GEOLOGICA BELGICA (2012) 15/3: 193-199

The characterization of sedimentary quartzite artefacts from Mesolithic sites, Belgium

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ABSTRACT. This work presents an extensive characterization study of quartzitic tools from different Mesolithic sites in Belgium (with several sites in the vicinity of Tienen). Their properties are compared with those of natural outcrops, i.e. the Wommersom and Tienen quartzite and a third unknown variety. Therefore, a detailed petrographical and geochemical study is performed by means of optical microscopy, point counting, image analysis, scanning electron microscopy, hot-cathodoluminescence microscopy, inductively coupled plasma – optical emission spectrometry and portable X-ray fluorescence spectroscopy. It is shown that the geological samples of the sedimentary quartzite varieties can be distinguished based on their texture and composition. The results of the grain size distribution indicate that there is a clear contrast between the fine-grained Wommersom quartzite versus the much coarser-grained Tienen quartzite. On the other hand, the concentrations of the chemical elements zirconium, titanium and iron show a difference between the three quartzite varieties, with the aid of discriminant function analysis. These criteria are applied to a number of archaeological artefacts showing that most of the investigated samples are composed of the fine-grained Wommersom quartzite. The provenance of the more coarser-grained artefacts is still unknown.

KEYWORDS: Wommersom quartzite, Mesolithic artefacts, provenance, grain size distribution and geochemical composition.

1. Introduction

Quartzitic tools can be found at several Mesolithic sites in Belgium, the fine-grained Wommersom quartzite being the most important one. This rock is very suitable for use in tools because of its smooth fracture surfaces, sharp edges and good quality in contrast with the more erratic flint (Caspar, 1984; Perdaen et al., 2009). Of this quartzite, there is only one area of outcrop known i.e. the "Steenberg" (literally translated as the "Stone Mountain") in Wommersom, 6 km east of Tienen. These stones are quartzitic silcretes belonging to the continental fluvio-lagoonal sediments of the Tienen Formation (55.8 – 54.8 Ma), earliest Eocene. The formation consists of coarse-grained white sands, lignitic dark clays and pale marls in fluviatile gullies and is in some places characterised by a significant silicification. This process has formed a massive sedimentary quartzitic bank (i.e. sandstones that have undergone secondary silicification in non-metamorphic environments (Skolnick, 1965; Bates & Jackson, 1980)) as well as petrified tree trunks at the top of the formation (Dormaal Member) (Sintubin et al., 2000).

The Wommersom quartzite was used, to a lesser extent, from the Middle Palaeolithic, with finds on nine known archaeological sites including Spy ('Grotte de la Bèche-aux-Roche') 40 km SW of the Stone Mountain (Di Modica, 2011). But the large increase of tools shaped of Wommersom quartzite took place from the Early Mesolithic with numerous sites at a distance of 20 to 25 km from the outcrop. During the Middle and Late Mesolithic, this distribution expanded over a total area of 40,000 km² (the entire Belgian territory and parts of the Netherlands, Germany and Luxembourg) with most of the artefacts found in the north and northeast of this area, i.e. the Kempen (distribution, see Perdaen et al., 2009, Fig. 22.1; Gendel, 1982).

In addition to this fine-grained Wommersom quartzite, another coarser-grained quartzite variety was used by the Mesolithic people. Archaeologists gave less attention to this stone probably due to its limited use in the Mesolithic and disagreements in nomenclature (Perdaen et al., 2009). A commonly used name for this stone is a "micaceous sandstone" which is a misnomer for the silicified rock without micas. Others call it a "Tienen quartzite" referring to the sedimentary quartzites found in the vicinity of Tienen which, just like the Wommersom quartzite, belong to the Formation of Tienen.

It is important to determine the origin of raw materials for tools in order to deduce the trade contacts and migration patterns of people in a certain time period. Important information can be obtained from the analysis of the distribution of raw materials from a localized outcrop (Gendel, 1983). In this respect, certainly the Wommersom quartzite is highly interesting because the rock is only exploited near the Stone Mountain at Wommersom, at least as far as we know, from the current knowledge.

2. Research aims

The investigation of archaeological artefacts is mainly done by means of macroscopic descriptions. Nevertheless there is need for petrographical and geochemical analyses to find out which materials belong to the same rock type and from where they probably originated (Di Modica, 2011).Various techniques, both destructive and non-destructive, are available taking into account the pros and cons concerning the usefulness of the available information, accuracy/precision and representativity of the results and degree of damage to the material.

A detailed petrographical and geochemical study is performed on the geological samples of three different sedimentary quartzite varieties from the vicinity of Tienen, i.e. the known Wommersom and Tienen quartzite and a third unknown quartzite, in order to establish unique criteria for each variety. Based on these results, several archaeological artefacts with Mesolithic age are examined to check whether the rock fragments belong to the same geological formation and may indeed be composed of the Wommersom (or Tienen) quartzite. This will enable confirmation or rejection of the proposed statements about the quartzite artefacts in earlier archaeological studies.

