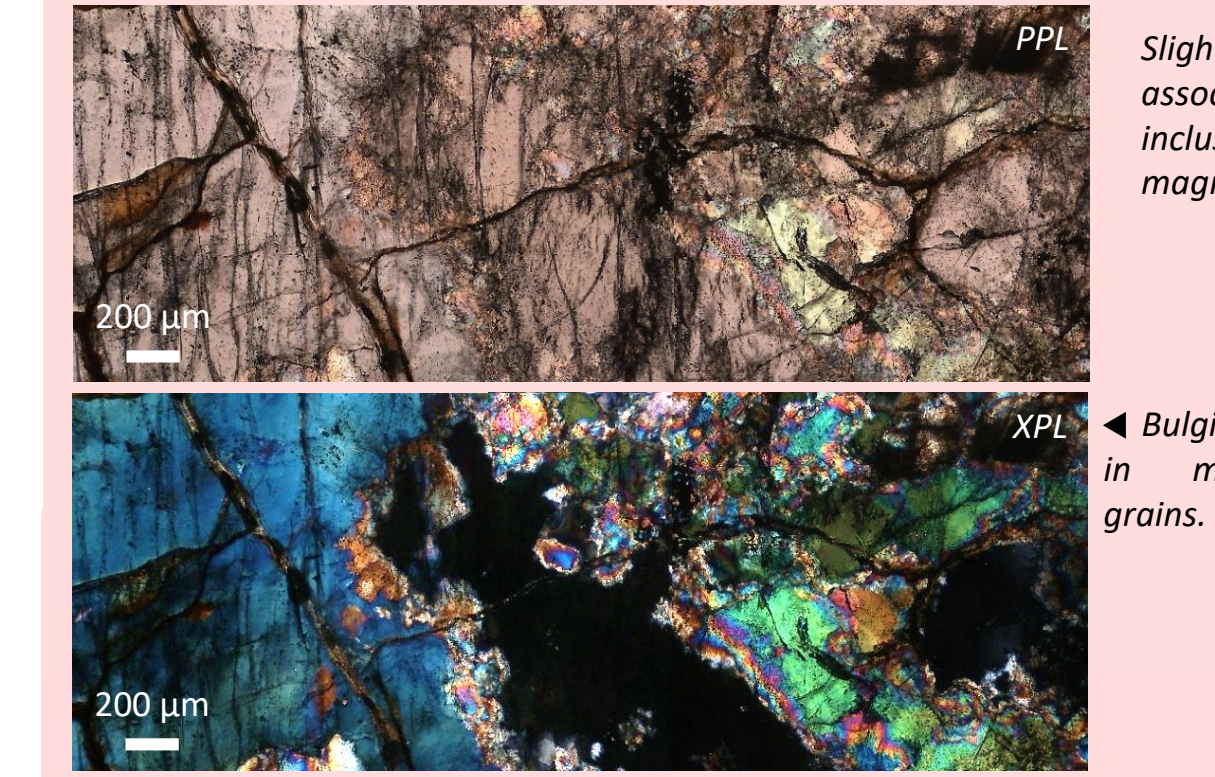
Quartz signatures

Based on rock petrology and quartz chemistry, six quartz types can be distinguished:

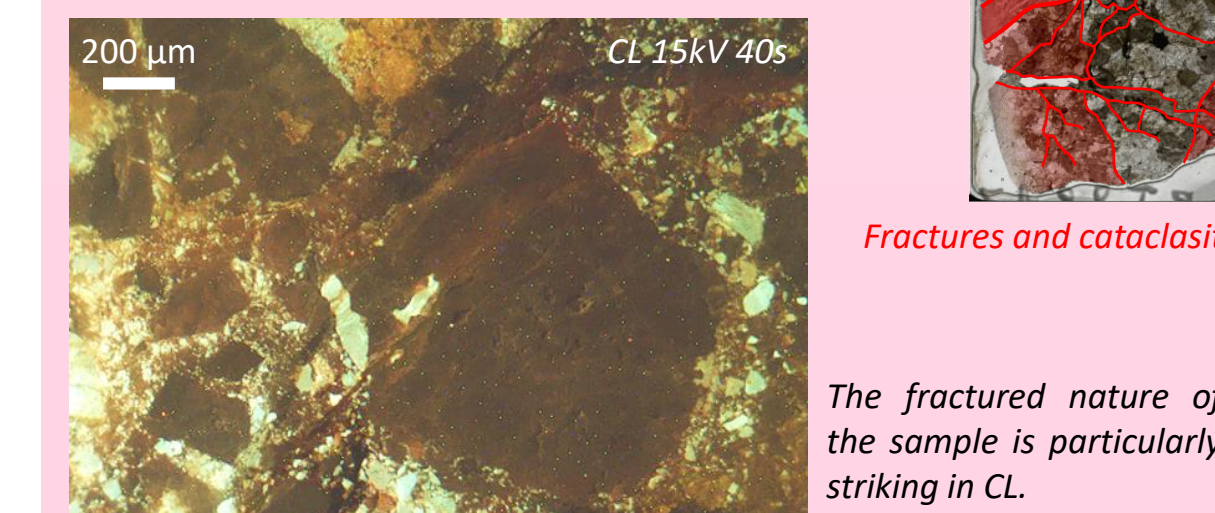
- Sedimentary
- Magmatic group 1
- Magmatic group 2
- Magmatic group 3
- Metamorphic
- Hydrothermal

Magmatic group 1: Unspecific granitic quartz

- Thannenkirch and Brézouard granites (samples STR22_15, 17, 20, 45)
- Magmatic and recrystallized quartz
- Dominant quartz type: magmatic
- Large (several mm Ø) magmatic quartz grains with local bulging recrystallization
- No distinctive chemistry difference between quartz types

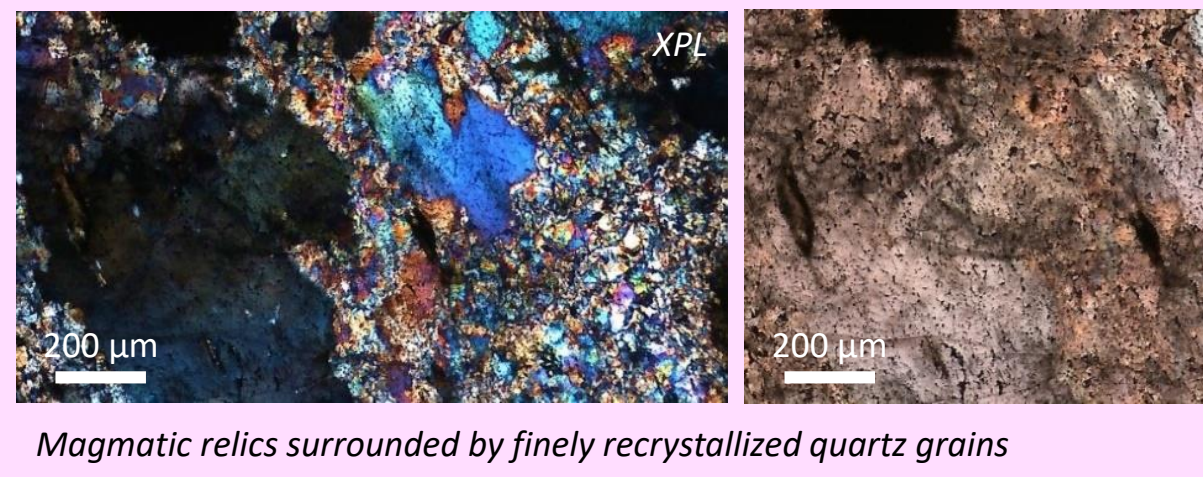


- STR22_17: Verreries facies
- Partial anatexis (locally granito-gneiss features)
- Sample intensely fractured
- Lower Al and Li concentration than the rest of magmatic group 1 closer to magmatic group 3 chemistry



