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Preliminary structural and chemical study of two quartzite varieties from the same geological formation: a first step in the sourcing of quartzites utilized during the Mesolithic in northwest Europe

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ABSTRACT. Wommersom and Tienen quartzite are found as varieties of lithified arenite banks within the Cenozoic Tienen Formation. These macroscopically distinct varieties were utilized as raw material for stone tool production during the Mesolithic period in the Rhine-Meuse-Scheldt area of northwest Europe. They were distributed over 80,000 km^2 between the Paris and North Sea basins for over four millennia. This distribution has been interpreted by archaeologists as a long-distance exchange network. In this work, samples from both outcrops have been examined by different characterization methods with the aim to develop an operator-independent and objective method to determine the origin of a certain artifact.

Petrographical study revealed a distinct difference in grain size of both quartzites. However, considering the results of the petrographical analyses, it is clear that there is a difference between the accessory minerals that are more or less irregularly distributed in the samples. Cathodoluminescence (CL) revealed additionally information on the presence of feldspars and facilitated the recognition of minerals such as apatite, zircons and kyanite. X-ray tomography was used to obtain in a non-destructive way, a structural overview of the samples as well as a detailed 3D grain-size distribution of some accessory minerals. The latter is important given that these non-destructive techniques could be used for sourcing of other geological material as well as archeological artifact.

This work is a first step in the sourcing of different quartzite varieties to their different outcrop locations and their specific facies within the same geological formation. However, when characterizing artefacts for sourcing purposes, it will remain crucial to provide attention towards a possible level of heterogeneity inside these samples. In order to do this correctly, besides a characterization of the artefacts themselves, also a detailed analysis of the entire geological formation is needed.

KEYWORDS: Quartzite artefacts, Wommersom, Tienen, microscopy, cold-cathodoluminiscence, X-ray computed tomography

1. Introduction

The Mesolithic (10,000-5000 BP) archaeological record from the Rhine-Meuse-Scheldt area of northwest Europe has yielded two different quartzite varieties distributed over an area of 80,000 km^2 between the Paris and North Sea basins (Robinson et al. in press). The area of Tienen in central Belgium has been their proposed origin of procurement, and temporal and spatial patterns in their distribution have led archaeologists to interpret them as evidence of long-distance exchange networks that played important roles in Mesolithic cultural identities (Crombé 1998; 2002; De Paepe 1998; Gendel 1982; Hamal-Nandrin 1945; Perdaen et al. 2008; 2009). These different varieties have been labelled 'Tienen' and 'Wommersom' quartzite on the basis of macroscopic analyses by experienced archaeologists and geologists based on texture, grain quality (e.g. 'coarse' versus 'fine', respectively), and colour. It has been hypothesized that these two varieties were different facies within the sands of the Dormaal Member in the Tienen Formation, Landen Group. According to the most recent geologic map and its lithostratigraphic units (Maréchal & Laga, 1988), the Tienen Formation is a Thanetian (upper Paleocene) continental deposit (Kaartblad Leuven), equivalent to the continental deposits in the province of Hainaut and northern France. With the lowering of the base of the international Ypresian stage from the base of the Mont-Héribu Member in Belgium to the carbon isotope excursion level (CIE) (ratified 2003), the Tienen Formation has an early Ypresian age according to De Geyter et al. (2006).

The Tienen Formation is a continental deposit, containing coarse sand and gravel in fluviatile gullies, lignite and well-sorted sands. Regional silicification gave rise to a stone bank and associated lithified tree trunks. Stone produced from this stone bank is called 'Rommersom quartzite' or 'Tienen quartzite'. De Geyter (1996) mentions that the Wommersom quartzite is a local fine-grained facies found in Wommersom which is frequently used as artefact (Fig. 1).

Quartzite can geologically have two forms: orthoquartzites (quartz-cemented sedimentary quartz grains) and metaquartzites (recrystallised grains with mosaic texture). In this case, we are dealing with quartzarenites or orthoquartzites, which underwent no metamorphic alteration. Dreesen and Dusar (2010) describe the Tienen quartzite as a fine-grained (average particle size between 0.125 mm and 0.250 mm) quartzarenite, which are pale-grey silcretes from the Gete Bassin. The term "silcrete" is used for a variety of (mostly) continental silicifications. There are two main categories of silcretes: *pedogenic* silcrete, which forms under semi-arid conditions and exhibits typical soil textures (illuviations, columnar structures, etc.), and *groundwater* silcrete, which forms at depths in relation to groundwater pathways and water-table levels under still unclear geochemical conditions, and develops typical "surface mamelonnée", such as in the Fontainebleau sands, Paris Basin (Thiry, 1999). No work has yet been done on detailed investigation of these quartzites to assess their pedogenic character. However, according to the study of Thiry (1999), the Tienen quartzites could be regarded as a groundwater silcrete.

The continental sands of Erquelinnes in the Mons Basin (province of Hainaut, ca. 70 km SE of Tienen) also contain quartzarenite banks, known as the 'Bray quartzite'. These are the time equivalents of the Tienen quartzite (De Geyter & Nijs,

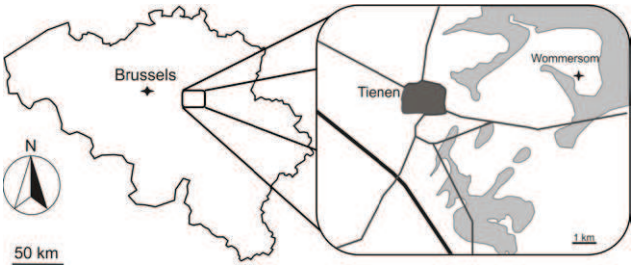

Figure 1. Map of Belgium with the localisation of the city of Tienen and the village Wommersom and subcrop beneath the Quaternary of the Tienen Formation according to the geological map (in grey, around the city of Tienen)

1982). Compared to the Tienen quartzite, this quartzarenite was also used as a local natural building stone, but on a smaller scale. It contains few root traces and it is generally less compact than the Tienen quartzite (Cnudde, 2005).

