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Trace elements in quartz: a tool for sediment provenance

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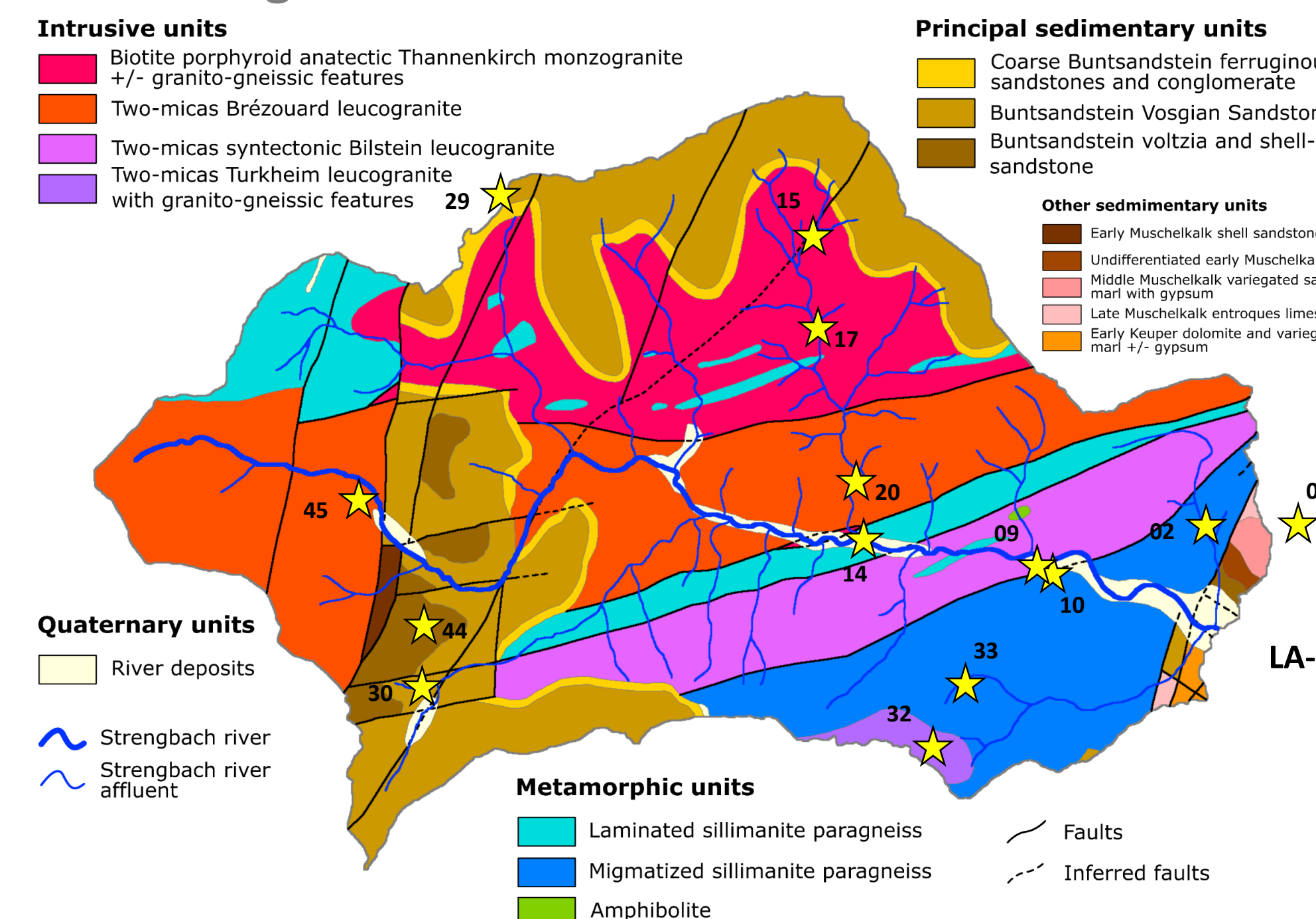
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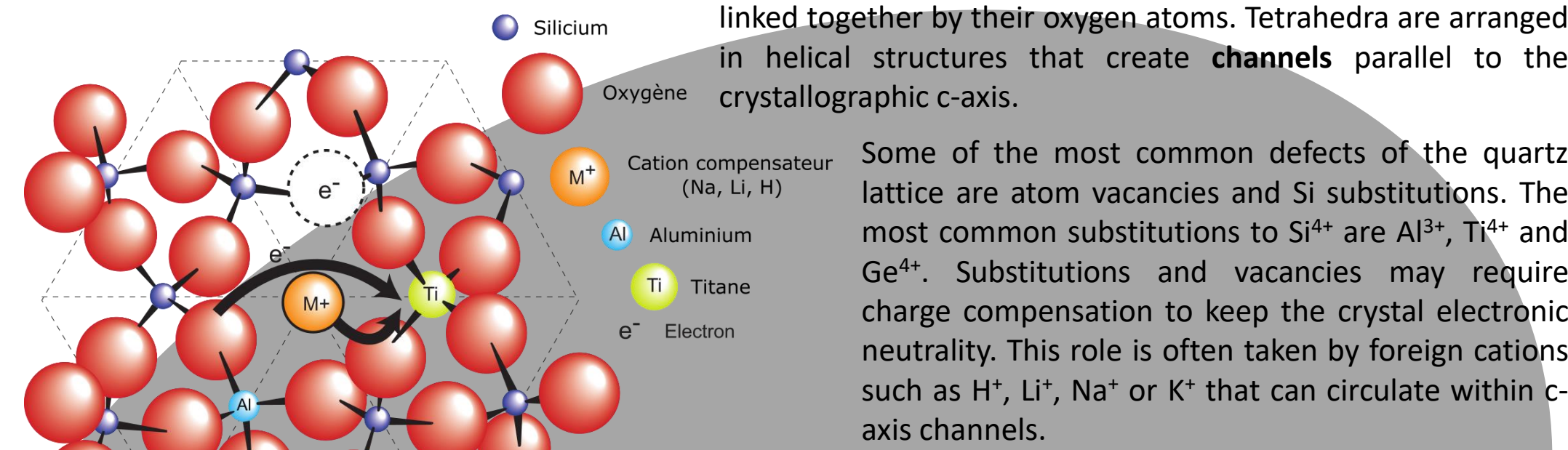
Quartz is ubiquitous within continental crust and can virtually be found within all rock types (plutonic, metamorphic and sedimentary). During erosion, weathering and sedimentation processes, it has a very high preservation potential and is therefore a good candidate to **trace sediment production and 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