3. Materials

The only known outcrop of the Wommersom quartzite is situated in Wommersom, the Stone Mountain. In 1901 de Loë and Raeymaekers have described an outcrop of the Wommersom quartzite as nodules enclosed by sandstone (Destexhe-Jamotte, 1950; also Rutot, 1901). Currently these rocks are only found as individual fragments coming to the surface by ploughing the fields near the Stone Mountain (Fig. 1A: 1) (Di Modica, 2011). Fifteen samples have been collected in the vicinity of this location (Fig. 1A: 1-3) with samples G1-1 to G1-4 (the first number refers to the location on Fig. 1) coming from an in situ sedimentary quartzite bank removed from the subsoil years ago, while the others are individual surface fragments. These hard stones are grey to light grey coloured often with light brown to reddish brown spots visible on the surface. Some samples show traces of plant roots while others have a pronounced lobbed surface. Samples G1-8 and G1-9 show a more greyish brown colour with a (sub)conchoidal fracture. In contrast with the other samples, these rocks feel very smooth with small pale structures and sparkling facets visible on the surface. Samples G1-10 and G1-11 contain both varieties combined in one sample. The collected samples consist of the Wommersom quartzite but only samples G1-8 to G1-11 correspond macroscopically to the raw material of certain archaeological artefacts.

The Tienen quartzite covers a much larger area of outcrop in the neighbourhood of Tienen with occurrences in Overlaar, Hoegaarden, Huppaye and other places (De Geyter & Nijs, 1983). The investigated samples of the Tienen quartzite originate from three different locations: three individual surface fragments from Wommersom (Fig. 1A: 4-5), two in situ fragments from a quarry at Rommersom – Outgaarden (Fig. 1A: 6) and six individual fragments from a field ("O.L.V. van Troost-kapel") at Hoegaarden (Fig. 1A: 7). Most of these rocks have a lighter grey colour and show coarser grains in comparison with the Wommersom quartzite. Four samples of an unknown quartzite variety in the form of individual small fragments are

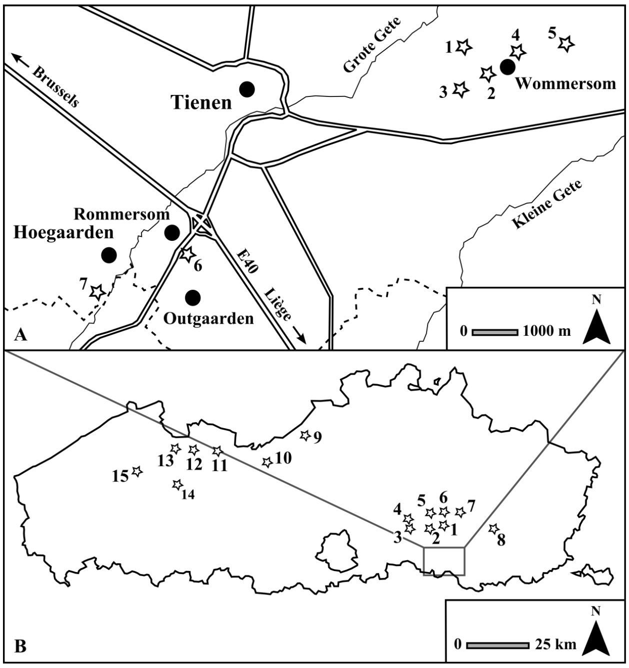

Figure 1. Geographical location of the samples in the Flemish Region (Belgium) with (A) geological (raw) material: 1-5. Wommersom; 6. quarry at Rommersom – Outgaarden; 7. field at Hoegaarden ("O.L.V. van Troost-kapel) and (B) archaeological material: 1. Bekkevoort; 2. O.L.V. Tielt; 3. Holsbeek; 4. Wezemaal; 5. Rillaar; 6. Scherpenheuvel; 7. Webbekom; 8. Stevoort; 9. Verrebroek; 10. Eksaarde; 11. Oost-Eeklo; 12. Eeklo; 13. Maldegem; 14. Aalter; 15. Oostkamp.

