Book of Tutorials and Abstracts

European Microbeam Analysis Society

EMAS 2019

16th

EUROPEAN WORKSHOP

on

MODERN DEVELOPMENTS AND APPLICATIONS IN MICROBEAM ANALYSIS

19 to 23 May 2019
at the
NTNU, Realfagbygget
Trondheim, Norway

Organised in collaboration with:
Norwegian University of Science and Technology
(NTNU)

EDS MICROANALYSIS: PUSHING THE LIMITS

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Thomas Aiglsperger obtained a PhD in 2015 from the University of Barcelona (UB), Spain, for his work on the geochemistry and mineralogy of platinum group elements (PGE), rare earth elements (REE) and scandium in Ni laterites. During his PhD he set up a HS-11 hydroseparation laboratory, making discoveries of minute amounts of small scaled heavy minerals (< 30 µm) in challenging rock types and soils possible. His research aims to understand enrichment processes observed in highly altered supergene ore deposits (e.g., Ni-laterites; bauxites) including innovative approaches such as the biological cycling of target metals. Since 2017 Thomas holds a position as an associated senior lecturer at the Luleå University of Technology (LTU) in Sweden where he is currently building up a QANTMIN (quantitative target mineralogy) laboratory that includes automated mineralogy facilities.

1. ABSTRACT

In this work, quantitative target mineralogy (QANTMIN) is introduced by showing a cross-cut through possible applications for automated mineralogy that is based on scanning electron microscopy (SEM). The technology for such SEM devices that offer the possibility of automated mineralogy exists since more than 4 decades. However, it was not until the last couple of years that this technique has also started to become a standard technique for mineral identification and quantification. Until then reliable results in sample characterisation were limited to the availability of experienced mineralogists who did this time-consuming task mostly by optical microscopy (OM). An experienced mineralogist is also needed for SEM-based solutions as the systems have to be accurately calibrated in the first place. If this is done properly, SEM-based automated mineralogy can be applied in a large number of fields. The purpose of this contribution is to highlight the advantages of QANTMIN approaches using SEM-based automated mineralogy by showing three case studies: (i) acid mine drainage prediction in environmental studies, (ii) dating of zircons in geochronology, and (iii) tracking target minerals in critical metals exploration. Special emphasis is given to a praxis-oriented description of the applied methodology.

2. INTRODUCTION

Quantitative target mineralogy (QANTMIN) is the combination of finding target minerals in trace mineralogy by applying innovative concentration techniques like hydroseparation and the numeric description of solid samples with respect to (i) their mineralogical composition, (ii) the chemical composition of identified minerals, as well as (iii) their general nature of appearance (Fig. 1).

For this purpose, QANTMIN merges different analytical techniques such as geochemistry (whole-rock and sequential extractions), X-ray diffraction (XRD), optical microscopy (OM), Raman spectroscopy, scanning-electron microscopy (SEM), electron probe microanalysis (EPMA) and laser ablation ion-coupled mass spectroscopy (LA-ICP-MS). Due to its multidisciplinary approach QANTMIN is a powerful tool for a wide range of applications including environmental studies, forensic geosciences, planetary geology, archaeology, ore deposit exploration as well as mining and mineral processing. However, the analytical part of QANTMIN is also a challenging task: Firstly, because of the need of a precise mineralogical characterisation for the totality of a given sample and secondly, because of the large amount of accumulated data that has to be interpreted. At a time when mineralogy was mainly done manually via a petrographic microscope, such demanding challenges forced mineralogist to work with estimations. As a consequence, quantitative results implied an error that could lead to wrong conclusions. The precision of QANTMIN-related methods increased dramatically when automated computing systems, based on SEM with energy-dispersive X-ray spectroscopy (EDS) technology, were introduced by CSIRO in the 1970´s [1]. This technology became known and