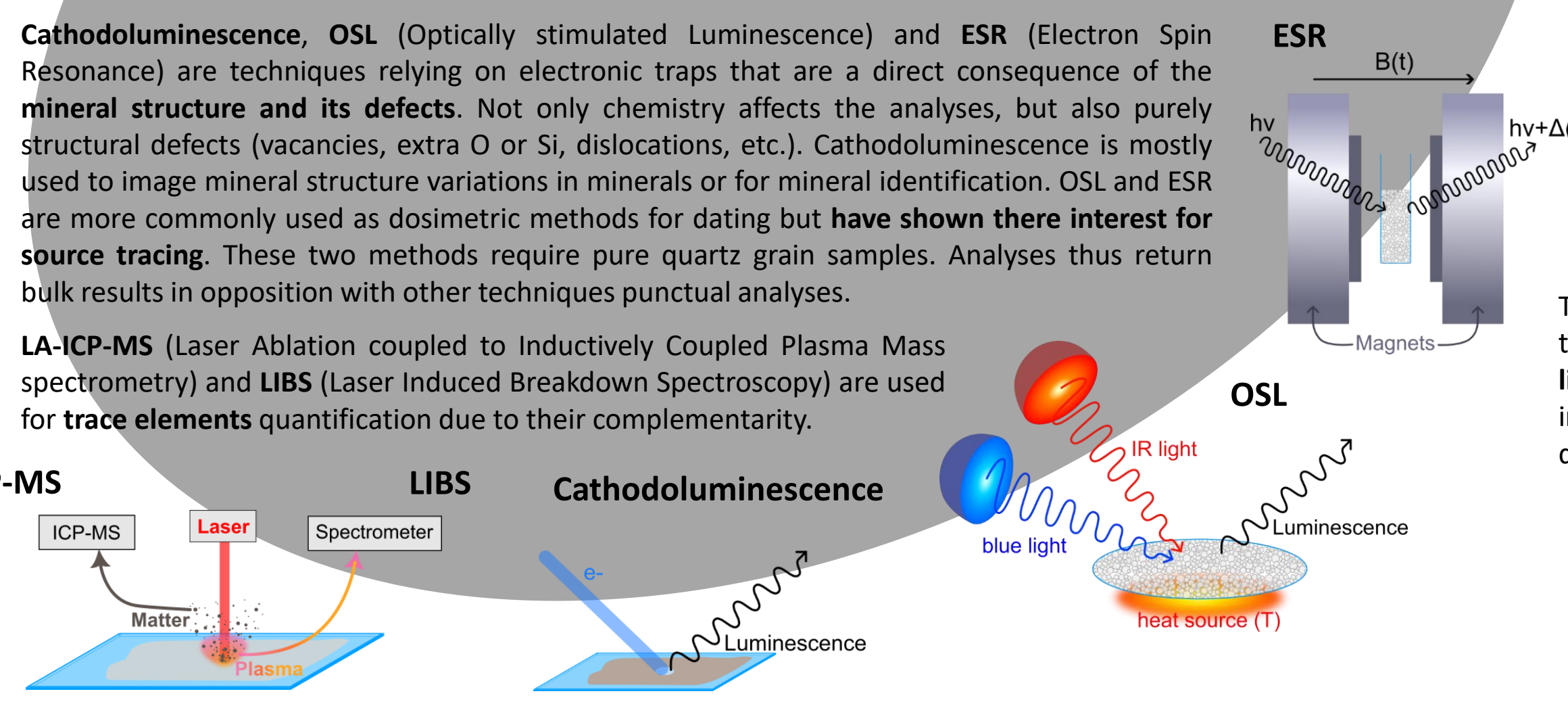
Quartz structure defects



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.



Cathodoluminescence, OSL (Optically Stimulated Luminescence) and ESR (Electron Spin Resonance) are techniques relying on electronic traps that are a direct consequence of the mineral structure and its defects. Not only chemistry affects the analyses, but also purely structural defects (vacancies, extra O or Si, dislocations, etc.). Cathodoluminescence is mostly used to image mineral structure variations in minerals or for mineral identification. OSL and ESR are more commonly used as dosimetric methods for dating but have shown their interest for source tracing. These two methods require pure quartz grain samples. Analyses thus return bulk results in opposition with other techniques punctual analyses.

LA-ICP-MS (Laser Ablation coupled to Inductively Coupled Plasma Mass Spectrometry) and LIBS (Laser Induced Breakdown Spectroscopy) are used for trace elements quantification due to their complementarity.

Quartz trace elements characterization

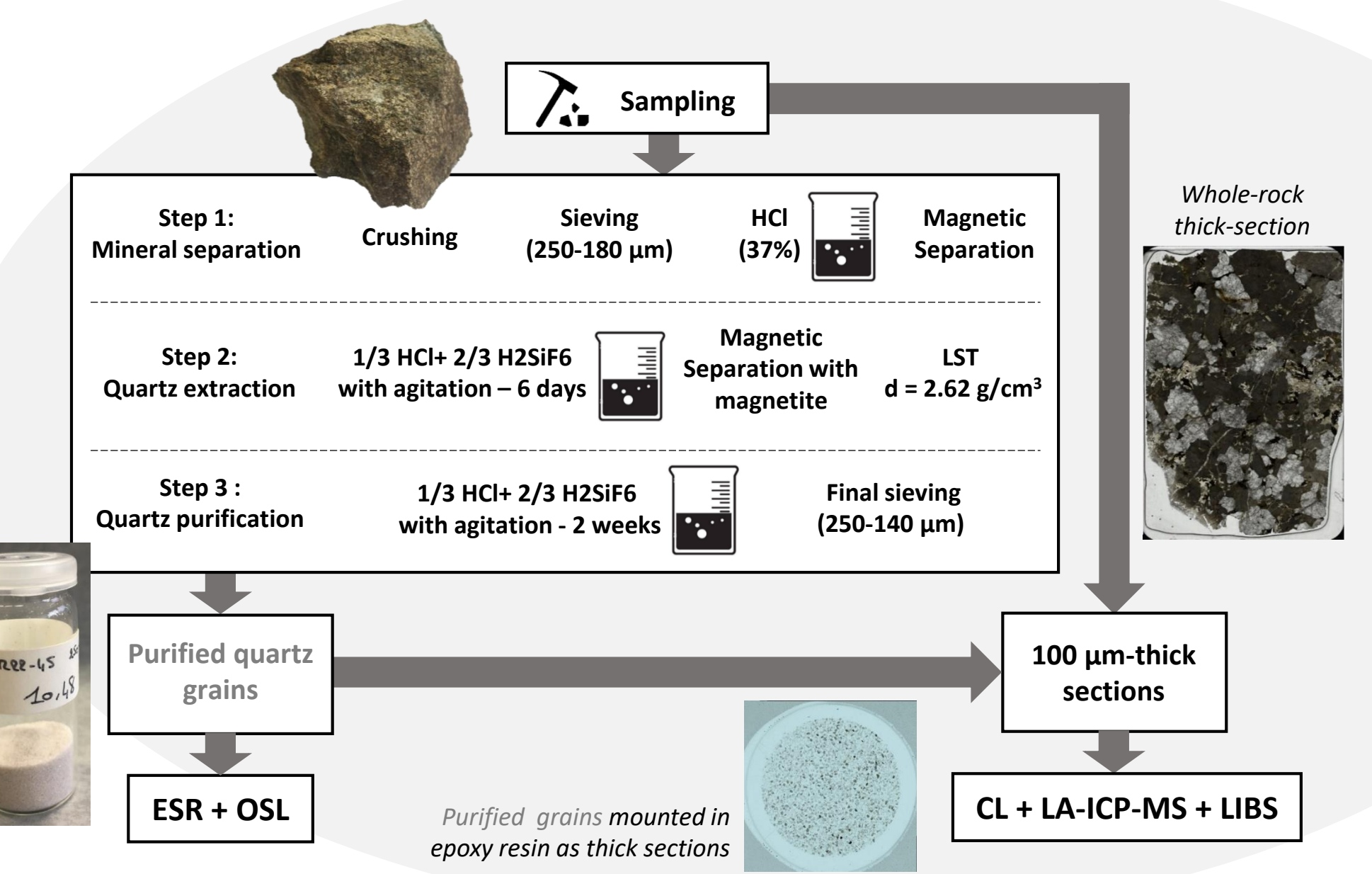
LA-ICP-MS analyses were carried out on an Agilent 8900 triple quadrupole ICP-MS coupled to a Teledyne Excite Excimer 193 nm laser in the BRGM (French survey) laboratories. Quartz being a difficult mineral to analyze with LA-ICP-MS due to its high resistance and its transparency, a particular setup had 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).