		Texture		*Composition (ICP-OES)*						*Composition (pXRF)*		
Sample no.	Quartzite type	% grains < 30 µm	Av. size grains > 30 µm	Al_2O_3	Ba	Fe_2O_3	Sr	TiO_2	Zr	$Fe_{(x)}/Fe_{(G2\text{-}1)}$	$Ti_{(x)}/Ti_{(G2\text{-}1)}$	$Zr_{(x)}/Zr_{(G2\text{-}1)}$
		%	*µm*	*wt%*	*µg/g*	*wt%*	*µg/g*	*wt%*	*µg/g*	-	-	-
G1-1	WQ	63	60	0.28	106	0.25	18	1.11	616	2.7	0.8	0.9
G1-2	WQ	59	61	0.16	102	0.16	16	1.06	696	1.6	0.8	1.2
G1-3	WQ	57	63	0.14	99	0.11	15	1.07	697	0.7	1.0	1.3
G1-4	WQ	57	66	0.15	93	0.20	15	1.06	695	0.9	0.9	1.3
G1-5	WQ	53	68	0.16	83	0.22	13	0.74	680	0.6	0.5	1.1
G1-6	WQ	65	66	0.15	65	0.10	11	0.98	546	0.7	0.9	1.1
G1-7	WQ	67	61	0.15	90	0.20	15	1.14	672	1.5	1.3	1.2
G1-8	WQ	69	73	0.17	109	0.25	16	1.15	505	3.1	0.9	0.9
G1-9	WQ	82	64	0.19	103	0.14	16	1.57	741	1.0	1.3	1.3
G1-10	WQ	83	54	-	-	-	-	-	-	-	-	-
G1-11	WQ	82	59	-	-	-	-	-	-	-	-	-
G2-1	WQ	64	64	0.22	100	0.14	16	1.58	688	1.0	1.0	1.0
G2-2	WQ	-	-	0.19	89	0.16	13	1.17	685	0.7	0.9	1.1
G3-1	WQ	59	56	0.18	90	0.18	13	1.08	558	1.1	0.8	0.9
G3-2	WQ	68	58	0.19	91	0.17	16	1.32	633	0.6	0.5	0.6
	Mean	*66*	*62*	*0.18*	*94*	*0.18*	*15*	*1.16*	*647*	*1.2*	*0.9*	*1.1*
G4	TQ	2	118	0.06	70	0.05	7	0.15	287	0.3	0.1	0.4
G5-1	TQ	7	83	0.09	90	0.06	11	0.44	546	0.5	0.3	0.7
G5-2	TQ	1	123	0.04	3	0.03	1	0.19	276	0.2	0.1	0.4
G6-1	TQ	3	116	0.06	64	0.03	7	0.19	293	0.3	0.2	0.3
G6-2	TQ	2	112	0.06	17	0.04	2	0.30	382	0.5	0.3	0.6
G7-1	TQ	-	-	0.06	84	0.05	6	0.23	467	0.5	0.2	0.5
G7-2	TQ	1	125	0.04	7	0.03	2	0.24	468	0.3	0.2	0.6
G7-3	TQ	7	115	0.07	171	0.04	7	0.34	312	0.5	0.3	0.4
G7-4	TQ	3	120	0.04	80	0.03	6	0.18	328	0.4	0.1	0.5
G7-5	TQ	4	138	0.09	65	0.13	5	0.18	228	0.7	0.1	0.4
G7-6	TQ	3	123	0.07	33	0.07	4	0.17	312	0.7	0.2	0.5
	Mean	*3*	*117*	*0.06*	*62*	*0.05*	*5*	*0.24*	*354*	*0.4*	*0.2*	*0.5*
G7-7	UQ	35	77	0.17	134	0.12	11	0.96	1052	0.6	0.8	1.5
G7-8	UQ	40	59	0.13	165	0.17	14	1.17	1110	2.0	0.7	1.7
G7-9	UQ	26	58	0.12	139	0.13	10	0.95	1164	2.1	0.5	0.9
G7-10	UQ	40	69	0.11	137	0.14	11	0.88	999	4.5	0.7	1.7
	Mean	*35*	*66*	*0.13*	*144*	*0.14*	*11*	*0.99*	*1081*	*2.3*	*0.7*	*1.5*

Table 1. Analytical data of the geological samples for the texture and composition (ICP-OES and pXRF) with WQ = Wommersom quartzite, TQ = Tienen quartzite and UQ = unknown quartzite. For the pXRF-data, each sample (x) is normalized by means of sample G2-1 to obtain ratios.

found at the last mentioned location. These dark rocks show a (sub)conchoidal fracture and contain small pale structures and sparkling facets on the surface similar to the samples G1-8 to G1-11 but feel less smooth. Contrary to the known Wommersom and Tienen quartzites, this third variety has never been examined before but resembles macroscopically the other two. So an additional question arises of whether this quartzite was known by the Mesolithic people or not.

Thirty-one artefacts were collected from archaeological sites with Mesolithic age. Figure 1B shows the geographical location of these sites. Some of the samples come from sites located at a distance of 20 to 25 km from Wommersom (Fig. 1B: 1-8) and the others were found at a distance of 75 to 130 km (Fig. 1B: 9-15). Starting from macroscopic similarities, the samples are divided into two groups. The samples of group 1 are hard, brown to grey stones with small pale structures visible on the surface. The rocks feel relatively smooth with a (sub)conchoidal fracture on which light sparkling facets are observable. The surfaces of some samples show a pale patina. Based on this macroscopic description, the samples are referred to by archaeologists as "Wommersom quartzite". The samples of group 2 are dark grey to greyish brown rocks often showing a purple shine. In some cases small pale structures are visible on the surface. In contrast to the samples of the other group, the grains are clearly perceptible and many sparkling facets can be observed. Based on this description, the samples are referred to by some archaeologists as "micaceous sandstone" and by others as "Tienen quartzite".

4. Methodology

In order to obtain an unambiguous characterization of the sedimentary quartzites, the samples are examined using both petrographical and geochemical methods.

The petrographical research is carried out by optical, scanning electron (SEM) and hot-cathodoluminescence (CL) microscopy to provide direct information about the texture (like grain size and shape) and the mineralogical composition. For determining the grain size distribution of the samples, the relative contribution of grains larger and smaller than 30 µm (Dott, 1964) is estimated by point-counting (with 500 points on each thin section) under the optical microscope while image analysis is used to determine the grain size distribution of the grains larger than 30 µm (Tables 1 & 2). Image analysis is based on composite images of a two-dimensional thin section on which the maximum Feret diameter of each grain is manually measured by means of the program *Image Pro Plus*® (500 to 600 grains on each thin section) (Mertens & Elsen, 2006). In addition, gold-coated surfaces of a few samples are observed using a JEOL JSM 6400 SEM with an accelerating voltage of 15 keV and a current of 300 µA. For the geological samples (G1-3, 1-6, 1-8, 6-1, 7-2, 7-7 and 7-8) a fresh fractured surface is used, in contrast with the raw surface of the archaeological samples (A1-2, 2-3, 3-1, 3-2, 3-3, 4-2, 5-1, 5-3, 6, 7, 8, 9-1, 9-2, 10, 11-1, 11-2, 12, 15-1, 15-2 and 15-3). This is because of the need for a non-destructive analysis. Finally the petrographical observations with the optical microscope are supplemented by Simon-Neuser HC3-LM hot-CL