Based on the literature (De Geyter & Nijs, 1982; Bassleer, 1985) and on previous work, a difference in grain size exists between the Wommersom (micro)quartzite and the Tienen quartzite, associated with the same geological formation. Bassleer (1985) mentions that based on their petrographical study, the average grain size in the microquartzite of Wommersom varies largely between 10 µm and 63 µm.

Although there is very little literature pertaining to the sourcing of quartzite, there is one paper, by Pitblado et al. (2008), which reports the results of pilot-study efforts to develop methods to profile quartzite, a rock type to which geochemical and other sourcing techniques have only rarely been applied. Pitblado et al. (2008) evaluated in their study petrography, ultraviolet fluorescence (UVF), wavelength dispersive X-ray fluorescence (WD-XRF), instrumental neutron activation analysis (INAA), and inductively coupled plasma mass spectrometry - both acid-digestion (AD-ICP-MS) and laser ablation (LA-ICP-MS) - as means to differentiate among the different specimens and the sources they represent. One sample was taken from each outcrop and their study suggests there is potential for petrography, INAA, and both versions of ICP-MS to discriminate among quartzites from different source localities in the Gunnison Basin. Another recent work concerning characterization of quartzite artefacts, is the work by Blomme et al. (2012) were quartzitic tools from different Mesolithic sites in Belgium were characterised.

In this paper we aim to develop a methodological framework to examine operator- independent methods to distinguish between a well-selected sample from different outcrops. Therefore we want to examine which analysis method or combined methods could be suitable for an objective discrimination between Wommersom and Tienen quartzite based on structural and/or chemical composition. A petrographical study based on optical microscopy, cold-cathode luminescence (CL) and scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) will be performed in combination with high-resolution X-ray tomography (HRXCT).

This study is an important first step in the operator-independent sourcing of different quartzite varieties to their different outcrop locations and their specific facies within the same geological formation.

2. Materials

Well-selected representative samples of Tienen quartzite and Wommersom quartzite were selected from their respective outcrop locations (Fig. 1) in Overlaar (Tienen) and Wommersom (Wommersom).

The quartzite of Tienen is found as isolated blocks (Fig. 2A) or as thick layers (up to 1 m thickness) with a very characteristic shape, known as “surface mamelonnée” (Fig. 2B) and is a light grey to green-grey massive compact stone. Locally, some very thin opal layers can be found at the surface. This stone is a very hard and compact material, with a compressive strength of 300 N/mm² and chemically consists almost out of pure SiO_2.

The Wommersom quartzite has a finer grained texture and varies in color from light grey to brown and black. Some fragments contain a few large angular quartz grains with a diameter of ± 100 µm, which are not touching each other and are imbedded in a fine-grained quartz cement containing dark impurities. Other fragments of the microquartzitic Wommersom contain only fine-grained quartz and those fragments start to show some resemblance with flint.

Thin sections from each of the samples were prepared using in-house thin section preparation methods, including cutting with a water-cooled saw and grinding with silicium carbide (carborundum) and polishing on cloths using 6, 3 and finally 1 µm diamond gels. These ± 30 µm-thick, polished thin sections underwent petrographical study and cathodoluminescence. Additionally, polished samples were analysed with scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) and from each sample two subsamples of different sizes (samples with a diameter of around 3 mm and 1.5 cm) were taken for high resolution X-ray CT.

Figure 2. Formation of Tienen. A: Bray sandstone from the Mons Basin, B: Tienen Quartzite from the Tienen region

3. Methods

3.1.Petrographical study

Petrographical research on thin sections of the quartzite of Tienen and Wommersom by optical microscopy allows a 2D study of the mineralogy and the texture of the stones. For the petrographical description, the European standard EN12407 (2000) was used as a guide. Optical microscopy was performed at the Geology department (Ghent University, Belgium) using an Olympus-BH2 microscope with total magnifications of x100 and x200.

3.2. Cathodoluminescence

Cathodoluminescence (CL) analysis was performed at the Geology department of the University of Mons (Belgium). The CL unit used in this study is a cold-cathode electron gun operating at 15 kV beam voltage and 500 µA current (model CITL Mk5). Helium was admitted in the vacuum chamber instead of air to support the electron discharge. This improves stabilization of the electron beam and limits heat effects when long exposures times are required, typically for the observation of weakly-luminescing minerals such as quartz. A high sensitivity camera allows direct observation and capturing of digital images. Optical spectroscopy of the CL emission was performed as a support for mineral identification after Marshall (1988). We used a CITL COS8200 spectrometer with a spectral resolution of 3.7 nm and a detection range of 380-1100 nm.

3.3. Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX)

Secondary electron imaging of the Scanning Electron Microscope (JEOL JSM-5310LV) was used to analyse the morphology and the surface topography of the Tienen and Wommersom quartzite, while backscattered electron imaging was applied to

visualise compositional contrast in detail. Since the SEM system is equipped with an energy dispersive spectrometer, qualitative and semi-quantitative compositional analysis results could be obtained and analysis of elemental composition of materials was accomplished with a high spatial resolution.

3.4. High resolution X-ray micro-CT in combination with Morpho+

While petrographical study by optical microscopy reveals the mineralogical composition and texture of the stone in 2D, X-ray high-resolution X-ray CT reveals the internal structure of the stone in 3 dimensions (Cnudde et al., 2011). X-ray tomography registers the X-ray attenuation, which depends on the internal density and atomic number of the elements of the constituent minerals. By means of the reconstruction software Octopus, this data is converted into 2D cross-sections that allow 3D renderings of the examined sample (Vlassenbroeck et al., 2007a). The in-house developed software Morpho+ was used for 3D analysis (Vlassenbroeck et al., 2007b, Brabant et al., 2011) and calculation of the porosity and concentration of high density particles. In addition, the high density particles were analysed based on their shape (spheres, blades, discs and rods) according to Tucker (2001) after Illenberger (1991). The shape of a grain is measured by calculating the Long (L) intermediate (I) and short (S) axes.

