

Supplementary Material 2 to:

Automated Quantitative Mineralogy Applied to Metamorphic Rocks

This file contains the Mineralogic method with screenshot figures of the method.

2.3. Mineralogic Method

The micro-analysis on the selected thin section was performed on a ZEISS SIGMA 300VP SEM equipped with a back-scattered electrons (BSE) detector and two Bruker XFlash 6130 EDX detectors, with 129 eV energy resolution and with the ZEISS Mineralogic automated quantitative mineralogy software platform located at the Geological Survey of Denmark and Greenland, Copenhagen, Denmark. Within each thin section a region of interest was selected and imaged to provide a high-resolution BSE mosaic. Also, in this region of interest, a quantitative mineralogical analysis was carried out using Mineralogic, creating a mineral map with a user defined step size (or pixel size) as well as a list with parameters for grains in the sample. The acceleration voltage of the primary electron beam was set to 15 or 20 kV, to ensure X-ray excitation for all relevant elements (e.g., Fe, Cu, Zn). The 120 μm aperture providing 80 μA beam current used was used to obtain a high input count rate for the EDX detectors. The EDX software is fully integrated with the Mineralogic software, allowing for matrix corrections of each mineral. Therefore, exact element concentrations can be calculated for each acceleration voltage. A detailed description of the Mineralogic method is given below.

2.3.1. Zeiss Mineralogic Mining

The ZEISS Mineralogic software platform has a Mining and a Reservoir rock plug-in, though analytical functionalities between both branches largely overlap. The difference between both lies in how obtained data are visualized, e.g., as target and byproduct (Mining), or integrated with porosity measurements (Reservoir). Here, the Mining part of the software was applied. The software offers a recipe-based solution for all steps in the analysis (SEM parameters, holders and stubs used, calibration for the EDX and BSE detectors, image analysis, morphological analysis, mineralogical analysis, lithological analysis, mining output parameters, and criteria that specify how and when the analytical run is performed and terminated). These recipes can be saved, mixed, and changed individually, thus adapting each analysis to the sample at hand. Recipes can also be in- and exported allowing for an exchange between different internal and external users. Routine analyses can be set up allowing a non-geologist/mineralogist to run samples from a batch of similar samples, while the more experienced user gets the freedom to vary many parameters for each analysis [8]. The description here is based on Mineralogic software version 1.6.

