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A new methodological approach (QEMSCAN®) in the mineralogical study of Polish loess: Guidelines for further research

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Abstract: This article presents in detail the methodology dedicated strictly to loess mineralogical investigation by automated mineralogy system QEMSCAN® (quantitative evaluation of minerals by scanning electron microscopy (SEM)), which couples SEM and energy dispersive X-ray spectrometry to automatically deliver mineral and phase mapping. The present study provides guidelines for further loess investigation in Poland, in order to maintain the complete comparability of results which will be obtained. The methodology is then used to obtain the data on complex mineralogical composition (heavy, light, transparent and opaque phases). In total 1,159,107 particles have been measured for five bulk loess samples and 4–6% of them were heavy minerals (c.a. 10,000 per sample). The bulk samples are dominated by quartz (57.3–62.9%) and contain plagioclase (7.8–9.2%), K-feldspar (7.9–8.7%), carbonates (5.0–7.8%), muscovite (3.2–6.2%), biotite (4.2–7.5%), heavy minerals (4.3–5.8%) and clay minerals (0.9–1.6%). The heavy minerals (as a group recalculated to 100%) are mainly represented by phases such as clinopyroxene (38–51%), garnets (14–21%), TiO₂ polymorphs (8–12%), Al₂SiO₅ polymorphs (3–7%), ilmenite (3–6%), iron oxides, e.g., hematite and magnetite (2–5%) and zircon (~2%). Nearly 50% of the heavy minerals is classified in the 16–31 µm fraction, which

determine the changes in the current research procedure traditionally used for Polish loess.

Keywords: loess, QEMSCAN®, SEM, EDS, automated mineralogy, Poland, Late Pleistocene

1 Introduction

Loess and paleosols are mixtures of mineral and rock particles derived from the source regions and weathered under the varying climatic conditions in both alimentation and deposition sites. It means that the loess–paleosol sequences contain data related to the paleoenvironmental conditions and the provenance of the material. The relevant information is fingerprinted in the specific features of mineral phases, such as mineral and rock particle assemblies, particle size distribution and shapes, crystal chemistry, mineral stability and mineral weatherability [1]. In order to access all of them, the bulk mineralogical composition should be investigated. However, the registration and analysis of such wide range of mineralogical data, particularly with a good statistical reliability, require fast and advanced measurement instruments and consistent methodologies.

The current worldwide mineralogical research depends strongly on scanning electron microscopy (SEM) and X-ray diffractometry techniques, and sometimes involves mineral pre-concentration in heavy liquids [2]. The automated mineral analysis, which integrates SEM and energy-dispersive X-ray spectrometry (EDS), provides unattended, reproducible and operator-independent mineral and phase maps of relatively large areas [3]. It has been already applied to a wide range of geological materials, including, e.g., igneous rocks, [4] raw materials [5] and sedimentary rocks [6]. However, the automated SEM-EDS analyzers have been used only a few times in the loess research [7–9], and to our best knowledge never in Europe, especially for the specific loess material.

The aim of the article is to apply, refine and exploit the automated SEM-EDS mineralogy for loess studies and to provide a relevant methodology. For this work, we used a

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Figure 1: Location of the Złota loess–paleosol successions on the map of loess distribution in Poland (a) and Europe (b) modified after Mroczek [13].

QEMSCAN[®] (quantitative evaluation of minerals by SEM) which is the automated analyzer by FEI Company (currently Thermo Fisher Scientific). We argue that most of the available Polish mineralogical studies, although important, suffer from the omission of some major minerals (or focusing only on the heavy minerals), failure to differentiate important mineral phases, and a tendency to focus on specific granulometric fractions. Because of the lack of complete mineralogical information, there is often difficulty to reconcile and fully interpret the results of the research. For this reason, prior to paleoenvironmental investigations of samples from different profiles (or many samples from the same profile), our focus was on refining the methodology. We have introduced a fully functional protocol, including sample preparation, measurement parameters selection and data analysis, dedicated to the loess.

2 Description of the profile and sampling

The samples for experiments were taken from the Late Pleistocene loess–paleosol sequence in Złota (21°39'E, 50°39'N) located in the south-eastern part of Poland, on the northern side of the Vistula river valley, and near the mouth of the San river (Figure 1). The 13 m Złota loess–paleosol sequence consists of five main units developed in the Late Pleistocene and Holocene [10,11]:

two paleosol complexes (S1 correlated with MIS 5 and L1SS1 correlated with MIS 3), two calcareous loess units (L1LL1 correlated with MIS 2 and L1LL2 correlated with MIS 4) and recent S0 soil at the top (Figure 2). To correlate the stratigraphic units used herein with the Polish loess stratigraphy, please refer to the previous articles [11] or [12]. More detailed information about the Złota loess–paleosol sequence can be found elsewhere [11].

