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# Ancient Potassium-Calcium Glass and its Raw Materials (Wood-Ash, Fern-Ash, Potash) in Central Europe

WILLEM B. STERN UND YVONNE GERBER

**Zusammenfassung: Historisches Kalium-Calcium-Glas und seine Rohmaterialien (Holzasche, Farnasche, Pottasche) in Zentraleuropa.** Während der knapp vier Jahrtausende der Herstellung von Hohl- und Flachglas war Natrium-Calciumglas der weitaus häufigste Typ. Vom 9. bis zum 19. Jahrhundert war im nördlichen Zentraleuropa jedoch sogenanntes Waldglas aus Pflanzenasche (Netzwerk wandler) und Quarzsand (Netzwerk bildner) weit verbreitet. Schriftliche Quellen berichten von Asche der Buche (*Fagus sylvatica*) und von Farn (*Pteridium aquilinum*), wobei zwischen Pflanzenasche und Pottaschenextrakt begrifflich oft nicht klar differenziert wird. Pflanzenasche enthält neben Kalium und Calcium Phosphat als Hauptkomponente, während Pottaschenextrakt zur Hauptsache aus löslichen Kalisalzen besteht und kaum Calcium oder Phosphate enthält. Die vorliegende Arbeit diskutiert mit Hilfe graphischer und statistischer Verfahren erstmals Analysen von historischem Kaliglas (n=340), um zwischen Aschenglas (aus Holz- oder Farnasche) und Pottaschenglas (aus Aschenextrakt) zu differenzieren. Darüber hinaus wird mit neuen Analysen von Glas aus der historischen Hütte von Chaluet (Berner Jura/Schweiz) gezeigt, dass farblose Fragmente aus Pottaschenglas, buntfarbene Gläser jedoch aus eigentlichem Aschenglas bestehen. Natronglas war unter den 106 analysierten Fragmenten nicht vertreten.

Der Kenntnisstand über die Zusammensetzung von Buchenholz- und Farnasche und deren stoffliche Variabilität ist insgesamt dürftig. Deswegen werden neue Analysen von Buchenholz- und Farnaschen vorgelegt, die eine beträchtliche chemische Variabilität aufweisen, sich aber so klar unterscheiden, dass auch die aus ihnen hergestellten Gläser klar voneinander abgrenzbar sein müssten. Die Ergebnisse zeigen, dass eigentliches Farnaschenglas im zentraleuropäischen Mittelalter ausgesprochen selten gewesen sein muss. Eine Erklärung hierfür ist die nach neu vorgelegten Erhebungen geringe Ernteausbeute von Farn pro Flächeneinheit im Gegensatz zu Holz sowie möglicherweise die Toxizität von *Pteridium aquilinum*.

**Abstract: Sodium-calcium glass has been the most common type for making hollow- or flat glass over the past four millennia.** But from the 9<sup>th</sup> to the 19<sup>th</sup> century AD potassium-calcium glass was in wide use in Central Europe. It was manufactured from whole-ash of plants like beech (*Fagus sylvatica*) or possibly fern (*Pteridium aquilinum*) containing not only potassium and calcium, but also phosphate as a main component. If potash, the extract from plant ash is used, neither lime nor phosphate are contributed, because these less soluble compounds remain in the residue of the leaching/extraction process.

By blending and melting whole-wood ash as a flux/network modifier with quartz sand as a network former, a glass results with several wt.-% phosphate. By using potash extract instead, a glass is obtained being virtually free of phosphate. The phosphate content of historical potassium-calcium glass may therefore be used as a criterion to distinguish whole-ash from potash glass which was not possible so far.

Chemical analyses of historical potassium-calcium glass exist in large numbers and can be screened statistically by applying the phosphate criterion, but reliable analyses of whole-plant ash and of potash are extremely scarce. The present paper presents hence not only new analyses on plant ash and discusses its natural variability, but it evaluates also statistically the phosphate content of Central European potassium-calcium glass (340 published analyses) and its preference for either whole-ash or potash extract. It discusses furthermore a set of 106 new glass analyses from one glass production

site in the Swiss Jura Mountains. By applying the phosphate criterion it was found that colourless fragments consisted of potash glass, whilst coloured fragments represented whole-ash glass; all fragments consisted of the potassium type, no sodium glass was observed.

Data on beech- and fern-ash are rare; the few old, and presented new data display a clear chemical difference between the two. The bulk of historical potassium glass has to be interpreted as whole-wood ash glass, not as fern-ash glass. The restricted use of fern for glass making is probably due to the small fern output per surface unit in contrast to wood growing per surface unit, as our new investigations show. Another reason is possibly the toxicity of fern.