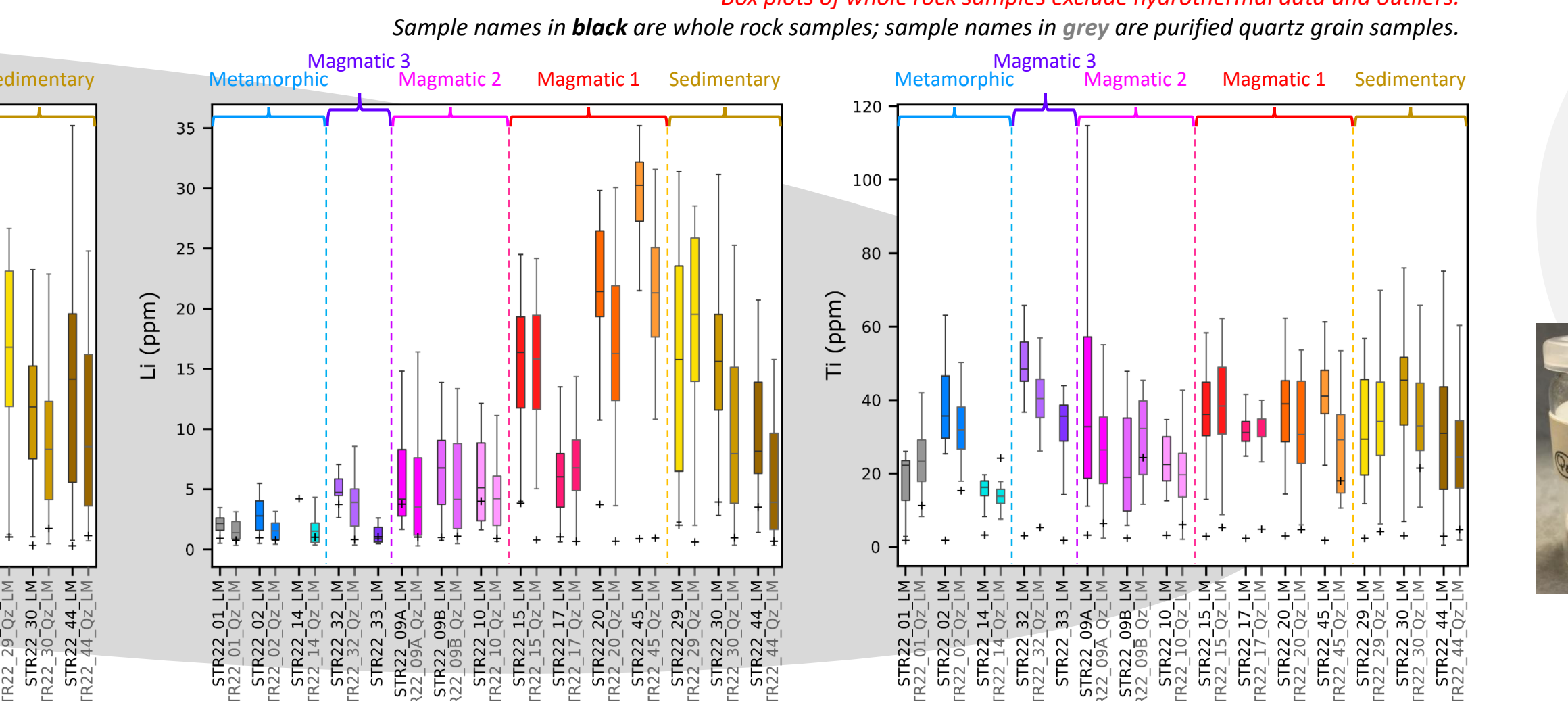
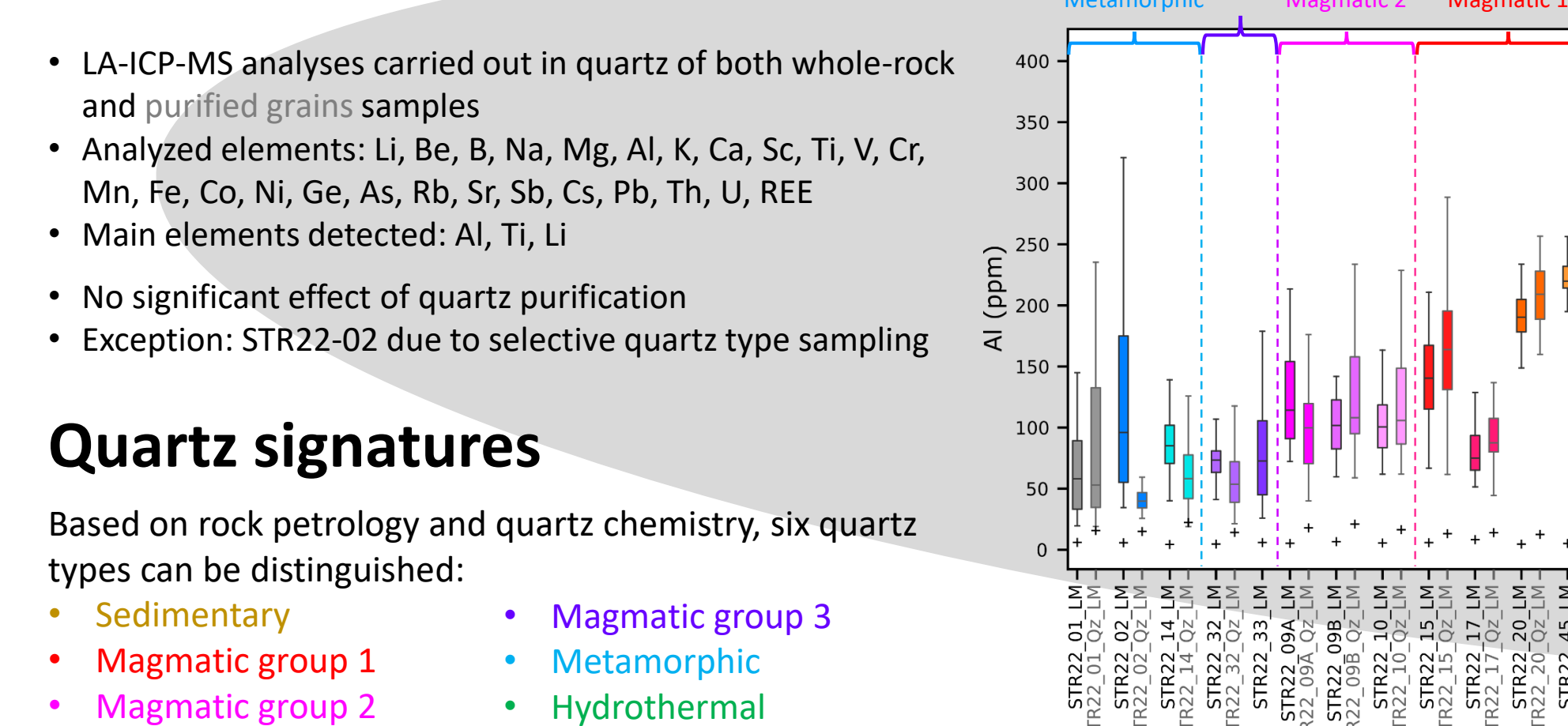
LIBS imaging instrumentation is based on the generation of a series of plasmas at different positions on the sample following a scan sequence. Each spectrum is then processed to build the corresponding elemental maps. The step size was between 40 et 50 μm for about a millions spectra allowing the analysis 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