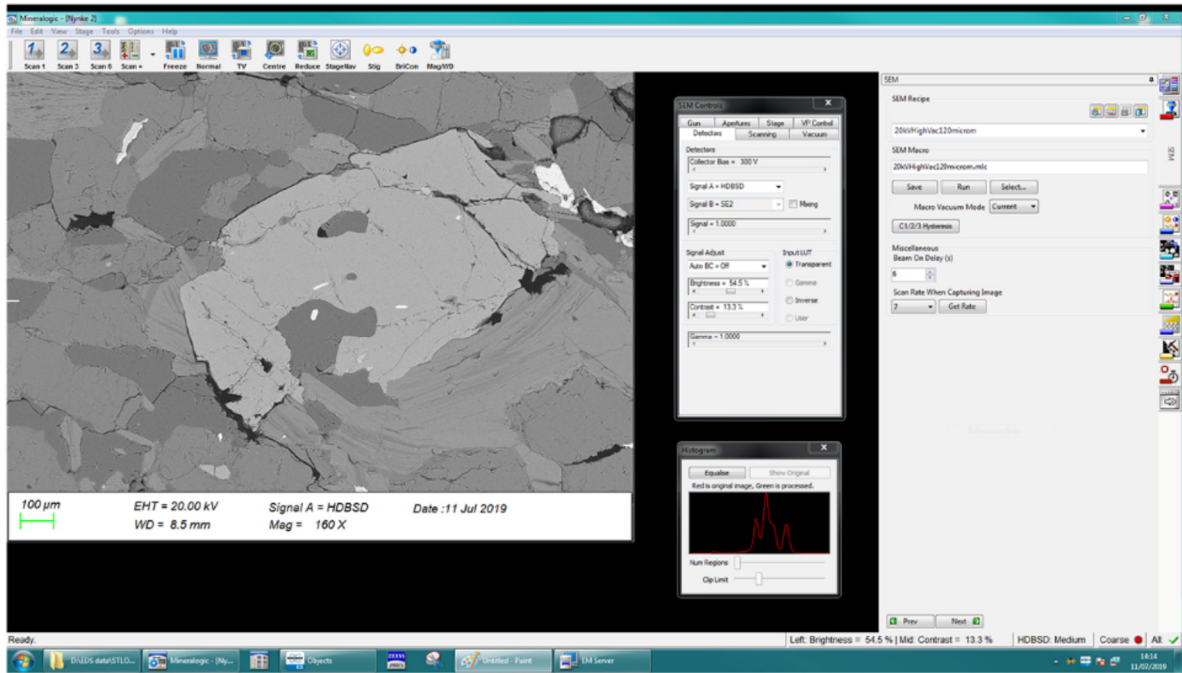


Figure S1. Overview of the SEM recipe (left) and the image navigation tool (right). The image navigation tool. is based on an optical or SEM image of the sample holder or sample and by defining points of reference on the sample holder and the image, the movements of the stage can be controlled from the navigation image. The SEM recipe saves the current settings of the SEM (like vacuum settings, beam parameters) and regulates the SEM imaging parameters (dwell time to allow for stage movements, scan speed).

2.3.2. Image Navigation

The Image Navigation tool of the ZEISS SEM applies digital images of thin sections, the entire sample holder, or overview SEM-images to navigate within the sample (Figure S1). The tool allows the user to define three fiducial points on the navigation image and connect those to stage coordinates. The tool is especially ideal to set up analyses on holders with several samples, or on fine grained material in a fast manner.

2.3.3. SEM Recipe

In this recipe, the SEM can be operated in a normal mode to set and save the operating conditions for the analysis. The sample can be placed to the correct position, the beam is focused and optimized at the required acceleration voltage (often 15–25 kV) and aperture size (often 60–120 µm). The brightness and contrast of the image are set. Thereafter, the conditions for BSE-imaging are determined, see Figure S1.

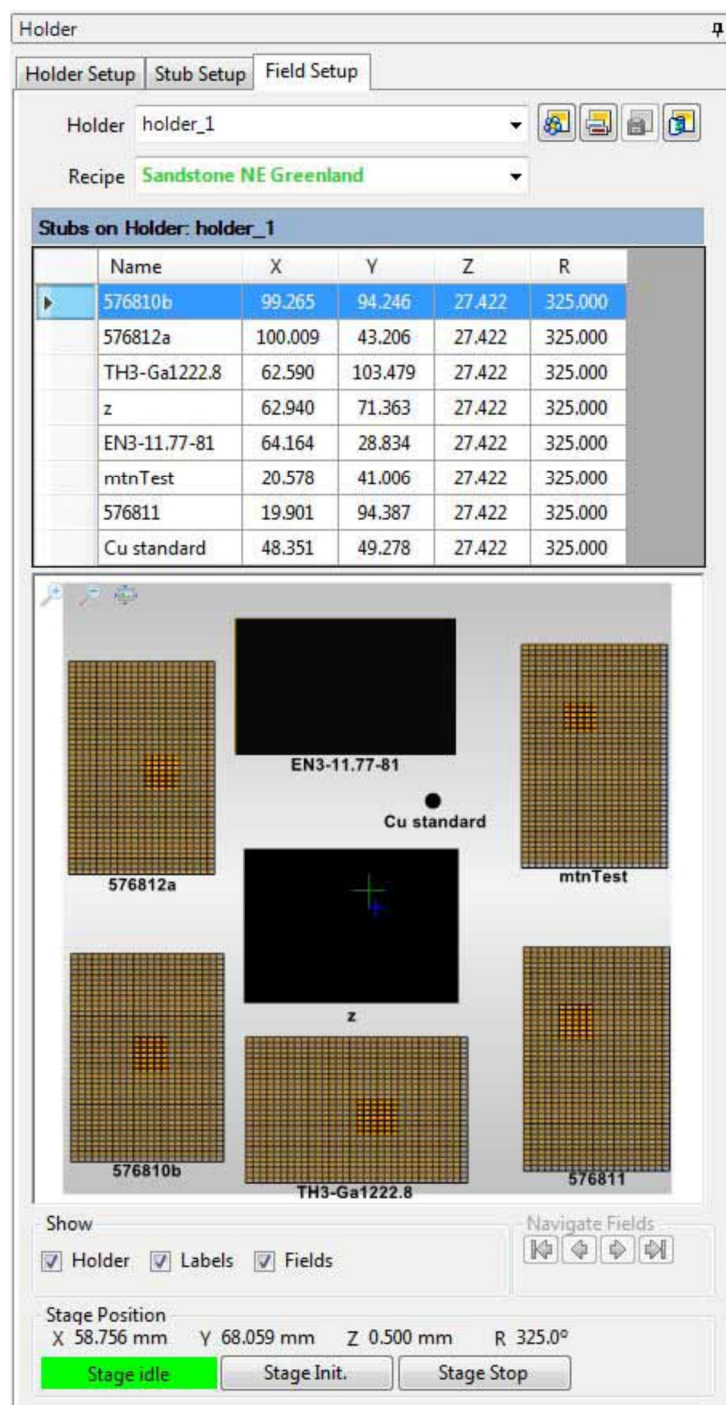


Figure S2. Within the Holder recipe the shape and size of holders and stubs can be defined with respect to the stage coordinates. First the size and shape of holder are defined (holder set-up), afterward the size and shapes of the individual stubs (stub setup). Then (stub details) each sample can be selected individually for analysis (here 5 samples have been defined), the area to be analysed (bright orange) and the step size are set by the user. In the central row the location of the Cu–Al standard for calibration is defined (black circle.).