4. Results

4.1. Petrographical study

4.1.1. Tienen quartzite

Tienen quartzite is a quartz arenite with a more or less unimodal grain distribution (Fig. 3). It consists almost completely of angular to subangular, equidimensional quartz cemented by a microquartz cement. Besides quartz grains, some zircon, rutile and tourmaline are randomly distributed throughout the sample. Additionally, some randomly distributed opaque minerals occur. Some enrichment in opaque minerals, Ti-oxides, occurs in fine-grained, finely stratified areas. These are interpreted as illuviation structures associated with decayed rootlets. Together with the angular morphology of the initial quartz grains (see cathodoluminescence), these observations provide evidences for the non-marine origin of the material.

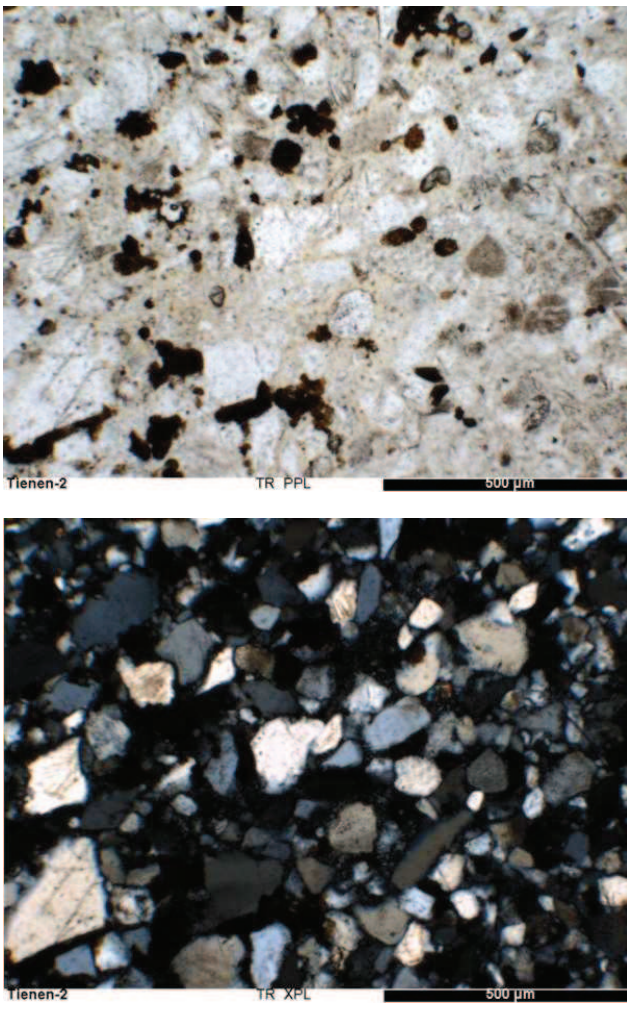

Figure 3. Tienen quartzite under plain light (A) and crossed-polarized light (B)

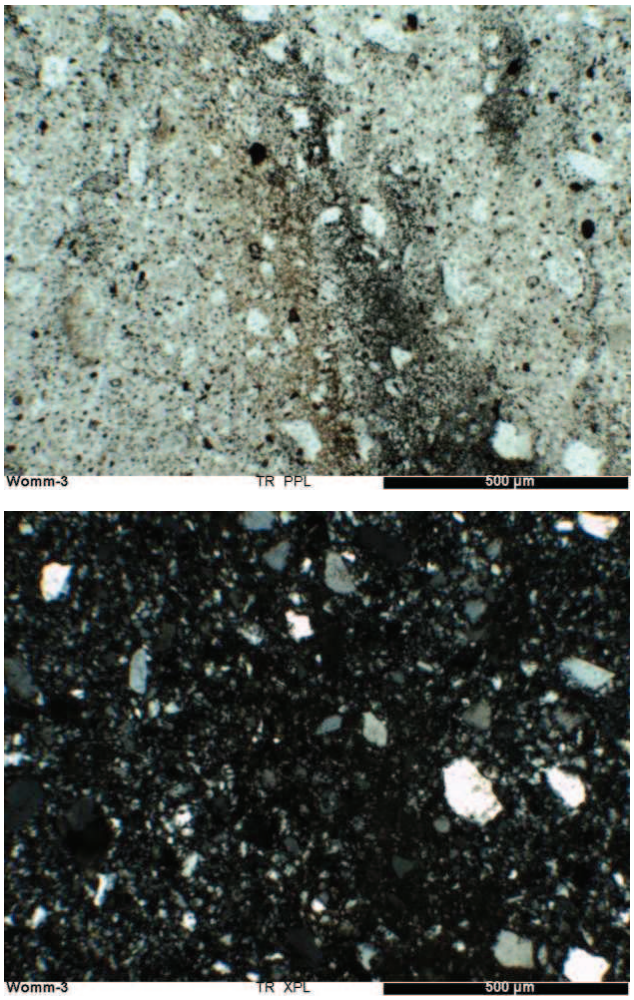

Figure 4. Wommersom quartzite under plain light (A) and under crossed-polarized light (B)

4.1.2. Wommersom quartzite

Wommersom quartzite is a fine-grained quartz arenite with a mixture of two unimodal distributions: the main size class consists of rather small, well-sorted subangular quartz grains, while the other class comprises of a small fraction of very large grains relative to the main size (Fig. 4). The whole has a quartzitic texture. As in the Tienen quartzite, some opaque structures can be found throughout the entire sample. This might be Ti-oxides from a similar pedologic origin (Summerfield, 1983).

