PRE-INDUSTRIAL GLASSMAKING IN SWISS JURA: THE REFRACTORY EARTH FOR THE GLASSWORKS OF DERRIÈRE SAIROCHE (CT. BERN, 1699-1714)

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Abstract

Refractory fragments of the melting furnace and crucibles of the glassworks of Derrière Sairoche are compared to the local raw materials. Geochemical, petrographical and grain-size affinities between the archaeological and natural materials demonstrate that local clayey sands (Hupper, Sidérolithique) were exploited to produce refractory materials for the melting furnace and crucibles. Availability in situ of good raw materials made unnecessary any tempering. Its high eutectic point (~ 1600°C) allowed good performances at temperatures up to 1500°C to work glass and low Fe_2O_{3tot} concentrations avoided batch-glass contamination.

Key words: Swiss Jura, pre-industrial glassmaking, refractory materials, Sidérolitique

INTRODUCTION

In Middle Ages the spreading of wood-ash glass production in northern Europe implied relevant changes from the natron glass produced in antiquity. Their high CaO (10-20 wt.%) required higher melting temperatures (up to 1400°C) than the 1000-1100°C for the ancient Na-Ca glasses (Turner 1956, Cable and Smedley 1987, Cable 1998, Brill 1999, Henderson 2000, Stern and Gerber 2004). In order to reach temperatures up to 1400°C, a more efficient pyrotechnology and more performing refractory materials were necessary (Charleston 1978, Cable 1998, Eramo in press).
Recent studies on the pre-industrial glassworks of Derrière Sairoche (1699 – 1714) discusses some aspects of glass technology in the Bernese Jura (Gerber 2003, Stern and Gerber 2004, Eramo in press). In this area, dozens of glassworks were active during the second half of the XVII century and the first half of the XVIII

century (Sveva Gai 1991, Sternini 1995). Here, glassmakers found pure quartz sand (see below), extensive forests and streams to transport wood (Amweg 1941, Michel 1989, Gerber et al. 2002). Stern (1991) reports a Ca-K composition for glasses coming from this area and made glass replica using local quartz sand and wood ash (Stern and Gerber, 2004). Several outcrops of pure quartz sand and refractory earth are historically known in proximity of Derrière Sairoche (Schlaich 1934, Amweg 1941); however, in order to better understand the role of the raw materials and their influence on local glass technology, an archaeometrical characterization appeared necessary. In a recent paper Eramo (submitted) showed that the crucibles samples of Derrière Sairoche were not tempered with recycled crucibles and refractory fragments as suggested by old glassmaking treatises. Nevertheless, processing of the raw materials can not be excluded (e.g. sand tempering). This article attempts to prove, by a multivariate analysis of the grain-size and chemical data, whether or not the local raw materials (*Hupper*, *Sidérolithique*) could be naturally suitable to produce the crucibles and the refractory and whether or not there are compositional differences between crucibles and refractory samples due to technological reasons.

THE SIDÉROLITHIQUE

The name *Sidérolithique* was introduced in geological literature by Thurmann (1836) and is still used to indicate a complex geological unit deposited during the Eocene (Lower Oligocene?) on the karstified surface of the Mesozoic limestones in Jura region. The accumulation of different lithologies (i.e. kaolinitic clays, iron pisoliths, quartz sand, etc.) occurring in karstic pockets, rarely as continuous beds (e.g. valley of Delémont) (Fleury 1909, Schlaich 1934, von Moos 1941, Aubert 1975, Pfirter 1997) marks the stratigraphic limit between Mesozoic limestones and Molasse sediments throughout the Jura region (Fig. 1). Generally, the outcrops are distributed along the flanks of the valleys of the Jura belt. Since these terrains do not have lateral continuity, they may occur in several associations or some lithologies may be lacking. The Sidérolithique is composed of red or yellow clays (rarely white, green or violet) called *Bolus*; levels rich in iron pisolithes (*Bohnerz*); quartz sands which can be sometimes clayey (*Hupper*) and calcareous conglomerate (*Gompholithe*) containing iron pisolithes.

The chemical composition of Hupper varies as a function of clay content. Al_2O_3 concentrations up to 15 wt% for clay-rich samples were reported by De Quervain (1969). Hoffmann and Peters (1969) report kaolinite as prevalent clay mineral (70 – 90 wt. %) and illite and montmorillonite as minor component (0 – 10 wt.%) in the grain-size fraction finer than 2 μm. Hupper layers rich in clay were quoted as suitable for refractory materials by Tobler (1897) and Fleury (1909). Their melting point exceeds 1500°C (Von Moos 1941, Hoffmann and Peters 1969). On the other hand, the quartz sand (up to 99 wt% of SiO_2) was exploited since the Middle Ages as raw material for glass (Fleury 1909, Amweg 1941, Kündig et al. 1997).

SAMPLING STRATEGY

The glassworks of Derrière Sairoche is located in the valley of Chaluet (Bernese Jura) with several outcrops of Hupper near by (Fig. 1). The exploitation of some of these outcrops for glass, refractory and ceramic production is known in literature (Fleury 1909, Schlaich 1934, von Moos 1941, De Quervain, 1969). In order to prove the utilization of natural raw materials suitable to produce the crucibles and the refractory, only the outcrops having somewhat plastic materials were chosen for sampling (Fig. 1). In some cases it was possible to sample sediments of different grain-size distributions (Lac Vert, Souboz-Montaigu and Sur Frête). Nine-teen samples of Hupper were collected (Tab. 1).
The analytical methods used in this study and a discussion about the precision of the grain-size analyses are described in Appendix 1.

RESULTS

Hupper

Petrography and mineralogy: The clastic portion of the samples consists of mono- and rare polycrystalline quartz. Grains are rounded to well rounded (Fig. 2b). The argillaceous matrix consists of kaolinite (XRD) and is sometimes brown due to iron-hydroxides and oxides. Some calcite is present in ER136, 253 and 256, and ferruginous aggregates were detected in ER126 and 248. This latter sample shows few quantities of K-feldspar, plagioclase, muscovite/illite and chlorite (Tab. 1).

Chemistry: Bulk chemical compositions of the samples are characterized by high percentages of SiO_2. Except for Al_2O_3, the other oxides are generally below 1 wt%. On a whole, the concentrations of the trace elements are low (< 100 ppm), but for Zr (Tab. 2).

Grain-size analysis (sieving): Table 3 displays grain-size data concerning Hupper. The cumulative frequency curves (Fig. 3) show the grain-size variability in the sampling area. Almost all of the samples are poor of coarse sand (-1ϕ and 0ϕ) and show a large dispersion of fine sand (3ϕ and 4ϕ) and "silt + clay" (pan) percentages. ER139 and 248 consist of more then 95 wt% of silt and clay. The samples from Lac Vert and Souboz – Montaigu show the widest grain-size variability in the same outcrop.

Crucibles and refractory

As reported by Eramo (in press; submitted) both the refractory and the crucible fragments are composed almost completely of SiO_2 and Al_2O_3. Weight percentages of Fe_2O_{3tot} and TiO_2 are generally below 1 wt% (Tab. 2). Monocrystalline and rare polycristalline quartz were detected as non-plastic inclusions originally present in the ceramic body (Fig. 2a). Quartz grains, partially substituted by tridymite and cristobalite, are surrounded by a low-birefringent matrix composed of cristobalite and mullite.

<u>Grain-size analysis (thin section):</u> The results of the grain-size analysis in thin section of the crucible and refractory fragments are shown in Table 4. Both types of samples are characterized by few

percentages of coarse sand and by an increase of standard deviation values for finer size classes. The cumulative frequency curves of crucible fragments are similar to one another (Fig. 4a) and show 3ϕ and 4ϕ values more dispersed than the refractory samples (Fig. 4b). The crucible samples ER23, 48 and 52 are richer in silt and clay than the other.