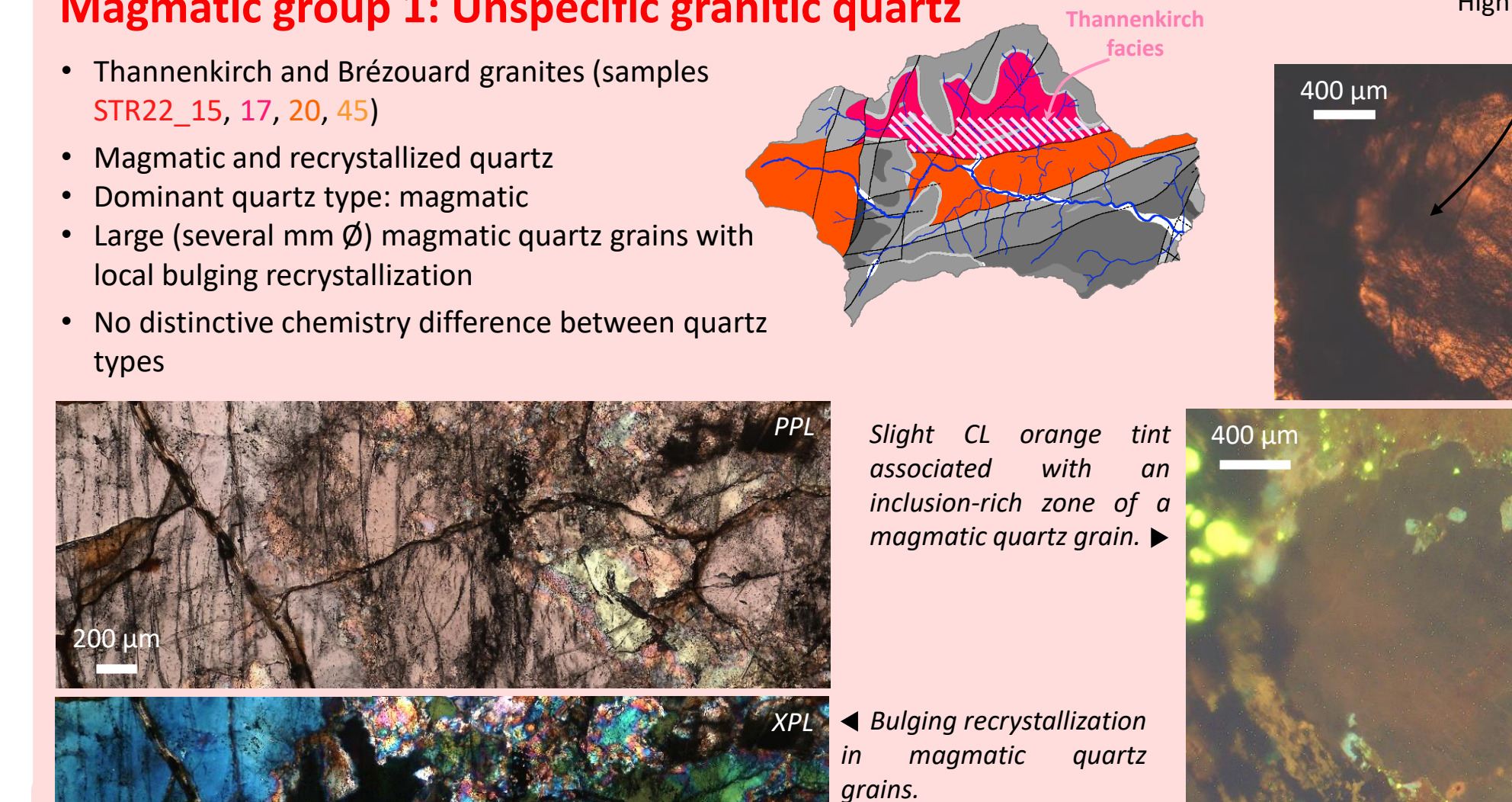
- LA-ICP-MS analyses carried out in quartz of both whole-rock and purified grains samples
- Analyzed elements: Li, Be, B, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Ge, As, Rb, Sr, Sb, Cs, Pb, Th, U, REE
- Main elements detected: Al, Ti, Li
- No significant effect of quartz purification
- Exception: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

Quartz signatures

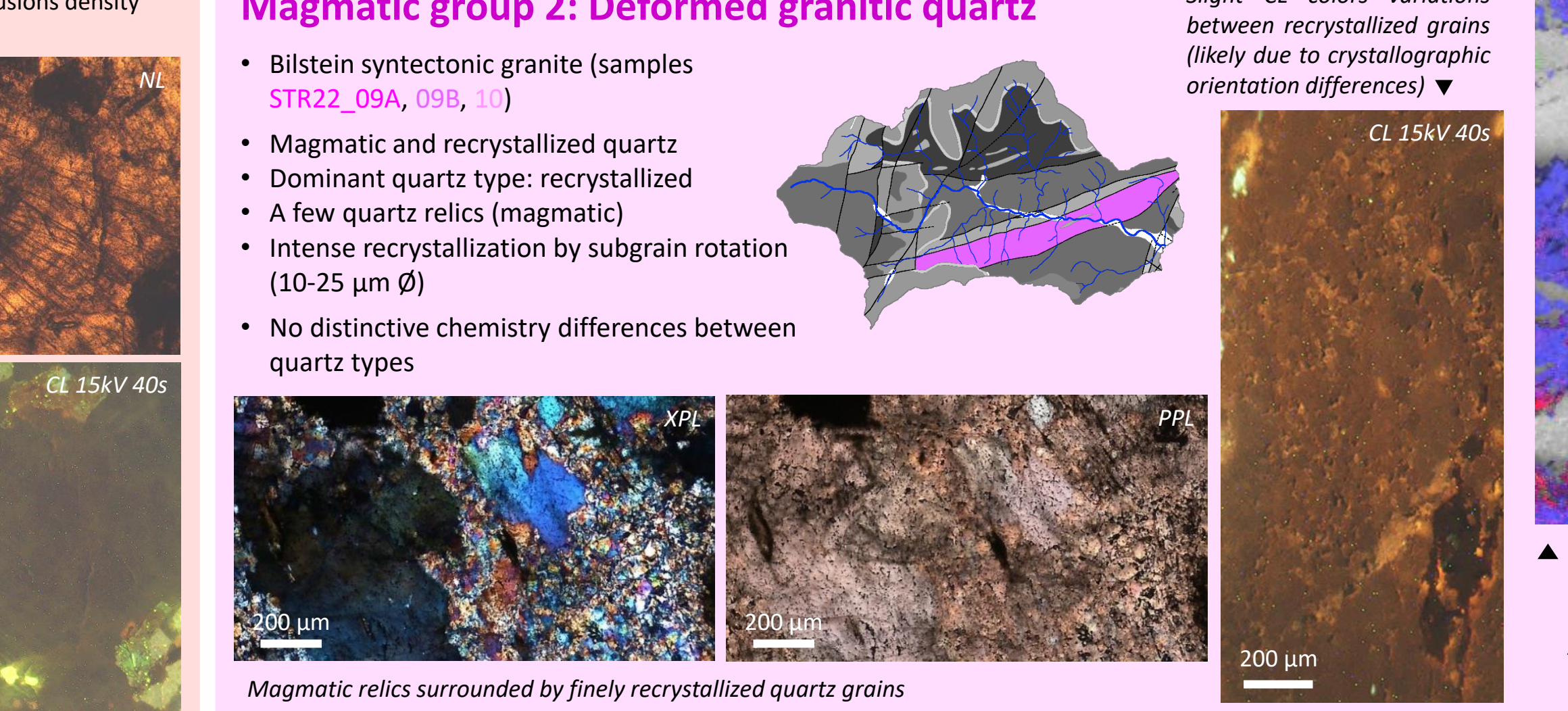
Based on rock petrology and quartz chemistry, six quartz types can be distinguished:

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

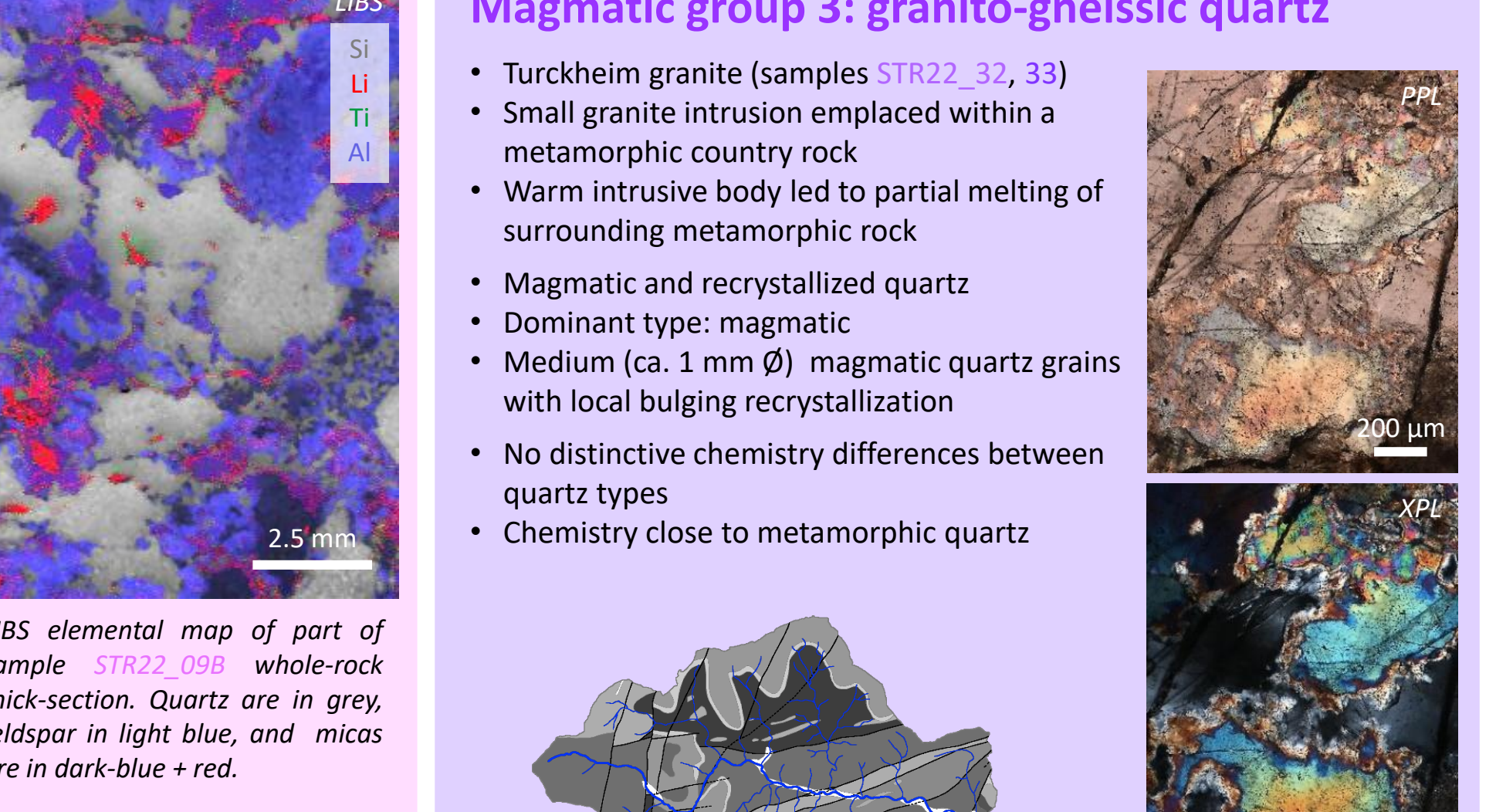
Magmatic group 1: Unspecific granitic quartz



