# Monitoring gravitational and particle shape settling effects on MLA sampling preparation

T. Heinig[1]*, K. Bachmann[1], R. Tolosana-Delgado[1], G. van den Boogaart[1] and J. Gutzmer[1,2]

[1] Helmholtz Center Dresden-Rossendorf, Helmholtz-Institute Freiberg for Resource Technology, Halsbrücker Str. 34, D-09599 Freiberg, Germany, t.heinig@hzdr.de
[2] Technische Universität Bergakademie Freiberg, Department of Mineralogy, Brennhausgasse 14, D-09596 Freiberg, Germany
*Thomas Heinig

**Abstract**

Automated mineralogy has become a standard method to quantify rock properties such as modal mineralogy and grain liberation in mining industry. As this method uses only little amounts of sample material, it is crucial that sample preparation guarantees representativity. The presented study evaluates this representativity for the last step of sample preparation, production of sample blocks with epoxy resin. Statistical treatment of mineral liberation analyzer data from different layers within the sample blocks indicate a significant variation of the quantitative data based on the amount of resin used to embed the sample material and the measured plane. These deviations in data are caused by different grain properties of the heterogeneous, unsorted sample material, i.e. grain density, shape and size and therefore gravitational separation. Precautions in sample preparation have to be taken to reduce settling effects to ensure comparability between data of samples and data translation into rock.

## 1 Introduction

Scanning electron microscope (SEM)-based automated mineralogy like a mineral liberation analyzer (MLA) by FEI provides access to geometric parameters as well as compositional data for a large number of particles in a relatively short time. Mineralogical studies are accelerated by using this method. Furthermore the amount and variety of data can be applied to run and/or check simulations. In the mineral processing industry the used epoxy blocks for automated mineralogy typically contain sorted or unsorted material from feeds, concentrates or tailings of the processing chain. Lastra & Petruk (2014) stated in their study that detailed observation of the quantitative mineralogical data obtained using polished sections prepared with sieved and un-sieved samples indicates that there are differences in the mineral quantities and the mineral liberation. Furthermore, the authors mentioned it is noteworthy that it is possible to reach the same diagnostic conclusions with either set of data. In these cases, accuracy and precision of SEM-based analytics not only depend on stable measurement parameters and conditions but also on sample preparation. The major aim of sample preparation is the production of representative, homogeneous specimen mounts in terms of geometric parameters and compositional data to generate valid information about the given sample materials. However, experiences in preparation indicate an influence of many factors such as resin type, resin viscosity, mineral grain density, grain shape and sample material/resin ratio on the analytical results.

The aim of this study is the evaluation of the influence on the representativity of a mineral sample caused by different material/resin ratios. In order to investigate possible gravitational and shape related settling effects during sample preparation, the material of choice is a homogenized greisens-type ore from Zinnwald/Germany. It is suitable as it provides sample material with a heterogeneous mineral composition, mineral density (Quartz – Topaz), grain shape (Mica – Quartz) and grain size (5 – 1000 µm). Eight specimens were prepared with equal weight aliquots of the same ore material, with increasing resin amount. These polished epoxy mounts were analyzed three times by MLA to evaluate their difference in modal mineralogy, grain sizes and grain shapes. This contribution presents the MLA results of the prepared samples which were further evaluated by statistical treatment, both conventional quantile-quantile plots (QQ plots) and Kolmogorov-Smirnoff (KS) tests for equality of distributions.

# 2 Material and Methods

Mineral Liberation Analyser measurements were performed to investigate gravitational and particle shape settling effects on MLA sampling preparation of greisen-type ore. The measurements were followed by statistical treatment.