4.2. Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX)

4.2.1. Tienen quartzite

A SEM image of the analysed polished surface of Tienen quartzite is shown in Fig. 5. Dense minerals and fossilised root structures are clearly distinguishable, while individual quartz grains are hard to characterise due to their uniform chemical composition throughout the analysed zone. EDS-Spectra of 28 dense minerals were collected from the groundmass. The spectra for the 10 brightest minerals (35 %) correlate with the characteristic spectra for Si and Zr, identifying these minerals as zircons, as could be observed under the petrographic and cathodoluminescence

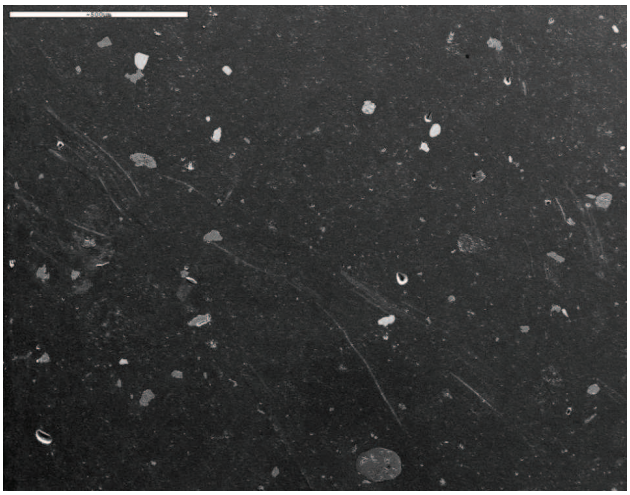

Figure 5. Image of an area of 1,75 x 1,37 mm of the Tienen quartzite, which was analysed with energy dispersive spectroscopy (EDS)

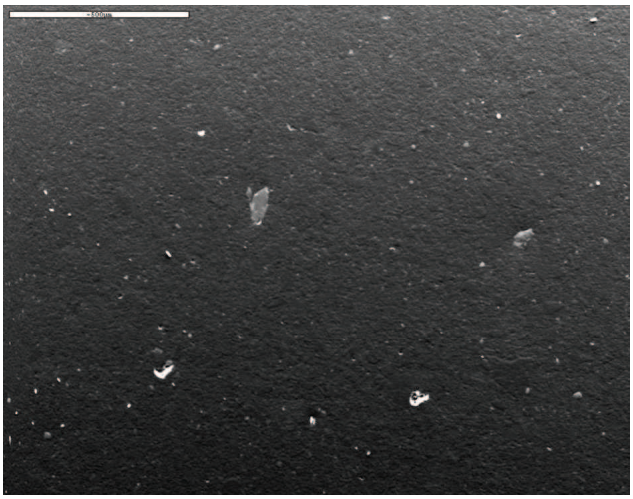

Figure 6. An area of 1,75 x 1,37 mm of the Wommersom quartzite was analysed with energy dispersive spectroscopy (EDS)

microscope. The other denser minerals (60 %) can be identified as titanium oxides (TiO_2).

4.2.2. Wommersom quartzite

In the SEM image of the Wommersom quartzite (Fig 6), the dense minerals are smaller, apart from some larger TiO2 minerals, and less abundant compared to the Tienen quartzite. Due to their smaller size and lower abundance, only 8 minerals in the prepared polished sample are suitable for analysis with EDS. Five of the analysed minerals could be identified as TiO2, two as zircon and only one mineral as kyanite.

4.3. Cathodoluminescence

The cathodoluminescence (CL) characteristics of the Tienen quartzite (Fig. 7) are exactly the same as that of Wommersom (Fig. 8), except for the grain size and distribution. In addition, the micro-quartz cement differs, which is not resolved in Wommersom due to the small grain-size. CL reveals the detrital quartz grains which weakly luminescence in different shades of blue, brown and, less frequently, in red. The shape of these grains appears highly angular under CL. The quartz cement is less luminescent than the grains, but becomes clearly visible by using high exposure times. This cement is mainly composed of microquartz exhibiting a distinctive red luminescence that gradually shows up as beam exposition is increased. An earlier, dark blue luminescent cement consisting of syntaxial overgrowth forms a discontinuous coating on the grains. This earlier cement may be in part inherited, i.e. it came with the initial quartz grains in the sedimentary system.

A small amount of bright-blue luminescent minerals were observed in the pore space. This mineral possibly represents kaolinite, which is compatible with the pedogenic origin of the sandstone (Thiry, 1999).

Many zircons were detected under CL. They display a white to greenish-white CL with variable intensities and a yellow irradiation halo in the surrounding quartz. Besides zircons, CL observation allowed the recognition of heavy minerals that are difficult to identify under classical microscopy such as monazite, apatite and kyanite. Kyanite could be also representing the mineral that was found in the SEM/EDX where an Al-silicate mineral was detected. Monazite occurs with a typical dark olive green luminescence and a yellow or red irradiation halo in the adjacent quartz grain and cement, respectively. Bright luminescent grains with reddish to pinkish CL were observed. These grains resemble to plagioclases, but spectroscopy revealed the typical sharp dual emission lines due to Cr^{3+} activation in the red region of the spectrum (feldspars show a broad, single emission in this region due to Fe^{3+} activiation), allowing identification as kyanite. Rare apatite grains exhibit a bright yellow-green luminescence (emission at 575 due to Mn^{2+} activation).

4.4. X-ray micro-CT in combination with Morpho+

From the original quartzite of Tienen and the quartzite of Wommersom, 2 small subsamples with a diameter of around 3 mm and 2 larger subsamples around 1.5 cm size were taken and were scanned with a resolution of respectively 6.63 µm and 22.18 µm. After scanning, the raw data of each scan was converted into reconstructed cross-sections (Fig. 9) by means of the reconstruction software Octopus (Vlassenbroeck, 2007a).