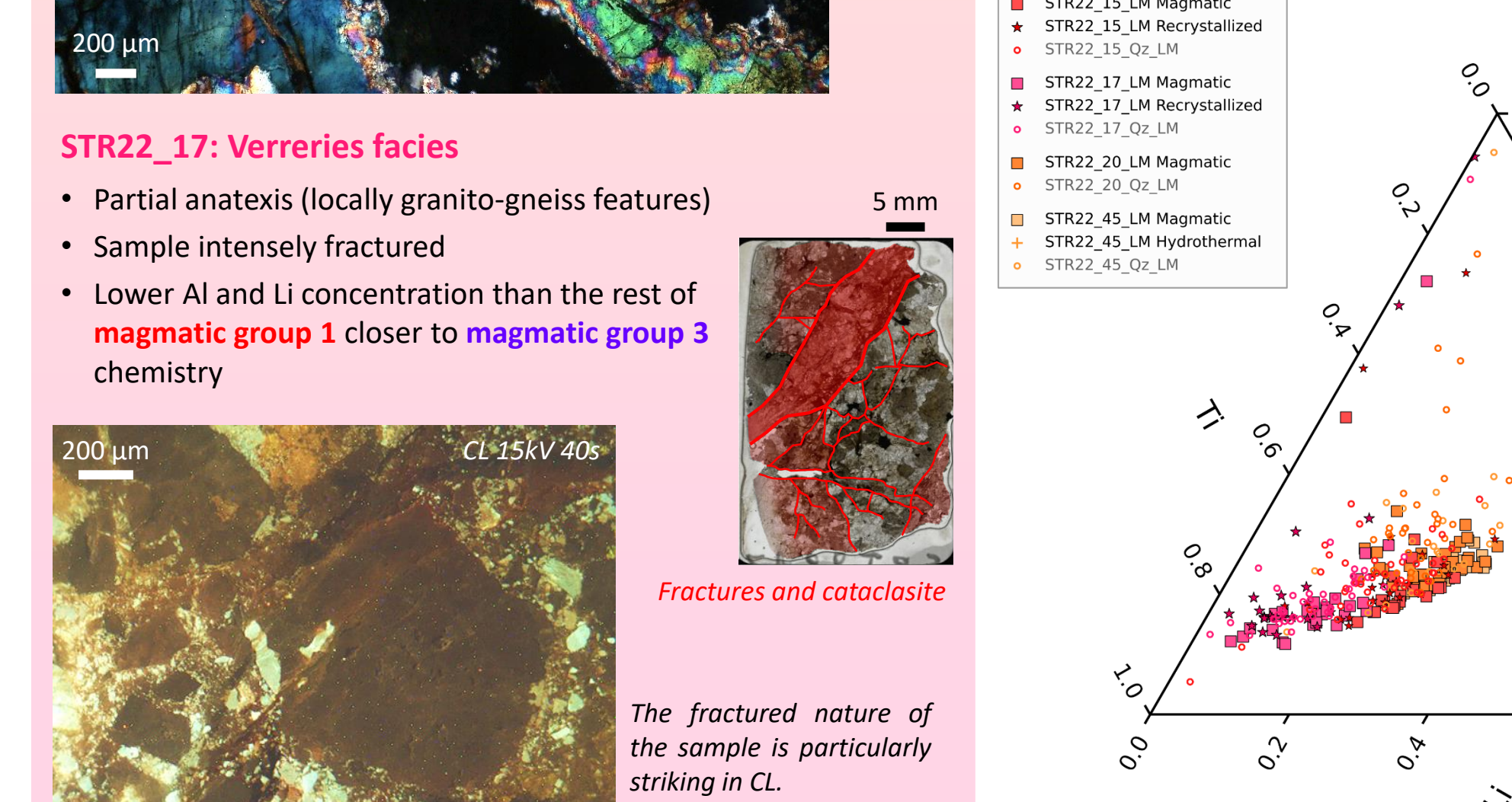
Magmatic group 2: Deformed granitic quartz



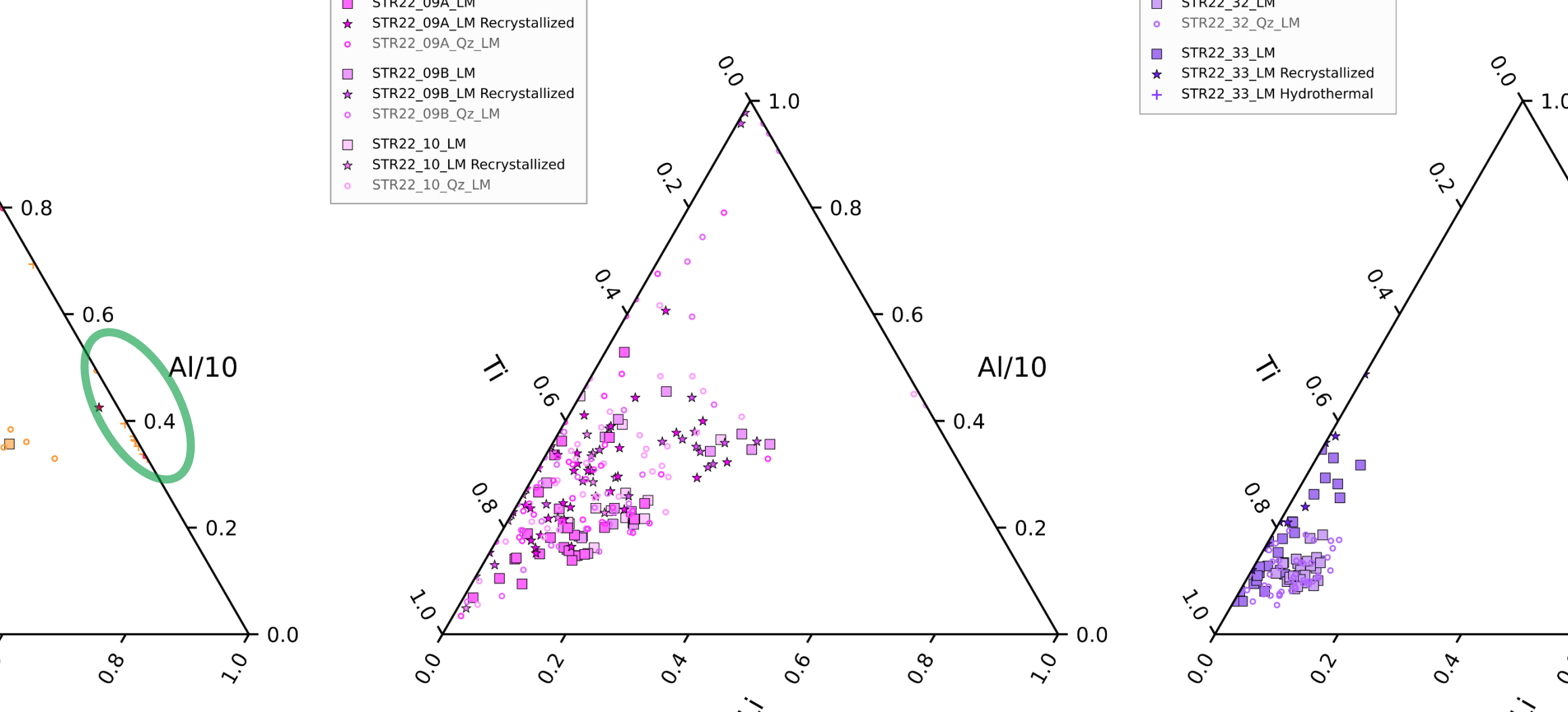
Magmatic group 3: granito-gneissic quartz



