Technology Note

Correlative Automated Quantitative Mineralogy (AQM) and LA-ICP-MS Workflows

for Geochronology, Vector/Indicator Minerals and Conflict Minerals

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Introduction

The use of Laser Ablation Induced Coupled Plasma Mass Spectrometry (LA-ICP-MS) is an actively growing and increasingly utilized technology within both academic and industrial geoscience. Typical applications include:

- Geochronology: U-Th isotope ratio measurements in zircons provide a geochronological clock to enable dating of geological horizons
- Vector and Indicator mineral: Garnet, epidote, magnetite, pyrite, etc.) and their trace element geochemistry are used to understand proximity of the analysed mineral to the ore deposit (vector) and/or as an indicator mineral, whereby the chemistry indicates whether you have potential for an economic resource.
- Conflict minerals: 3T minerals (cassiterite, wolframite, coltan) – as defined by the US Dodd-Frank Act – and gold are minerals that extracted from regions of conflict. As such, to ensure legitimacy of supply it is possible to use trace element geochemistry to “finger print” the deposit or location of the extracted minerals as a means to validate the supply chain.

Regardless of the application, a precursor to the LA-ICP-MS analysis is typically investigation on a Scanning Electron Microscope (SEM) such as the ZEISS Sigma 300. The utilization of the SEM in these applications is for 3 main reasons:

Zircons in Geochronology – Typically on the SEM, cathodoluminescence (CL) is used in combination with the backscattered electron detector (BSE) to identify:

- Growth zones: these zones record specific times during zircon crystal formation, the history of crystal growth and age at the time of zone formation. As such, specific zones may be of interest for age dating.
- Defects: identification of defects in a crystal is critical in screening samples for isotope analysis, increasing confidence in measured ages, as fractures can result in “leaking” of 207Pb.

Vector or Indicator minerals – Recent work has shown how the trace element geochemistry of specific minerals can be used as a vector to locate and understand ore deposits, or as an indicator mineral suggesting a deposit may exists in a particular suite of rocks. Minerals such a garnet (used during diamond exploration), epidote (used during porphyry copper exploration) and magnetite (used during the exploration of magmatic nickel sulphide) are examples of such minerals. The SEM is required for the following reasons:

- Mineral identification: crucial to ensure the trace element analysis on the LA-ICP-MS will be valid.
- Chemical quantification: valid chemical measurement from the centre of the mineral grain where the LA-ICP-MS spot analysis will be carried out is needed to act as an internal chemical standard for trace element calibration. It is also valuable in ensuring no alteration which would adjust the trace element signature or the major elements has occurred.
- Textural setting of the grain: in some applications a certain textural setting or a mineral texture is indicative of the target mineral. Measurements are carried out to ensure they satisfy the criteria for a LA-ICP-MS analysis
- Precise determination of laser spot location: typical LA-ICP-MS systems require the operator to identify the laser spot location manually using a compound microscope. The SEM can automatically output co-ordinate locations of mineral grains of interest with nanonmeter precision to avoid this manual process and guarantee an unbiased, error free analysis.

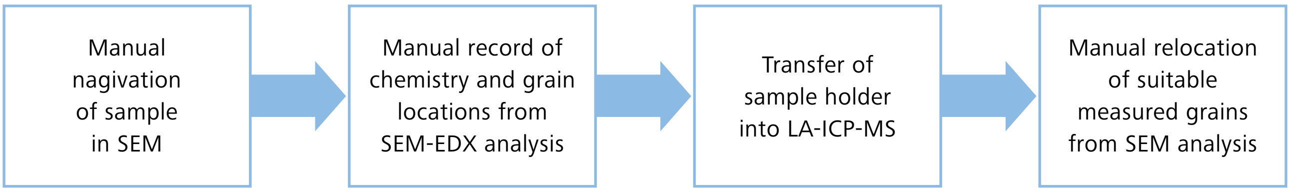

Figure 1 *Existing SEM Workflow*

- Sufficient grain area: the laser diameter can be around 30 microns and therefore it is important that the mineral grain that is analysed is large enough to accommodate the laser spot without contamination of the LA-ICP-MS occurring with contributions generating a LA-ICP-MS signal from surrounding minerals.
- Contextual mineralogy: while LA-ICP-MS gives detailed information about local isotopic geochemistry, SEM analysis can complement this by giving automated analyses over a large area. This allows for the location of the target mineral and an understanding of its distribution, textural character and relation to other structures within the sample.

Conflict Minerals – The origin of coltan, cassiterite, wolframite and gold can be determined through the measurement of trace element concentrations within the mineral matrix. As EDX is unable to measure the concentration of elements below 0.1 wt%, a correlative workflow to LA-ICP-MS enables the measurement of the indicator elements down to ppb levels. Using ZEISS Mineralogic Mining to identify coltan, cassiterite, wolframite and gold grains enables their rapid relocation in the LA-ICP-MS and enables auditors to exclude the sample origin as being from conflict zones.

