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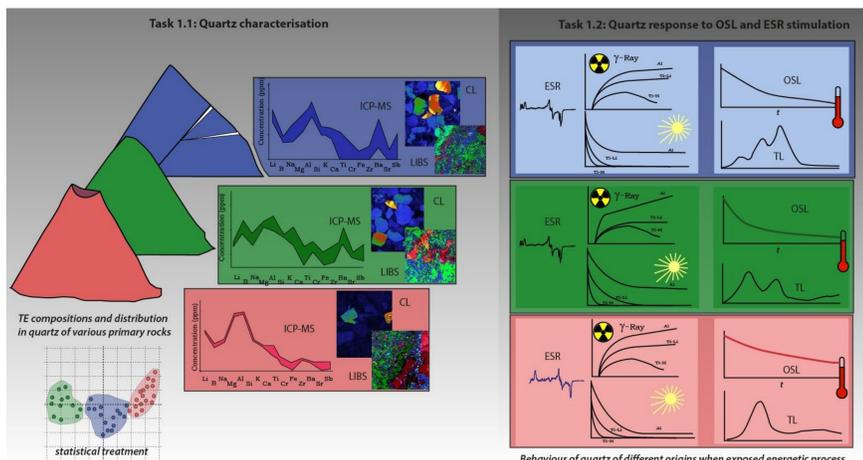
Creation of Quartz ID cards for source tracing using a multi-method approach as part of the ANR Quartz project: Lithium as a key element

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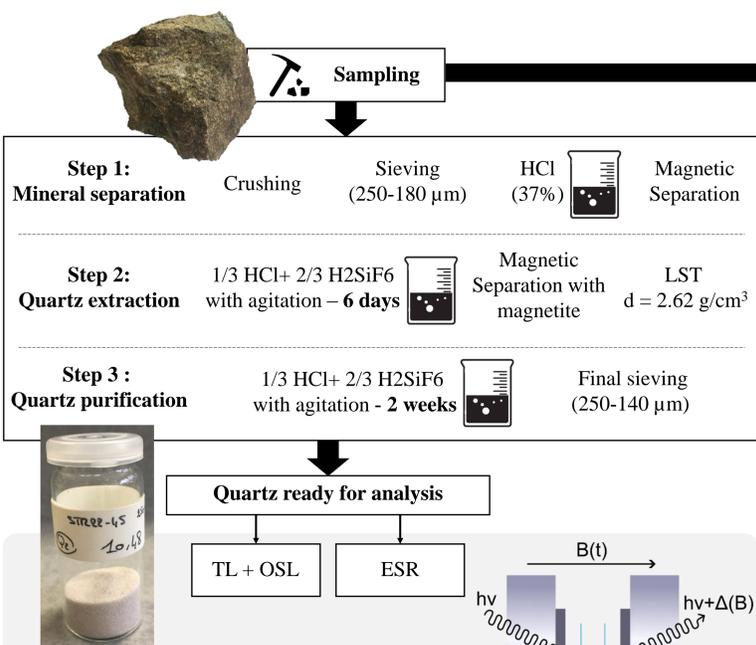
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Quartz, because of its high resistance to weathering, is ubiquitous and abundant in fluvial sediments. Its chemistry and physical properties provide information on its formation context and subsequent history making it an interesting marker of fluvial dynamics in a source to sink approach.

One of the main objectives of the French ANR Quartz project is to use the characteristics of quartz to trace its origin within fluvial sediments by combining conventional characterization methods with dosimetric methods such as Electronic Spin Resonance (ESR) and Optically Stimulated Luminescence (OSL) usually used for dating.



The first step to this is the characterization of the quartz signature of each of the bedrocks of the watershed of interest.



Analyses are made on purified quartz grains to remove any foreign mineral signature. Especially feldspar, that has a strong OSL signature overprinting quartz signal. This is less critical for ESR.

These techniques rely on the activation of electronic traps formed by structural defects in the mineral lattice either using magnetic, luminous or thermal energy.