**Key words:** potassium-calcium glass, wood-ash, fern-ash, potash, phosphate.

### 1. Introduction: The material «glass»

Terminology: Potassium-calcium glass and sodium-calcium glass are designated as K-Ca glass and Na-Ca glass respectively throughout the text. K-Ca glass as a general term for forest glass comprises both, glass made from the whole-ash of plants, and glass made from the extract of plant ash as discussed in the text. «Ash» is defined to be the inorganic part of burnt plant tissue, rich in alkali and earth-alkali carbonates, phosphates, sulphates and chlorides. The term «plant» is used as a general, botanical designation comprising trees, shrubs, fern, etc.

The technology of extracting potash from the whole-plant ash was a significant refinement process within one part of the Medieval glass production (Wegstein 1996, Maus 1997/98, Wedepohl 2003; Stern and Gerber 2004; Gerber et al. forthcoming). Potash is a very important potassium supplier – yielding a higher potassium content than whole-plant ash. A likely criterion for discriminating between potash glass and potassium glass will be discussed in this paper. The potash technology has not yet achieved recognition in the English-speaking literature. Conventional wisdom regarding high potassium content in Medieval glass analyses held that fern, or an addition of fern, which also yields high potassium values, was the main potassium supplier. The aim of this paper, which is focussed on K-Ca glass, not on the wide-spread Na-Ca glass, is to investigate aspects of potash technology versus fern, and the plausibility of potash as an alternative potassium supplier for specific glasses.

Because the raw materials for glass-making and their precise mixing recipes are known from literature sources only to a very limited degree, the final product – glass – has attracted scientific curiosity since the early days of modern chemistry and physics. The complex chemical composition of ancient glass is considered to be a clue to the character of applied raw materials, their mixing proportions, questions of recycling, and glass-making technology.

Besides Na-Ca glass a second type became important in Central and Northern Europe between the 9<sup>th</sup> and 19<sup>th</sup> century AD, namely potassium-calcium-glass. Instead of soda, potassium carbonate acts as a network modifier. Because  $\text{KHCO}_3$  (kalicinite) is highly soluble in water, it does practically not occur in nature under moderate climatic conditions. It had to be obtained by ashing terrestrial plants like beech, pine, oak, or possibly bracken. Large-scale wood-burning provided the necessary ash. Glass huts for making «forest glass» were installed «in the woods» where ash for glass-making and firewood for the furnaces could be obtained. Hence ideal spots for glass-making were woods close to river banks, where also quartz sand was available, e.g. in the Black Forest (SW Germany). Because terrestrial plants – in contrast to, e.g., *Salicornia* growing on sea shores – take up not only potassium, but also calcium from the substratum, the addition of lime as a stabiliser was not strictly necessary. The production process became hence somewhat simpler. K-Ca glass was predominant in Central Europe until the 19<sup>th</sup> century when cheap soda became available through the Solvay process (1860).

Although the production of Alkali-Ca glass seems technologically simple, the prerequisites are not trivial:

- the essential raw materials quartz sand, lime, alkali, and fuel occur seldom together, and hardly at the place where glass is finally used,
  - the impurity of natural raw materials and their chemical variability impede a predictable product quality,
  - the high melting temperature involved (900 to over 1400°C) asks for refractory materials for melting pots and furnace linings,
  - the large but unknown and variable amount of volatile components in ash renders a defined and reproducible glass-making recipe with a fixed ash-to-sand ratio difficult, if not impossible,
  - glass-making needs, as a consequence, sophisticated technical skills and much experience.
- When whole-wood ash (plant after burning/calculating, without further extraction processes) is used for glass-making, several compounds besides potassium salts enter the glass-making process, notably phosphate, sulphate, chloride, lime, magnesia, silica, manganese and iron in various constellations and proportions. If, however, wood ash is processed/extracted, i.e. washed, relatively pure «potash» (chemically  $K_2CO_3$ ) results on one hand, and a residue rich in phosphate, sulphate, lime, iron etc. on the other hand. When potash extract is used for glass-making, colouring elements like manganese and iron are avoided, but lime is also lost and has subsequently to be added as a stabiliser.

Ancient sources are not aware of the difference between sodium, potassium, and their compounds; written texts need hence detailed interpretation. Part of even modern glass literature ignores the obvious difference between «potassium» and «potash», although the terms are clearly defined: «potash = potassium carbonate especially from wood ashes» (Webster's New Encyclopedia 1995).