2.3.4. Holder Recipe

In the Holder recipe the size and shape of both the sample holder and of the individual stubs can be defined and adjusted. The recipe lists a number of standard sample holders, but own holders can be defined as well (Figure S2a). In the stub details part of the menu, the geometrical parameters for the analysis of each particle can be defined: Z-coordinate of the stage, magnification during the

analysis, step size for the mapping of the sample, and the area or areas in the sample that are analysed, (Figure S2b).

2.3.5. Calibration Recipe

Both the BSE brightness and the EDS peak position can be monitored and corrected during larger mapping sessions. The BSE brightness is regulated using a standard with a bright- and a dark phase next to each other, f.e., a copper-aluminium stub. The brightness of the BSE image is set such that the bright phase in the standard (e.g., copper) has grey-values in the upper grey-level segment, but is not completely white, while the dark phase (e.g., aluminium) has grey values in the dark-grey segment. The interval for monitoring can be selected, e.g., every hour and for every new sample. At each monitoring event, the SEM resets the brightness and contrast values of the SEM to match the predefined values for the bright and dark phase in the standard (Figure S3).

The EDS peak position can be monitored by regularly measuring a suitable EDS peak, typically Cu K α , for the beam energy settings chosen for the analysis.

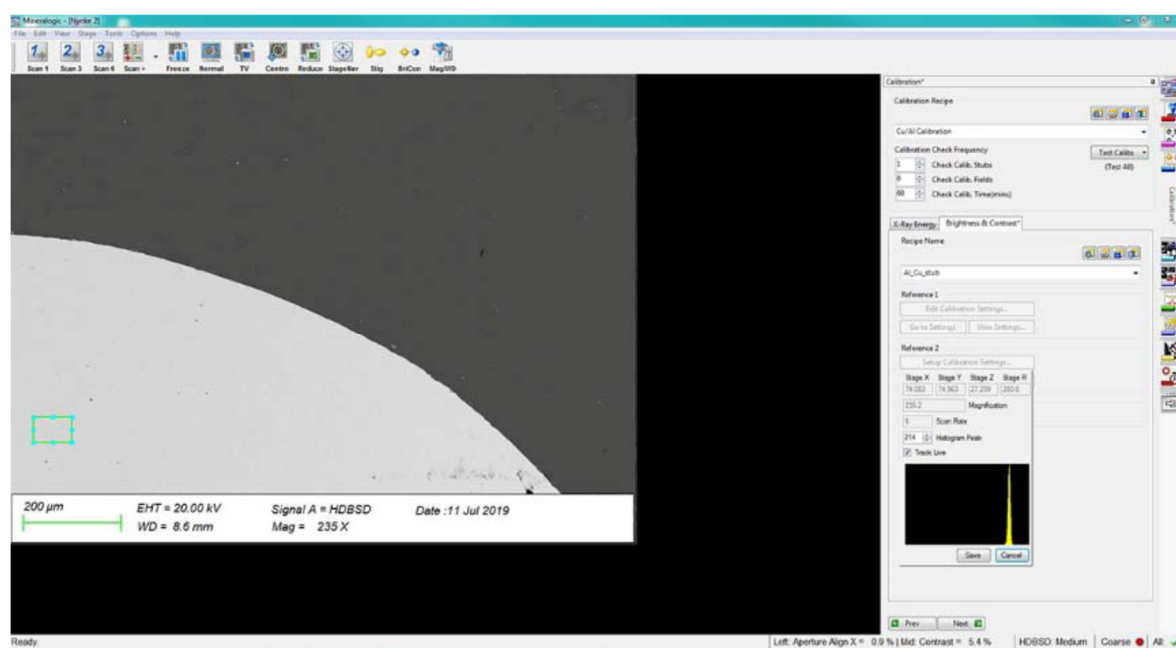


Figure S3. BSE brightness and contrast monitoring can be defined in the Calibration recipe to compensate for drift in the BSE signal. In the Figure the control area for a bright phase (here copper metal) is defined as Reference 2.