These analytic methods are typically used for dating purposes but have shown potential for provenance studies. The origin of the OSL signal is poorly known, however the most used dating ESR centers are Al, Ti-Li, and Ti-H centers.

Principle of Optically Stimulated Luminescence (OSL) and Thermoluminescence (TL)

Principle of Electronic Spin Resonance (ESR)

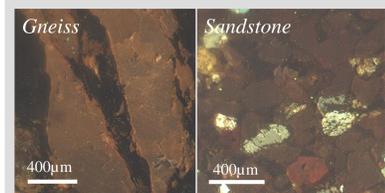
Principle of Cathodo-Luminescence (CL)



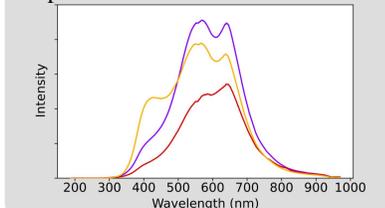
Thick sections
 LA-ICP-MS
 LIBS

Principle of Cathodo-Luminescence (CL)

Cathodo-luminescence's principle relies on similar electronic traps as OSL, activated this time by an electronic beam.

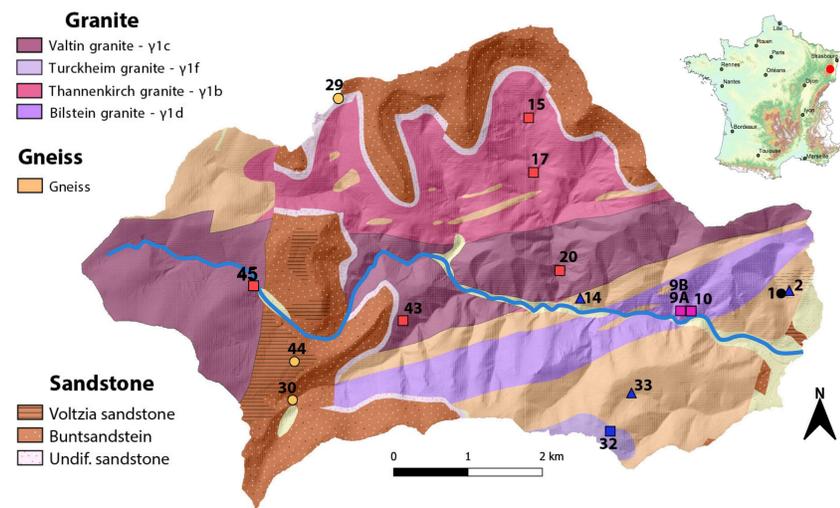


Quartz CL emission is weak but varies according to mineral orientation and quartz origin. CL-spectra can be obtained using a spectrometer.



The Strengbach Watershed:

The Strengbach is a small river from the Vosges Moutains (France). It has a relatively small catchment (ca. 40 km²) with a relatively simple bedrock lithology.

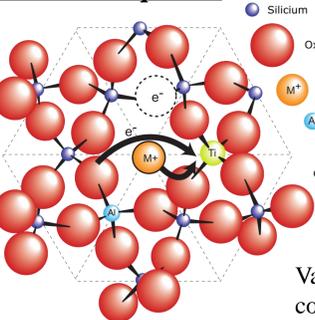


Principle of Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) vs Laser Induced Breakdown Spectroscopy (LIBS)

Laser ablation requires thick material to work on (at least 100   m) as it removes matter from the sample. Quartz is a challenging mineral for laser ablation due to its hardness and transparency. To prevent excessive tearing of the sample, a more powerful laser setting is used. This precaution is not necessary with LIBS as the laser energy required to produce plasma is much lower and does not damage the sample surface as much.

LIBS and LA-ICP-MS are complementary techniques. LIBS is more sensitive to light and volatile elements while LA-ICP-MS is most performant with heavy elements. LIBS produces quick elemental maps while LA-ICP-MS is best at punctual analyses.