		Texture		*Composition (ICP-OES)*						*Composition (pXRF)*		
Sample no.	Group	% grains < 30 µm	Av. size grains > 30 µm	Al_2O_3	Ba	Fe	Sr	TiO	Zr	$Fe_{(x)}/Fe_{(G2-1)}$	$Ti_{(x)}/Ti_{(G2-1)}$	$Zr_{(x)}/Zr_{(G2-1)}$
		%	*µm*	*wt%*	*µg/g*	*wt%*	*µg/g*	*wt%*	*µg/g*	-	-	-
A1-1	1	82	55	0.21	99	0.14	16	1.41	598	4.9	0.9	0.7
A1-2	1	-	-	0.19	100	0.11	16	1.32	564	5.3	1.2	1.2
A1-3	1	83	53	0.20	87	0.18	14	1.40	494	0.6	1.2	1.1
A2-1	1	84	52	0.24	104	1.02	16	1.38	559	9.2	1.4	0.8
A2-2	1	-	-	0.19	112	0.14	16	1.19	527	4.4	1.1	1.0
A2-3	1	-	-	0.19	195	0.79	17	1.21	506	1.4	1.2	1.0
A3-1	2	19	101	0.08	124	0.32	9	0.34	869	6.2	0.2	1.1
A3-2	2	-	-	0.35	175	0.36	15	0.32	839	2.1	0.3	1.3
A3-3	1	69	62	0.18	105	0.11	16	1.10	656	2.0	0.9	1.0
A4-1	1	84	62	0.21	103	0.26	16	1.57	566	1.8	1.9	1.2
A4-2	1	-	-	0.20	105	0.09	16	1.53	660	2.3	1.5	1.4
A4-3	1	-	-	0.19	95	0.15	15	1.44	642	0.7	1.1	1.1
A5-1	1	83	66	0.30	130	0.31	19	2.34	588	2.0	1.1	0.9
A5-2	1	79	55	0.18	98	0.12	15	1.63	653	2.4	1.0	0.9
A5-3	1	-	-	0.24	92	0.21	15	2.13	752	3.8	1.3	1.3
A6	1	54	66	0.17	96	0.09	15	1.06	740	1.8	1.0	1.3
A7	1	84	52	0.22	95	0.14	15	1.53	704	4.0	1.2	1.2
A8	1	84	54	0.20	98	0.25	16	1.50	543	0.5	0.9	0.8
A9-1	2	19	110	0.08	117	0.08	10	0.27	697	2.4	0.2	0.9
A9-2	2	-	-	0.09	141	0.17	11	0.25	724	0.6	0.1	1.0
A9-3	1	-	-	0.22	97	0.40	16	1.45	577	2.4	1.5	1.2
A9-4	1	59	65	-	-	-	-	-	-	0.9	0.7	1.1
A10	1	-	-	-	-	-	-	-	-	1.0	1.5	0.7
A11-1	2	-	-	0.08	141	0.32	9	0.30	755	0.7	0.3	1.3
A11-2	1	-	-	0.22	94	0.10	15	1.23	397	0.8	1.1	0.8
A12	1	-	-	0.23	98	0.76	17	1.58	628	1.5	1.4	1.2
A13	1	72	54	-	-	-	-	-	-	0.8	1.4	1.3
A14	1	-	-	0.20	106	0.14	17	1.47	633	2.2	1.4	1.2
A15-1	2	12	109	0.08	100	0.15	10	0.27	802	1.1	0.3	1.7
A15-2	1	-	-	-	-	-	-	-	-	1.2	1.4	1.2
A15-3	1	-	-	-	-	-	-	-	-	0.7	1.2	0.6

Table 2. Analytical data of the archaeological samples for the texture and composition (ICP-OES and pXRF) with indication of the group. For the pXRF-data, each sample (x) is normalized by means of sample G2-1 to obtain ratios.

with a potential of 13.5 keV, current of 0.20 mA to 0.30 mA and vacuum of < 10^{-3} Torr to distinguish the overgrowths from their detrital quartz grains.

The geochemical data of the samples are obtained by an inductively coupled plasma – optical emission spectrometry (ICP-OES) analysis with a Varian 720 ES instrument. After removing the exposed surface, each sample is pulverized using a SPEX mill. Although only 100 mg is needed for the bulk chemical analysis, up to 500 mg is prepared to aim at chemical homogenization. The lithium metaborate procedure (Suhr & Ingamells, 1966) is exerted on these pulverized homogenous samples to determine the major elements Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, and TiO_2 (in wt%) and the trace elements Ba, Cr, Cu, Sc, Sr and Zr (in µg/g) (standards: NBS 688, AGV-1, BCS 267, DR-N and NBS 278). Only the elements Al_2O_3, Ba, Fe_2O_3, Sr, TiO_2 and Zr are used for the characterization of the quartzites because of the high precision of less than 2% (Tables 1 & 2). A discriminant function analysis is used to determine which elements most discriminate between the quartzite varieties. This multivariate technique is suitable to distinguish groups with respect to the average of specific variables. A maximum separation between different groups can be automatically obtained by means of optimal linear combinations of certain variables, the so called discriminant functions (StatSoft Inc., 1984-1994).