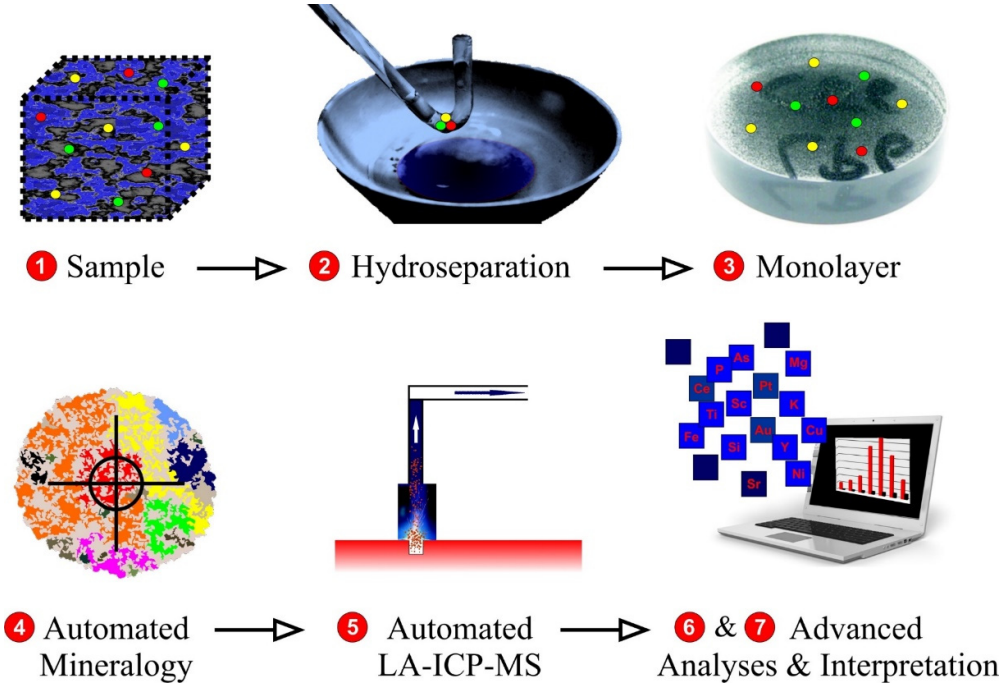

Figure 1. Flowsheet showing an example for QANTMIN: (1) initial sample material hosting (heavy) target minerals; (2) target mineral concentration (down to < 30 µm) via highly sensitive hydroseparation; (3) polished monolayer production (d = 2.5 cm) from highly concentrated target minerals; (4) mineral identification, quantification and position determination via automated mineralogy; (5) automated LA-ICP-MS measurement of point of interest retrieved from imported automated mineralogy data; (6) and (7) high-precision isotope analyses and multi-element analyses with subsequent interpretation.

patented as the so-called QEMSEM (quantitative evaluation of minerals by scanning electron microscopy) that was further developed until 2001, when CSIRO started the commercialisation of the technology with the brand name QEMSCAN (quantitative evaluation of minerals by scanning electron microscopy) (currently owned by FEI Company, which also owns a similar technology named mineral liberation analyser; MLA, but stopped further production). Today, several companies offer automated mineralogy solutions (e.g., Bruker, FEI, Oxford Instruments, TESCAN and Zeiss) and a look on the number of scientific publications dealing with automated mineralogy shows that the application of this technique has significantly increased especially during the last 15 years (Fig. 2).

A simplified explanation of what a SEM-based automated mineralogy facility does is that it scans the surface of a sample for its chemical composition via a defined raster and creates ultimately maps and tables that show the mineral phase assemblage of the sample. For the mineral identification, the chemical composition together with information of backscattered electron (BSE) brightness and X-ray count rates are used. Nevertheless, due to the complexity of mineralogy an experienced mineralogist is always needed for initial calibration and quality