2.3.6. Image Processing Recipe

Mineralogic analyses are typically performed overlying a BSE image, but other types of images based on EM detector input, like secondary electrons or cathodoluminescence (CL) signal can be applied too, where required. The image can be thresholded to only include certain grey levels for the forthcoming Mineralogic analysis, e.g., with the aim only to investigate the brightest phases in the sample, or to exclude epoxy and porosity from the analysis. The quality of the image can be improved with a large number of image processing techniques like arithmetic functions (e.g., addition, subtraction, inversion), logical operations (e.g., image AND image, image OR constant), convolution and filters (e.g., median filter, sharpening, edge detection), histogram and threshold operations, morphological operations (e.g., dilation, opening, hole fill, skeletonize), segmentation and region based operations (e.g., watershed), or geometric and linear transformations (e.g., downsize with a power of two).

The image processing recipe tap can also be applied on pre-set functions like the search for bright phases in the sample (Figure S4), which can be applied to find suitable zircon or monazite minerals

for isotope dating or certain ore minerals). Here, the BSE signal is thresholded to only find the brightest particles in a large sample and to store their chemistry and coordinates.

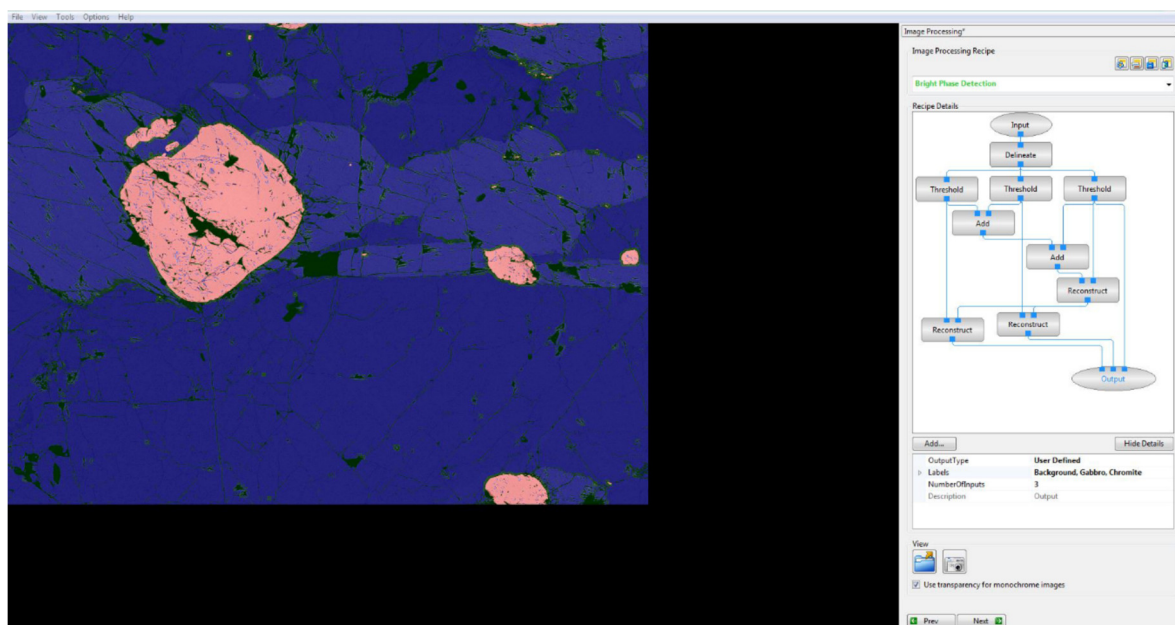


Figure S4. Image processing recipe tap that can be applied to manipulate the BSE image to only measure the required parts of the sample. Here the bright phase detection function is shown, where the sample can be thresholded to three different grey levels that can be defined by the user. Here the grain boundaries and holes are shown in green, plagioclase and hornblende minerals are shown in blue and the brightest phases – chromite – are shown in red.

2.3.7. Morphology Recipe

In the Morphology recipe the grain size, grain shape and other physical parameters of the sample that are analysed can be selected. The software offers following possibilities: area, length, breadth, elongation, roughness, Feret maximum, minimum and mean length, Feret maximum, minimum and mean angle, porosity, grey value (Figure S5). These grain morphology parameters are provided as output data for every individual analysed grain and can therefore be correlated to grain mineralogy or chemistry. Morphological analyses are performed on the BSE (or other input) image of the sample, not on the map produced during the analysis.

The morphological parameters can be classified such that grains full-filling certain size or shape parameters are registered separately. The grains fulfilling these parameters can be filtered out after the analysis.