Finally the samples are examined with a portable X-ray fluorescence (pXRF) spectrometer to determine the chemical composition of the rocks in a non-destructive and fast way (Tables 1 & 2). The measurements are performed on a BRUKER TRACER III-SD instrument with a radiation time of one minute in vacuum conditions between 1 and 40 keV and 10.90 µA (with a Rh X-ray tube). The method consists of a qualitative and quantitative analysis based on the connection between the concentration of an element in a sample and the intensity of that element in the X-ray spectrum (Potts & West, 2008). XRF measurements are highly matrix dependent due to different absorption coefficients of the elements, requiring standards with a similar composition to the unknown material for quantitative analysis (Skoog et al., 2007). Nevertheless in order to study the chemical data in the absence of suitable standards, all samples will be normalized by means of a random sample (i.e. sample G2-1) to compare the ratios. As in the petrographical analyses a freshly fractured surface of the geological samples is measured, to avoid contamination in contrast with the raw surface of the archaeological samples, to prove the non-destructive nature of the technique. All samples have a surface area greater than the spot size of the detector (> 7 mm²).

5. Results

5.1. Petrography

5.1.1. Geological samples

The mineralogical very mature sedimentary quartzites consist almost completely of the mineral quartz. The Wommersom quartzite is characterized by a limited number of large quartz grains floating in a fine-grained silica matrix (Fig. 2: A1, 2) exhibiting a floating (F) fabric when using Summerfield's (1983) terminology. The rather irregular shape of the quartz grains is caused by fretting of the grain surfaces and sometimes by secondary overgrowths around the detrital grains. On the other hand, the Tienen quartzite consists mainly of large interlocking quartz grains (Fig. 2: B1, 2) with irregular shapes due to common authigenic overgrowths exhibiting a grain-supported (GS) fabric. The sizeable cavities between the quartz grains are eye-catching and often show a typical triangular shape. Finally the unknown dark quartzite combines features of both the Wommersom and Tienen quartzite. The rock is composed of several large quartz grains with frequently authigenic overgrowths floating in a very fine-grained silica matrix (Fig. 2: C1, 2).

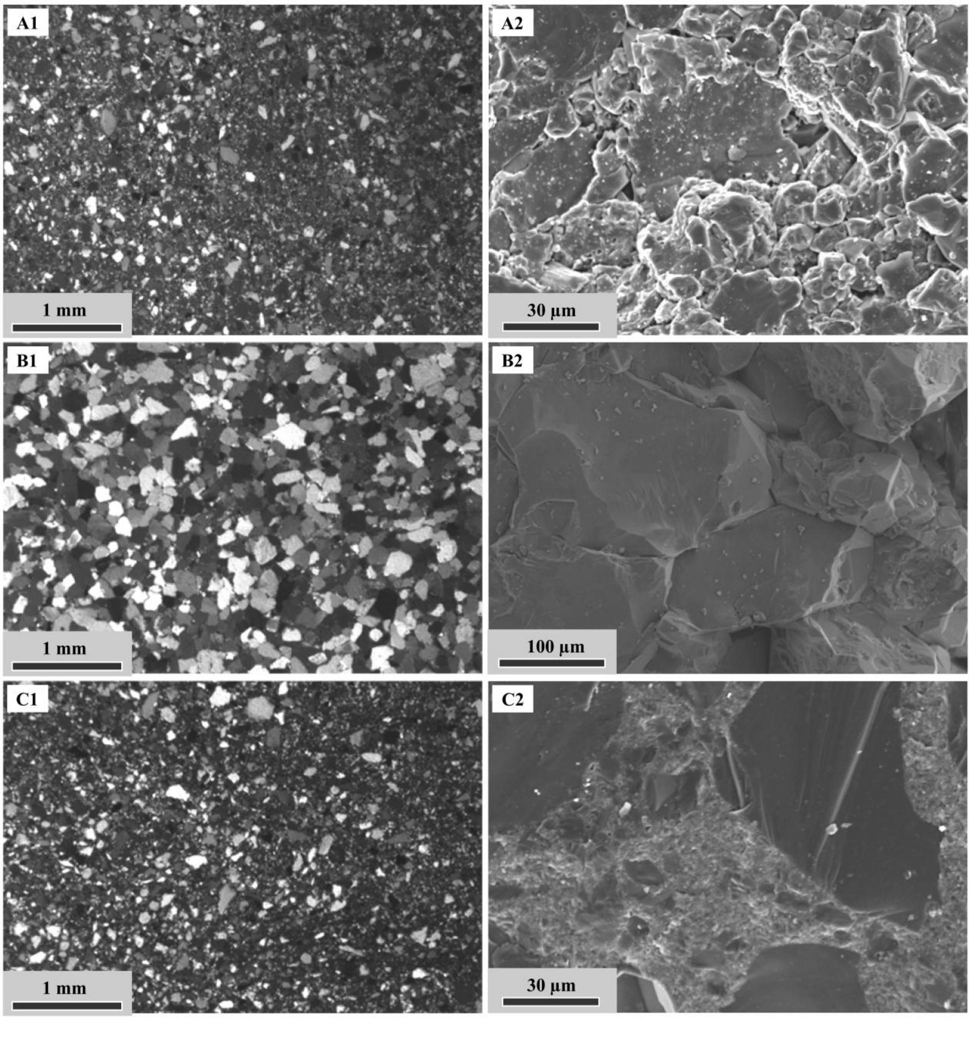

Figure 2. Microphotographs under (1) the optical microscope (crossed-polarized light) and (2) the scanning electron microscope of (A) the Wommersom quartzite G1-3, (B) the Tienen quartzite G6-1 and (C) the unknown quartzite G7-7.