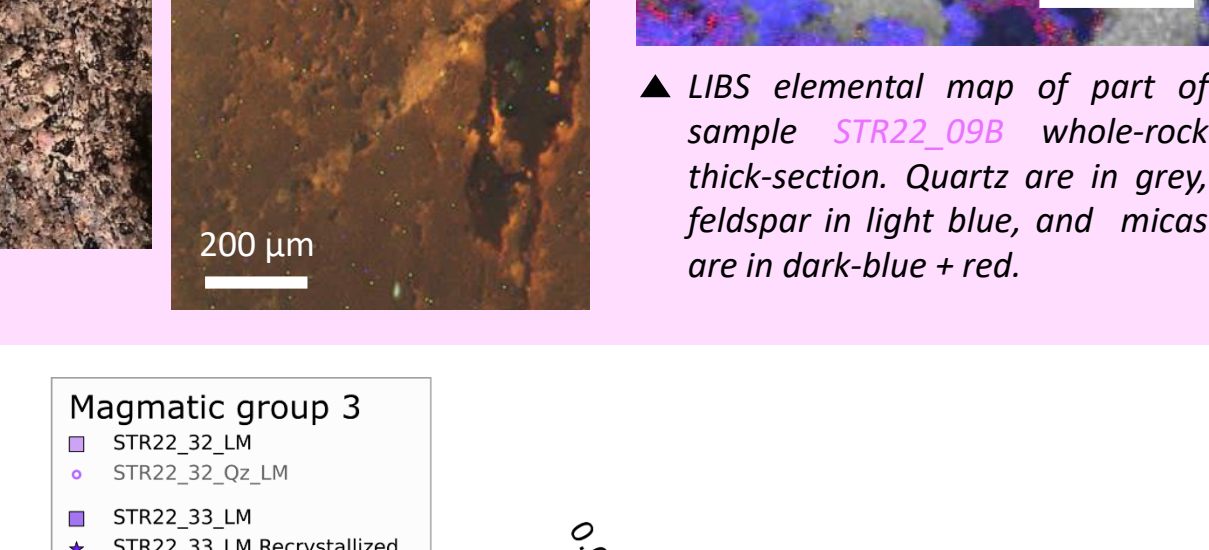
Magmatic group 2: Deformed granitic quartz

- Bilstein syntectonic granite (samples STR22_09A, 09B, 10)
- Magmatic and recrystallized quartz
- Dominant quartz type: recrystallized
- A few quartz relics (magmatic)
- Intense recrystallization by subgrain rotation (10-25 μm Ø)
- No distinctive chemistry differences between quartz types