The loess–paleosol sequence in Złota was sampled in 2011 (with the interval of 5 cm), and, after some tests were done, they were stored in the samples' warehouse of the Department of Physical Geography of the University of Wrocław. In the current work, five samples were selected for QEMSCAN[®] analysis from the whole collection (with the total number of 260 samples). Three samples (s200, s400 and s605) were taken from the L1LL1 loess (MIS 2) and two (s825 and s925) from the L1LL2 loess (MIS 4). The sample names correspond to the depth of their sampling (centimeters below the surface level).

3 Description of the developed protocol

3.1 Instruments

The bulk loess samples were analyzed with QEMSCAN[®] – an automated SEM-EDS mineralogy system in Łukasiewicz

Figure 2: Examples of the main and additional mineral phases found in the loess from Złota. They are BSE images (carbon tape) of individual minerals (1–6), BSE images (carbon tape) with EDS maps of individual minerals (7–10), BSE images (carbon tape) with EDS maps of mixed minerals and aggregates (11–14) and BSE images of polished sample surface (15–17).

Research Network – PORT Polish Center for Technology Development in Wrocław, Poland. The system integrates a special software, a Quanta 650 FEG SEM microscope

(Thermo Fisher Scientific) and two EDS XFlash detectors (Bruker Inc.) with an energy resolution of 133 eV. The QEMSCAN[®] system scans the electron beam over the sample

Figure 3: The successive components and steps of the preparation process – (a) Jones divisor, (b) samples mounted in special molds and embedded in resin, (c) CitoVac chamber for removal of air bubbles from samples, (d) sample grinding and polishing samples with Tegramin 25, (e) surface quality check under a light microscope, (f) sample carbon coating in EM ACE 600 coater and (g) sample introduction to the QEMSCAN® system.

area with the small micron-scale step size and acquires backscattered electron (BSE) signal and EDS X-ray intensity. The BSE SEM image provides material contrast due to its dependence on the atomic number, while EDS provides the local elemental composition. The final results, i.e., mineral or phase maps are obtained after processing the raw data by the iDiscover software which classifies a mineral by comparing EDS data at each pixel against a species identification protocol (SIP) database.

3.2 Preliminary manual analysis of mineral composition

The energy of the beam electrons (equivalent to acceleration voltage) is the most important parameter for any successful QEMSCAN® analysis. The fundamental requirement is that the energy should be enough to generate X-rays from all the elements in the sample, which depends on the sample composition, particularly on the content of the heavy elements. To determine the primary beam energy, the samples were placed on a carbon tape (the excess was removed with a compressed air) and manually BSE imaged in SEM followed by EDS investigation in several micro areas and EDS mapping. The exemplary results for the Złota loess samples are shown in Figure 2.

We identified that the heaviest elements found in the sample were minerals Au, Pt and Ag that could be assigned

to native gold, native silver and the so-called platinum gold. That information is important for the proper assignment of the standards or the proper functioning of the databases such as SIP in QEMSCAN®, because of, e.g., the unambiguous analysis of Au and Pt requires their EDS L lines. Their effective generation requires the beam energy of minimum 25 keV. This point is also relevant for setting the appropriate contrast for the BSE signal. The BSE calibration was accordingly performed on Au (one of the heaviest elements found in the samples) and SiO₂ standards (most frequent phase in the samples).

3.3 Sample preparation for QEMSCAN® measurements

The QEMSCAN® system requires specially prepared samples, so the measurements were preceded by sample preparation process (performed mostly with the use of Struers preparation line). The first step was to homogenize the sample using Jones divisor. Jones' divisor also known as riffle splitter [14] is a box divided by an even number of compartments into narrow compartments with a sloping bottom and outlets facing alternately in opposite directions. The shredded sample is poured into the apparatus from a shovel, the width of which should match the divisor width. On the shovel, the material

Figure 4: Example of data processing for the selected particle.