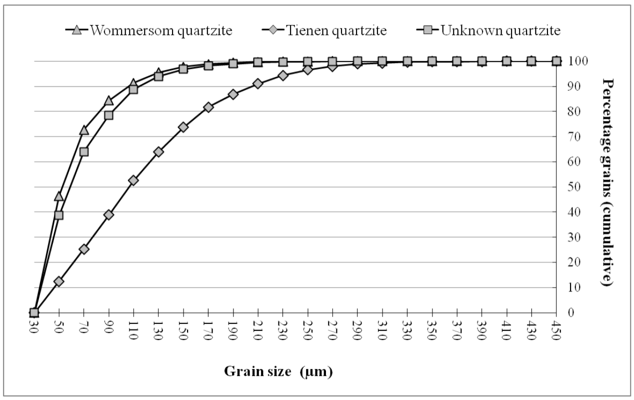

Figure 3. Average two-dimensional grain size distribution of the quartz grains larger than 30 µm (cumulative graph) of the Wommersom, Tienen and unknown quartzite.

The above mentioned texture differences can be emphasized by determining the (two-dimensional) grain size distribution of the quartzites. In accordance with the aim of the study, the size of the detrital grains including the secondary overgrowth is determined. Using point counting we could deduce that the quartzites are clearly distinguishable showing volume percentages of the grains smaller than 30 µm between 53% and 83% for the Wommersom quartzite (average of 66%), at most 7% for the Tienen quartzite (average of 3%) and between 26% and 40% for the unknown quartzite (average of 35%). The grain size distribution of the quartz grains larger than 30 µm is determined by means of image analysis. The results can be observed in Fig. 3. The distribution of each quartzite variety is non-symmetric because of the larger amount of smaller grains showing a mean value of 62 µm for the Wommersom quartzite, 117 µm for the Tienen quartzite and 68 µm for the unknown quartzite (Table 1). Consequently we could infer that the grain size distributions of the Wommersom and unknown quartzite are broadly the same whereas the grain size distribution of the Tienen quartzite is considerably different with a higher mean value and a greater dispersion than the other two quartzite varieties. As may be seen from Fig. 2, this can also be observed on the SEM-images.

In addition to quartz, the sedimentary quartzites contain small amounts of chert fragments, feldspar, accessory minerals (like zircon, rutile and tourmaline), iron oxides (like goethite, limonite and hematite), organic matter and other impurities. Some small differences between the quartzites can be noted. Only in the Wommersom quartzite, numerous small rutile crystals are occurring in the fine-grained quartz matrix beside the 'big' rutile crystals. Furthermore the Wommersom quartzite (and also the unknown quartzite) is characterized by numerous minute impurities in the fine-grained silica matrix and by the presence of bioturbations (root fragments) and oxidized organic matter which are totally absent in the Tienen quartzite. Nevertheless, the literature reports the presence of numerous traces of roots visible on the surface of the Tienen quartzite (Nijs & De Geyter, 1984).

5.1.2. Archaeological samples

The microscopic texture of the samples belonging to group 1 consists of a few irregular shaped large grains floating in a fine-grained silica matrix. The percentage of grains smaller than 30 µm varies between 54% and 84% with most of the samples showing a rather large percentage. The average size of the grains larger than 30 µm ranges between 52 µm and 66 µm (Table 2). The rocks mainly consist of quartz with small amounts of feldspar, zircon, tourmaline, rutile and sometimes chert fragments. Furthermore iron oxides, organic matter and numerous minute impurities are present in the fine-grained silica matrix and frequently bioturbations can be observed.

The samples of group 2 are composed of many isolated large grains, often in combination with authigenic overgrowths and surrounded by very fine grains. The percentage of grains smaller than 30 µm is around 17% which is relatively low and the average size of the grains larger than 30 µm lies between 101 µm and 110 µm (Table 2). The rocks mainly consist of quartz with small amounts of feldspar, chert fragments, zircon, tourmaline, rutile and iron oxides. In most cases the matrix is composed of very fine-grained quartz but also sometimes of chalcedony. Also organic matter, bioturbations and fine-grained opaque impurities are missing from all samples.

5.2. Geochemistry

5.2.1. Geological samples

The chemical composition of the sedimentary quartzites is rather simple, comprising more than 96 wt% silica with minor concentrations of titanium, aluminium and iron oxides (Table 1). In addition to these major elements, the trace elements zirconium, strontium and barium show evidence of typical concentrations for each quartzite variety. The Tienen quartzite is easily recognisable due to the very low concentrations of the chemical elements except silica, in contrast with the relatively high amounts in the Wommersom and unknown quartzite. The unknown quartzite differs from the Wommersom quartzite by a higher content of zirconium and barium.

Using a forward stepwise discriminant analysis, it was found that the elements zirconium, titanium and iron were the most appropriate variables to separate the different groups as much as possible (with Wilks' Lambda = 0.012). Subsequently this model supplies two statistically significant discriminant functions with the first function accounting for over 80.7% of the explained variance and for that reason being the most important one. From the discriminant plot (Fig. 4), which is a scatterplot with the two discriminant functions, it is seen that the first function mostly discriminates between the Tienen quartzite and the two other quartzites while the second function provides a difference between the unknown quartzite and the other two.