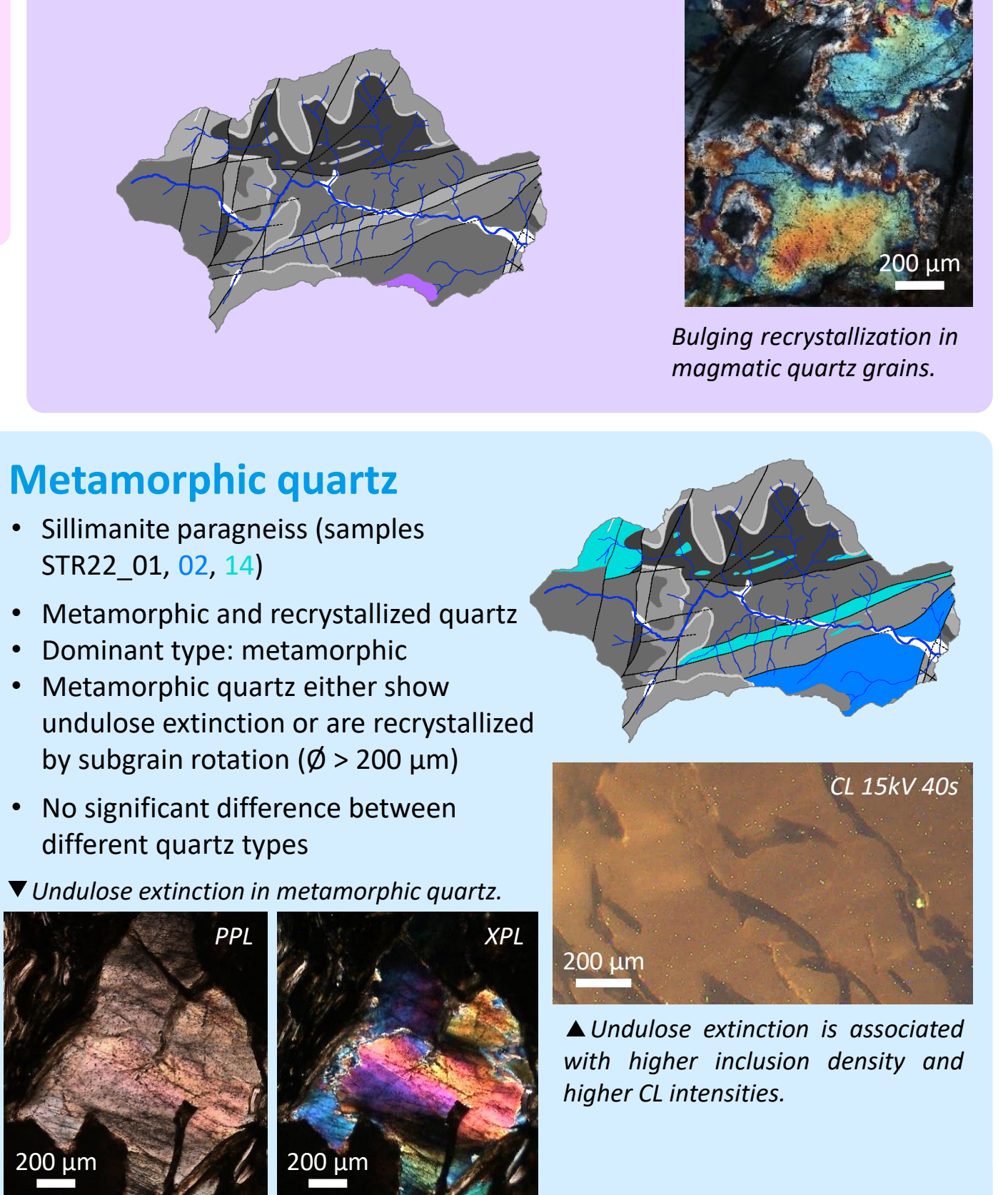
Magmatic group 3: granito-gneissic quartz

- Turkheim granite (samples STR22_32, 33)
- Small granite intrusion emplaced within a metamorphic country rock
- Warm intrusive body led to partial melting of surrounding metamorphic rock
- Magmatic and recrystallized quartz
- Dominant type: magmatic
- Medium (ca. 1 mm Ø) magmatic quartz grains with local bulging recrystallization
- No distinctive chemistry differences between quartz types
- Chemistry close to metamorphic quartz