Figure 5: Location of the randomly selected research fields for the s660 sample.

should be evenly distributed so that they get to individual compartments with equal portions. Spilled through divisor material is collected in two containers placed on both sides of the divisor under the compartment outlets. Material from one container is treated as a sample and from the other is a recoil [15,16] (Figure 3a). Representative and homogenized material was mounted in epoxy resin in special mold (Figure 3b). To avoid the

air bubbles within the resin, CitoVac vacuum chamber was used (Figure 3c). After resin binding, the samples were ground and polished using Tegramin-25 unit (Figure 3d). In this order, various types of grinding disks and polishing cloths were used. The samples were then checked for surface quality with an optical microscope (Figure 3e). The lack of any scratches and chipping significantly improves the quality of SEM measurements.

Figure 6: The variability of the main mineral phases or groups of phases in the bulk loess samples from Złota.

The last step was to use a high-vacuum coater Leica EM ACE 600 (Figure 3f) for coating with a conductive thin carbon layer (~20 nm) in order to avoid the charging

problems. For regular measurements (see Section 3.4), the QEMSCAN[®] system was used (Figure 3g).

3.4 QEMSCAN[®] measurement parameters

QEMSCAN[®] analysis requires several parameters to be properly set, e.g., primary beam energy, beam current, scanning step size and total sampled area. The measurement settings for QEMSCAN[®] elaborated herein for loess studies have been double-checked to provide reliable and reproducible results within optimal time. As input information, we propose to take into account a sediment type and preliminary chemical and mineralogical composition of samples, mostly the heavy elements content (see Section 3.2). For the current work, the measurements were performed at a relatively high voltage of 25 keV due to the presence of heavy elements such as Pt, Au and Ag in the samples.

The measurement step size (pixel spacing), i.e., the distance between the consecutive EDS measurements within each analyzed grain, was set to 3 µm. This step should be directly related to the interaction volume of beam electrons in the sample. Too small a step would result in the EDS spectra interferences between pixels difficult to deconvolute. The interaction volume depth and width in the heaviest minerals in loess (native gold, rare earth elements [REE] minerals) for 25 keV is close to 1.5 µm. No charging effects due to carbon coating allow all SEM-EDS measurements to be performed in a high-vacuum mode, which avoids the beam spreading issues known for low vacuum [17].

The threshold number of EDS pulses, i.e., the accumulated number of pulses at a current pixel before the beam is moved to a new pixel, was set to 3,000, which still provides relatively meaningful spectra as for this type of analysis. Regarding the total investigated area, for each sample, the surface consisting of 25 randomly selected square fields has been analyzed. That parameters influence the total analysis time most extensively (in this case c.a. 5 h per sample). It should be remembered that all limitations of EDS spectrometry hold [18], including inefficient detection of light elements and mediocre detection limits in general. The latter are even more compromised by low spectrum counts.

3.5 Data processing

The EDS measurements cannot be directly used for the mineralogical investigation. To assign the mineral or

Figure 7: The percentage share of heavy minerals in s200, s400, s605, s825 and s985 Żłota loess samples (s-sample, 200 – sample collection depth [cm]).

phase to EDS spectrum, the standards or the databases are needed. The collected data were therefore analyzed by QEMSCAN® software iDiscover package containing a mineral database called SIP. The SIP includes specific physical and chemical properties such as density and chemical composition for thousands of mineral types. It is natively created by the software supplier based on the reference materials and can be customized.

The initial results of iDiscover processing of raw loess data against the native SIP database resulted in a significant share of the “undefined” particles, meaning that there were no database hits for them and they were not recognized. To improve the identification efficiency, the native SIP database was expanded with new phases or the original spectra for some phases were modified based on the manual EDS measurement results (see Section 3.2). In this way, the synthetic EDS spectra were generated utilizing spectral engine which exploits the standard-based algorithm and uses strictly defined beam parameters for spectrum calculation (here beam current of 10 nA and accelerating voltage of 25 keV). The comparison of the actual and theoretical spectra of minerals allowed to obtain an accurate estimation of the elemental and mineralogical composition of the investigated samples. In most cases, the original SIP phases

were only slightly changed, usually by extending the composition range of some elements to accommodate the natural chemical variability of minerals. The customized SIP improved the hit rate and allowed the accurate determination of elemental and mineralogical composition of the samples. We consider that the confidence values exceeding 90% means that the fit is satisfactory (Figure 4).