## 2.1 Greisen-type ore

Greisen-type ore used in this study was obtained from a large bulk sample, about 2 t in weight, collected underground in the old mine workings of the Zinnwald/Cinovec deposit. The polymetallic (Li-Sn) greisen deposit of Zinnwald/Cínovec is located in the eastern Ore Mountains at the German-Czech border, 40 km south from the town of Dresden. Ore mineralization is developed as lodes and massive greisen bodies. Ore minerals are various Sn-W-Mo minerals. The greisenization resulted in a replacement of feldspar and magmatic micas by topaz, fluorite and zinnwaldite, a group of lithium-bearing, trioctahedral dark micas of the siderophyllite-polylithionite series (Rieder et al, 1998). The Greisen material was comminuted to a maximum particle size of 1 mm in the steps jaw crusher – gyratory crusher – cone crusher –pin mill by the MVTAT, TU Bergakademie Freiberg. Grain mounts of greisen material were prepared for quantitative mineralogical analysis using a MLA. For this purpose, aliquots of 2.1 g of solid material were mixed with 0.4 g graphite and different amounts of epoxy resin. Eight samples were prepared with increasing amounts of epoxy resin starting at 1.5 g till 5.0 g (step-widths of 0.5 g) as well as grounded and polished (series A, XY plane) in the Erzlabor of the Helmholtz Institute Freiberg for Resource Technology (Fig. 1). After MLA measurements the samples were halved along the XZ plane, and re-embedded into epoxy resin, grounded and polished again. Due to the cutting and polishing both half-blocks display new, different surfaces. Re-analyzation of these eight sample blocks resulted in 16 MLA measurements (2 analyses per sample, one for every halved-block, orthogonal to the XY plane, series B1 and B2).

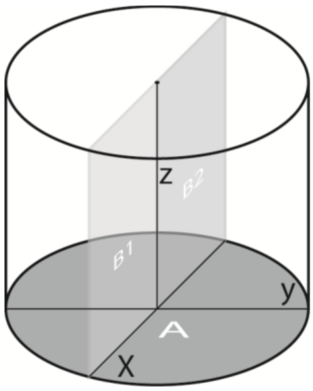


Figure 1. Sketch of a sample block. x-,y,-z-axes are marked.

## 2.2 Mineral Liberation Analyzer

The MLA system combines a scanning electron microscope FEI Quanta 650F equipped with two Bruker Quantax X-Flash 5030 energy-dispersive X-ray spectrometers and the specific software MLA Suite 3.1.4 for automated data acquisition. The MLA measurements were carried out at the Helmholtz Institute Freiberg for Resource Technology. Consistent operating conditions applied are listed in Table 1.

Table 1. Summary of MLA parameters

| SEM parameters | | MLA parameters | |
|---|---|---|---|
| Mode | GXMAP | Scan speed | 16 |
| Voltage (kV) | 25 | Resolution (pixels) | 1k x 1k |
| Working dist. (mm) | 13 | Pixel size (µm/px) | 1.0 |
| Probe current (nA) | 10 | Acq.time (ms) | 5 |
| Spot size | 5.68 | Minimum EDX-count | 2000 |
| HFW (µm) | 1000 | Step size (px) | 6x6 |
| Brightness | 93.79 | GXMAP trigger | 20 |
| Contrast | 18.45 | Min. particle size (px) | 4 |
| BSE calib. | Au 244 | Min. grain size (px) | 4 |
| Horizontal field width - HFW | | Particle count | >3,500 |

As a result, the analysis of one single sample with MLA can deliver several Megabytes of data, covering a wide range of properties which describe the sample material. In the case of grain mounts, this is a list of all particles contained in the sample, each related to its constituent mineral grains (i.e. with a mineral phase attached). Particles and grains are all measured with several size properties. This allows computing modal the mineralogy, particle or grain size distribution, and several mineral association indices. The present study focuses on particle size distributions, in particular based on the equivalent circle diameter (coextensive circle of the particle area).

### 2.3 Statistical treatment

For each amount of epoxy resin used, three lists of particles exist: A, B1 and B2 (which can be merged in a single B list). These will be compared with conventional quantile-quantile plots (QQ plots) and Kolmogorov-Smirnoff (KS) tests for equality of distributions. All calculations were done with standard commands from the statistical language R (R Core Team, 2014). Recall that QQ plots are produced by ordering each sample separately, and identifying and plotting pairs of data placed in each list in the same relative position in the ordered list, i.e. leaving the same proportion of the sample below. KS test, on the contrary, calculates the difference between relative positions on these lists (i.e. the cumulative probabilities) of each possible diameter value, and then takes the largest of these differences. In this study the KS test statistic is used but no associated p-value was computed, because the typical MLA analysis delivers so many particles that each formal test would almost always reject the null hypothesis of equal distributions. The lack of this formal assessment is compensated by including a B1-B2 comparison, which gives an assessment of how large can the KS statistic be.