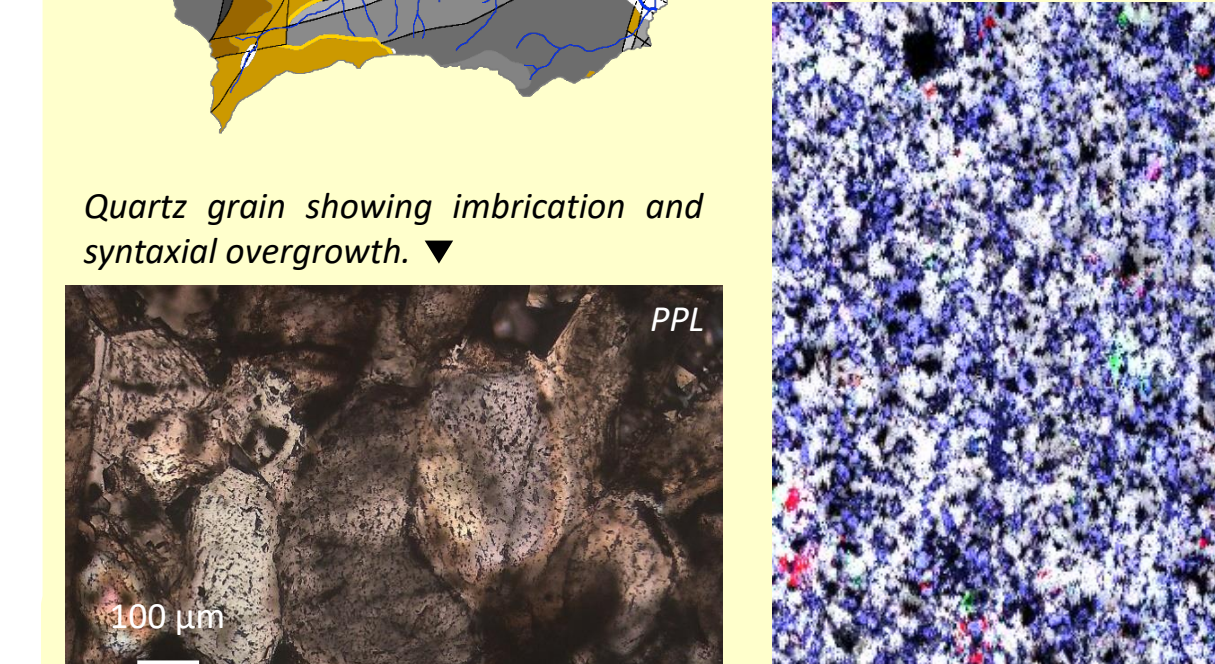
Metamorphic quartz

- Sillimanite paragneiss (samples STR22_01, 02, 14)
- Metamorphic and recrystallized quartz
- Dominant type: metamorphic
- Metamorphic quartz either show undulose extinction or are recrystallized by subgrain rotation (Ø > 200 μm)
- No significant difference between different quartz types
- Undulose extinction in metamorphic quartz
- Undulose extinction is associated with higher inclusion density and higher CL intensities.