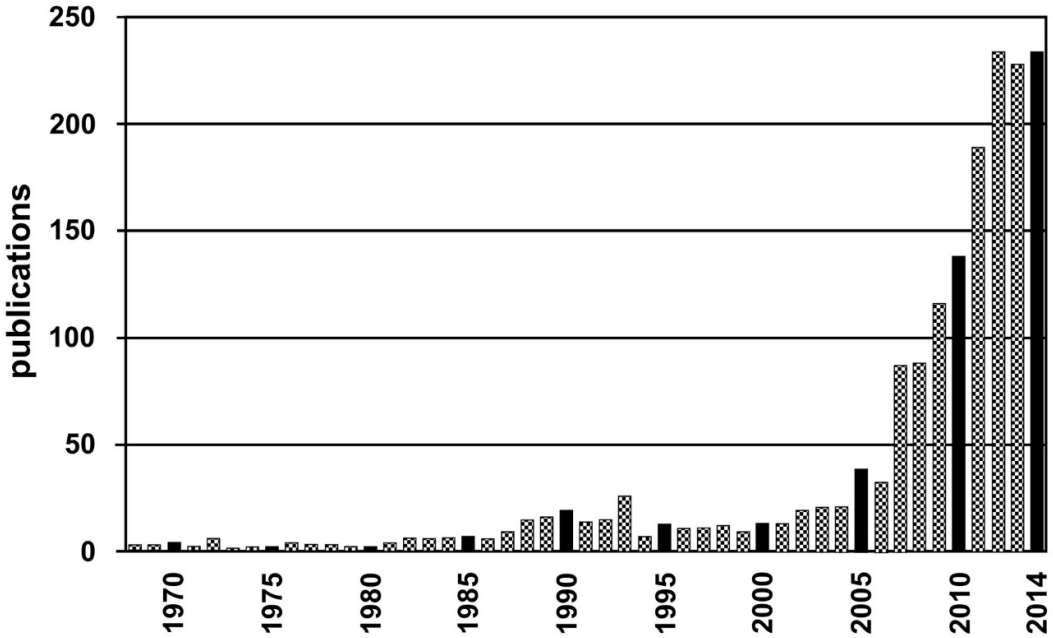

Figure 2. Time series (1968-2014) of publications related to automated mineralogy (modified after [2]).

control. Beside the mineralogical composition, multiple additional information is collected, visualised and quantified such as mineral grain size, mineral shape, mineral textures, mineral liberation, mineral associations, mineral density and elemental ratios. The numeric report of a completed scan is then used for data processing depending on the scope of investigation.

3. FROM MANUAL TO AUTOMATED TARGET MINERALOGY

Geological rock samples collected in field can occur highly heterogeneous with e.g., veins that cross-cut the main fabric, zones of alteration, contacts between different lithologies and hence different mineralogy. Therefore, traditionally any detailed mineralogical study starts with a careful sample preparation. This implies selecting one or several representative area(s) of interest that is (are) cut with a diamond rock saw for subsequent polished thin section and/or polished section production.

Depending on the particular scope of investigation, complementary sub-samples may be collected and used for additional analyses such as whole-rock geochemistry and/or XRD. However, the polished (thin) sections are usually first studied under a standard petrographic microscope which has the advantage of gaining rather fast multiple information (e.g., mineral identification and mineral abundances, grain sizes, alteration processes and general relations between minerals) at relatively low costs. The main drawback of this standard manual technique

is its operator dependency paired with the previously mentioned need to estimate when it comes to quantification. Therefore, attempts were undertaken to make this powerful tool of optical microscopy less operator dependent. One example in this context is the optical image analysis (OIA) for ore minerals characterisation that uses multispectral and colour images [3]. The main limiting factor for such automated mineralogy solutions that are based on optical properties of minerals, is the challenge to discriminate minerals with similar optical properties. Identifying differences in the chemical composition between such minerals is then often the next logical step to proceed and EDS technology at a SEM is usually applied. However, without a SEM facility that offers automated mineralogy, also this step is operator dependent and can become very time-consuming. Extremely time-consuming becomes a manual screening with SEM for scarce and small-scaled target minerals (e.g., platinum-group minerals (PGM); see example below). Depending on the complexity of the sample and the used magnification a careful manual screening can take up to days for a single standard polished section (d = 2.5 cm). As PGM contain platinum-group elements (PGE) that have significantly higher atomic numbers compared to the main elements of their host minerals (e.g., Cr in chromite), brightness and contrast settings on the SEM can be used to find PGM that occur usually much brighter in BSE images. However, as other heavy minerals and/or native elements that might occur beside can have a similar BSE brightness as PGM, spot analyses with EDS have to be applied manually for confirmation and mineral identification. Of course, every analysis and every grain of interest has to be saved manually for future quantification and interpretation that demands a lot of patience and persistence from the operator. This is only one of many examples explaining in a nutshell why automated SEM-based mineralogy facilities have become essential tools for quantitative mineralogy.