The reconstructions of the 4 samples reveal a quite homogeneous matrix containing dense inclusions, indicating the presence of minerals with a higher attenuation for X-rays. More highly attenuating minerals are present in the Tienen sample than in the Wommersom sample. After reconstruction, 3D volumes of

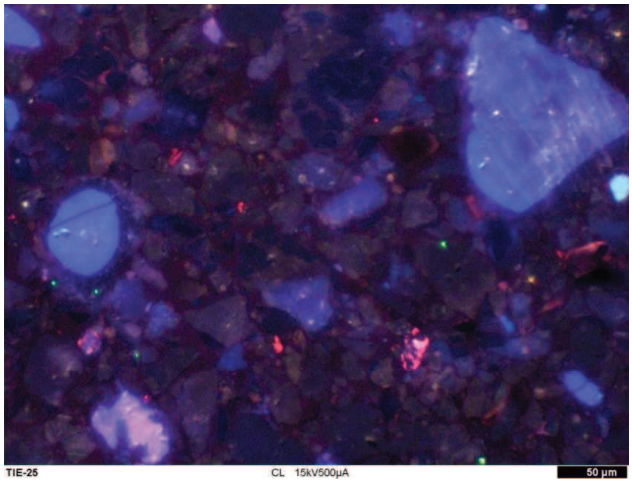

Figure 7. CL image of Tienen quartzite

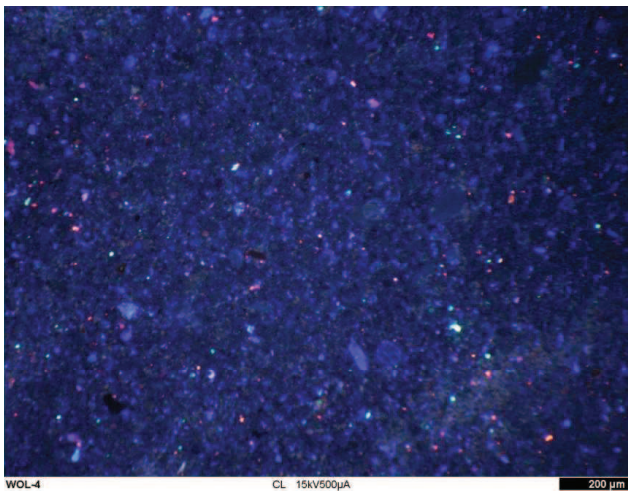

Figure 8. CL image of Wommersom quartzite

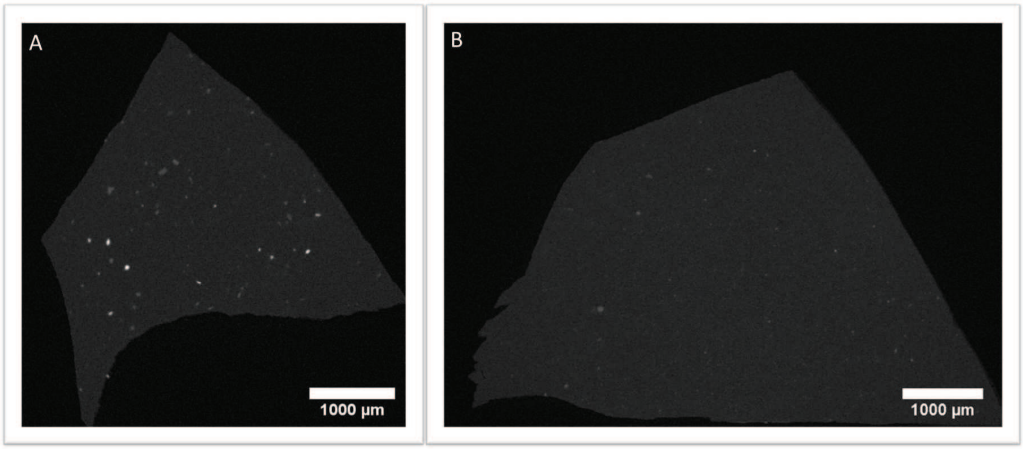

Figure 9. Reconstructed cross-section of the small Tienen subsample (A) and the small Wommersom subsample (B)

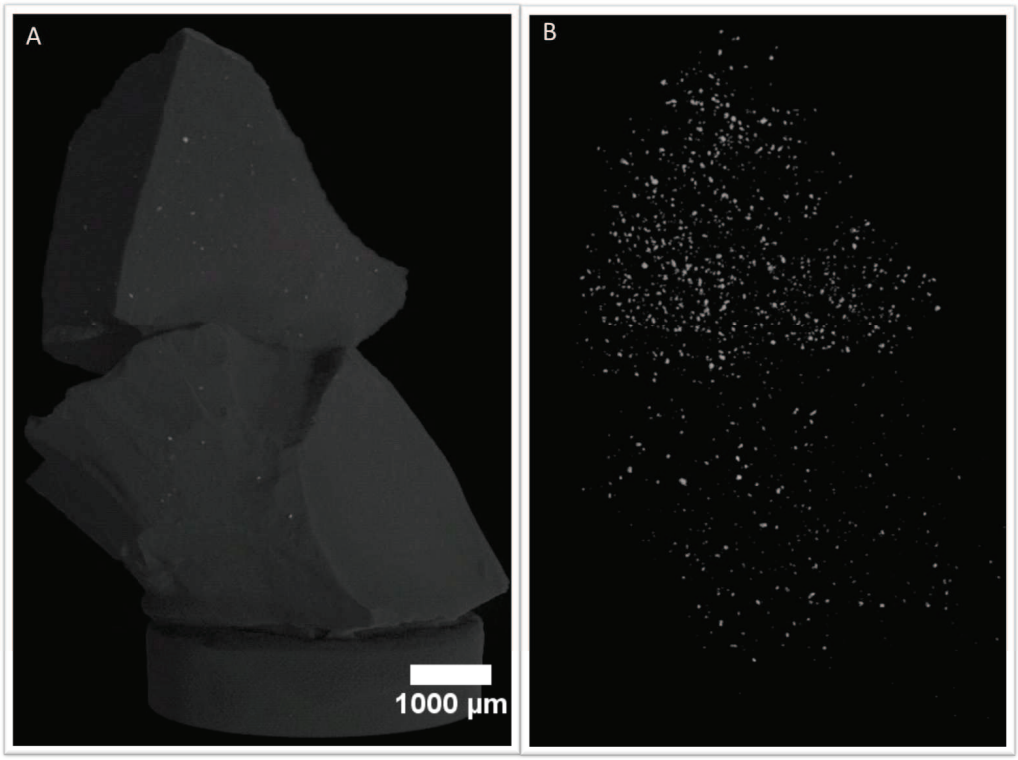

Figure 10. A) 3D rendered volume of the small Tienen (top) and Wommersom (bottom) subsamples; B) 3D rendered volume of the dense inclusions inside the small Tienen (top) and Wommersom (bottom) subsample

the scanned samples were rendered (Fig. 10). Fig. 10A represents the 3D rendered volume of the small Tienen (top) and the Wommersom (bottom) subsample, while in figure 10B the virtual removal of the matrix was performed, visualising the localization of the dense inclusions, which are highly attenuating minerals. In addition, Fig. 11 shows a larger rendered subvolume of both quartzites. The Tienen quartzite (top) clearly demonstrates its dense concentration of highly attenuating minerals. For both samples in the figures, the same clip-value was used. In this way, the same quantity of matrix was virtually removed, allowing us to compare both volumes in an unambiguous way.