Sedimentary quartz

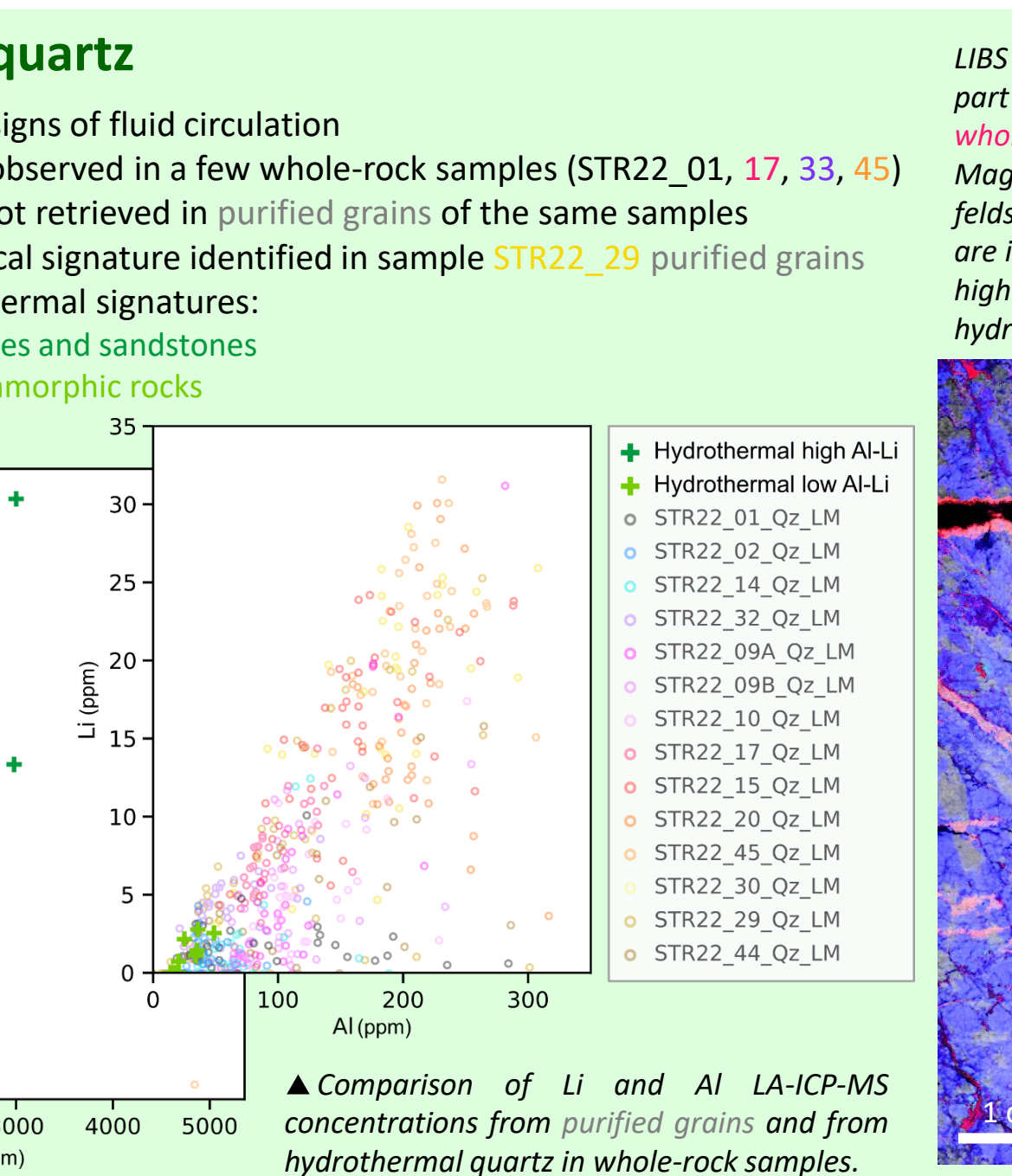
- Buntsandstein sandstones (samples STR22_29, 30, 44)
- Detrital grains of various origins
- Sub-rounded to well-rounded grains
- Syntaxial overgrowth
- Grains imbrication
- Similar chemical signature as magmatic group 1



▲ LIBS elemental map of STR22_44 whole rock thick section. Quartz are in grey and feldspar in blue. Other bright color spots identify other phases such as oxides and micas. Some light colored spots highlight variations in quartz composition.

Hydrothermal quartz

- Most samples show signs of fluid circulation
- Hydrothermal veins observed in a few whole-rock samples (STR22_01, 17, 33, 45)
- Chemical signature not retrieved in purified grains of the same samples
- Hydrothermal chemical signature identified in sample STR22_29 purified grains
- Two types of hydrothermal signatures:
 - Al+Li rich in granites and sandstones
 - Al+Li poor in metamorphic rocks