## 3 Results and Discussion

Automated mineralogy is used to receive detailed data on rock/sample composition and grain properties. In the best case scenario, this data acquired from a few grams of sample material should represent or translate into tons of material mined for large volumes beneficiation. This leads to many challenges during sample acquisition and preparation to ensure representativity.

Table 2 illustrates one of these challenges. Despite using the same material, preparation method and preparation machinery, the modal mineralogy of the displayed samples differs significantly. The only difference during preparation was the usage of varying amounts of epoxy resins. There is an apparent negative correlation between the amount of quartz and zinnwaldite in the A series. With increasing amounts of epoxy the fraction of quartz increases while the amount of zinnwaldite decreases. The data shows a drop of zinnwaldite content when using more than 2 g of resin. The reason could be related to their different grain shapes, which could produce a different sorting behavior with higher epoxy volume and more space to sort and sink. While quartz and zinnwaldite have similar densities (2.65 – 3.01 g/cm$^3$) their grain shape is very different. Quartz has an often round or elliptical habitus and zinnwaldite is usually sheeted, forming thin plates during comminution (Fig. 2). In the settling phase after steering the sample material into the resin the quartz grains are likely to sink faster than the more buoyant zinnwaldite particles. A second indicator of this theory is the consistently higher zinnwaldite to quartz ratio in the sample series B compared to the series A. The measured surfaces of B resulted from cutting the series A orthogonal respectively in the direction of particle settlement. Therefore, settling effects have no influence on the modal mineralogy of series B.

Table 2: Modal mineralogy of sample series A and B. A is representing the XY-plane of the sample while B represents the XZ-plane. Numbers indicate the amount of epoxy resin in g. Mineral content is given in wt%. Trace minerals contain minerals like cassiterite, remnants of feldspars, florencite, monazite, scheelite, wolframite, xenotime and zircon.

| series-resin | Fluorite | Kaolinite | Muscovite | Quartz | Topaz | Trace Minerals | Zinnwaldite | Total |
|---|---|---|---|---|---|---|---|---|
| A-1.5 | 0.62 | 1.70 | 4.45 | 66.28 | 7.23 | 2.77 | 16.95 | 100.00 |
| B-1.5 | 0.58 | 1.27 | 5.12 | 66.50 | 5.84 | 2.49 | 18.20 | 100.00 |
| *A-2.0* | *0.57* | *1.43* | *4.59* | *65.67* | *7.84* | *2.29* | *17.60* | *100.00* |
| *B-2.0* | *0.54* | *1.82* | *5.04* | *64.20* | *5.31* | *1.11* | *21.97* | *100.00* |
| A-2.5 | 0.53 | 1.37 | 3.52 | 71.07 | 8.28 | 1.73 | 13.51 | 100.00 |
| B-2.5 | 0.62 | 0.85 | 5.07 | 65.75 | 4.46 | 0.75 | 22.49 | 100.00 |
| *A-3.0* | *0.37* | *1.94* | *3.76* | *71.15* | *6.63* | *2.71* | *13.44* | *100.00* |
| *B-3.0* | *0.62* | *1.44* | *4.88* | *69.06* | *5.15* | *0.76* | *18.10* | *100.00* |
| A-3.5 | 0.42 | 1.36 | 3.45 | 73.54 | 5.31 | 2.17 | 13.75 | 100.00 |
| B-3.5 | 0.58 | 1.45 | 4.43 | 63.98 | 5.76 | 1.20 | 22.60 | 100.00 |
| *A-4.0* | *0.44* | *1.36* | *3.79* | *74.18* | *6.07* | *1.45* | *12.70* | *100.00* |
| *B-4.0* | *0.54* | *1.30* | *5.08* | *64.17* | *4.80* | *0.81* | *23.29* | *100.00* |
| A-4.5 | 0.32 | 1.49 | 3.89 | 74.20 | 6.47 | 1.30 | 12.33 | 100.00 |
| B-4.5 | 0.50 | 1.14 | 4.71 | 69.35 | 3.78 | 0.73 | 19.79 | 100.00 |
| *A-5.0* | *0.36* | *1.63* | *3.49* | *69.67* | *7.42* | *3.23* | *14.19* | *100.00* |
| *B-5.0* | *0.57* | *1.39* | *5.39* | *65.07* | *4.82* | *0.85* | *21.91* | *100.00* |