DATA PROCESSING

On a whole, the petrographical and chemical features of the Hupper samples here analyzed are consistent with those of the refractory and crucible samples reported by Eramo (in press, submitted). In both natural and archaeological materials, monocrystalline quartz forms their actual or original non-plastic portion, whereas Al_2O_3 percentages are related to actual or pre-firing kaolinite.
Furthermore, the grain-size analysis carried out on both the archaeological and natural materials shows that most of the samples have similar size-distribution curves (Figg. 3 and 4).
A multivariate statistical analysis using both chemical and grain-size variables appeared useful to compare the Hupper with the

crucibles and refractory samples. Principal component analysis (PCA) was carried out on the entire dataset (84 samples: 43 crucibles, 22 refractories, 19 Hupper) using chemical and grain-size variables which have few missing values and higher variance (Tab. 5). The “< 0.01” in the data set were approximated to 0.01. Since the eleven variables (SiO_2, TiO_2, Al_2O_3, Fe_2O_{3tot}, MgO, CaO, K_2O, Cr, Sr, Zr, 2ϕ, 3ϕ, 4ϕ and *pan*) used for the PCA are expressed in different units, standardization was necessary to ensure a similar order of magnitude and variance. The contributions to the total variance and the loadings of the first three PCs are shown Table 6. PC1 is very strong and accounts for 41.78% of total variance. This component is characterized by negative loadings of SiO_2 and sand fractions and by the association of Al_2O_3, K_2O, Cr and pan fraction. Although some associations occurring in PC1 are still present, PC2 features higher variance of 2ϕ and 4ϕ. Three ϕ is neutral in both PC2 and PC3. While PC2 is characterized by high loadings of 2ϕ and 4ϕ, PC3 features high loadings of Zr, MgO, Al_2O_3 and Sr. The component plot PC1 vs PC2 (Fig. 5a) shows strong positive correlation between K_2O and pan fraction, TiO_2 and Zr, Fe_2O_{3tot} and MgO and between SiO_2 and 3ϕ. The latter association of variables is negatively correlated to K_2O and pan fraction and in a lesser extent to the other variables located in the positive quadrants of the diagram. The PC1 vs PC3 diagram shows less obvious correlation, such as Zr – MgO or Sr – Al_2O_3 (Fig. 5b). These relations between variables may be interpreted as the chemical and grain-size signature of the studied materials. PC2 provides a more grain-size-sensitive fingerprint of the dataset, whereas PC3 is rather chemistry-sensitive. The Al_2O_3, K_2O and pan fraction positive correlation reflects the presence of these two oxides in clay minerals, whereas those of CaO, MgO and Sr may be explained as a co-occurrence in minor amounts of calcareous clasts eventually present. Although PC1, PC2 and PC3 account only for 66.07 % of total variance, their bivariate plot shows a close distribution and a complete overlap of the refractory and crucibles data points (Fig. 5c, d). On the contrary, Hupper data points are more dispersed and only ER125 and 251 fall in the region of crucible and refractory if PC1 and PC2 are considered (Fig. 5c), whereas in the PC1 vs PC3 plot also ER131, 249, 250 and 254 fit the archaeological materials (Fig. 5d). According to the position of the data points, it can be inferred that the archaeological materials are characterized by high content of fine quartz sand and low content of clay, Fe-oxides and calcareous fragments. Summarizing, a large number of natural samples fit the archaeological materials from a chemical point of view, whilst the grain-size distribution is a more stringent factor to fit the archaeological materials.

DISCUSSION AND CONCLUSIONS

Grain-size analysis by sieving and by point counting on natural and archaeological samples respectively, added the grain-size distribution variable as a tool non commonly used in provenance studies of ceramic materials. Multivariate statistics involving chemical and grain-size variables revealed that the refractory and the crucible samples analyzed were made with the same raw materials.

Chemical, petrographical and grain-size characteristics of the Hupper samples collected in proximity of Derrière Sairoche show their compatibility with crucibles and refractory. It was quoted in the introduction chapter that there are historical notices about refractory earth and pure quartz sand exploitation in Berner Jura. Even if it was not possible to locate exactly the old pits, since they are no more accessible today, it was shown that the analyzed samples cover a wide grain-size and chemical range. Only ER125 and ER251 are really consistent with the archaeological materials if the first two PCs are taken into account. Sur Frête (ER125) is the nearest Hupper deposit to the glassworks, whilst Monible-Côte lies about 15 km away. It is reasonable to think of Sur Frête as the most probable source of clayey sand. However, the occurrence of other suitable raw materials at a greater distance signals that these features may be found in several places in the area. It must be kept in mind that the heterogeneity of Hupper and its stratigraphical position made possible the occurrence of the good raw material almost everywhere in the Swiss Jura. Furthermore, availability in situ of good clayey sand made unnecessary any further treatment. The absence of recycled refractory and crucible fragments in refractory and crucible samples (Eramo submitted), as reported by old glassmaking treatises, suggests that this practice was not economically and technologically relevant because of the abundance of suitable refractory earth deposits.

The differences between crucibles and refractory samples are minimal, which indicate that the natural raw material was retained technologically valid for both. They are characterized by fine monocrystalline quartz sand which minimized the thermal expansion problems and gave more stability to the artifacts (Hübner 1991). Normative calculation of the original mineralogical compositions for the crucible fragments points to about 20 wt.% of kaolinite (Eramo submitted). This clay mineral supplied enough plasticity to the raw material to form the crucibles and bricks and to be applied as a plaster in the melting chamber. Moreover, its low shrinkage reduced the formation of cracks in the artifact increasing the mechanical resistence. Such a composition (i.e. Qtz 80 wt.% + Kln 20 wt.%) has an eutectic point of about 1600 °C and guarantees good refractory behavior in service conditions (up to 1500 °C). A low Fe_2O_{3tot} content is very important for refractory materials used in glassmaking. Even few percents of Fe_2O_{3tot} may compromise the color of glass and of course lower the eutectic point of the refractory materials.

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APPENDIX 1

Sample weight: The Hupper samples were quartered until a 75 g portion was obtained. This portion was used for sieving (50 g), for thin-section preparation (~ 5 g) and for XRD and XRF (~ 20 g, powdered).

Petrographic analysis: Five samples of Hupper (ER125, 136, 248, 250 and 255) were impregnated with epoxy resin to obtain thin sections, which were analyzed under a Carl Zeiss Standard polarising microscope.

X-Ray diffraction (XRD): The mineral composition was resolved by XRD analyses carried out on a Philips PW1800 diffractometer with Cu-K_{α} radiation at 40 kV and 40 mA (step angle of 0.02°, 2θ from 2° to 65°, measuring time 1 s per step).

Loss on ignition (LOI): 3 g of dry powdered sample were calcined at 1000°C for one hour and were weighed to determine the LOI.

X-Ray fluorescence (XRF): Analyses were carried out on glassy tablets, which were prepared by melting 0.700 g of calcined samples, 0.350 g of Li fluoride and 6.650 g of Li tetraborate at 1150°C in a Pt crucible. Bulk chemical analyses for major and trace elements were performed by a Philips PW 2400 X-ray fluorescence spectrometer equipped with a Rhodium X-ray tube. Since the standards used do not cover the very high percentages of SiO_2 in the samples, deviations up to 4 wt.% from the 100 wt.% occur (Tab. 2)

Grain-size analysis by sieving: Grain-size distribution data were obtained by wet sieving. Fifty grams of each Hupper sample were analyzed. The samples were dispersed in water and exposed to ultra-sound waves to clean sand grains from clay. Six sieves with different opening sizes (63, 125, 250, 500, 1000 and 2000 μm) and a terminal pan to retain the < 63 μm fraction were used. The analyses were performed with the aid of a Fritsch shaker for 30 minutes per each sample. The size fractions (pan content included) were dried and weighed and their percentages were normalized to 100 wt.%. The precision of the sieving method was assessed by repeating three times the analysis on sample ER125, 136, 248, 250 and 255 (Tab. 7).