The SIP modifications have actually allowed to create the “loess mineral database,” which also includes the mineral admixtures and the “boundary” phases between the most common minerals in the loess samples (e.g., the quartz grain with incorporated rutile can be averaged in 50/50 or 75/25 proportion for both the chemical composition and density). Even the mineral aggregates were separated into individual particles by iDiscover software and assigned separately to the appropriate mineral phase and granulometric fraction. However, for some minerals with slight differences in chemical composition below EDS sensitivity (e.g., hematite/magnetite), only one general phase was created. In addition, due to the small spatial resolution of the measurement energy and resolution of the QEMSCAN® measurements (see Section 3.2), the individual clay minerals cannot be analyzed, but the

Figure 8: Native silver and carbon particles in a cigar-shaped aggregate. In the upper left corner: BSE image of the aggregate; in the upper right corner: Ag and Si elemental map distribution; in the bottom left corner: C elemental map distribution; in the bottom right corner: EDS spectrum.

Figure 9: The graph of the distribution of particles in individual fractions summarizing all five investigated samples of Złota loess.

recognition of clays as a general group is not a problem. The QEMSCAN® data for all the samples were reclassified through the newly developed “loess mineral database” to extract the final results.

3.6 Analytical reproducibility

To confirm the reliability of the methodology, a repeatability test was performed on the sample no. s660. Five separate measurements were conducted with randomly selected 25 square fields (Figure 5). Relative standard deviation (RSD), as estimated from the five measurements of the sample s660, is less than 5.5% for most main mineral phases (quartz, biotite, muscovite/sericite, plagioclases, K-feldspars, clay minerals) and some additional minerals (e.g., clinopyroxene and cordierite). RSD for other more abundant additional minerals (and also for carbonates included to the main phases) is less than 10% (e.g., ilmenite, rutile with polymorphs, kyanite with polymorphs and amphiboles) and 15% (carbonates, titanite, zircon, REE minerals group or garnets). For Fe-oxides, RSD is less than 20%. Minerals with low abundance in the bulk sample have RSD of less than 35% (e.g., Fe native, other native elements such as Au or Ag and apatite). As expected, the lowest repeatability was found for minerals at extremely low concentrations, e.g., for olivines RSD is below 63.5% and for ulvospinel 75%. To conclude, the reproducibility for most relevant phases and minerals in the

Figure 10: Particles separated by iDiscover software into five granulometric fractions for loess sample s200 (particle size in microns).

loess is satisfactory. However, the rare phases should be concentrated prior to the QEMSCAN[®] analysis for better reproducibility.

4 Results and discussion – pros and cons of the developed methodology

4.1 Number of analyzed particles

In total, 1,159,107 particles have been measured for five samples and 4–6% of them were heavy minerals. For each sample at least 2,00,000 particles were identified, including ca. 10,000 particles of heavy minerals. These numbers already show that the automated SEM-EDS mineralogy has a huge advantage over traditional methods' insignificance. The previous “traditional” studies of loess in Poland were usually based on about 300 particles of heavy minerals [19].

4.2 Set of mineral phases

The mineral compositions of the loess samples are summarized in Figure 6. The investigated bulk loess material is dominated by quartz (57.3–62.9%) and contains plagioclase (7.8–9.2%), K-feldspar (7.9–8.7%), carbonates (5.0–7.8%), muscovite (3.2–6.2%), biotite (4.2–7.5%), heavy minerals (4.3–5.8%) and clay minerals (0.9–1.6%). The

concentration of clay minerals is most probably underestimated due to the not sufficient spatial resolution (see Section 3.4). The content of the undefined phases reaches maximally 1.4% and is assigned mostly to the finest granulometric fraction.

The heavy mineral group is controlled mostly by clinopyroxene (1.6–2.7% of the bulk sample), garnets (grossular = 0.44–0.86%; almandine = 0.1–0.45%) and polymorphs of TiO₂, i.e., rutile, anatase and brookite (0.48–0.65%). The more important additional minerals are amphiboles (0.14–0.19%), ilmenite (0.26–0.38%), zircon (0.12–0.17%), magnetite + hematite (0.14–0.24%) and kyanite + sillimanite + andalusite (0.18–0.28%). The other heavy minerals do not exceed 0.1% of the bulk sample. The relations of these phases exclusively in the heavy mineral group (not in the bulk sample) are shown in Figure 7.

Many other rare and/or complicated mineral phases (not shown in the Figure 7) were also found, such as REE-bearing allanites, platinian gold, etc. Moreover, we observed heavy phases such as native Au and native Ag associated with light-density phases and even organic matter (Figure 8). Some of them have been confirmed additionally by Raman spectroscopy.