Furthermore, there is not only a difference between different samples but also within one sample depending on the measured plane (Fig. 2). In general, all series A measurements contain more quartz and topaz (higher density and round grains) than the B series while their series B counterparts contain relatively more muscovite and zinnwaldite (lower density – plate shape), i.e. the ratio of sheety-to-round minerals increases in sections B with respect to sections A, irrespective of the amount of resin. Topaz with its relatively high density is an additional indicator for gravitational separation as it is concentrate at the bottom of the sample (XY-Plane) resulting in higher measurement values for series A compared to series B.

In theory, the reason for less settlement or gravitational effects using lower resin amounts is the contact between particles hindering each other from freely settling. Shifting the proportion of sample material and epoxy in the direction favoring resin leads to more space for particles to turn and freely settle. The comparison of quartz and topaz highlights this effect. Throughout all samples the weight percentage of topaz in the series A is between ~1.5 – 3.5 higher than in series B. Quartz on the other hand shows similar weight percentages for A-1.5 and B-1.5 and A-2.0 and B-2.0, respectively, but varies between 4.5 – 10 wt% for the samples with more resin. Compared to quartz, the topaz grains of the sample material are usually very small and able to move freely even in samples with lower resin content. Therefore, settling effects due to gravitational pull apply fully on topaz while large quartz grains are not able to settle freely leading to an enrichment of topaz in the XY-plane.

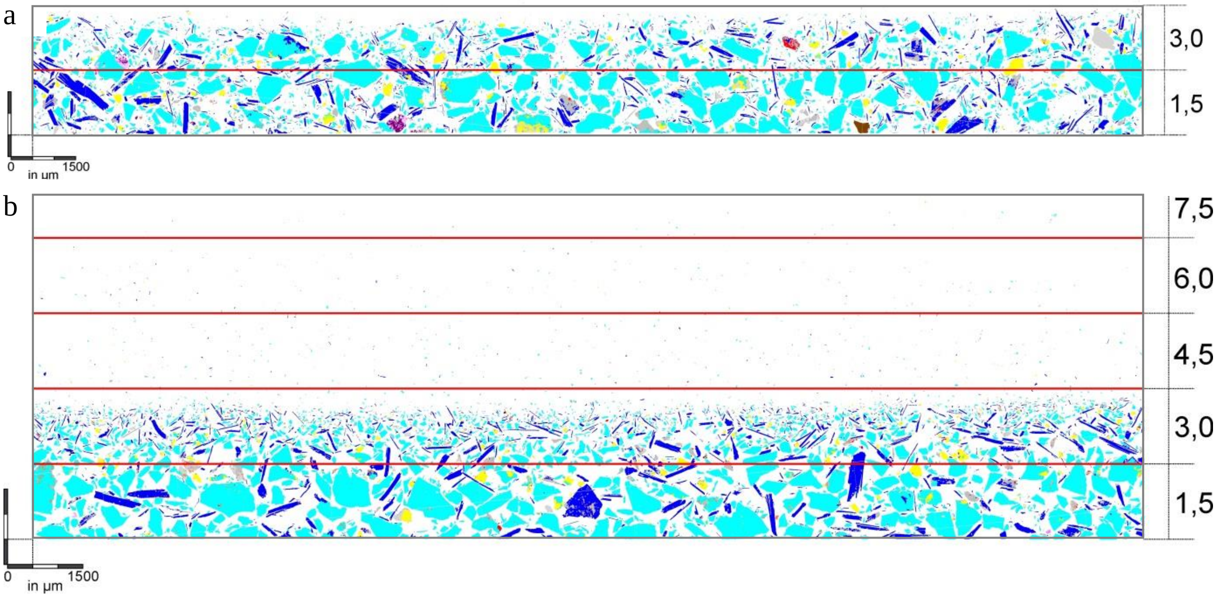


Figure 2: MLA processed image of XZ plane (series B1) 1.5 (a) and 5.0 (b). Classified mineral phases: Quartz – cyan; Zinnwaldite – dark blue; Topaz – yellow; Muscovite – grey. Right side scale displays sample block thickness in mm.