Grain-size analysis in thin section: Twenty-two thin sections of refractory materials (unit ζ, Eramo in press) and 43 of the melting crucibles (Eramo submitted) were analyzed. Moreover, five thin sections of Hupper samples (ER125, 136, 248, 250 and 255), with different grain-size distribution, were analyzed in order to estimate the precision of this method (Tab. 7). A Swift & Sons point-counter, mounted on the petrographical microscope, was used (1/3 of mm as line distance and as lateral step). The maximum apparent diameter of grains was measured with the aid of a micrometer eyepiece at x20 magnification. The same size classes as in sieving were distinguished. Between 500 and 600 points per thin section were counted as minimum number of counts necessary for routine analyses (Friedman, 1958). Grain-sizes data were reported in ϕ values (Tab. 3 and 4) and represented by cumulative frequency curves (Fig. 3 and 4).

Precision of the grain-size analyses: The two methods provide grain-size frequencies from weight percentages (sieving) and from number of counts (thin section). The grain-size frequencies obtained by the two methods on the five test samples are plotted one against each other in Fig. 6. The correlation coefficient ($r^2 = 0.98$) is highly significant and only one out of 35 observations lies outside the 95% confidence limits. Such a result shows that the grain-size analysis data in thin section have a precision comparable at the 95% level of significance with that of sieving. Underestimation of the particle size in thin section due to sectioning effect (Krumbein 1935) was not relevant in PCA because of standardisation of variables.

REFERENCES

Amweg, G., 1941, Verrerie. In: Les Arts dans le Jura bernois et à Bienne, Tome II Arts appliqués. Porrentruy.

Aubert D. (1975) - L'évolution du relief jurassien. Eclogae geol. Helv., 68/1, pp. 1-64.

Brill R.H., 1999, Chemical analysis of early glasses, Vol.2, Tables of analyses, The Corning Museum of Glass, New York.

Cable, M., 1998, The operation of wood fired glass melting furnaces. In: Prehistory and history of glassmaking technology, Ceramics and Civilisation, American Ceramic Society, Westerville.

Cable, M., and Smedley, J.W., 1987, Liquidus temperatures and melting characteristics of some early container glasses, Glass Technology, 28, 94-98.

Charleston, R.J., 1978, Glass furnaces through the ages, Journal of Glass Studies, 20, 9-33.

De Quervain, F., 1969, Die nutzbaren Gesteine der Schweiz, Kümmerly and Frey, Geographischer Verlag, Bern, 248-250.

Eramo, G., in press, The melting furnace of the Derrière Sairoche glassworks (Court, Swiss Jura): heat-induced mineralogical transformations and their technological signification, *Archaeometry*.

Eramo, G., submitted, The glass-melting crucibles of Derrière Sairoche (1699-1714 AD, Ct. Bern, Switzerland): a petrological approach, *Journal of Archaeological Sciences*.

Fleury E. (1909) - Le Sidérolithique suisse. Mém. Soc. fribourg. Sci. nat., 6, pp. 260.

Friedman G.M., 1958, Determination of sieve-size distribution from thin-section data for sedimentary petrological studies, Journal of Geology, 66, 394-416.

Gerber C., Portmann M. & Künding C. (2002) - Fours à chaux, four à fer et charbonnières dans le Jura bernois. Direction de l'istruction publique du canton de Berne. Berne, pp.132.

Gerber, C., 2003, Court-Chaluet bei Moutier (Berner Jura, Schweiz): eine Schwarzwälder Glashütte. In: Glashütten im Gespräch. Berichte und Materialien vom 2 Internationalen Symposium zur archäologischen Erforschung mittelalterlicher und frühneuzeitlicher Glashütten Europas, Ed. by Peter Steppuhn, Verlag Schmidt-Römhild, Lübeck, 64-69.

Henderson J. (2000) - The Science and Archaeology of Materials. An investigation of inorganic materials. London , Routledge, pp. 334.

Hoffmann, F. and Peters, T., 1969, Untersuchungen über die Verwendbarkeit schweizerischer Rohstoffe als Bindetone für Giessereiformsande, Beiträge zur Geologie der Schweiz, Geotechnische Serie, Lieferung 47, p. 27.

Hübner G., 1991, Natural and synthetic raw materials for technical ceramics, European Journal of Mineralogy, 3, 651-665.

Krumbein W.C., 1935, Thin-section mechanical analysis of indurated sediments, Journal of Geology, 43, 482-496.

Kündig R., Mumenthaler T., Eckardt P., Keusen H.R., Schindler C., Hofmann F., Vogeler R. and Guntli P. (1997) – Die Mineralischen Rohstoffe der Schweiz. Schweizerische Geotechnische Kommission, Bern.

Michel, G. J., 1989, Verriers et verreries en Franche-Comté au XVIII^{ème} siècle (2 tomes), Editions ERTI.

Pfirter U. (1997): Feuille 1106 Moutier. – Atlas géol. Suisse 1:25.000, Notice expl. 96.

Schlaich E., 1934, Geologische Beschreibung der Gegend von Court im Berner Jura : mit Berücksichtigung der Molassebildungen, Beiträge zur geologischen Karte der Schweiz, 26, 1-41.

Stern, W.B., 1991, Zur chemischen Analyse der Bieler Gläser, in *Hohlglasfunde der Region Biel, Zur Glasproduktion im Jura* (ed. R. Glatz), 83-86, HAUPT, Bern.

Stern, W.B., and Gerber, Y., 2004, Potassium-Calcium Glass: New Data and Experiments. *Archaeometry*, **30** (1), 137-156.

Sternini, M., 1995, La fenice di sabbia. Storia e tecnologia del vetro antico, Edipuglia, Bari.

Sveva Gai, A., 1991, La produzione del vetro preindusrtriale in Germania sudoccidentale. Stato delle ricerche e prospettive, in *Archeologia e storia della produzione del vetro preindustriale* (ed. M. Mendera), 375-410, All’insegna del Giglio, Firenze.

Thurmann J. (1836) - Essai sur les sulèvements jurassiques. 2eme chaier, avec la carte du Jura bernoise. Porrentruy.

Tobler A. (1897) – Ueber fossilführende Qarzite aus der eocäenen Hupperde von Lausen (Ctn. Baselland). Berocht über die 30. Vers. Des Oberrhein. Geol. Vereins zu Mühlhausen i. E am 22 april 1897.

Turner, W.E.S., 1956, Studies in Ancient Glasses and Glassmaking Processes. Part V. Raw Materials and Melting Processes, *Journal of the Society of Glass Technology*, 40, 277-300.

von Moos A., 1941, Über Vorkommen und Abbau von Giessereiformstoffen in der Schweiz, Eclogae Geologicae Helvetiae, 34 (2), 229-240.

