2017 GeoQuEST Grant Report:
Chemical fingerprinting of trace elements in quartz

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Initial Aim: *To collect baseline measurements of trace elements in quartz from a variety of volcanic, plutonic and metamorphic rocks. These measurements will be used to develop a methodology for provenance analysis of sedimentary quartz.*

Background

Despite the abundance of quartz in clastic sediments, quartz is not routinely analysed to determine sediment provenance in the rock record. This is because no rapid, reliable and inexpensive analytical techniques are available for this purpose.

Determining the ratio of quartz and feldspar in a clastic sedimentary rock is widely used to estimate the tectonic setting of deposition (e.g., Dickinson & Suczek 1979). This technique was based on the tectonic setting of sedimentary rocks from the western USA, and is not considered reliable in other parts of the world, such as tropical regions or basins with a high volcanic contribution (Smyth et al. 2008). Other quartz-based provenance techniques include using the texture or colour of quartz under cathodoluminescence to approximate whether quartz is derived from a volcanic, plutonic or metamorphic source (e.g., Seyedolali et al. 1997; Augustsson & Bahlburg 2003). However, these techniques have limitations and can provide ambiguous results (Boggs et al. 2002; Augustsson & Reker 2012). These quartz-based techniques are not routinely used for provenance analysis.

The cathodoluminescence-based methodologies were developed because it is notoriously difficult to quantitatively analyse the trace element composition of quartz. This is because quartz grains may contain multiple generations of growth and/or healed fractures, as well as fluid and/or mineral inclusions. Therefore, trace element geochemistry of quartz requires *in situ* techniques. Most laser ablation ICP-MS systems use a 197 nm laser beam, which does not effectively couple with translucent quartz, resulting in irregular ablation and producing large quartz chips (cf. Chenery & Cook 1993). This is why there are few studies on the trace element chemistry of quartz.

Tanner et al. (2013) achieved homogenous ablation of quartz using a purpose-built 157 nm laser ablation ICP-MS system at the Australian National University; our findings demonstrated that a wide range of trace elements can occur above analytical detection limits and substitute into the quartz lattice. These include: Li, B, K, Al, P, Ti, Fe, Rb, Be, Ge, Zr, As, Sb and Th.

Project design

Multiple samples of quartz from the ANU research collection were mounted into polished resin blocks, and analysed in-house using the SEES Phenom XL scanning electron microscope to obtain analytical targets. Once the quartz crystals were targeted for analysis, polished mounts were carbon-coated and analysed using the Gatan MonoCL4 panchromatic cathodoluminescence system at the Electron Microscopy Centre. Cathodoluminescence images mapped the structure and colour variation within each grain (which will later be coupled with quantitative trace element data). The characterised quartz targets were then taken to Canberra and analysed using the 157 nm laser ablation ICP-MS at the Research School of Earth Sciences, Australian National University.

Results and Impact

The collection of the LA-ICP-MS data coincided with the installation of the new TOF-SIMS facility at the UOW Innovation Campus. I recruited a 2nd year Dean's scholar student Ryan North to be part of this project. I mentored Ryan, training him to both use electron microscopes and then write his first scientific research paper.

As part of this project, we collected TOF-SIMS maps to correlate with each LA-ICP-MS track. This then **became the first Australian study to** leverage a time of flight mass spectrometer (ToF-SIMS) in a dual-beam electron microscope to **map the chemistry of minerals at up to 65 nm resolution** (for reference, fingernails grow at 1 nm/sec). This is the first time quartz chemistry has been mapped on this scale: the results are already resolving questions on impurities in quartz.

The data collected in this study was used to create the following output:

- Undergraduate Research Report (EESC260): North, R. (2018) *A pilot study to evaluate time-of-flight secondary ion mass spectrometry (TOF-SIMS) as a supplementary method for quartz grain provenance analysis.*

Which then led to the following publication:

- North, R., Tanner, D., Nancarrow, M., Pasic, B. & Mavrogenes, J. A. Resolving sub-micrometer-scale zonation of trace elements in quartz using TOF-SIMS. *American Mineralogist* 107, 955–969 (2022).

And two external grant applications:

- Tanner, D. *Cryptic crystallisation: the key to deciphering hydrothermal proxy records*: DE200100499
- Alard, O., Foley, S., Chatzaras, V., Tanner, D., Grave, P., O'Reilly, S.Y., Payne, J., Davis, G. Gore, D., Jacob, Z., Paterson, J. *Probing our living planet: a frontier Electron MicroProbe*: LE200100113

It also provided the foundation for TOF-SIMS studies of other minerals:

- North, R. White, L, Nancarrow, M., Dosseto, A., Tanner, D. (*under review*) Sub-micrometre resolution FIB-SEM-based TOF-SIMS used to map geochemical zoning in four zircon reference materials. *Geostandards and Geoanalytical Research*

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