4. APPLICATIONS

4.1. Application of QANTMIN in environmental studies: Acid-base accounting in acid rock drainage prediction

Mining for metals guarantees the life standard of our modern high-tech society. At the same time, mining activities also account for the production of huge amounts of mine waste (note: a porphyry Cu mine with a grade of 1 % Cu produces 99 % of wastes) that is mostly represented by (i) waste rocks, mined to access the ore deposit and deposited on waste rock piles, and (ii) tailings that accumulate during the ore production process (e.g., flotation) and that are subsequently deposited in tailings impoundments. The management of such huge amounts of heterogeneous material is a challenging task and preventing of water pollution is one of the highest priorities. Acid mine drainage (AMD), or more general acid rock drainage (ARD), occurs when sulphide-rich waste rocks and/or tailings are exposed to the atmosphere, leading to the oxidation of the sulphides, which results in high element concentrations in the water and acidification [4]. However, there are minerals such as carbonates, hydroxides and silicates that can buffer these processes by neutralizing protons. In acid-base accounting (ABA), the amount

of moles of protons that could be liberated by this process (i.e., acid potential, AP) are calculated and compared to the amount of minerals that can neutralise the produced protons (i.e., neutralisation potential, NP). The result of this calculation is the so-called net neutralisation potential (NNP = NP - AP) and if the NNP is negative the material will form ARD, whereas a positive value means that the material has enough NP to maintain the material neutral. Most standard ABA calculations are limited by the assumption that all sulphur measured in whole-rock analyses is associated to pyrite. This, however, ignores the possible occurrence of other S-bearing minerals such as no acidity producing sulphides (e.g., sphalerite and galena) and/or sulphates (e.g., anhydrite-gypsum). Furthermore, there is also a substantial difference if calcite (neutralising one mole of protons per mole of calcite at neutral pH) or other carbonates such as siderite (acting as neutraliser or acid producer depending on the conditions) are present. It is, therefore, fundamental to have a precise knowledge of the mineralogy, and especially of the complete mineral abundances, in order to predict if a waste rock or tailings will produce an acid, neutral or alkaline environment (Fig. 3).

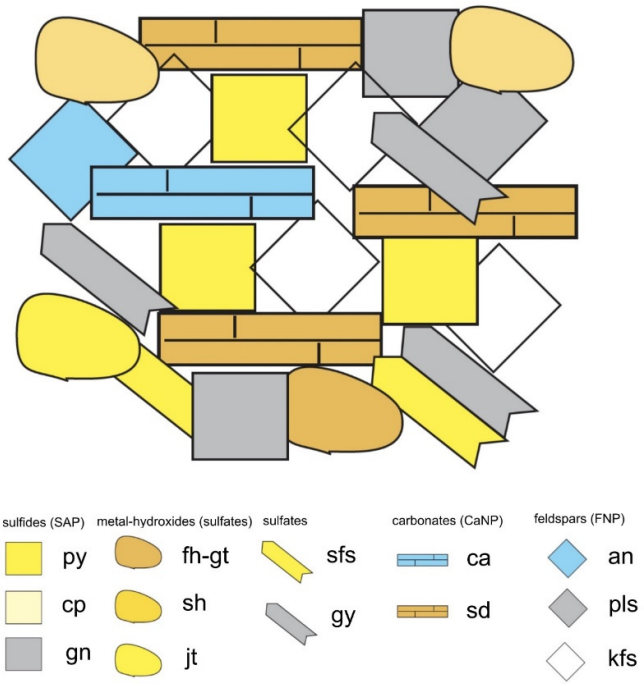

Figure 3. Schematic illustration of minerals and mineral groups showing their potential for producing either acidity or for protons neutralisation. Yellow colours indicate acid potential, blue neutralisation potential and grey and white none of both. Abbreviations: py - pyrite; cp - chalcopyrite; gn - galena; fh - ferrihydrite; gt - goethite; sh - schwertmannite; jt - jarosite; gy - gypsum; sfs - sulphosalts; ca - calcite; sd - siderite; an - anorthite; pls - plagioclase; kfs - K-feldspar. SAP = sulphide acid potential; CaNP = carbonate neutralisation potential; FNP = feldspar neutralisation potential. Modified after [4].

To evaluate possible element pollutions (different elements behave differently at different geochemical conditions) also minor and trace element compositions of target minerals have to be determined. Hence, due to the high complexity of the task, SEM-based automated mineralogy has proven to be the most appropriate technique [4], after through quality control [5]. Other techniques such as e.g., optical microscopy (experienced mineralogist needed; slow; expensive) or XRD (insufficient detection limit around 2 - 5 wt%) can only serve as complementary methods as they are not suitable for reliable mineral (and element) quantification needed for prediction purposes.