Table 1 Analyzed samples of Hupper (Sidérolithique)

Sample	Coordinates	Locality	Mineral content
ER125	591.510/231.200	Sur Frête	Qtz + Kln
ER126	591.510/231.200	Sur Frête	Qtz + Kln + Goe
ER127	591.510/231.200	Sur Frête	Qtz + Kln
ER131	591.075/233.150	Lac Vert	Qtz + Kln
ER136	591.075/233.150	Lac Vert	Qtz + Kln + (Cal)
ER137	591.075/233.150	Lac Vert	Qtz + Kln
ER138	591.075/233.150	Lac Vert	Qtz + Kln
ER139	591.075/233.150	Lac Vert	Qtz + Kln + Ill/Mus
ER140	590.300/233.625	Champoz- P. Mont Girod	Qtz + Kln
ER141	590.300/233.625	Champoz- P. Mont Girod	Qtz + Kln
ER248	579.620/235.230	Forêt de Bérole	Qtz + Kln + Ill/Mus + Chl + Kf + Pl
ER249	581.370/235.510	Châtelat	Qtz + Kln
ER250	581.370/235.510	Châtelat	Qtz + Kln
ER251	582.140/235.490	Monible-Côte	Qtz + Kln
ER252	582.140/235.490	Monible-Côte	Qtz + Kln
ER253	580.100/232.700	La Fuet	Qtz + Kln + Cal
ER254	580.100/232.700	La Fuet	Qtz + Kln
ER255	586.750/235.875	Souboz-Montaigu	Qtz + Kln
ER256	586.700/236.000	Souboz-Montaigu	Qtz + Kln + (Cal)

Mineral abbreviations: Qtz = quartz, Kln = kaolinite, Cal = calcite, Goe = goethite, Chl = chlorite, Ill = illite, Mus = muscovite, Kf = potassium feldspar, Pl = plagioclase

Table 2 Chemical composition of the Hupper samples and the means and standatr deviations for the crucibles (n = 43) and the refractory (n = 22) (LOI = Loss on ignition)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_{3tot}	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Sum	LOI	Ba	Cr	Cu	Nb	Ni	Pb	Rb	Sr	Y	Zn	Zr
Sample	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
ER125	85.33	1.03	9.78	0.33	<0.01	0.04	0.10	<0.01	0.02	<0.01	96.68	3.64	<12	61	<2	24	15	14	<3	26	22	3	304
ER126	79.5	0.67	10.4	6.52	0.03	0.26	0.35	<0.01	0.37	0.08	98.26	5.14	64	97	7	14	40	27	29	107	22	49	263
ER127	92.49	0.45	3.95	0.93	<0.01	0.14	0.17	<0.01	0.08	0.03	98.29	2.36	<12	34	<2	9	19	14	4	35	17	8	267
ER131	87.71	0.47	6.95	0.53	<0.01	0.06	0.05	<0.01	0.05	<0.01	95.86	2.65	14	47	<2	11	20	10	<3	23	17	12	222
ER136	78.93	0.77	12.47	1.83	<0.01	0.88	1.52	<0.01	1.77	0.07	98.34	4.70	111	91	13	16	68	20	118	58	15	96	241
ER137	91.46	0.25	3.40	0.23	<0.01	0.09	0.05	<0.01	0.14	<0.01	95.64	1.24	<12	11	<2	7	8	12	<3	26	15	17	185
ER138	93.94	0.26	3.60	0.32	<0.01	0.19	0.07	<0.01	0.26	0.01	98.68	1.14	34	16	3	7	12	10	17	23	15	14	133
ER139	65.31	1.25	26.11	1.24	<0.01	0.28	0.32	0.07	2.29	0.26	97.28	7.32	396	121	77	21	28	114	119	328	27	35	255
ER140	95.43	0.24	2.85	0.08	<0.01	0.10	0.02	<0.01	<0.01	0.01	98.77	0.94	<12	10	7	9	8	13	<3	16	15	3	275
ER141	94.54	0.91	3.80	0.10	<0.01	0.10	0.03	<0.01	<0.01	0.01	99.54	1.25	<12	20	19	26	9	15	<3	17	16	<2	329
ER248	80.23	1.07	9.49	3	0.05	0.85	0.56	0.84	1.75	0.29	98.28	2.68	256	112	27	19	39	26	89	85	28	84	596
ER249	88.65	0.47	8.35	0.63	<0.01	0.19	0.15	<0.01	0.36	0.04	98.89	2.81	47	65	<2	9	17	18	23	35	23	13	180
ER250	85.83	0.47	8.59	0.42	<0.01	0.14	0.13	0.22	0.31	0.02	96.19	2.88	36	57	<2	11	12	9	12	32	15	9	193
ER251	81.48	0.78	13.73	0.30	<0.01	<0.01	0.09	<0.01	0.04	0.03	96.50	5.05	<12	71	<2	18	16	27	<3	38	22	4	333
ER252	90.54	0.34	5.31	0.43	<0.01	0.10	0.07	0.04	0.08	0.02	96.96	2.19	<12	26	<2	10	13	13	<3	24	17	7	199
ER253	89.55	0.46	4.22	0.73	0.03	0.24	3.72	<0.01	0.16	0.2	99.38	4.61	<12	28	<2	13	14	16	16	320	18	16	226
ER254	92.66	0.32	3.17	0.17	<0.01	0.08	0.08	<0.01	0.05	0.02	96.58	1.78	<12	<5	<2	9	9	8	<3	52	14	3	161
ER255	80.16	0.75	14.82	0.45	<0.01	0.07	0.29	<0.01	0.32	0.03	96.94	5.30	51	73	<2	13	5	20	11	61	19	5	163
ER256	94.65	0.22	3.17	0.13	<0.01	0.12	0.51	<0.01	<0.01	0.02	98.85	1.68	<12	13	<2	7	5	11	<3	12	14	<2	177
Crucibles*																							
mean	90.08	0.81	8.89	0.43	0.01	0.12	0.21	0.19	0.29	0.02	101.08	0.14	59.21	70.93	2.86	17.58	30.07	6.86	12.91	37.79	12.84	27.56	307.88
σ	1.39	0.23	1.25	0.13	0.00	0.05	0.07	0.19	0.16	0.03	0.39	0.06	15.09	8.89	2.66	4.22	12.86	2.13	6.69	44.16	1.73	88.57	40.49
Refractory**																							
mean	87.98	0.79	8.81	0.60	0.01	0.14	0.36	0.13	0.21	0.03	99.07	0.15	14.45	62.77	7.36	15.45	25.64	6.91	10.05	29.77	17.32	14.41	232.82
σ	1.49	0.24	1.21	0.26	0.00	0.11	0.12	0.19	0.11	0.01	0.58	0.07	7.60	11.34	9.59	4.04	14.72	6.23	10.34	7.08	1.49	25.41	32.83

* Chemical data for crucibles from Eramo (in press)

** Chemical data for refractory from Eramo (submitted)

Table 3 Grain-size data of the Hupper samples by sieving (wt.%)

ϕ	**< -1**	**-1 - 0**	**0 - 1**	**1 - 2**	**2 - 3**	**3 - 4**	**> 4**
mm	>2	**1 - 2**	**0.5 - 1**	**0.25 - 0.5**	**0.125 - 0.25**	**0.063 - 0.125**	**< 0.063**
ER125	0.00	0.23	1.65	9.35	22.19	21.33	45.24
ER126	7.47	0.46	1.45	9.30	19.09	9.40	52.82
ER127	0.54	0.05	2.80	16.79	28.97	21.70	29.16
ER131	0.14	0.32	1.38	6.48	24.76	1.22	65.71
ER136	0.78	0.02	0.23	8.07	14.72	9.01	67.18
ER137	0.02	0.27	3.97	26.09	38.81	15.77	15.07
ER138	0.00	0.18	2.34	25.61	39.18	15.59	17.10
ER139	0.00	0.04	0.22	0.85	1.50	2.56	94.84
ER140	0.02	0.22	3.24	35.81	21.84	16.50	22.37
ER141	0.00	0.02	1.22	23.39	34.85	23.37	17.16
ER248	0.04	0.04	0.06	0.30	0.98	1.96	96.62
ER249	0.34	0.80	4.28	16.76	25.76	14.40	37.66
ER250	0.30	0.86	3.46	15.54	28.96	14.58	36.30
ER251	0.90	0.78	1.06	7.46	33.14	19.58	37.08
ER252	0.08	0.82	4.20	16.38	28.74	19.38	30.40
ER253	3.76	0.32	1.96	7.30	16.86	22.72	47.08
ER254	0.00	0.02	1.00	5.48	15.32	16.20	61.98
ER255	0.30	0.32	0.82	2.62	21.06	8.14	66.74
ER256	1.68	0.84	4.60	20.70	35.10	17.88	19.20