The QQ plots described in chapter 2.3 are displayed in Figure 2. While the QQ plot of B1-B2 shows extremely similar particle size distributions (PSD) along the whole range of added epoxy (i.e. good aligning of points along the 1:1 line), the comparison of the PSDs between the sections A and B display major differences. For any given quantile, the value of the associated diameter on the A section is (almost always) larger than on the B section, (i.e. curves below the 1:1 line). This confirms the starting hypothesis that sections A might present biases towards larger particle sizes induced by settling effects.

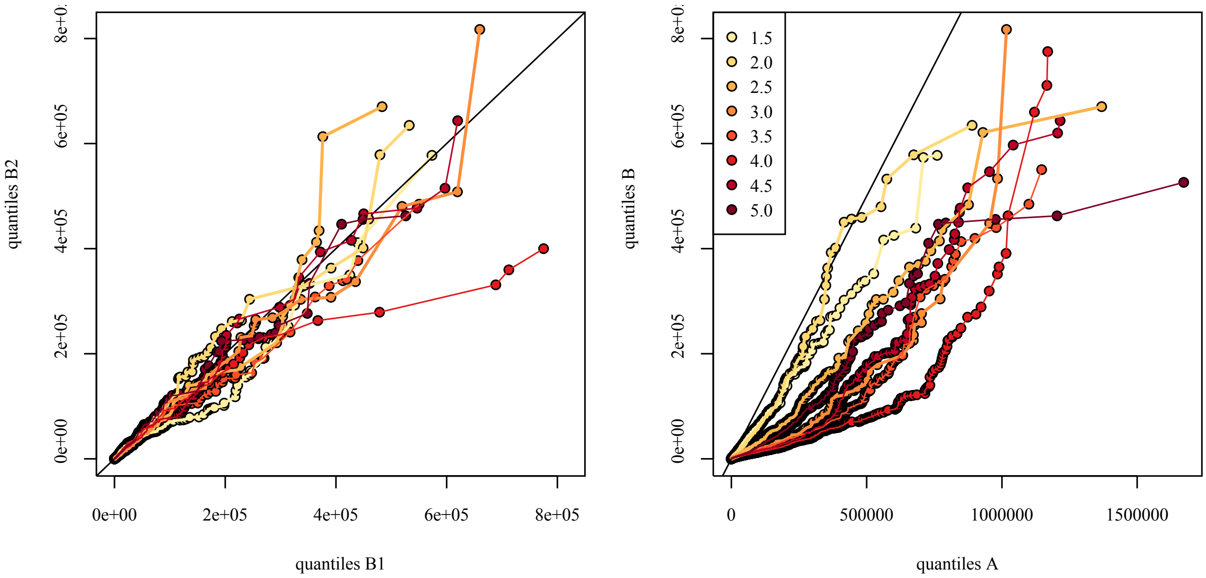


Figure 3: QQ plots of the analysed samples. (a) Comparison between area B1 and B2. (b) Comparison between area A and B. The legend is given in graph b. Numbers give the amount of epoxy resin in g used for each sample.

Figure 3, right, suggests that perhaps the bias is lower for 2 g of epoxy than for 1.5 g, because the associated PSD better plots along the bisector. However, the KS statistic (Fig. 4) show that the difference on this statistic between 1.5 g and 2.0 g of epoxy is not relevant at all, of a comparable magnitude to the differences shown in the comparison B1-B2 (which can be considered as the possible range of stochastic variation of this statistic). This figure also displays that PSDs are much more similar on sections B1-B2 than between A-B. Thus, there is no proportion of epoxy which reduces the settling bias in section A to statistically acceptable levels.