Written sources (for Theophilus, Agricola, Biringuccio, Neri, Kunkel see e.g. Frank 1982, Smedley et al. 1998, Wedepohl 2003, Kurzmann 2004) describe ancient glass-making techniques in some detail. But literature (ancient up to the

early 19<sup>th</sup> century) leaves a number of points open: to what extent a distinction was made between soda (Na-salts) and kali (K-salts), to what extent whole-plant ash was used for glass-making, or ash extracts, what the mixing recipes of quartz sand and ash have been in practice, and to what extent plant ashes other than from beech, fern or lichen have been used.

The present paper discusses K-Ca glass with a focus on the following questions:

1. What criteria exist to distinguish between whole-ash glass and potash glass made from ash extract? Can such data be validated statistically?
2. If indeed two ancient production techniques for making K-Ca glass did exist, was one preferred regionally above the other?
3. Was either one preferred in relation to the making of a specific glass type?
4. What was the impact of whole-ash on glass quality in terms of, e.g., colour? Are elevated manganese contents always a proof of intentional decoloration, or do they merely proceed from a high Mn-content in wood?
5. Do criteria exist to prove the use of fern ash in glass-making, and possibly for a purpose-specific usage?
6. What was the forest consumption for making K-Ca glass?

## 2. Potassium glass: the significance of whole-plant ash and of ash extract

Medieval literature sources like Theophilus Presbyter (12<sup>th</sup> century, citation in Frank 1982, Wedepohl 2003, Kurzmann 2004) indicate a mixture of two parts beech ash with one part river sand for making forest glass. We tried both mixture proportions (2 parts ash [weight] to 1 part purified sand, and 1:1) when producing glass in the laboratory (see also Stern and Gerber 2004).

Our own experiments with beech, birch and pine ash, and extracts from these ashes, have shown that glass made from these ashes and quartz sand can be produced at temperatures between 1000 and 1350°C on a laboratory scale (Stern and Gerber 2004). The process of extrac-

ting ash for making potash is easy, and was known in Medieval times for making soap, among other usages. But was it also in routine use for making glass? Is the reported «potash» from ancient literature sources indeed a potassium-rich extract from plant ash, or just a semantic confusion between potassium as a chemical element and potassium-carbonate?

The advantage of using processed alkali salts is their relative purity and hence low colouring effect on the final glass. It might also be easier to optimise mixing recipes in order to obtain eutec-

tica, i.e. low-melting temperatures around 900°C. The temperature difference between low-melting and high-melting K-Ca glass is of the order of 300 to 500°C (Morey et al. 1930), the technological impact is thus far from negligible.

This comes at an added cost in labour, and the absence of lime which has to be added in the further glass-making process (see table 1, with a schematic overview over the main procedures for making common alkali-calcium glass, the most wide-spread glass type during the past 3 to 4 millennia; and fig. 1a).

Glass Type	<b>Na-Ca 3 Glass</b>	<b>Na-Ca 3 Glass</b>	<b>K-Ca 2 Glass</b>
Raw materials	Sodium-calcium 3	Sodium-calcium 3	Potassium-calcium 2
Network former	Quartz sand	Quartz sand	Quartz sand
Network modifier	<b>Inorganic soda</b> from evaporites or Solvay Process	<b>Organic soda</b> from halophile plant ash	Organic K-salts from plant ash: wood, fern
Stabiliser	Limestone, marble or shells, dolomite	Limestone, marble or shells, dolomite	Earth alkali from plant ash
Discriminative elements	<b>much Na, Ca</b> no/little P	<b>much Na, Ca</b> some K, Mg, P	<b>much K, Ca, Mg, P</b> some Na, Fe, Mn
Special procedures	washing → soda extract no P	washing → soda extract no P	washing → potash extract no P
Production period	Egypt, Roman, modern	Mesopotamian, Venetian	MA C-Europe, Bohemian
Use	3rd millennium BC– today	3rd millennium BC– 19th c. AD ?	9th–19th c. AD
Colouring / decolouring agents and additives not mentioned. Lead-, borate-glass not considered.			

**Tab. 1:** Common alkali – Earth alkali glass; a schematic overview.

If a certain amount of the residue from the potash production was taken as a stabiliser (rather than crushed limestone), the phosphate and e.g. iron and manganese content would have been augmented accordingly. The same can happen when adding cullet or bone ash.