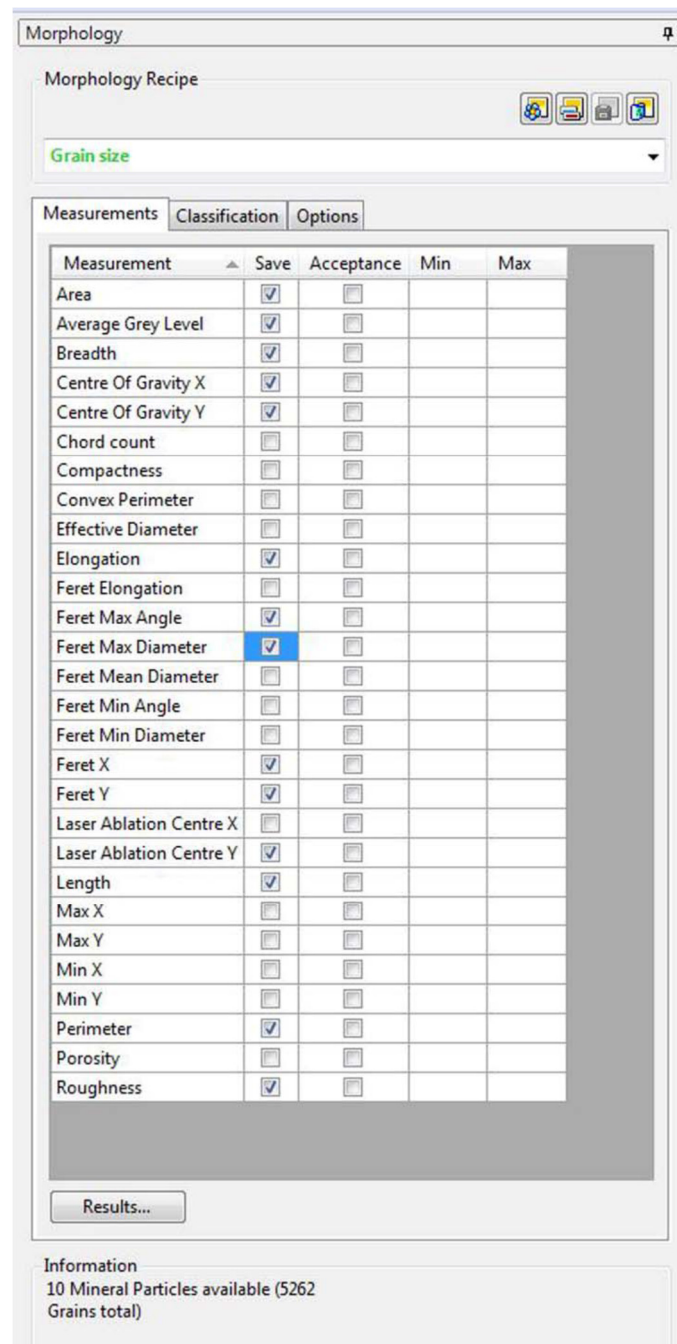


Figure S5. Morphology recipe where required morphology parameters that need analysis can be selected and acceptance values for individual parameter can be set.

2.3.8. Mineral Recipe

The Mineral recipe is the central part of the Mineralogic Mining plugin. It regulates the EDS and mapping type parameters, holds the list of minerals, and allows for morphochemical classification criteria (Figure S6). The Mineralogic analysis can be performed in five different ways:

- Mapping analysis, where the user defines the step size (pixel size) for the EDS map, and an analysis is performed for every single point (pixel) of the map. Typical pixel sizes are 5–30 μm , but can be larger for coarse grained, homogeneous samples, or as small as 200 nm [20]. This method provides the full detail of the sample but is also the most time-consuming method.
- Spot centroid analysis, where the sample is segmented by BSE value of the grains. The method is typically used on grains in an epoxy matrix. For each grain determined, the

geometrical centre of the grain is calculated, and a single EDS analysis on this point is performed. This method is especially suitable for homogeneous grains, as a small variation in the chemistry, like inclusions or zonations, will not be picked up.