Although no direct chemical information of the different minerals is given with X-ray CT, the attenuation of the minerals is an indicator for its density and the atomic composition. The theoretical linear attenuation coefficient as a function of the energy for the minerals analysed with optical microscopy, SEM-EDX and CL is given in Fig. 12. This figure illustrates that the minerals with the highest X-ray attenuation are zircon and rutile. For the TiO_2 minerals, anatase, brookite and rutile respectively with an average density of 3.9, 4.11 and 4.25, the minerals with the lowest density will have the lowest theoretical linear attenuation coefficient and the one with the highest density will have the highest theoretical linear attenuation coefficient. However, on the basis of CT images it will be very difficult to distinguish rutile from anatase or brookite. By means of Raman spectroscopy this could however be clarified (Ohsaka et al., 2005). However, the TiO_2 minerals are most likely to be rutile, since this is the most abundant species in detrital grain assemblages.

Each reconstructed data-set of the scanned samples was analyzed individually to obtain quantitative information about the abundance of the dense grains and their distribution. The measurements of the grain size and their orientation were only performed on the highest resolution scans of the smaller subsamples, since those obtained a higher resolution.

By performing first some binary operations, the volume of interest of each sample was selected by dual thresholding. The average grey value inside the volume of interest (83.96 mm^3) of the small Tienen subsample was 6947 ± 1548, while this was 7115 ± 1100 for the small Wommersom subsample. This average grey value is influenced by the volume of dense inclusions and their composition as well as the composition of the matrix. Therefore, these volumes of interest were thresholded in order to quantify only the dense inclusions. When analysing the dense minerals, several minerals with a different attenuation value could be distinguished (Fig. 13). The total amount of highly attenuating minerals in the Tienen sample was 1.2% for the larger sample and 1.09% for the smaller sample. The large Wommersom sample contained 0.25% high attenuating minerals and the small one 0.36%. The difference in abundance between the small and large samples can be explained by a difference in resolution used combined with the fact that natural stone have a natural heterogeneity and more small samples should be analysed in order to obtain a representative volume element. For the high resolution scans on the small subsamples, two groups of dense minerals could be identified. By combining the data of the linear attenuation coefficient with the chemical information and the

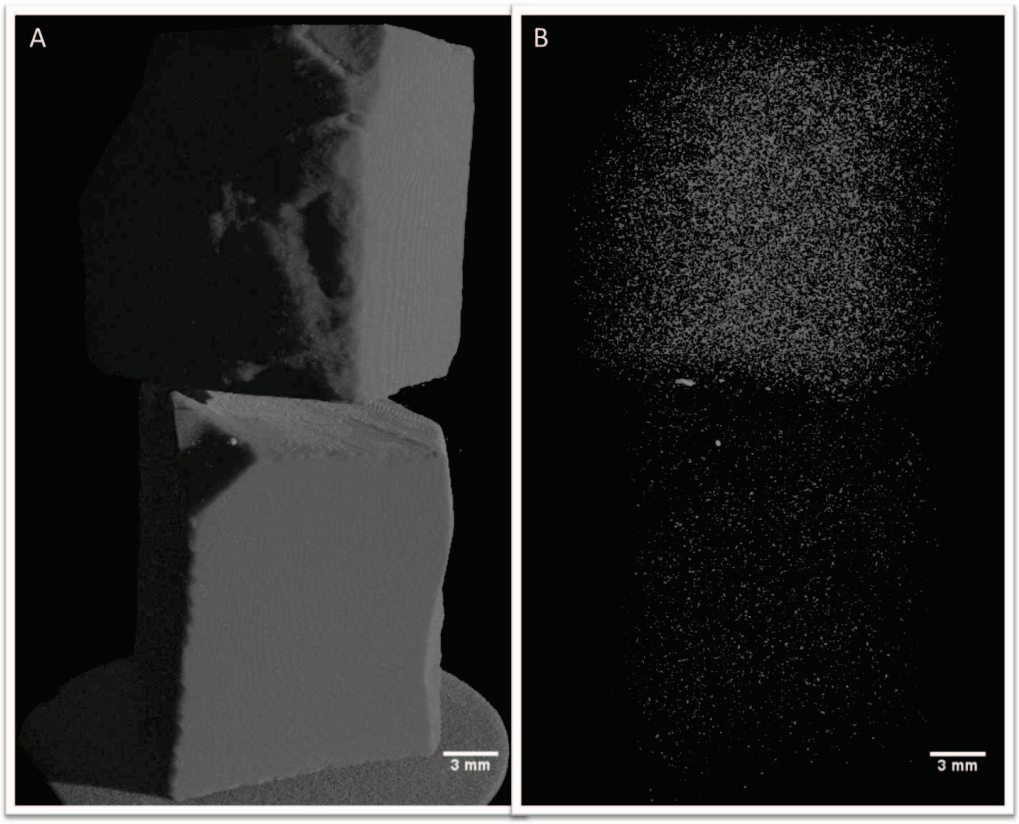

Figure 11. A) 3D rendered volume of the large Tienen (top) and Wommersom (bottom) sample; B) 3D rendered volume of the dense inclusions inside the large Tienen (top) and Wommersom (bottom) sample

information obtained by optical microscopy, CL and SEM, the group with the highest attenuation can be identified as zircons, while the less dense minerals are Ti-oxides. Some other mineral phases are present in the CT images with a slightly higher attenuation than the quartz matrix and a lower attenuation than the TiO_2. These minerals can be identified as tourmaline, apatite and kyanite, based on the information of the SEM/EDX, CL and optical microscopy. When analysing the zircon minerals, they were identified eight times more in the Tienen subsample than in the Wommersom subsample. While for the Ti-oxides, this is a factor of 2.8 more.