Existing SEM
LA-ICP-MS Workflow

With each application outlined, SEM analysis (imaging or chemical analysis) is a prerequisite to LA-ICP-MS. At present, each of these analyses is manually carried out by an operator. This workflow is time consuming and laborious and can result in user error and a drop in efficiency. Furthermore, the time consuming manual investigation can lead to low discovery rates of suitable minerals of interest with the correct chemistry, grain size and textural location. This ultimately determines the number of grains which can be identified for LA-ICP-MS analysis and thus limits the population statistics critical for these applications.

In addition, once the imaging or chemical identification is complete, there is a manual workflow that involves moving the samples from the SEM to the LA-ICP-MS, requiring the removal of samples from the SEM sample holder and repositioning on the LA-ICP-MS stage. As a result, sample orientation and relocation of the grains of interest is challenging.

New Workflow Development
The Introduction of New Automated Quantitative Mineralogy Capabilities

Automated mineralogy / automated quantitative mineralogy (AQM) has been a widely applied technique since its original development in the early 1980s. These software solutions provide an automated analysis where the software packages control a combination of the SEM and EDS to perform analysis to then quantify the mineralogy across the samples. Despite its age and application in process mineralogy, it has received little notable technological and methodical developments.

ZEISS launched Mineralogic in July 2014, which incorporated a new analytical framework that utilizes both modern day energy dispersive spectrometry (EDS) technology and quantitative X-ray spectrum analysis algorithms. This development caused a paradigm shift in AQM analysis, whereby each is classified from a fully quantitative chemical analysis This quantification has been independently verified by Rio Tinto, comparing electron probe microanalysis (EPMA) to mineral quantification using ZEISS Mineralogic (Figure 1) (Ryan and Hill, 2016).

ZEISS Mineralogic is therefore specialized and uniquely placed to provide the research-quality quantitative chemical measurements needed as a precursor to, and an internal calibration of, LA-ICP-MS.

Fully Quantitative Chemical Analysis – Each analysed point within the mineralogical software has an EDS spectrum acquired. This EDS spectrum is then quantified to provide the normalized or un-normalized wt% contribution of the elements present. This is done through the utilization of modern EDS principles whereby matrix corrections (PB-ZAF or PhiRoZ), peak deconvolutions and standards based quantification are all used to bring accurate and precise quantified chemical compositions to each analysis point. As such, for a particular analysed point in a mineral, the Mineralogic software can tell you elemental abundance (e.g. for epidote it gives the concentration of Al, Si, Fe, Ca and O).

The second major development within automated mineralogy has been that of textural-based measurements, enabling:

- Morphochemical mineral classifications – combining the initial mineralogy grain classification with a textural quantification of the grain produces a "morphochemical" classification whereby feature such as area, feret max diameter, feret min diameter, length, porosity, compactness, etc., can be used to provide an extra valuable layer of data to the analysis. This can identify different textural types of minerals with the same chemistry (Ward et al. 2017) and/or be used to ensure the mineral classified has suitable size, i.e. > 30 microns, for LA-ICP-MS analysis.
- Lithology: This enables textural data and entire particle mineralogical information to be combined into a particle level classifier. This is important and specific minerals or specific mineral assemblages may need to be accepted or discarded. The ability to use the lithology classification to identify these particle types is the first step in providing a suitable workflow to the LA-ICP-MS system.