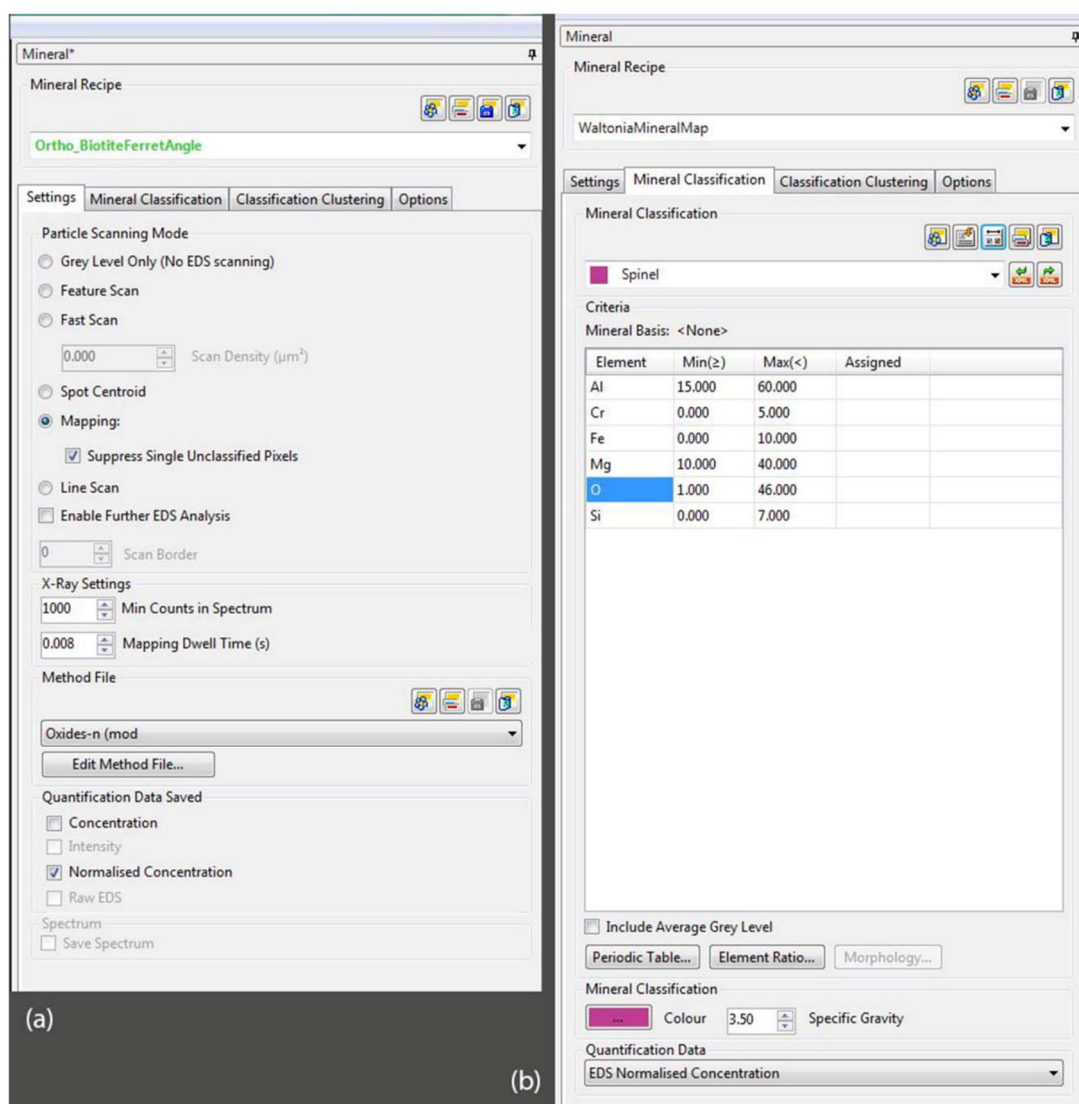


Figure S6. Mineral recipe set-up. (a) The settings for the mineral analysis can be defined by choosing the particle scanning mode and settings, as well as the EDS quantification method. (b) In the mineral classification list, individual minerals can be defined by element concentration and element ratios. After a mineral is defined, the classification can be refined by defining morphological criteria to the mineral definition. Mineral classifications can be imported and exported between projects.

- Feature scan analysis, where—like for the spot centroid analysis—the grain boundaries are determined by segmenting the BSE image. In this analysis mode, the beam is rastering within the boundaries of the grain, giving an average chemical composition. In case of zonations, a more correct average grain chemistry will be found; for heavily included samples, a false mineral classification might be generated. The method can be nearly as fast as a spot centroid analysis, depending on the pre-set amount of counts in the spectrum.
- Fast scan is an intermediate form of Feature scan and spot centroid analysis. It scatters a series of point analyses across a grain and thus arrives at an average composition of the grain. The user gets to determine the density of the spots for the analyses in an area, but each grain is analysed at least once, independent of its size.

- Line scan analysis, where all EDS analyses are made along a line with a pre-defined step-size across the centre of a particle or frame. All variations in composition are accounted for, and a first impression on the grain size and texture can be obtained. The method is very fast compared to a full Mapping analysis.
- Grey level mapping, where the sample is imaged (usually with BSE), without applying EDS measurements. For samples with a simple chemistry, grey values can be used to separate individual minerals. The method is very fast, but less precise than EDS-based investigations.