Table 4 Grain-size data of the refractory and crucible samples by thin-section analysis (vol.%)

	ϕ	< -1	-1 - 0	0 - 1	1 - 2	2 - 3	3 - 4	> 4
	mm	>2	1 - 2	0.5 - 1	0.25 - 0.5	0.125 - 0.25	0.063 - 0.125	< 0.063
Crucible fragments	ER21	0.00	0.00	3.92	8.81	16.15	26.10	45.02
	ER22	0.00	0.09	1.04	12.16	22.51	26.50	37.70
	ER23	0.00	0.00	1.71	7.62	9.14	12.95	68.57
	ER24	0.00	0.77	1.93	10.89	27.12	19.32	39.98
	ER25	0.00	0.00	2.25	13.30	24.75	14.85	44.85
	ER26	0.00	0.19	4.08	6.21	21.17	31.26	37.09
	ER27	0.00	0.00	2.96	11.50	23.98	17.48	44.08
	ER28	0.00	0.00	4.64	12.96	28.43	23.98	29.98
	ER29	0.00	0.00	3.50	8.47	26.34	29.10	32.60
	ER30	0.00	0.00	1.38	10.80	33.45	23.43	30.93
	ER31	0.00	0.00	2.64	7.91	21.66	23.16	44.63
	ER32	0.00	0.00	1.88	4.33	29.94	23.35	40.49
	ER33	0.00	0.00	1.09	3.83	25.32	23.68	46.08
	ER34	0.00	0.00	0.39	7.56	26.16	26.16	39.73
	ER35	0.00	0.00	0.39	5.10	23.92	41.18	29.41
	ER36	0.00	0.20	2.15	10.67	27.25	19.86	39.87
	ER37	0.00	0.00	0.86	6.39	21.59	42.31	28.84
	ER38	0.00	0.00	2.75	9.17	21.83	29.54	36.70
	ER39	0.00	0.25	3.96	9.66	28.15	18.14	39.84
	ER40	0.00	0.00	1.99	7.40	22.56	34.84	33.21
	ER41	0.00	0.00	1.43	6.51	21.75	31.11	39.21
	ER42	0.00	0.00	0.98	5.69	26.67	32.55	34.12
	ER43	0.00	0.27	1.43	9.17	33.05	22.79	33.29
	ER44	0.00	0.00	0.98	3.54	25.20	36.61	33.66
	ER45	0.00	0.00	1.28	4.95	27.11	33.88	32.78
	ER46	0.00	0.00	3.57	5.35	23.53	27.81	39.75
	ER47	0.00	0.00	0.51	8.81	22.37	32.88	35.42
	ER48	0.00	0.00	2.51	5.20	16.67	20.79	54.84
	ER49	0.00	0.00	1.62	7.94	21.48	25.27	43.68
	ER50	0.00	0.00	2.66	6.45	22.77	32.26	35.86
	ER51	0.00	0.00	2.91	4.73	20.18	24.00	48.18
	ER52	0.00	0.72	0.72	4.15	14.26	19.49	60.65
	ER53	0.00	1.71	0.57	7.60	25.67	33.08	31.37
	ER54	0.00	0.00	0.91	6.92	26.05	32.24	33.88
	ER55	0.00	0.00	1.48	3.87	29.52	33.76	31.37
	ER56	0.00	0.00	1.69	4.14	21.09	25.05	48.02
	ER57	0.00	0.00	1.47	7.56	29.46	24.79	36.72
	ER58	0.00	0.00	1.98	5.49	28.51	39.02	25.00
	ER59	0.00	0.00	1.13	7.16	26.74	32.39	32.58
	ER60	0.00	0.10	0.93	8.55	31.12	25.11	34.20
	ER61	0.00	0.00	0.56	6.40	19.59	39.36	34.09
	ER62	0.00	0.00	1.19	5.25	21.02	37.63	34.92
	ER65	0.00	0.00	0.97	4.65	25.78	38.57	30.04
	mean	0.00	0.10	1.84	7.32	24.21	28.08	38.45
	σ	0.00	0.30	1.11	2.58	4.80	7.29	8.53
Refractory fragments	ER 63	0.00	0.00	2.23	4.28	19.74	31.47	42.27
	ER 64	0.00	0.00	2.11	6.01	22.24	30.68	38.96
	ER 66	0.00	0.00	1.47	7.89	30.09	28.81	31.74
	ER 67	0.00	0.00	2.64	6.78	28.44	37.66	24.48
	ER 68	0.00	0.00	4.85	5.04	30.22	32.09	27.80
	ER 69	0.00	0.00	1.60	8.53	21.31	22.91	45.65
	ER85	0.00	0.00	1.20	5.60	22.40	21.80	49.00
	ER86	0.00	0.00	1.52	7.77	21.79	24.83	44.09
	ER87	0.00	0.00	1.51	8.47	22.22	24.11	43.69
	ER88	0.00	0.00	0.53	5.49	23.72	30.27	40.00
	ER89	0.00	0.00	1.49	5.65	21.99	25.71	45.17
	ER90	0.00	0.00	0.00	3.14	25.65	41.14	30.07
	ER91	0.00	0.00	0.00	1.17	20.43	38.72	39.69
	ER102	0.00	0.00	0.59	2.55	27.50	43.42	25.93
	ER103	0.00	0.00	1.91	5.53	27.48	42.37	22.71
	ER267	0.00	0.00	0.95	7.44	33.21	34.92	23.47
	ER276	0.00	0.00	0.36	4.55	20.91	31.64	42.55
	ER277	0.00	0.00	0.54	4.83	20.75	31.13	42.75
	ER278	0.00	0.00	0.70	5.04	22.26	36.35	35.65
	ER279	0.00	0.00	3.02	4.34	25.66	40.00	26.98
	ER280	0.00	0.00	0.55	4.62	26.06	41.77	26.99
	ER281	0.00	0.00	3.91	4.84	26.82	35.75	28.68
	mean	0.00	0.00	1.53	5.43	24.59	33.07	35.38
	σ	0.00	0.00	1.24	1.87	3.74	6.66	8.54

Table 5 PCA of the archaeological and natural samples: eigenvalues of the correlation matrix

Component	Eigenvalue	% of Variance	Cumulative %
1	5.85	41.78	41.78
2	2.00	14.31	56.09
3	1.40	9.97	66.07
4	1.33	9.53	75.59
5	0.91	6.49	82.09
6	0.68	4.84	86.92
7	0.64	4.61	91.53
8	0.36	2.56	94.09
9	0.33	2.32	96.42
10	0.25	1.77	98.18
11	0.15	1.10	99.29
12	0.07	0.51	99.79
13	0.03	0.18	99.98
14	0.00	0.02	100.00

Table 6 PCA of the archaeological and natural samples: loadings of the first three PC