To judge the usefulness of the geochemical technique pXRF, the results (Table 1) are compared with the data of the ICP-OES for the geological samples. First there is a good correlation in case of the element titanium measured with ICP-OES and pXRF ($R^2 = 0.83$). The minor deviation between the two methods can be attributed to the fact that pXRF is carried out at one specific point of the sample while the measurements with the ICP-OES comprise more average values. Also the results for zirconium yield a relatively good correlation ($R^2 = 0.71$), contrary to the case of the element iron ($R^2 = 0.32$). Summarized, the analysis by pXRF provides relatively good results with respect to the titanium and zirconium content of the samples. Hence the different quartzites can be distinguished in a similar way as in the case of the ICP-OES technique.

5.2.2. Archaeological samples

With respect to group 1, the titanium content measured with ICP-OES ranges from 1.0 wt% to 1.6 wt% with the exception of two samples from Rillaar (samples A5-1 and A5-3) which exhibit higher values (Table 2). The zirconium concentrations are between 400 µg/g and 750 µg/g and iron shows values ranging

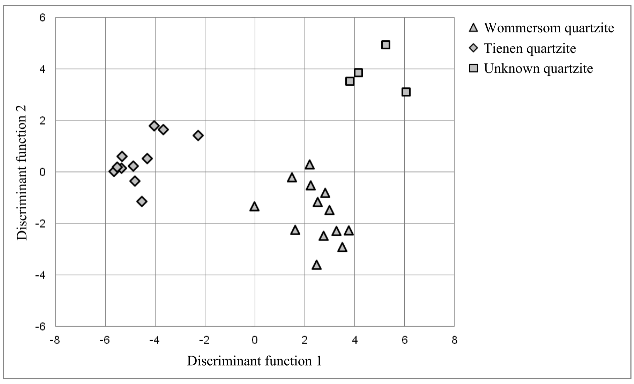

Figure 4. Discriminant plot using linear combinations of the variables Zr, TiO_2 and Fe_2O_3 to separate the different quartzites with discriminant function 1 = -8.90 + 0.008 Zr (µg/g) + 2.95 TiO_2 (%) + 15.64 Fe_2O_3 (%) and discriminant function 2 = – 1.72 + 0.010 Zr (µg/g) – 4.57 TiO_2 (%) – 7.08 Fe_2O_3 (%).

from 0.1 wt% to 1.0 wt%. Furthermore, the concentrations of aluminium ranges between 0.15 wt% and 0.30 wt%, barium between 85 µg/g and 200 µg/g and strontium between 13.5 µg/g and 18.5 µg/g.

The concentrations of the elements for group 2 measured with ICP-OES are clearly different with a relatively low titanium content of about 0.3 wt%, zirconium around 800 µg/g and iron in the range 0.1 wt%-0.4 wt%. In addition, aluminium shows a concentration around 0.08 wt% except for one sample of Holsbeek (sample A3-2) with a value of 0.34 wt%, barium lies between 100 µg/g and 140 µg/g with an outlier of 173 µg/g in case of sample A3-2 and strontium around 10 µg/g with an outlier of 15 µg/g in case of sample A3-2.

Contrary to the results of the geological samples, there appears a less good correlation between the results of ICP-OES and pXRF (titanium: $R^2 = 0.65$ and zirconium: $R^2 = 0.24$).

6. Discussion

The results of the archaeological samples from group 1 match very well with the results of the geological samples of the Wommersom quartzite. The petrographical composition of the samples is almost the same for the archaeological and geological samples. Also the texture is quite similar which is confirmed by the percentage of grains smaller than 30 µm and the average size of grains larger than 30 µm. Nevertheless one can notice from Table 2 that these values are relatively low in comparison with the geological samples. Webb and Domanski (2008) have proven that there is a strong positive correlation between the amount of matrix and the compressive strength for comparable materials. The very mature mineralogy together with the small grain size of the sedimentary quartzites increase the compressive strength of the tools and in this way the flaking quality. This makes the rocks suitable to shape which may explain why they were more frequently used as a raw material for prehistoric tools.

With respect to the geochemical data some problems arise because of the high concentrations of iron in the samples which makes the statistical analysis with the elements titanium, zirconium and iron less successful (Fig. 5A). Probably this high iron content is due to contamination of the pulverized materials by eroded material of the raw surface. This could not be avoided because of the small dimensions of the artefacts. A possible solution to this problem is to perform the discriminant analysis with the element aluminium instead of iron which yields statistically significant results as well (with Wilks' Lambda = 0.017). On the plot in Fig. 5B one can distinguish relatively well the three geological quartzite groups from each other and the archaeological samples of group 1 match well with the group of Wommersom quartzite. There are two samples (from Rillaar, already mentioned above) which immediately catch the eye by their higher values of both the discriminant functions due to higher titanium concentrations. Finally the titanium and zirconium contents measured by pXRF also point in the direction of the group of the Wommersom quartzite but this assignment is less obvious than with ICP-OES. Probably the differences between the results of pXRF and ICP-OES can be attributed to factors related to the nature of the samples. In the analysis with pXRF, the raw surface of the samples was measured instead of a fresh fractured surface. The degree of corrosion and the surface roughness are two important factors to take into account. Also the size of the samples can have an influence on the measurement since the artefacts are very small in comparison with the large fragments of the geological samples.

