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▶ To cite this version:

Claire Aupart, Damien Desvisme, Philippe Lach, Florian Trichard, Magali Rizza, et al.. Trace elements in quartz: a tool for sediment provenance. European Workshop on Laser Ablation (EWLA) 2024, Jul 2024, Ghent, Belgium. 2024. hal-04667768

HAL Id: hal-04667768 https://hal.science/hal-04667768v1

Submitted on 5 Aug 2024

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Trace elements in quartz: a tool for

sediment provenance



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Titane

Electron

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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 use 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

Intrusive units

- Biotite porphyroid anatectic Thannenkirch monzogranite +/- granito-gneissic features Two-micas Brézouard leucogranite
- Two-micas syntectonic Bilstein leucogranite Two-micas Turkheim leucogranite with granito-gneissic features 29

Principal sedimentary units

Coarse Buntsandstein ferruginous sandstones and conglomerate Buntsandstein Vosgian Sandstone Buntsandstein voltzia and shell-rich sandstone

Other sedmimentary units

Early Muschelkalk shell sandstone differentiated early Muschelkalk Middle Muschelkalk variegated sandy marl with avpsum Late Muschelkalk entroques limestone Early Keuper dolomite and variegated

rengbac

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. Oxygène

Some of the most common defects of the quartz Cation compensateur lattice are atom vacancies and Si substitutions. The (Na, Li, H) most common substitutions to Si⁴⁺ are Al³⁺, Ti⁴⁺ and Aluminium 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 nineral 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 there interest for source tracing. These two methods require pure quartz grain samples. Analyses thus return bulk results in opposition with other techniques punctual analyses.

Silicium

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.

Magnets

ESR B(t)

Quartz trace elements characterization

LA-ICP-MS analyses were carried 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 on thick sections (100-150 µm thickness) instead of more common thin sections (30 µm thickness). Spot size used from measurements was 50 µm for wholerock samples and 35 μ m in the case of grain samples.



Comparison of

Whole-rock

thick-section

LIBS imaging analyses were carried out using an ABLATOM microLIBS equipment (ELM-XS-I) allowing micrometric chemical 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

• Medium (ca. 1 mm Ø) magmatic quartz grains

No distinctive chemistry differences between

Magmatic quartz grains can be found in inclusion in

Their chemical signature is not retrieved in purified quartz grains.

Magmatic quartz grains have a chemical signature close to

pseudomorphs in STR22_02 whole rock thin section.

Magmatic group 3.

Götze et al., 2021; Minelli et al., 2021; Shimada et al., 2013; Tissoux et al. 2015

• Chemistry close to metamorphic quartz

with local bulging recrystallization

quartz types



No distinctive chemistry differences between

quartz types

types



CL 15kV 40s tint inclusion-rich zone of a magmatic quartz grain. 🕨





200 µm

CL 15kV 40s

▲ 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 guartz 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





I(Ti-Li) (a.u.)

Full symbols with a black outline are LA-ICP-MS results for the different quartz types identified in the whole rock thin sections. Hollow circles are LA-ICP-MS results of unknown quartz type(s) from purified quartz grains thin sections.

Comparison to ESR and OSL



I(Ti-Li) (a.u.)

quartz.

▲ The diversity of CL colors reflects the

diverse origins of the minerals

composing the sandstones. Bright

colors are associated with feldspar and

dark color shades are associated with