For all EDS-based methods, the EDS spectrum deconvolution can be specified in the same way as for regular EDS analyses. Thus, elements can be excluded from quantification (e.g., carbon used for coating is set to deconvolution-only), matrix quantification methods can be chosen (ZAF vs. Phi-Rho-Z), spectra output data can be normalized, and elements can be chosen to be always or never included, if wished for, thus potential sources of peak overlap can be avoided. EDS dwell time, and detector throughput rate can be chosen by the user. Every single generated spectrum during the analysis is fully quantified and the weight percentages of each element in each pixel on the false coloured mineral map is available after the analysis. User can choose to add standards-based quantification of the spectra. These latter two points are unique for the Mineralogic software. The matrix quantification for each spectrum also allows the user to switch between different acceleration voltages in between samples, without the need to specify a new mineral list. Most AQM systems require the user to make separate mineral lists for each acceleration voltage.

The mineral list for the sample analysis is created by the user based on the element wt% of the mappable phases, and can be used to produce a variety of visualizable informative image and data outputs. For each mineral the range of tolerated concentrations for each element, as well as for ratios between two elements, can be used to define the mineral phase. Minerals are placed in a list, which is checked against the chemistry of each analysed point, following a first-match principle and based on the order of minerals in the mineral list, which is defined by the operator. The same principle to build mineral lists, can also be used to define element concentration maps or element ratio maps, for where individual phases are identified and coloured by the concentration of one or a few elements. Mineral lists can be exported and imported between projects and adjusted to fit the exact mineral specifics for the sample area of interest, allowing for slight differences in mineral chemistry resulting from different whole rock compositions or metamorphic temperatures.

In an addition tab in the recipe, minerals can be clustered into groups (f.e. albite, labradorite and anorthite as plagioclase). Clustered minerals can be integrated as a group when particle data is exported after the analysis.

Additionally, morphological criteria can be used in the classification of minerals. For example, textural properties can be defined based on the chemically mapped grains, where the grain size or shape properties are used to synergize the chemical and textural characteristics. For example, zircons of a size large enough to be dated with a laser connect to a mass spectrometer can be classified from the main zircon population separately. All different ways of describing the sample (e.g., element map, mineral map, morphochemical map) can be calculated offline from the generated data. There is no need to reanalyze the sample after the mineral list was changed.

Many parameters affect the speed and quality of an AQM analysis, and a Mineralogic analysis is no different. Each analysis must be optimized prior to an AQM run. Different types of analyses (see above) will yield a difference in analysis speed and data quality. Acceleration voltage and aperture size both control how much signal is reaching the EDX detectors, where a high acceleration voltage and a large aperture size result in more signal. These parameters are typically tailored to the nature of the question (i.e., the data required), according to which the resolution and speed can be adapted. Detector throughput rate can be adjusted to optimize the measurement accuracy and precision. The throughput amount (i.e., counts input) impacts the elemental energy peaks Full Width Half Maximum (FWHM) and therefore the accuracy and precision. The dwell time (time the beam stays at one spot before moving on) has a major impact on the analysis speed. The lower a dwell time, the faster the analysis is. However, if the dwell time is too low it will result in insufficient spectrum

counts for a good quality analysis. Image capture time, determining the quality of the BSE image, and frame magnification, determining the amount of stage movements, also affect the analysis time, but these effects are minor and have no real influence during a mapping analysis. The last parameter to affect the analysis speed, is the step size (pixel size) in the mineral map, where a smaller step size will increase the analysis time, but at the same time will provide a more detailed in-depth analysis.