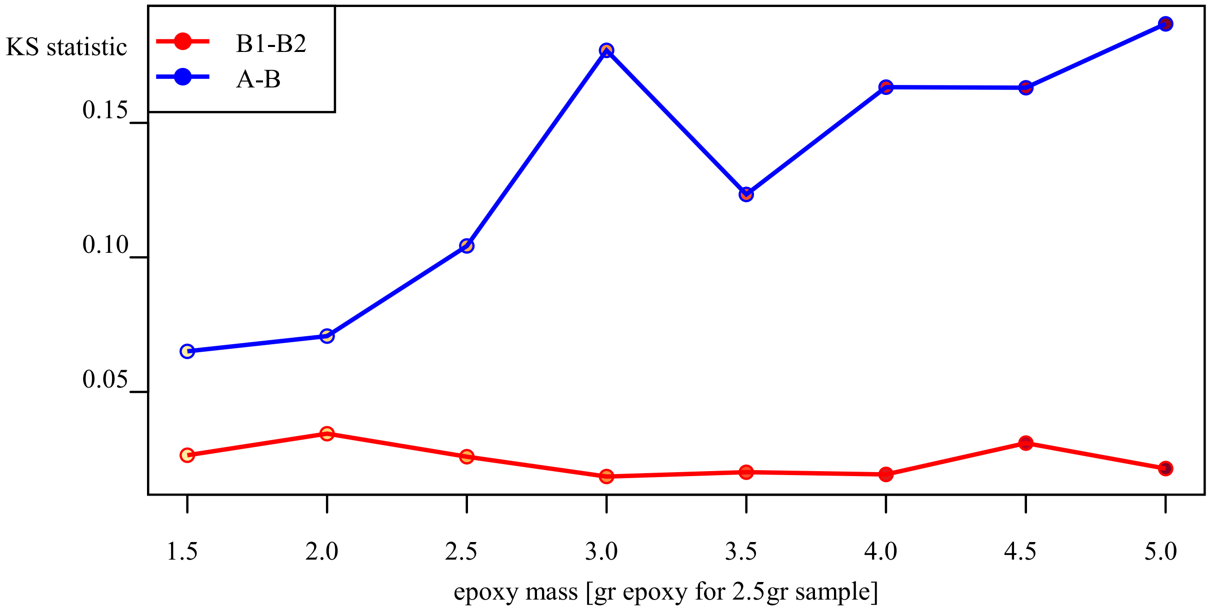


Figure 4. KS statistics showing the comparison between area B1-B2 and between A-B.

## 4 Conclusion

Automated mineralogy should provide data for heterogeneous and unsorted samples in terms of particle shape, size and density which represent the “true” composition of a rock or sample. With the currently applied method of sample preparation this representativity is not fully given for heterogeneous, unsorted samples and precautions have to be taken to reduce the effect of gravitational separation due to shape, size and density. This study showed that a wrong sample material - resin proportion leads to data with significant biases towards larger particles and heavier minerals with increasing resin proportion. Negative effects of particle settling on grain distribution were reduced by using less epoxy resin but are still present. A first step to further decrease the separation due to settling would by the measurement of the plane within the vector of the settlement direction. This would basically cancel all density related settlement effects caused by gravitational pull. Unfortunately, this does not cancel the size related effects like blocking for samples with low amount of resin and the shape related effects of adjustment for plate shaped grains with more epoxy.

Due to the used sample material, the described effects added up and had a big influence on the large differences in the modal mineralogy. Further work is needed, for instance to quantify separately the effects of settling on modal mineralogy or on grain size distribution of certain minerals measured on A sections, or to quantify the possible rotation biases on B sections. Future work will be done on homogeneous material with defined properties to control density, shape and size and to quantify their individual influence.

## References

Lastra, R., Petruk, W. (2014) Mineralogical Characterization of Sieved and Un-Sieved Samples. Journal of Minerals and Materials Characterization and Engineering 2, 40-48.

R Core Team (2014) R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, http://www.R-project.org/

Rieder, M, Cavazzini, G, D'yakonov, YS, Frank-Kamenetskii, VA, Gottardi, G, Guggenheim, S, Koval, PV, Mueller, G, Neiva, AMR, Radoslovich, EW, Robert, J, Sassi, FP, Takeda, H, Weiss, Z and Wones, DR (1998) 'Nomenclature of the Micas', Canadian Mineralogist, vol. 36, pp. 905–912.