Lithium in quartz:



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

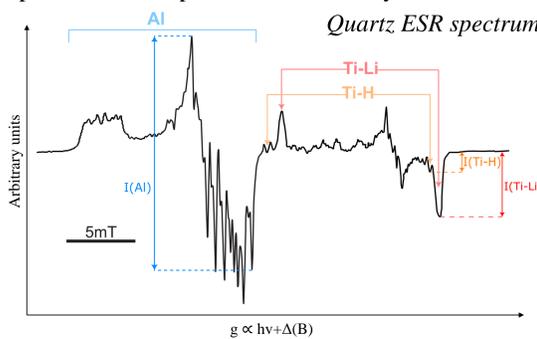
Some of the most common defects of the quartz lattice are atom vacancies and Si substitution.

Common substituting atoms in quartz: Al, Ti, Ge.

Vacancies and substituting atoms may require a charge compensation to keep electronic neutrality.

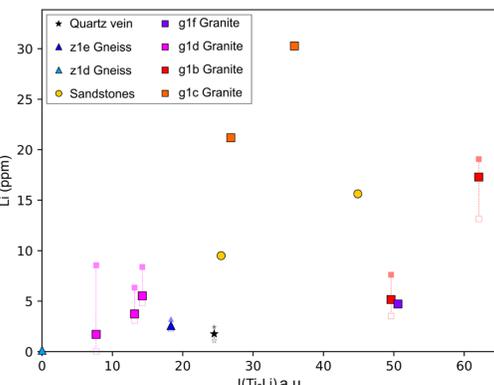
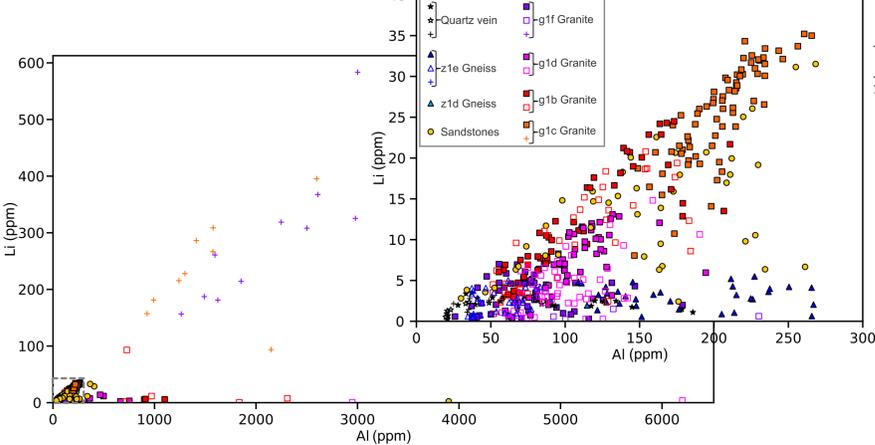
This role is taken by foreign cation circulating through the quartz structure in the c-axis channels.

Li is a common charge compensating ion. As such, it contributes to one of the main ESR centers used for dating.



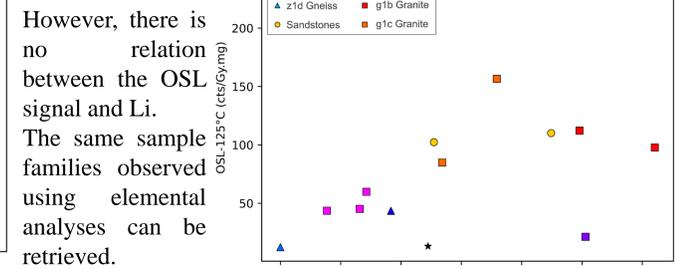
First results:

Li is critical to identify families of quartz types and origin. Its maximum content is correlated to Al content.



No strong correlation between ESR Ti-Li intensity and Li concentration.
 -> Li not limited to being a compensator for Ti in Ti-Li ESR centers

The best correlation between OSL and ESR signals is obtained with the Ti-Li center intensities.



A lot more to do:

- LIBS data, spectral CL data to acquire and treat
- Statistical treatment (ACP)
- Identify trace elements responsible for OSL and ESR signal
- Application to Strengbach fluvial sediments for provenance study