4.2. Application of QANTMIN in geochronology

Geochronology is the determination of the age of a geologic feature. It can be divided into relative geochronology (e.g., tectonic or stratigraphic relationships) and absolute geochronology that calculates the absolute age of e.g., a rock by using the half-time of a radioactive isotope that occurs as trace amounts in the structure of appropriate target minerals. Zircon ($ZrSiO_4$) for example contains trace amounts of U (but no Pb at the time of formation) that decays to Pb following two separate decay chains: (i) ^{238}U to ^{206}Pb; half-life 4470 ma and (ii) ^{235}U to ^{207}Pb; half-life 710 ma. As a consequence, the ratio of radiogenic Pb versus U can be used to determine the age of the zircon (and hence the age of the host rock).

The measurement of the Pb and U contents in zircons can be done by different methods such as via an ion microprobe using secondary-ion mass spectrometry (SIMS) or via laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS). However, dating laboratories of either kind request in general to send in zircons that are already mounted in epoxy, grain after grain following a line, and polished (Fig. 4).

This implies the main challenge to find, separate and mount enough zircons for the dating analysis. Finding zircons in acidic rock types such as granites is considered a rather easy task but it becomes extremely difficult in mafic to ultramafic rock types. Due to the relatively high specific gravity of zircons (4.7 g/cm^2) gravimetric techniques such as shaking tables and/or heavy liquids are normally applied to concentrate these target minerals. For challenging rock samples, such as for example highly Zr-depleted ophiolite-related ultramafic rocks, hydroseparation can be applied. However, time-consuming handpicking and subsequent "in line" mounting of the zircons is then the last step before polishing and sending for analyses. Due to SEM-based automated mineralogy technology this process can be significantly simplified. Modern LA-ICP-MS laboratories, as for example at the Instituto Andaluz de Ciencias de la Tierra (IACT) in Granada, only request a polished (thin) section (e.g., a heavy mineral concentrate) containing zircons of sufficient size (say 50 - 100 µm in diameter). The section is then routinely scanned for zircon grains that are subsequently documented and coordinates are automatically saved for final LA-ICP-MS measurements. This has great benefits for the overall workflow when it comes to zircon dating.

Figure 4. BSE image of a typical polished section (d = 2.5 cm) as generally requested by dating laboratories with zircons from 9 different rock samples (and three standards) ready for geochronological measurements.

4.3. Application of QANTMIN in exploration for critical metals

Technological advances have a great influence on mining and exploration operations. The development of catalysts for the automobile industry for example lead to a significant increase of interest for the so-called platinum-group elements (PGE; i.e., Os, Ir, Ru, Rh, Pt and Pd). However, PGE ore deposits are scarce and currently the global supply for PGE is dominated by major ore deposits in only two countries: (i) South Africa, producing approx. 70 % of the global Pt and approx. 37 % of the global Pd demand in its mines from the Bushveld Igneous Complex, and (ii) Russia, producing approx. 40 % of the global Pd demand as by-products from Ni deposits of the Norilsk Complex [6]. The situation of high economic significance of materials paired with supply risks led to the definition of so-called critical raw materials for the European Union (EU) by the European Commission [7]. In the most recent report on critical raw materials for the EU, 27 materials are listed and PGE as well as rare-earth elements (REE) are included [8]. REE is a group of 15 elements with similar chemical properties that occur together in the periodic table from lanthanum to lutetium as the lanthanide elements. They represent a top priority for the EU due to their essential usage in sophisticated high-tech applications such as related to renewable energy and laser technology. The supply risk for the EU with respect to REE is explained by a Chinese monopoly, as China hosts the largest active REE ore deposits on a global stage (i.e., the Bayan Obo ore deposit and ion-adsorption REE clay deposits). To minimise the supply risks for PGE and REE in the future new ore deposits have to be discovered and