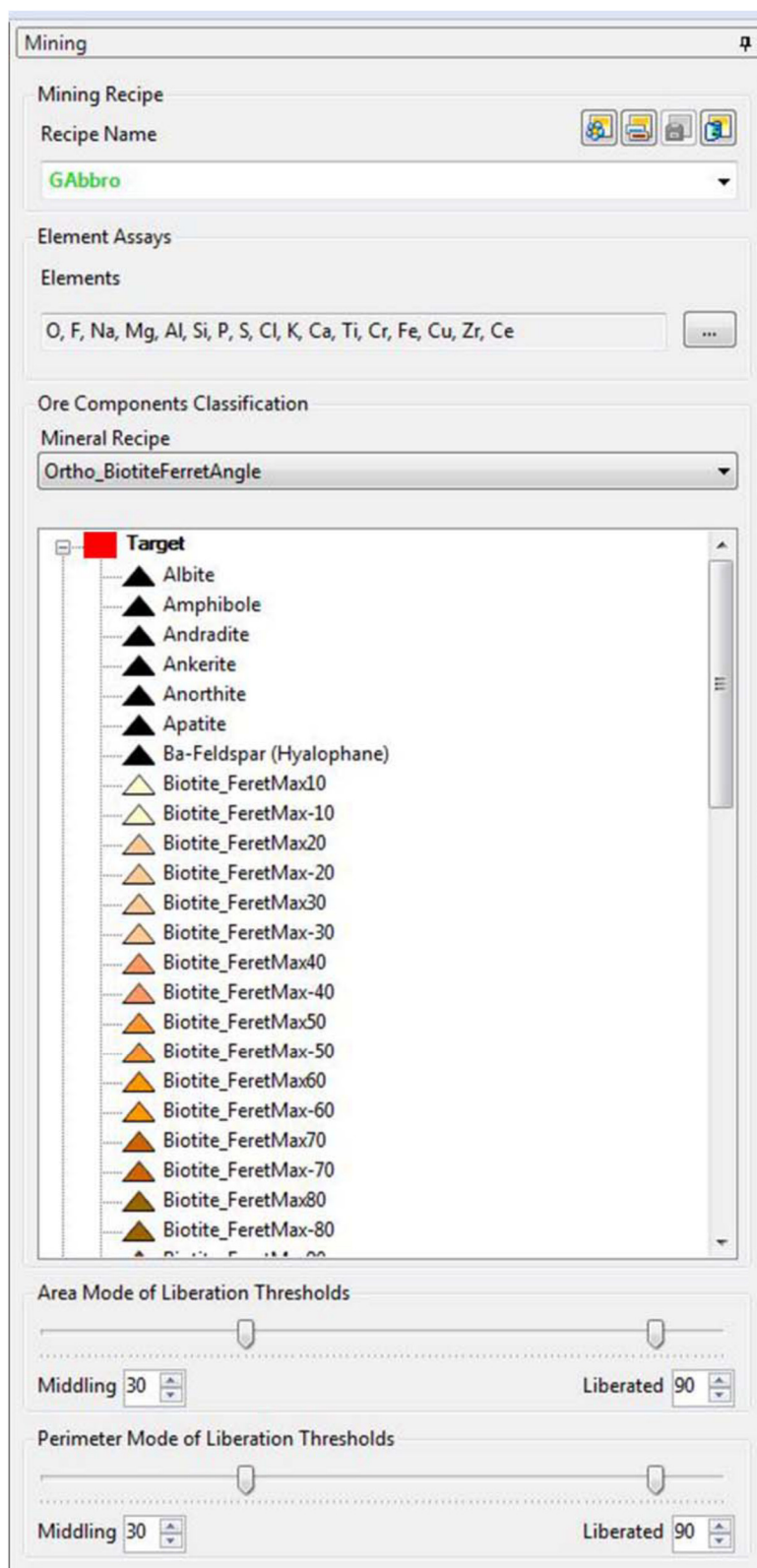


Figure S7. In the Mining recipe the elements of interest for assay calculations, the target mineral list, and liberation threshold values can be set for the analysis.

2.3.9. Mining Recipe

In this part of the software, particular minerals of interest and elements can be selected to perform advanced textural and chemical quantification. In the “Assay” part of the user interface, the user has the ability to select the elements of interest in this sample (Figure S7). The software will then perform an assay measurement whereby the chemical quantified pixel data and the specific gravity (data that is added to each mineral classification) are used to calculate a mass. This is done for all pixel / elements selected across the sample and is used to calculate an assay. This can therefore be used as a rough “bulk rock assay” where the analysis is based on a single 2D plane throughout the entire sample.

Additional value can be gathered from this aspect of the software whereby “elemental distribution” data can be gathered. This is where the chemical distribution is quantified. For example, when the chemical distribution of Mn is of interest: the data will give the wt% amount of Mn in all specified minerals, and also a distribution percentage based the total percentage of Mn found in each phase. This data is provided from the directly chemical quantification during the automated analysis and not from idealized or pre-defined concentrations. This provides researchers with a more reliable AQM technique to understand and quantify chemical and mineralogical variations. However, in cases where element concentrations cannot be measured reliably (e.g., for Boron in tourmaline), a concentration can be assigned in the mineral list for that specific element.

The minerals to be analysed for the map can be selected, as Target minerals. Byproducts and Gangue minerals can also be defined. The example shows a sample with a mineral list with a morphochemical classification (Figure S7). The mutual interconnection between minerals can be described by defining the liberation parameters, which can be exported for all minerals after analysis, together with the association and interlocking data.