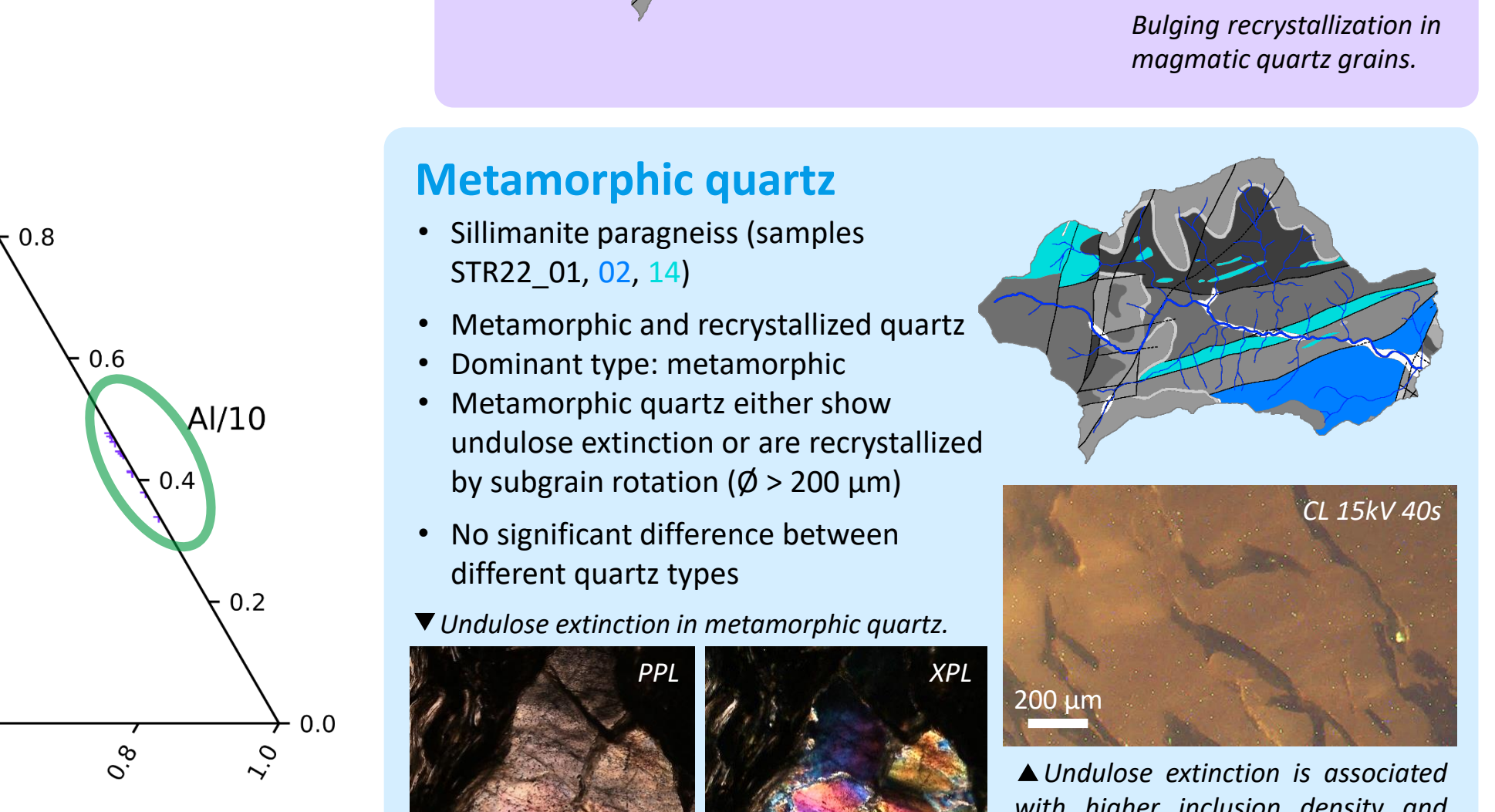
STR22_17: Verreries facies



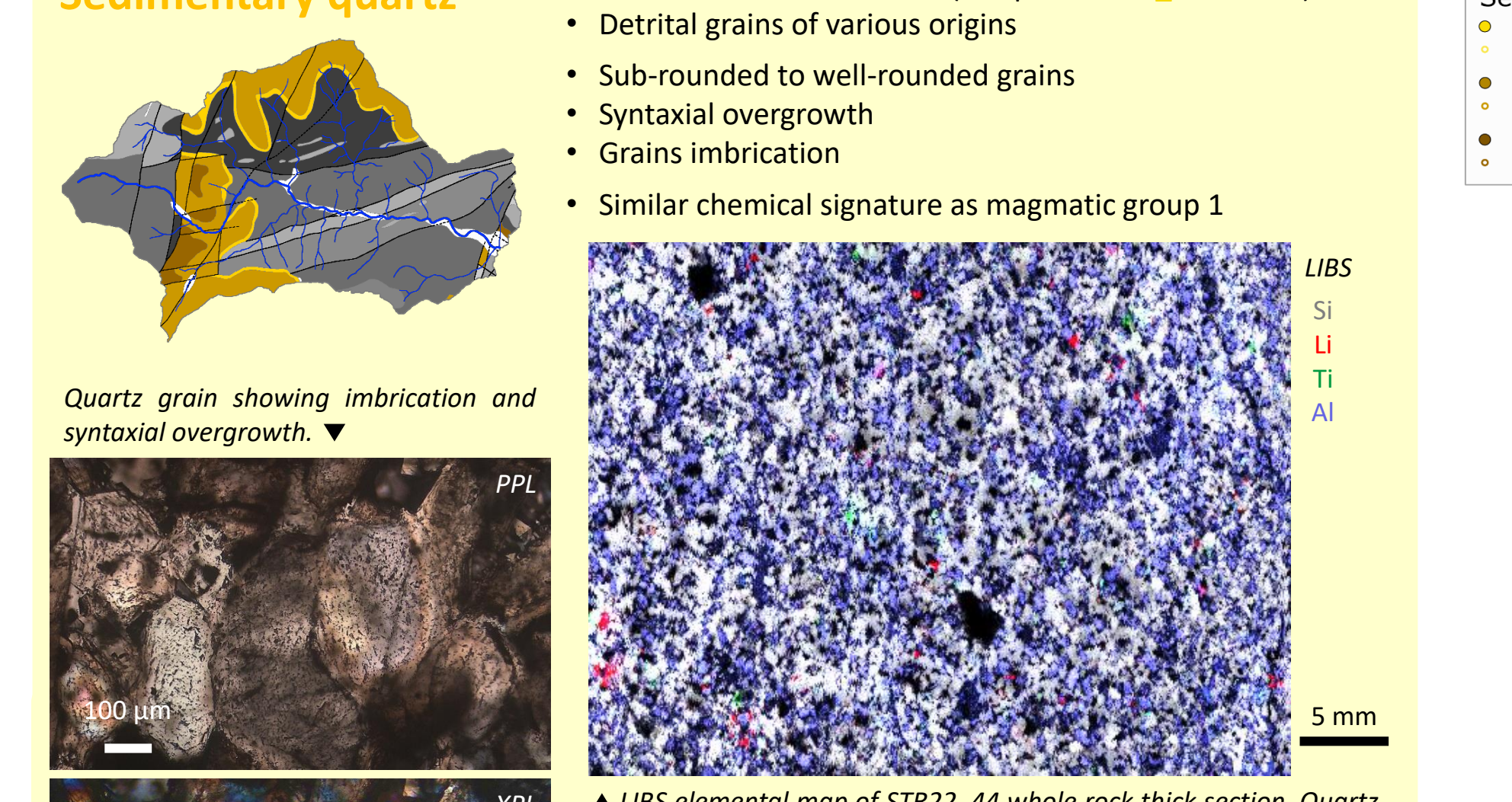
Metamorphic quartz



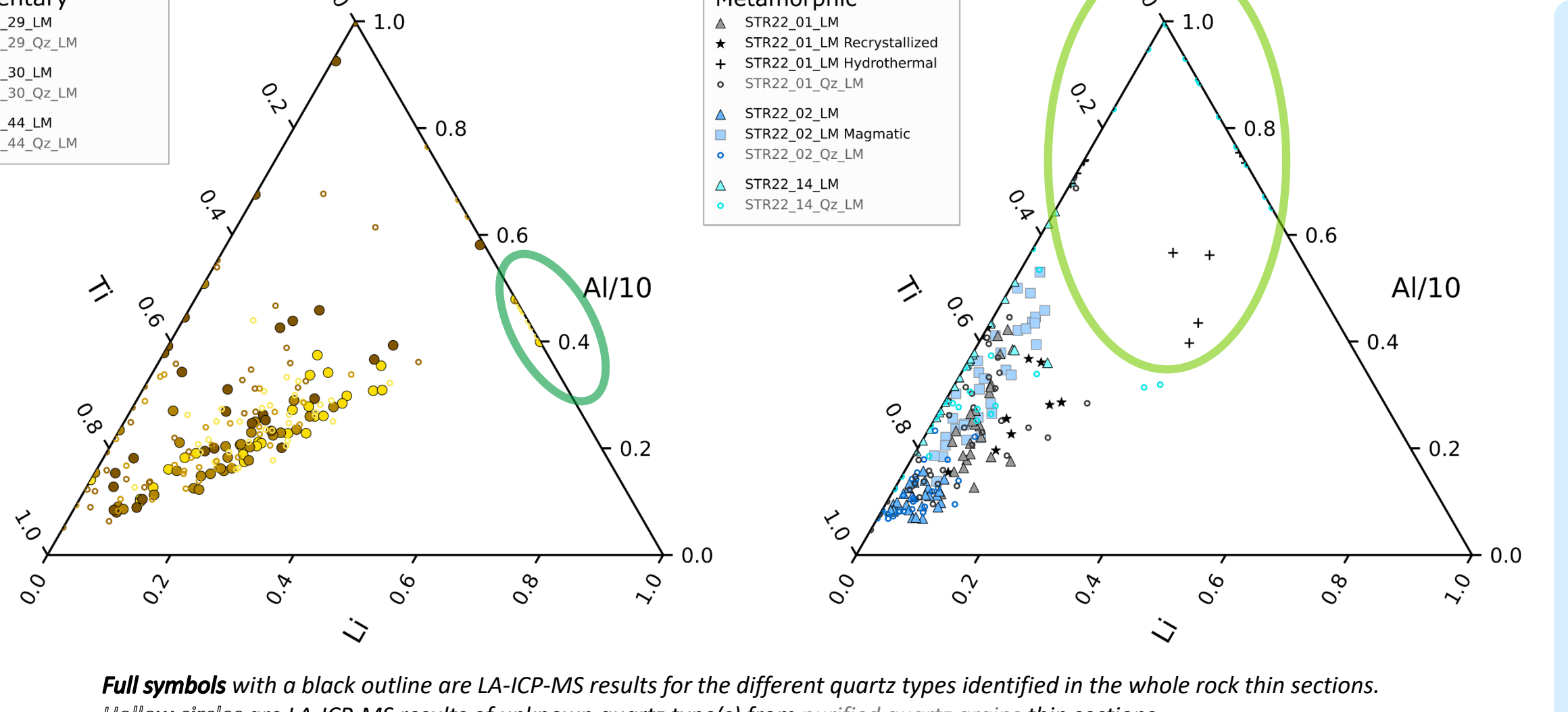
Sedimentary quartz