Analyses of ancient glass are abundant (see e.g. Barrera and Velde 1989, Brill 1999, Maus 1997/1998, Wedepohl 2003) and are an essential basis for the research of ancient glass technology. Analyses of raw materials like beech ash or fern ash (network modifier) are, however, scarce and often incomplete, and hardly representative. Many hark back to the very early days of analytical chemistry (Wolff 1847, 1871). Because also recent analytical data on plant ash are very limited, not only new analyses of these raw materials were carried out (Stern and Gerber 2004, and this paper), but also glass consisting of previously analysed raw materials was manufactured on a laboratory scale (table 2) and used as a reference for assessing literature data.

For the sake of a reasonable statistical basis, the data presented here must also comprise analyses from the literature which are quoted on table 2; old and new data sets are marked as such. Plant ash shows a wide variation of chemical composition, which depends primarily on the soil where the plant is growing, and on plant habitat in general, to a certain extent also on plant species (Sanderson and Hunter 1981, Smedley et al. 1998, Stern and Gerber 2004).

Our data and the literature data on beech ash («B» in fig. 1b, *Fagus sylvatica*) and fern ash/bracken («F» in fig. 1b, *Pteridium aquilinum*), two plant species reportedly used in ancient potassium glass-making, are presented in fig. 1b. Beech ash and fern ash compositions vary to a large degree, but occupy distinct areas. The final composition of the glass made of it, therefore, will be dominated by these variations. A second defining factor is the recipe for glass-making, i.e. the mixing ratio of ash and quartz sand. A third factor is dressing, i.e. calcining ash prior to mixing with sand; volatile-free ashes change the final glass composition and its melting behaviour strongly. The sand composition also has an impact on the final glass chemistry, as it may contain not only quartz but also feldspar which

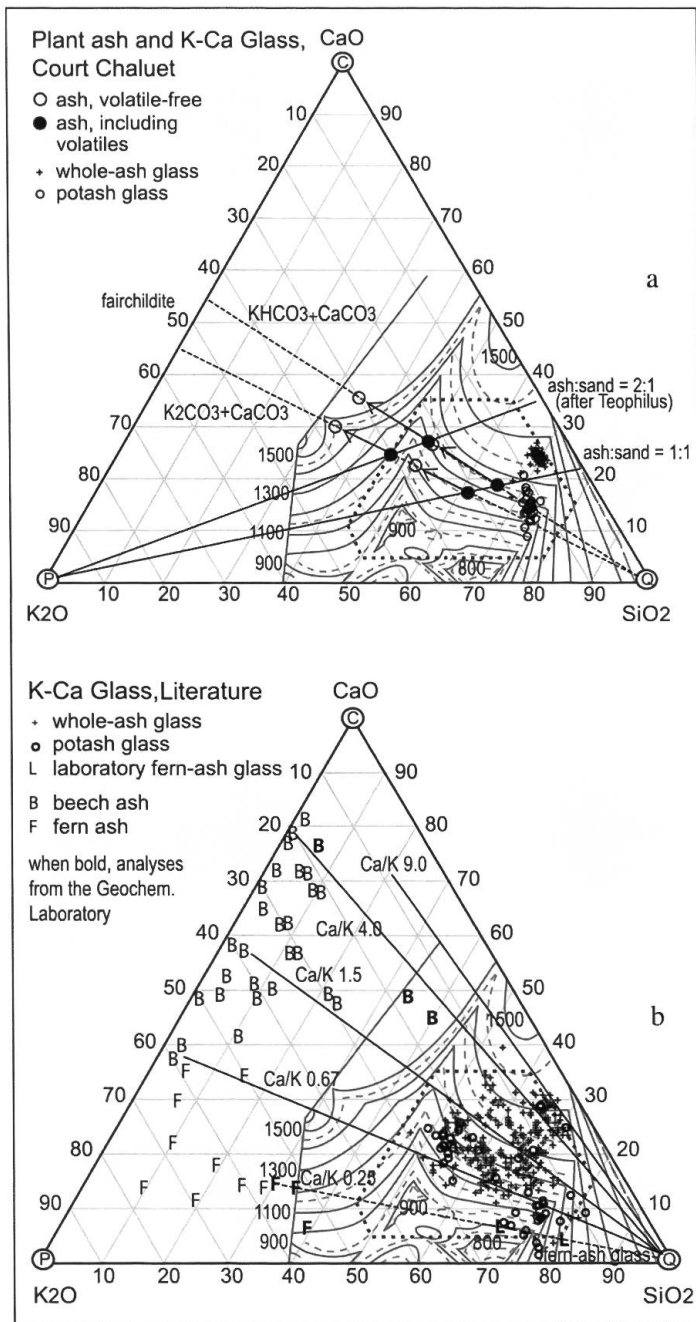
contributes alumina, lime and alkalis besides silica.