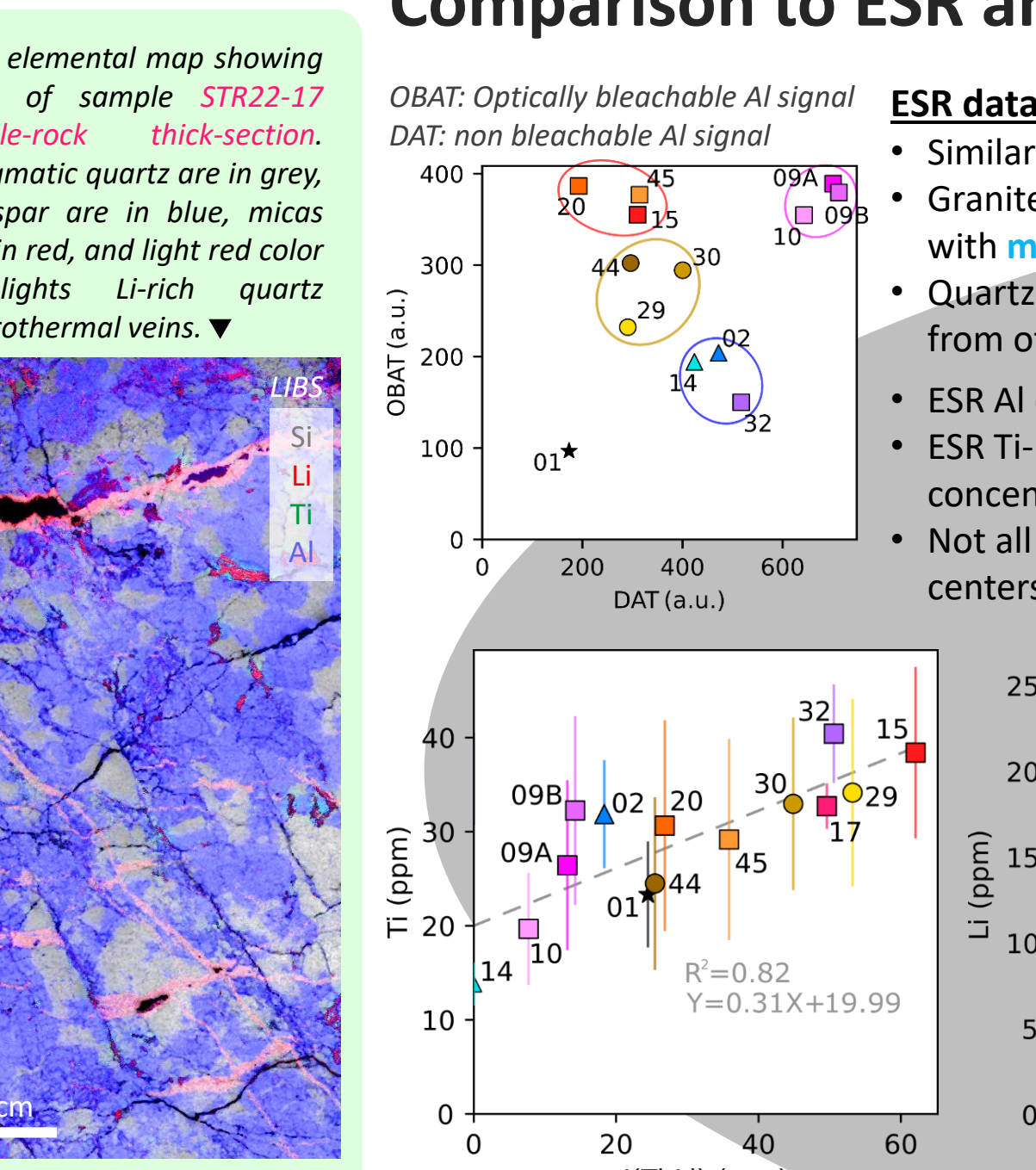


Comparison to ESR and OSL

OBAT: Optically bleachable Al signal
 DAT: non bleachable Al signal

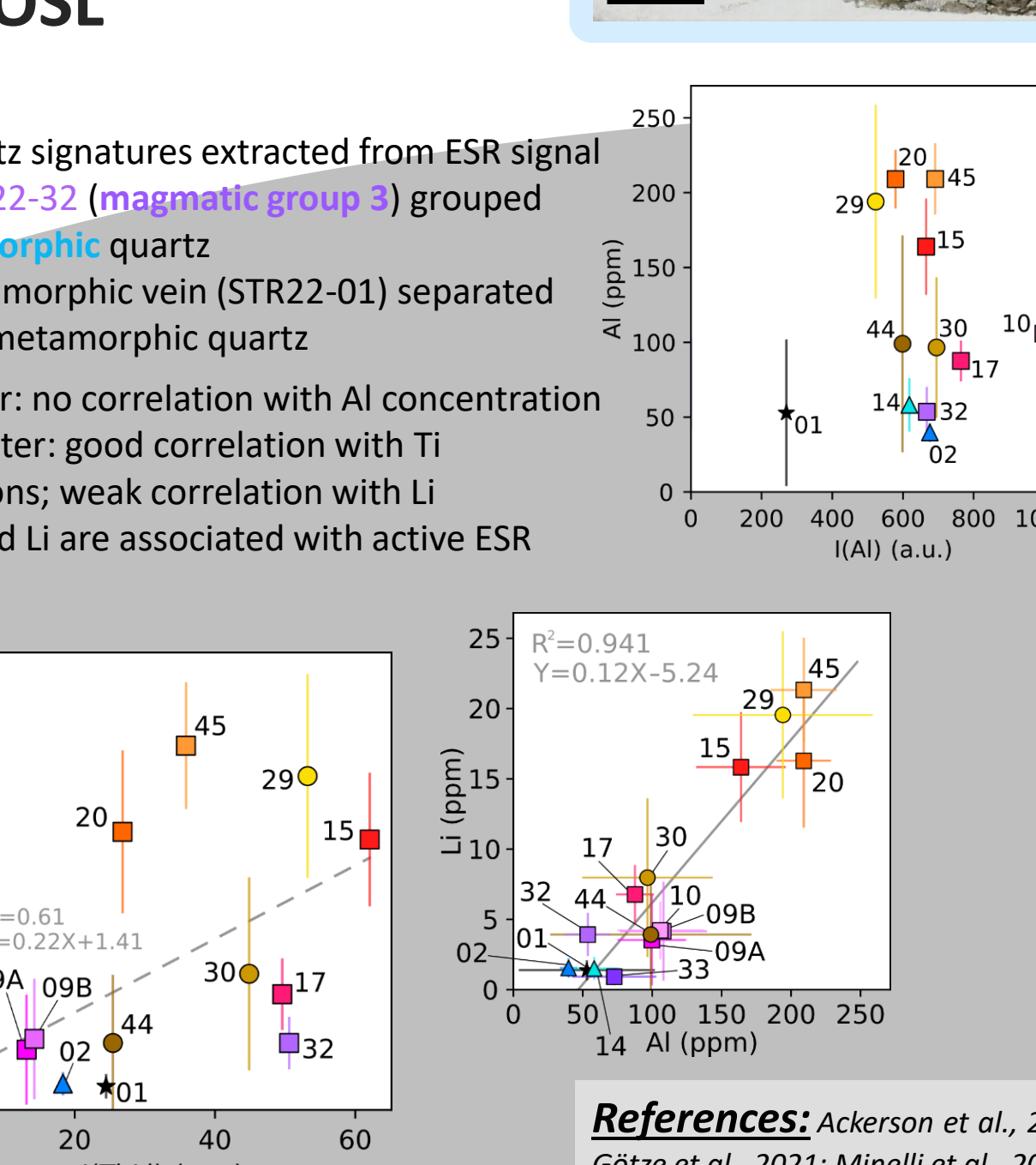
ESR data:

- Similar quartz signatures extracted from ESR signal
- Granite STR22-32 (magmatic group 3) grouped with metamorphic quartz
- Quartz metamorphic vein (STR22-01) separated from other metamorphic quartz
- ESR Al center: no correlation with Al concentration
- ESR Ti-Li center: good correlation with Ti concentrations; weak correlation with Li
- Not all Al and Li are associated with active ESR centers



OSL data:

- Low OSL signal: metamorphic or magmatic group 2 and 3 quartz
- High OSL signal: magmatic group 1 or sedimentary quartz
- Granito-gneiss signature of STR22-17 (Verreries facies) not visible
- Correlation between OSL and Al concentration



References:

Ackerson et al., 2015; Augustsson & Reker, 2012; Boele et al., 2016; Boggs et al., 2002; Duttine et al., 2002; Götzte et al., 2021; Minelli et al., 2021; Shimoda et al., 2013; Tissoux et al., 2015