The mean equivalent diameter of the zircons is more or less similar: 45.8 µm ± 12.3 µm for the small Tienen subsample and 43.07 µm ± 12.6 µm for the small Wommersom subsample, with a maximum equivalent diameter of 112.71 µm and 99.45 µm, respectively. The mean maximum opening of the zircons is also comparable: 30.87 µm ± 10.3 µm for the small Tienen subsample and 27.6 µm ± 10.35 µm for the small Wommersom subsample, respectively, with for both samples a maximum inscribed diameter of 72.93 µm for the largest zircon.

The mean equivalent diameter of the Ti-oxides is 31.45 µm ± 14.40 µm for the small Tienen subsample and 21.60 µm ± 9.80 µm for the small Wommersom subsample, with a maximum equivalent diameter of 125.97 µm and 139.23 µm, respectively. The mean maximum opening of these minerals is 16.12 µm ± 8.80 µm for the small Tienen subsample and 10.60 µm ± 6.50 µm for the small Wommersom subsample. The largest inscribed diameter inside Ti-oxides was 72.93 µm for the small Tienen subsample and 59.67 µm for the small Wommersom subsample.

All dense minerals (zircons + Ti-oxides) were analysed together as a group as well and in general their average equivalent diameter was higher for the small Tienen subsample than for the small Wommersom subsample. The orientation of the largest grains (with an equivalent diameter larger than 10 voxels) appears to be random. In Fig. 13, the volume of the dense minerals with a certain maximum opening divided by total volume of the object is plotted against the maximum opening of the dense minerals. The dense minerals are more abundant and larger in size in the Tienen samples compared to the Wommersom samples. In both Wommersom and Tienen samples, however, there is a shift towards a larger average maximum opening of dense minerals in lower resolution scans (larger samples). Due to the difference in resolution, analysis of size and shape of the minerals needs to be performed on the smaller samples at high resolution. By comparing the scans at lower and at higher resolution, it seems possible to discriminate Tienen and Wommersom based upon the number of dense mineral inclusions, independent of the sample size and resolution. Concerning the shape analysis, four different

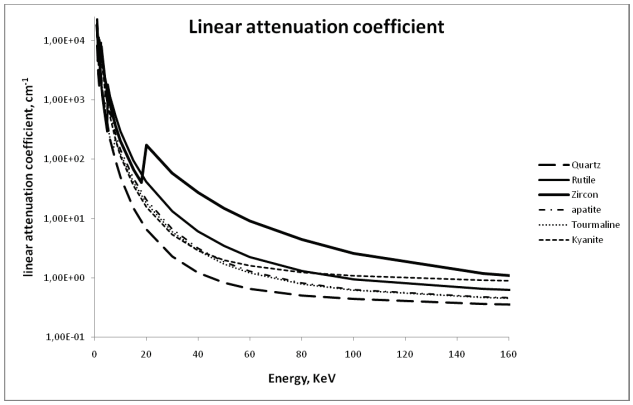

Figure 12. Linear attenuation coefficient of the main minerals in the quartzite of Tienen and Wommersom

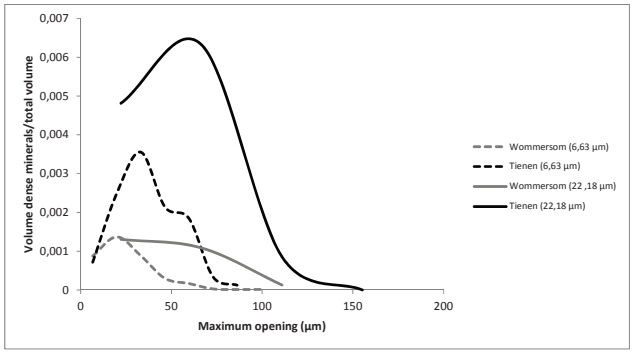

Figure 13. Graph of the analysed dense minerals inside the Wommersom and the Tienen quartzite, derived from CT analysis

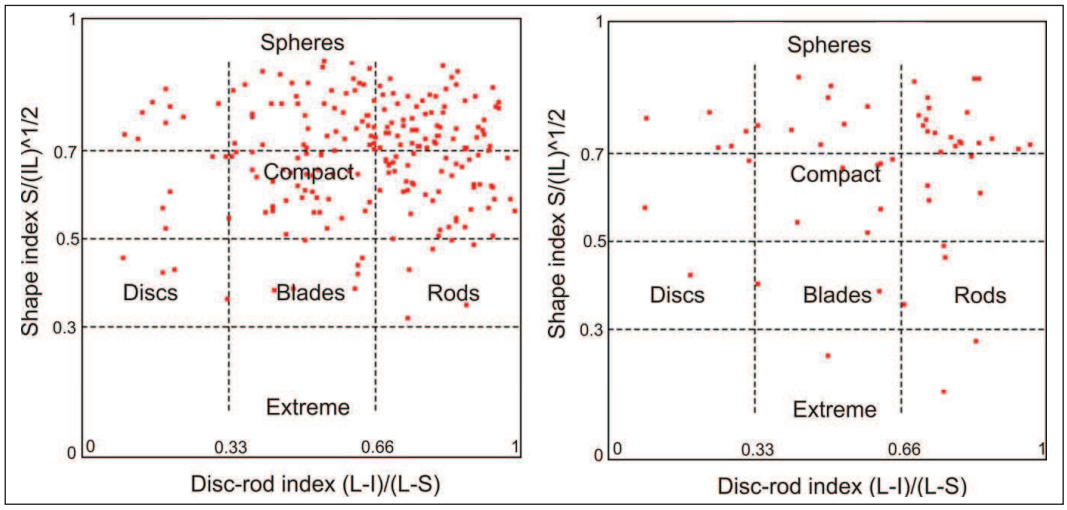

Figure 14. Shape plot of Tienen (left) and Wommersom (right). Each dense mineral was plotted in the graph according to the relation of their short (S), intermediate (I) and long (L) axes