On the average, fern ash contains more potassium and less lime than beech ash, as already stated by Wedepohl (2003). When mixing one part ash with one part quartz sand, fern-ash glass and wood-ash glass would probably be chemically different. But with higher quartz proportions or with the addition of a third component (lime) that difference might possibly be obscured.

When ash extract/leaching of terrestrial plants, i.e. potash, is used for glass-making, the recipe becomes more important. In theory, using chemically well-defined ingredients, a defined glass of virtually any suitable composition may be achieved. This is not possible in a straightforward way with whole-plant ash of unknown and varying composition. In the Medieval and recent periods an exact «defining and composing» of raw glass batches was not yet possible because knowledge of the chemical and mineralogical composition of the raw materials was lacking and still is today. Successful glass batches depended on traditional knowledge, experience and observations of and by the glassmakers involved.

It is evident from our laboratory-scale glass manufacturing experiments that both educts, whole-plant ash (beech, fern; table 2) and ash extract (beech; Stern and Gerber 2004), can be used for potassium glass-making, but the question remains whether the product glass reflects the initially used raw materials. Based on the premise that washing/leaching ash of terrestrial plants like beech and fern separates soluble potassium salts from less soluble phases like Ca-Mg phosphates, it follows:

1. glass made with whole-plant ash is rich in phosphate because terrestrial plants contain 2.7 to over 15.6 wt.-%  $P_2O_5$  (average of beech ash = 7 wt.-%, dry; table 2),
2. glass made with potash (ash extract) is depleted of phosphates,  $P_2O_5$  ranging between 0 and 0.3 wt.-% (experimental data in Stern and Gerber 2004),
3. glass made with potash and residues from potash extraction contains some phosphate, but probably less than 1 wt.-%  $P_2O_5$ ,



**Fig. 1:** a) Ternary diagram with network former  $\text{SiO}_2$ , network modifier  $\text{K}_2\text{O}$  and stabiliser  $\text{CaO}$ , combined with melting temperatures after Morey et al. (1930). The trapezoid displays the compositional field of K-Ca glass. Calculated K-Ca glass composed with theoretical raw materials (potassium carbonate and silica) are symbolised as circles representing mixtures of  $\text{KHCO}_3 + \text{CaCO}_3$  and  $\text{SiO}_2$ , and mixtures of  $\text{K}_2\text{CO}_3 + \text{CaCO}_3$  (mineralogically fairchildite) and  $\text{SiO}_2$  respectively. Mixtures of volatile-free raw materials (as listed in many compilations) are represented as empty circles, mixtures of «native», volatile-containing ash are represented as filled circles. Whether volatile-free or volatile containing ash is considered for calculating a K-Ca glass has a large impact on the final glass composition and its predicted melting composition.

K-Ca glass from Court-Chaluet (Swiss Jura) occupies two distinct areas. One (+) represents 74 % of the analysed total and is coloured, phosphate-rich ( $\text{P}_2\text{O}_5 > 1$  wt.-%) whole-ash glass, the other (o) represents predominantly colourless, phosphate-free potash glass ( $\text{P}_2\text{O}_5 < 1$  wt.-%).

b) The same ternary graph with 340 K-Ca glasses from literature, as indicated in the text. Projection points of beech ash (B) and of bracken (F) scatter widely, but occupy distinct areas. The K/Ca ratio of beech ash varies from 0.67 to 10, the ratio of fern ash is around 0.25. Suitable mixtures of fern ash and quartz sand might display eutectic melting temperatures around 900°C, but mixtures of beech ash with sand display much higher temperatures between 1100° and 1450°C. These statements are valid for the ternary system  $\text{SiO}_2$ - $\text{K}_2\text{O}$ - $\text{CaO}$ . The presence of additional main components like  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$  will most probably influence the melting behaviour.

4. glass made with potash and added recycled wood-ash glass (cullet) may contain approx. 0.3 to 1 wt.-%  $\text{P}_2\text{O}_5$ , and
5. glass made with potash and added bone ash will contain not only elevated lime combined with low magnesia, but again also much phosphate stemming from bone.