SEM-based automated mineralogy is of great help for exploration activities also for rather unconventional exploration targets. Weathering products for example have shown a certain affinity to accumulate critical metals that could be mined as sub-products: in the case of PGE, limonite-rich Ni laterites characterized by Fe-rich soils that developed above ultramafic protoliths due to tropical weathering [9] and in the case of REE bauxites, Al ores developed due to the weathering of Al-rich protoliths [10]. However, the main challenge in both cases is not only to find anomalies in whole-rock geochemical analyses but also to subsequently find their mineralogical explanations. In general, target minerals in this kind of materials are scarce and rather small in grain size (e.g., platinum-group minerals (PGM) usually occur in the < 50 µm range). Due to their relatively high specific weight, PGE- or REE-bearing minerals can be concentrated via gravimetric methods. For the concentration of PGM and REE minerals a successful approach is to use hydroseparation technologies that simulate natural beach placers by separating heavier minerals from the lighter fraction in a V-shaped glass tube (for a detailed description of this technique see Rudashevsky *et al.* [11] and visit www.hslab-barcelona.com). In order to concentrate the heaviest (and not the biggest) grains of a sample showing a geochemical anomaly, the sample has first to be sieved into appropriate grain sizes in the range of 125 µm to < 30 µm. During the subsequent concentration process, an initial sample amount of a few kilograms is separated into tailings (kg-range) and extremely concentrated concentrates of each size fraction (mg-range). These concentrates are then mounted on a metallic cylinder (d = 2.5 cm), included in epoxy and polished. The resulting polished monolayer (every grain is exposed to the surface) of the heavy mineral concentrate can then be studied under the microscope for mineral examination and quantification. However, if we think of a final concentrate in the size range of 50 µm the amount of grains that have to be analysed in one single polished section is enormous and can easily reach 100,000 grains (Fig. 5). Without the help of an automated mineralogy facility the task to find and identify target minerals (and their quantification) is challenging and extremely time consuming even for experienced mineralogists. Depending on the quality of the concentrate this task can take many hours to days per polished section. Furthermore, there is always the risk to overlook grains that might have game-changing relevance. A well calibrated SEM-based automated mineralogy facility guarantees that all target minerals are discovered, identified and quantified which will directly lead to more reliable conclusions in exploration projects.

QANTMIN combines different techniques with the aim to get the maximum of mineralogical information of a given sample and SEM-based automated mineralogy is a key-technology for this task.

5. *ACKNOWLEDGEMENTS*

The authors are grateful for the invitation by the European Microbeam Analysis Society (EMAS) to present this contribution at the 16th European Workshop on Modern Developments and Applications in Microbeam Analysis in Trondheim, Norway.

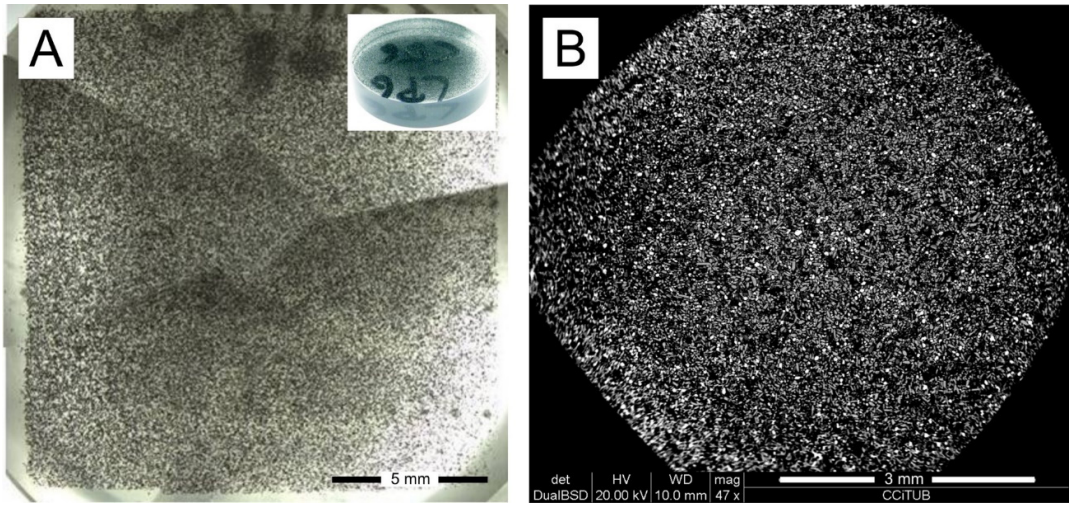

Figure 5. A: stereomicroscope image of a typical polished monolayer (insert; d = 2.5 cm) after heavy mineral concentration; B: BSE image of a polished monolayer with heavy minerals < 53 µm showing an approx. 16 mm^2 section that is representative for the entire monolayer. Note the great amount of bright occurring mineral phases that could be target minerals containing e.g., PGE or REE.

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