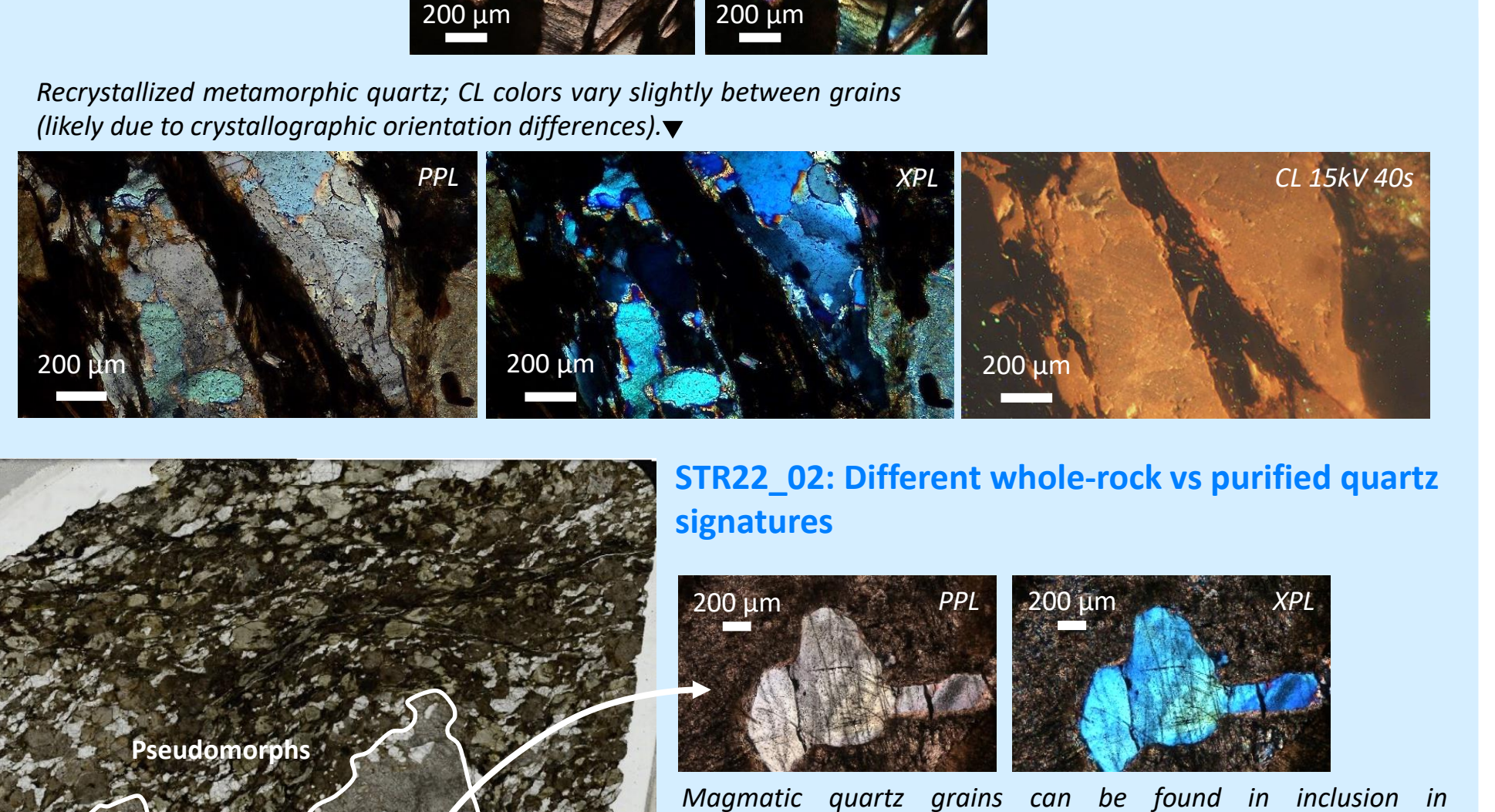
STR22_02: Different whole-rock vs purified quartz signatures



Comparison to ESR and OSL



Hydrothermal quartz



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