	PC1	PC2	PC3
SiO_2	-0.834	0.113	0.276
TiO_2	0.596	0.552	0.201
Al_2O_3	0.759	0.245	-0.384
Fe_2O_{3tot}	0.535	-0.266	0.269
MgO	0.592	-0.273	0.517
CaO	0.234	-0.456	-0.297
K_2O	0.785	-0.188	0.147
Cr	0.788	0.421	0.005
Sr	0.545	-0.361	-0.368
Zr	0.448	0.409	0.608
2ϕ	-0.547	-0.536	0.353
3ϕ	-0.790	0.066	0.057
4ϕ	-0.374	0.654	-0.222
pan	0.856	-0.206	-0.017

Table 7 Precision of the grain-size analyses by point counting (pc) and sieving (s). Means of the percentages of three-time repeated analyses and the standard deviations are shown

		ϕ	**< -1**	**-1 - 0**	**0 - 1**	**1 - 2**	**2 - 3**	**3 - 4**	**> 4**
		mm	>2	**1 - 2**	**0.5 - 1**	**0.25 - 0.5**	**0.125 - 0.25**	**0.063 - 0.125**	**< 0.063**
ER125pc	mean		0.00	0.00	0.87	7.00	15.16	19.48	57.49
	σ		0.00	0.00	0.58	1.03	0.39	0.93	1.25
ER125s	mean		0.00	0.23	1.65	9.35	22.19	21.33	45.24
	σ		0.00	0.15	0.52	0.35	2.67	1.43	3.02
ER136pc	mean		0.00	0.00	0.06	2.98	16.59	10.98	69.39
	σ		0.00	0.00	0.10	0.57	0.23	0.21	0.81
ER136s	mean		0.78	0.02	0.23	8.07	14.72	9.01	67.18
	σ		0.08	0.01	0.01	2.45	0.89	1.33	1.93
ER248pc	mean		0.00	0.00	0.00	1.56	3.19	1.72	93.53
	σ		0.00	0.00	0.00	0.47	0.91	0.32	0.71
ER248s	mean		0.04	0.04	0.06	0.3	0.98	1.96	96.62
	σ		0.01	0.02	0.01	0.65	0.80	0.97	1.23
ER250pc	mean		0.00	0.00	3.78	12.91	30.11	19.15	34.05
	σ		0.00	0.00	0.71	2.01	1.55	2.55	2.93
ER250s	mean		0.27	0.85	4.00	16.44	27.58	12.99	37.88
	σ		0.15	0.20	0.62	1.24	1.71	1.82	2.24
ER255pc	mean		0.00	0.00	1.46	2.61	18.54	11.87	65.52
	σ		0.00	0.00	0.12	0.57	0.43	0.67	0.36
ER255s	mean		0.23	0.64	1.03	2.98	17.87	7.99	69.25
	σ		0.08	0.28	0.18	0.37	2.79	0.46	2.44

Captions :

Fig.1 – Schematic geological map of the Court area (black rectangle), in the northern part of canton Bern (shaded area). Location of the Hupper samples: A = Sur Frête, B = Lac Vert, C = Champoz - P. Mont Girod, D = Forêt de Bérole, E = Châtelat, F = Monible - Côte, G = La Fuet, H = Souboz-Montaigu.

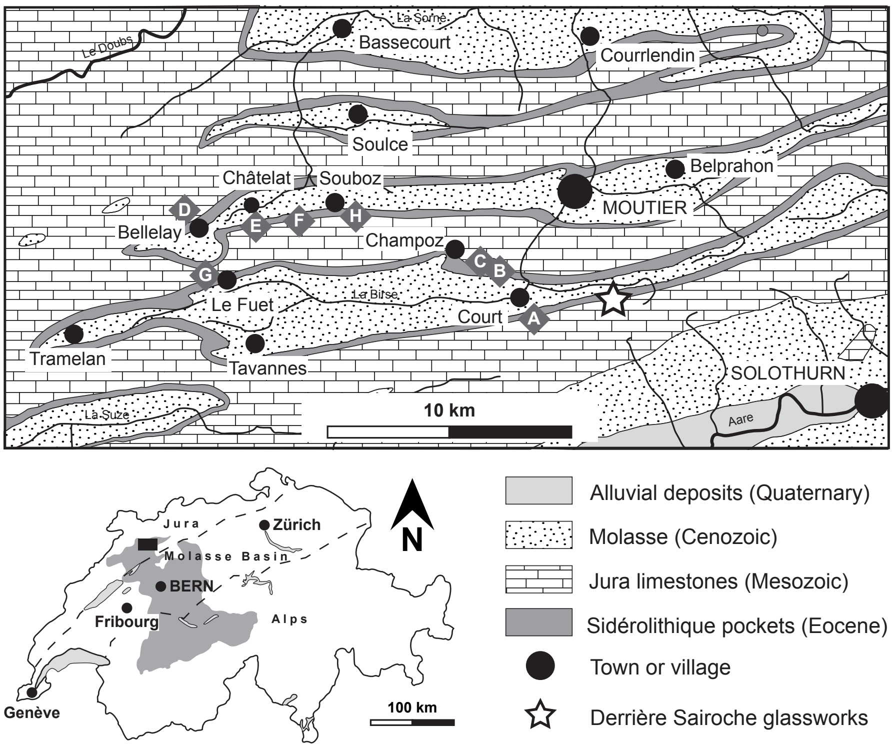
Fig. 2 – Microphotos under the petrographic microscope (x5, plain light) of a crucible fragment (a, ER52) and of a Hupper sample (b, ER250).

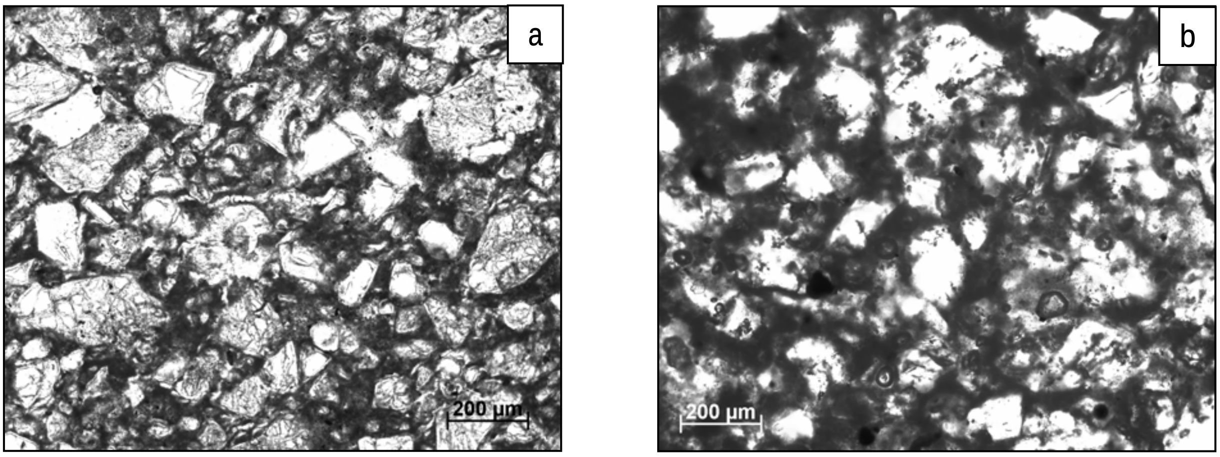
Fig. 3 – Cumulative grain-size frequency curves of the Hupper samples (sieve analysis).