Sample	Spheres (%)	Discs com/mid/extr (%)	Blades com/mid/extr (%)	Rods com/mid/extr (%)
Tienen	52	4	21	24
		63/37/0	83/17/0	87/13/0
Wommersom	60	6	18	16
		67/33/0	70/20/10	45/33/22

Table 1. Overview of the amount of spheres, discs, blades and rods in Wommersom and Tienen. A subdivision of compact (com), middle (mid) and extreme (extr) is shown.

classes (spheres, discs, rods and blades) were taken into account. Each dense grain was plotted on a diagram according to Tucker (2001). The shape index (S/(IL)^0.5) was plotted against the disc-rod index ((L-I)/(L-S). Subgroups were obtained for extreme, middle and compact shapes. The results for both Wommersom and Tienen are represented in Fig. 14. It is clearly visible that for the Tienen quartzite (left) more dense minerals were measured (223) than for the Wommersom quartzite (left) (55). The amount of each shape class is given in Table 1. For the Tienen quartzite 52 % of the dense grains are spheres, 4 % are discs, 21 % are blades and 24 % are rods. In case of the Wommersom quartzite, 60 % of the dense minerals are spheres, 6 % are discs, 18 % are blades and 16 % are rods. No extreme shapes are present in the Tienen quartzite, while inside the Wommersom quartzite some extreme shaped grains are visible (Fig. 14). In case of the Wommersom the average disc rod index is 0.65 (± 0.20) and for Wommersom 0.62 (± 0.22). The average shape index of Tienen is 0.69 (± 0.12) and 0.67 (± 0.17) for Wommersom.

5. Discussion and conclusion

This structural and chemical preliminary study of two quartzite varieties, the Tienen and the Wommersom quartzite, demonstrated that both a chemical as well as a structural difference can be detected between both. The selected sample were representative for these varieties and despite assessing just only a few well-selected samples, this study indicated that each sample was distinguishable The different techniques employed in this study provide the initial foundation for further work that needs to be performed on multiple sample in order to estimate the variance of the results in each of the selected varieties. However, there are some features which are really a method for characterization. The petrographical study reveals that both samples show a distinct grain size distribution. Tienen quartzite has a larger average grain size with a more unimodal distribution, while Wommersom quartzite has a smaller average grain size with a bimodal distribution. This is in correspondence with De Geyter (1980, 1996), who mentioned that the Wommersom quartzite is a local fine-grained facies compared to the coarser grain facies of the Tienen quartzite. Note that the large-sized quartz fraction from this bimodal distribution is larger than grain fractions from the Tienen quartzite in contrast to the smaller overall-grain size of the Wommersom quartzite.

CL reveals the presence of feldspars which cannot be distinguished by normal optical microscopy due to lack of twinning. Furthermore, this technique facilitates the recognition of minerals such as apatite, zircons and kyanite. In order to double check the presence of kaolinite, detected by CL, XRD spectra can be made. Except for the grains-size and their distribution, which is also accessible with other methods, like optical microscopy or X-ray CT, the CL results were exactly the same for both examined samples.

SEM-EDX measurements clearly show that two heavy mineral phases are omnipresent in both the Tienen and the Wommersom sample. These mineral phases could be identified as TiO_2 and as zircon, where in both quartzites TiO_2 is more abundant than zircon. There is a large discrepancy in the amount of heavy minerals in Tienen quartzite compared to Wommersom quartzite, which is noticeably higher in the Tienen quartzite.

The X-ray CT images could not reveal the average grain size of the quartz minerals, compared to optical microscopy and CL. However, in the X-ray CT image the heavy minerals can be clearly distinguished due to their higher X-ray attenuation compared to the surrounding SiO_2 matrix. Two differently attenuating mineral phases that can be identified as TiO_2 and zircon, supported by the SEM-EDX information were quantified. In order to determine if this is due to the difference in outcrop or due to internal heterogeneity of the stone, much more samples should be tested. This analysis method is operator independent and could be very practical in daily practice, since it is also a non-destructive method. The plot of the disc-rod index against the shape index, based on the X-ray CT images, is also a useful operator independent parameter. For the Wommersom and Tienen quartzite only the dense minerals could be thresholded and thus quantified. Because the amount of dense minerals is far less in the Wommersom quartzite, only 55 grains were measured inside the entire sample. In case of the two quartzites, no significant difference could be seen from the results of the shape classes. The averages, with their standard deviations, are not significantly different and thus, this parameter cannot be used to differentiate the Wommersom and Tienen quartzite. However, this approach of defining for each grain a shape class is very useful and can be used in an unambiguous way for all kind of rock types.

The conclusion of this study revealed that each of the examined methods has its pros and cons, and by combining the different analysis results it is possible to distinguish these quartzites from one another. Optical microscopy for sure is an important technique when one wants to perform detailed analysis of the different stone facies. However, when rare archeological findings are obtained, destructive thin section analysis is sometimes far from evident. Therefor X-ray CT was implemented in this study to reveal its possible value in characterization and determination of the different quartzites in a non-destructive manner. This latter is important given that this non-destructive technique could be used for sourcing of other geological material as well as archeological artifact. Having now established the

methodological foundation for discriminating between these different quartzite varieties, we must now employ these different instrumental techniques on a more robust sample set in order to get to the heart of contemporary archaeological questions concerning the specific locations of procurement during the Mesolithic period. Pertinently for this study as well as for the study performed by Pitblado et al. (2008), we can confirm that petrography remains an important basic technique in combination with the chemical analysis. The non-destructive HRXCT allows the first steps towards obtaining an operator-independent way to determine the grain-size distribution and chemical composition. The potential for application of HRXCT in archaeological research is very promising. By combining the selected techniques, more detailed information can be obtained and will be a step towards future research that will facilitate an operator-independent, and thus objective method to determine to which outcrop a certain geological sample or archeological artifact can be linked.

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