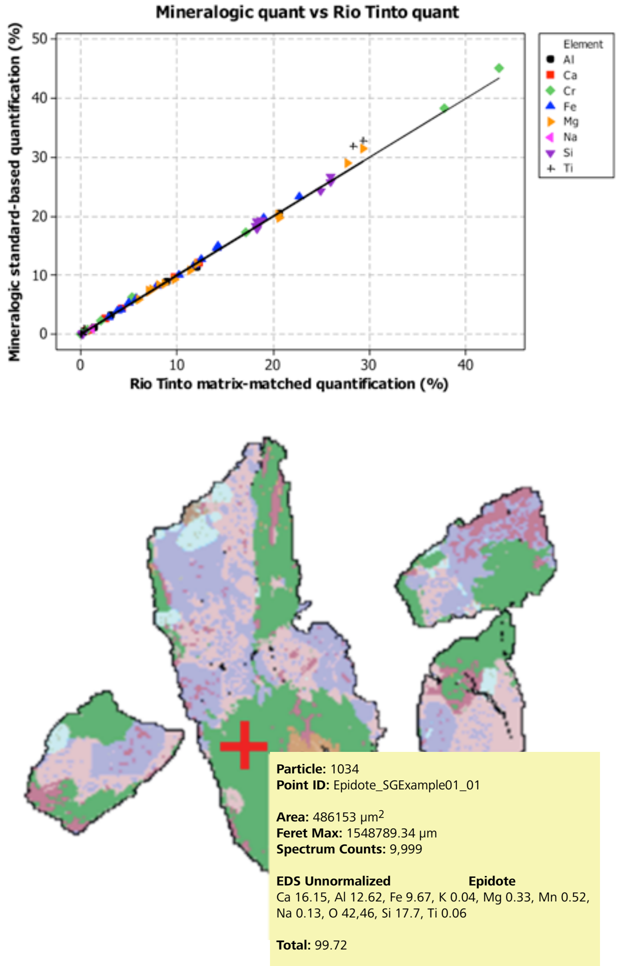

Figure 2 *Examples of the types of measurement quality that can be achieved by ZEISS Mineralogic and example data from an epidote analysis using ZEISS Mineralogic software with chemical data displayed.*

For more information of the standards-based quantitative capabilities of ZEISS Mineralogic and the textural capabilities described above, the reader is referred to Ryan and Hill (2016). ZEISS Mineralogic developments have provided direct, accurate and precise chemical measurements and mineralogical classifications into automated mineralogy and a textural analysis capability. It is now possible to combine and automate these large areas measurements and data into a correlative workflow with the LA-ICP-MS system.

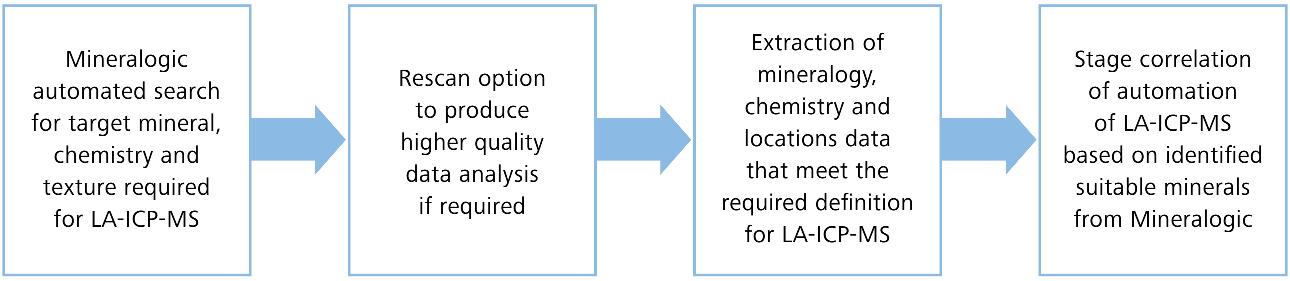

Figure 3 *New Workflow*

New Workflow Development

The Introduction and Correlation of Automated Quantitative Mineralogy with LA-ICP-MS

The correlation between AQM and LA-ICP-MS is streamlined using a common sample holder that can be used inside both the SEM and LA-ICP-MS, removing the first challenge of sample movement and relocation.

The automated mineralogy analysis can scan across the sample at a low spatial resolution to identify minerals of interest. ZEISS Mineralogic software can then perform a "re-scan" analysis whereby high quality measurement definitively quantifies the chemistry of the mineral grain (for the internal LA-ICP-MS standard), classifies the measured chemical composition and utilizes the textural quantification on the grain to fully understand the mineral textural occurrence and chemistry.

Predefined rules in the software can then be used to extract the mineral grain coordinates and abundances in a suitable format to be moved over to the LA-ICP-MS system. Through software development with ESI Lasers, it is possible to directly feed these coordinates into the LA-ICP-MS and convert and correlate ZEISS Mineralogic identified grain positions with the LA-ICP-MS stage. Crucially, the standards based EDX data from the Mineralogic system is then used as an internal calibration standard for the LA-ICP-MS system. This enables a fast and effective workflow between ZEISS Mineralogic AQM software and the LA-ICP-MS system.

This automation of the mineral analysis allows for a huge increase in the number of suitable locations for LA-ICP-MS to be carried out and thus greatly improves the population statistics and throughput capabilities of the instrument. It also removes the need for a devoted operator on the SEM to locate the grains of interest.

Summary

ZEISS Mineralogic has unlocked the correlation between AQM and LA-ICP-MS by providing a seamless correlative workflow to automate the identification of mineral grains of interest and subsequently analyse them using LA-ICP-MS. Through the unique ZEISS standards-based mineral quantification technology, the automated mineralogy system provides an internal standard for the LA-ICP-MS system. Automating the mineral grain identification and a common sample holder can therefore provide vast throughput improvements.

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