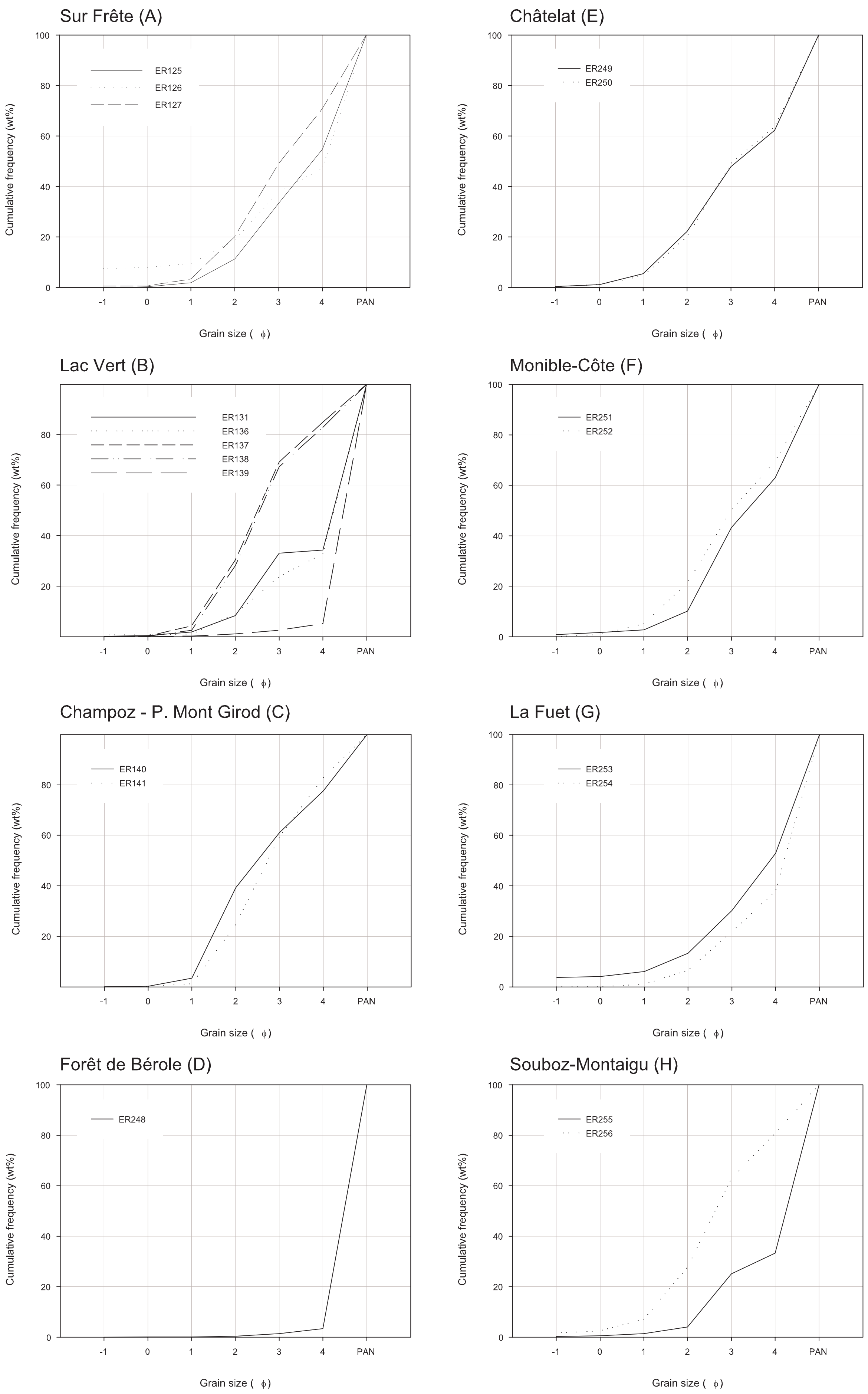
Fig. 4 – Cumulative grain-size frequency curves of refractory and crucible samples (thin-section analysis).

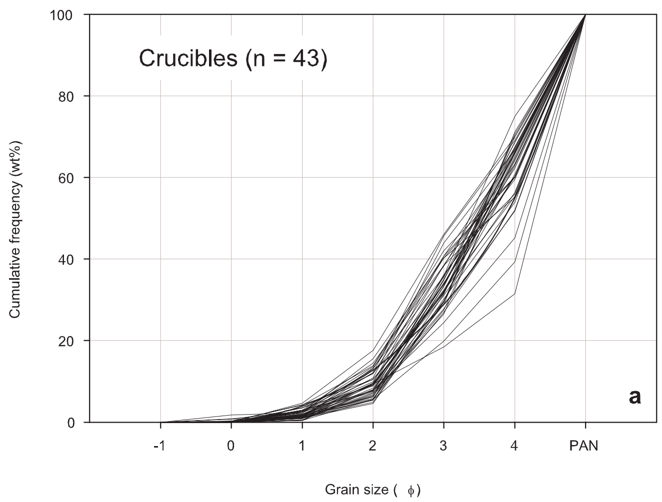
Fig. 5 – The component plots of PC1 vs. PC2 (a) and PC1 vs. PC3 (b) show the contributions to the PC variance and the correlations between variables (see text for details). Scatter plots of the PC scores using PC1 vs PC2 (c) and PC1 vs. PC3 (d). In plot c only two Hupper samples (ER125 and 251) fit to crucible and refractory samples, whilst in plot d other four samples (ER131, 249, 250 and 254) are compatible with the archaeological materials. White area: crucibles; grey area: refractory; black triangles: Hupper.

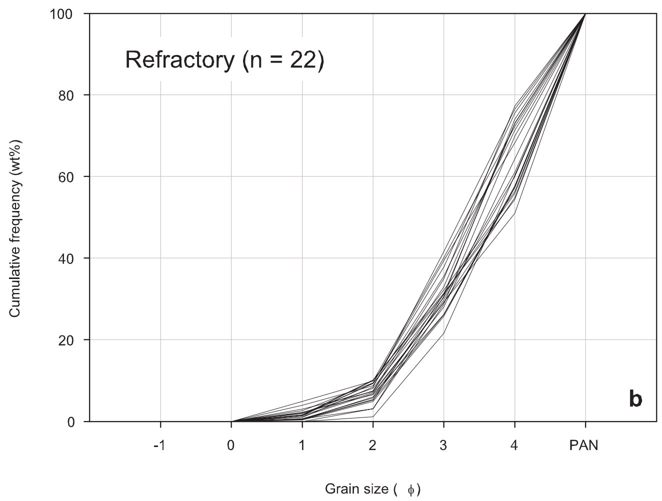
Fig. 6 – Linear regression of the thin-section vs sieving frequencies determined on the five test samples. The standard deviation bars based on the three-time repeated measures are reported. Dotted lines represent the 95% confidence limits around the regression line.