The archaeological samples of group 2 do not correspond with the Wommersom quartzite nor with the Tienen or unknown quartzite. Based on the texture and petrographical composition, the samples resemble well the studied quartzite varieties but many differences can be noticed. The same conclusions can be drawn from the statistical discriminant function analysis where the samples do not match with one of the quartzite groups except for the sample of Holsbeek (A3-2) (Fig. 5B). Unfortunately sample A3-2 is assigned to the wrong quartzite group, the unknown quartzite, due to its higher aluminium concentration. As a consequence, the origin of these artefacts is still unknown but in view of the petrographical and geochemical similarities to the studied quartzites, one can suppose that the source is probably situated in the vicinity of Tienen. Like the unknown quartzite, these rocks may possibly be a variety of the Tienen and Wommersom quartzite. However, the larger average grain size, and hence the less good flaking quality of these rocks, may be the reason for their rather limited use as prehistoric tools. The choice of a quartzite type was clearly influenced by its petrographical properties, besides proximity of source and availability of material (Webb & Domanski, 2008).

On the basis of these findings, it is conceivable that there is a high intra-formation variability of the sedimentary quartzites over a larger region in the vicinity of Wommersom. The macro- and microscopic data indicate that the sedimentary quartzites are most probably groundwater silcretes, which are related to the presence of a contemporary or former drainage feature or groundwater table, with the simple massive structure of the silicified rocks and the absence of pedogenic features being the most prominent indications (Nash & Ullyott, 2007). The variability in petrographical and geochemical features of the sedimentary quartzites can be attributed to a number of factors such as spatial variations in composition of the host sediment and the complex processes in the formation of the silcretes. Further research is required to confirm this statement.

7. Conclusion

In the vicinity of Tienen, numerous silicified rocks are found within the fluvial deposits of the Tienen Formation, earliest Eocene. The characterization study of the known Wommersom and Tienen quartzite and an unknown quartzite indicates that the rocks can be distinguished by means of the petrographical and geochemical data. The best results are derived from optical microscopy by determining the grain size distribution of the samples and from ICP-OES, in particular the elements titanium (derived from the mineral rutile), zirconium (derived from the mineral zircon), iron and/or aluminium, with the aid of discriminant function analysis. But, as non-destructive and fast methods are most suitable in an archaeological study, the results of the SEM and pXRF are of great importance. Both techniques

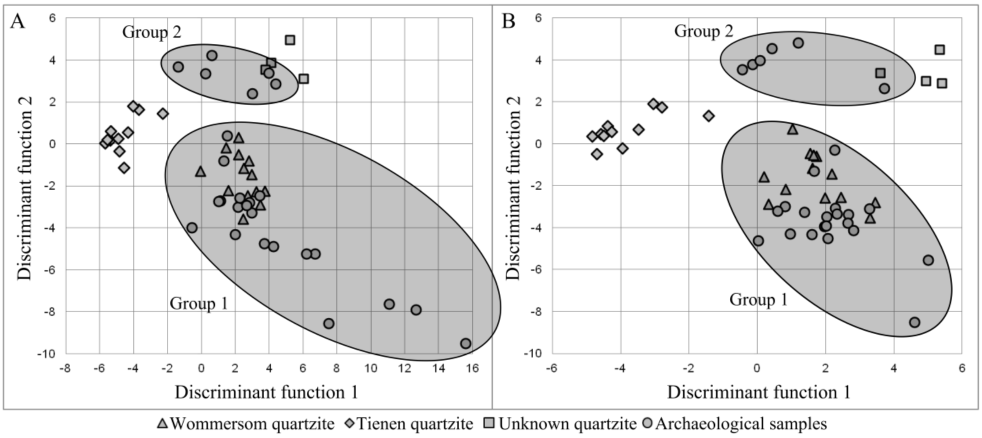

Figure 5. Discriminant plots using linear combinations of the variables (A) Zr, TiO_2 and Fe_2O_3 with discriminant functions see Fig. 4 and (B) Zr, TiO_2 and Al_2O_3 with discriminant function 1 = -8.08 + 0.009 Zr (µg/g) + 1.78 TiO_2 (%) + 10.65 Fe_2O_3 (%) and discriminant function 2 = – 1.01 + 0.009 Zr (µg/g) – 4.51 TiO_2 (%) – 7.66 Fe_2O_3 (%) to separate the different quartzite groups with adding the archaeological samples of group 1 and 2.

certainly provide useful information, in particular, the titanium signal of the pXRF, but nevertheless destructive methods are still inevitable for the characterization of the samples.

Two different quartzite varieties can be found at several archaeological sites of Mesolithic age in Belgium. A large number of artefacts are investigated using the criteria of the studied sedimentary quartzite varieties. Based on results related to texture and composition, we can conclude that the fine-grained Wommersom quartzite most probably represents the raw material for the majority of artefacts (group 1). However additional investigations of a larger number of different quartzite types should reveal whether the Wommersom quartzite is only outcropping at the Stone Mountain in Wommersom. Also more research is needed to find the supply source of the other artefacts (group 2) which, just like the considered unknown quartzite, are supposedly varieties of the Tienen and Wommersom quartzite occurring in the same area.

8. Acknowledgements

We would like to express our gratitude to P. Crombé for supplying a part of the archaeological artefacts and to F. Gullentops and G. Andries in the search for suitable geological samples. We are also very grateful to the research group of the division Geology of the University of Leuven (Belgium), especially H. Nijs for preparing the thin sections, E. Vassilieva for her help with the ICP-OES measurements and D. Braekmans for his assistance in using the pXRF.

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Manuscript received 17.03.2012, accepted in revised form 07.05.2012, available on line 15.06.2012