It should be noted that the set of mineral phases found above with QEMSCAN[®] analysis seems inclusive. Indeed, no assumptions or exclusions on phases were made such as the density (light or heavy), optical property (transparent or opaque) or abundance (major, minor or trace). The simultaneous analysis of all phases is the most important and desired advantage of the automated EDS-SEM mineralogy.

Figure 11: The distribution of heavy minerals in granulometric fractions of sample 200 (panel a) and in the 8–16 μm one of each sample (panel b).

The traditional approach, as described below and in the next section, faces many problems related to heavy phases, particularly the opaque and fine-grained ones. It

is an important topic because these phases are commonly used for the paleoenvironmental interpretations of the Polish loess [20]. These studies most often deal

with light microscopy of only transparent phases [21] and the lack of the opaque fraction resulted from the limited access to adequate equipment. Obviously, the composition of heavy minerals without the opaque phases (whose content can constitute up to 75% of the heavy fraction) can be misestimated and any further interpretations can be incorrect [21]. Similar problems are related to the size, shape and specific density of the minerals, especially the heavy ones. The most popular traditional way to separate heavy phases from the sample is to use heavy liquids (e.g., bromoform -2.89 g/cm^3 or polytungstate -2.97 g/cm^3 [22]), with density lower than that of the heavy minerals but greater than that of the main phases. However, in this separation method, the lamellar particles, even with density more than the liquid, can remain suspended and will not sink. Furthermore, some phases can be “heavy” or “light,” depending on their chemical composition, even in different parts of the same particle, e.g., the density of biotite can decrease from 3.08 to 2.5 g/cm^3 , during the weathering process by oxidizing iron and losing potassium cations [23]. Thus, some biotite can be found with this method but not the others. The same problem also holds for the transition phases or heavy minerals that overgrow the light phases. Other common methods are also available to separate heavy minerals (flotation, table concentration, spiral concentration, electromagnetic concentration or combinations of these methods), but they are unable to sufficiently and accurately separate heavy phases from fractions below $20 \mu\text{m}$ (frequently founded in the loess) or require too much input material [24–27]. The huge amount of material, averaged from significant interval of loess profile, cannot be investigated due to the need of obtaining the high-resolution record of paleoenvironmental changes.

4.3 Mineral composition in individual granulometric fractions

For the traditional mineralogical investigations, the heavy mineral analysis is conducted only on one selected granulometric fraction [28]. It is related to the technical issues during the standard mineral separation procedure in heavy liquids (see Section 4.1). It is well-known that particles not exceeding $20 \mu\text{m}$ tend to remain in the filter paper, which can prevent their recovery. The analysis of the smaller fractions (which are very

important for loess paleoenvironmental investigation) is therefore prone to errors. This is mainly due to granulometric analysis, which shows that nearly 50% of heavy minerals are associated with the fraction $16\text{--}31 \mu\text{m}$ (Figure 9).

The iDiscover software of the QEMSCAN® package allows to swiftly differentiate the mineralogical phases of bulk sample into individual granulometric fractions. The procedure is based on the sizing of the BSE images. As an example, we used the particles from sample s200, classified into five granulometric fractions, i.e., $4\text{--}8 \mu\text{m}$, $8\text{--}16 \mu\text{m}$, $16\text{--}31 \mu\text{m}$, $31\text{--}63 \mu\text{m}$ and $>63 \mu\text{m}$, are shown in Figure 10. The $0\text{--}4 \mu\text{m}$ fraction was not measured due to the limited spatial resolution of the method (see Section 3.3). As another example, we depicted the distribution of heavy minerals within all granulometric fractions of s200 sample and within $8\text{--}16 \mu\text{m}$ fraction of all samples (Figure 11). Some significant differences were found in the content between the samples and/or individual granulometric fractions. However, the interpretation of the results is beyond the scope of this article.

5 Conclusions

We elaborated the full methodology including sample preparation and the guidelines for QEMSCAN® analysis parameter determination and further measurement. The methodology may be found useful by other groups related to paleoenvironmental research. Further, we compared the automated EDS-SEM mineralogy with the traditional approaches that have been utilized. We identified the strong and weak points of the technique. We argue that QEMSCAN® avoids the commonly found problems such as low statistics, the lack of opaque heavy phases, separation-related losses of information, issues related to the fine particles, etc. The most significant limitation of QEMSCAN® stem from limited spatial resolution which affects the clay-sized particle analysis. We successfully applied the methodology for studying Polish loess from Złota region, and we obtained meaningful results. Their interpretation is beyond the scope of this article.

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