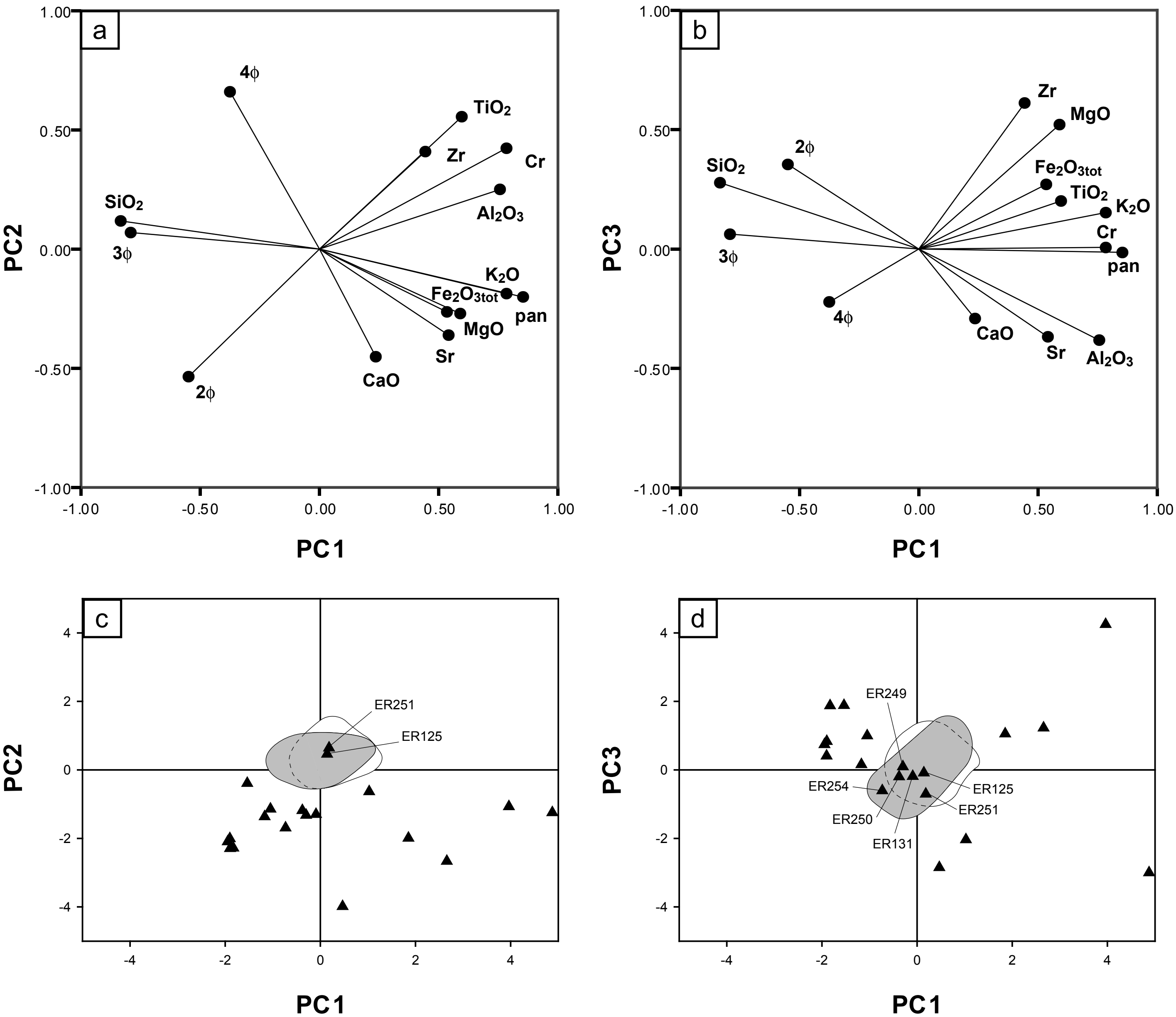

Le Doubs
La Sorne
Bassecourt
Courrlendin
Soulce
Belprahon
Châtelat
Souboz
MOUTIER
Bellelay
Champoz
Le Fuet
La Birse
Court
Tramelan
Tavannes
SOLOTHURN
La Suze
Aare
10 km
A
B
C
D
E
F
G
H
Jura
Zürich
Molasse Basin
BERN
Fribourg
Alps
Genève
100 km
N
Alluvial deposits (Quaternary)
Molasse (Cenozoic)
Jura limestones (Mesozoic)
Sidérolithique pockets (Eocene)
Town or village
Derrière Sairoche glassworks


a
200 µm
b
200 µm

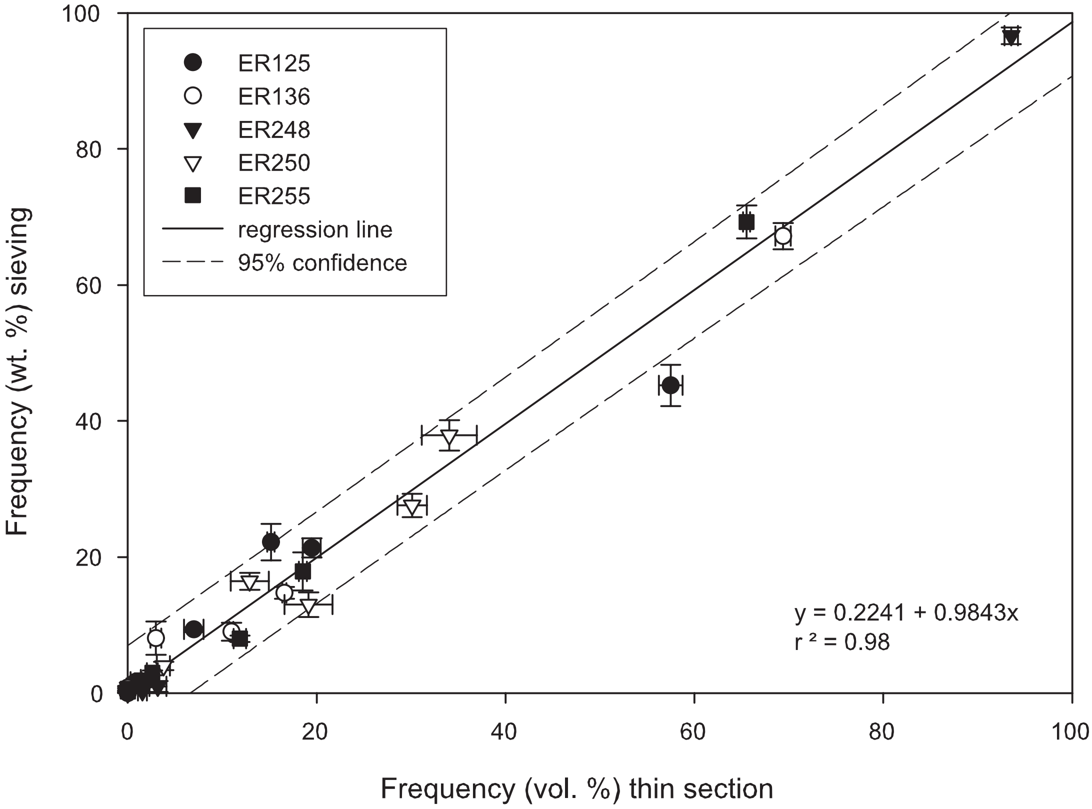

Sur Frête (A)
ER125
ER126
ER127
Châtelat (E)
ER249
ER250
Lac Vert (B)
ER131
ER136
ER137
ER138
ER139
Monible-Côte (F)
ER251
ER252
Champoz - P. Mont Girod (C)
ER140
ER141
La Fuet (G)
ER253
ER254
Forêt de Bérole (D)
ER248
Souboz-Montaigu (H)
ER255
ER256
Cumulative frequency (wt%)
Grain size (ϕ)
-1
0
1
2
3
4
PAN
0
20
40
60
80
100


Crucibles (n = 43)
a
Cumulative frequency (wt%)
0
20
40
60
80
100
-1
0
1
2
3
4
PAN
Grain size (ϕ)


Refractory (n = 22)
b
Cumulative frequency (wt%)
0
20
40
60
80
100
-1
0
1
2
3
4
PAN
Grain size (ϕ)



a
b
c
d
PC1
PC2
PC3
4ϕ
TiO2
Zr
Cr
Al2O3
SiO2
3ϕ
K2O
Fe2O3tot
pan
MgO
Sr
CaO
2ϕ
ER251
ER125
ER249
ER254
ER250
ER131


ER125
ER136
ER248
ER250
ER255
regression line
95% confidence
y = 0.2241 + 0.9843x
r ² = 0.98
Frequency (wt. %) sieving
Frequency (vol. %) thin section
0
20
40
60
80
100