Observations 1 and 2 point to the conclusion that the phosphate content of K-Ca glass is a clue to the understanding of ancient glass-making. The

lowest phosphate content of beech ash, known so far, is 2.7 wt.-% (see table 2). Assuming a one-to-one mixture ratio of sand and whole-ash, the phosphate content of the resulting K-Ca glass will be halved: a  $\text{P}_2\text{O}_5$  content of at least 1.35 wt.-% will result. A conservative mark of 1 wt.-%  $\text{P}_2\text{O}_5$  may be tentatively applied as a rough criterion for separating whole-ash glass from potash glass (fig. 2). The 1 wt.-% phosphate argument has never been brought forward before as a criterion for

assessing published analyses of ancient glass, and it is used here for the first time to interpret technological aspects of ancient glass-making.

### 3. The phosphate content: Statistical considerations

The overall  $P_2O_5$  distribution appears at first to be continuous gaussian, except for a distinct packet of outliers at the lower extremity (fig. 3a). These prove to be data near or at the detection limit, and their assigned values are usually artificial constructs.

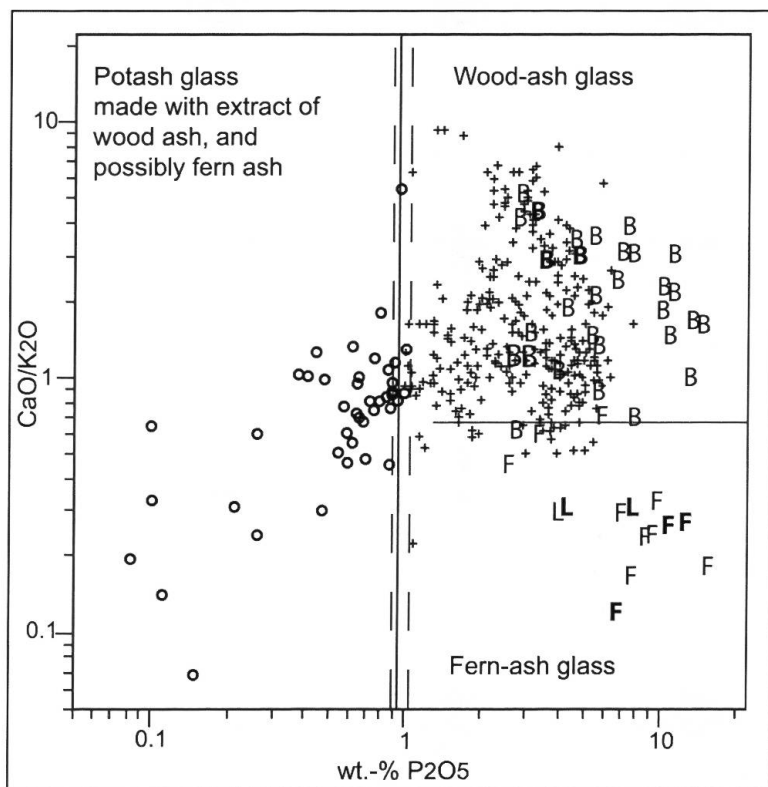
Can the  $P_2O_5$  threshold level postulated by theoretical calculation (see above) be substantiated through statistical analysis and simulation? The challenge resides in identifying a plausible probabilistic cut-off range discriminating between potash and whole-ash glass in accordance with the theoretical 1%-phosphate-threshold criterion. Ideally, all potash glass data should lie below the threshold, and all whole-ash glass above it. In practice, a transitional zone with upper and lower probabilistic cut-off thresholds seems likely, following a multi-modal Normal Mixtures model (Marin et al. 2005).

Exploratory Data Analysis (EDA) strongly suggests that the perceived continuous  $P_2O_5$  distribution may in fact be modelled by a series of overlapping lognormal distributions. Lognormalisation also compensates for the heteroscedasticity of correlated variables, and it serves to unclutter the dense packet of detection limit outliers (the latter being additionally jittered by a small lognormal random factor). Group dissection/identification and, hopefully, probabilistic segmentation conducive to maximum-likelihood cut-off thresholds ought to be achieved by multidimensional clustering.

The preferred tool for evaluating this assumption is an instance of the several variants of Normal Mixtures / EM algorithms (Wolfe 1970, 1971; Everitt 1979, McLachlan 1987; see Technical Note).

Excluding the unspecific Na and the ubiquitously abundant Si, K-means multidimensional clustering reveals that cluster formation depends mostly on P and Mg compounds, chiefly as a consequence of the range spread of  $P_2O_5$  and the variance of MgO.

Principal Components Analysis (PCA) on covariance shows that roughly 88 % of variance on Principal Component 1 (PC1) is explained by

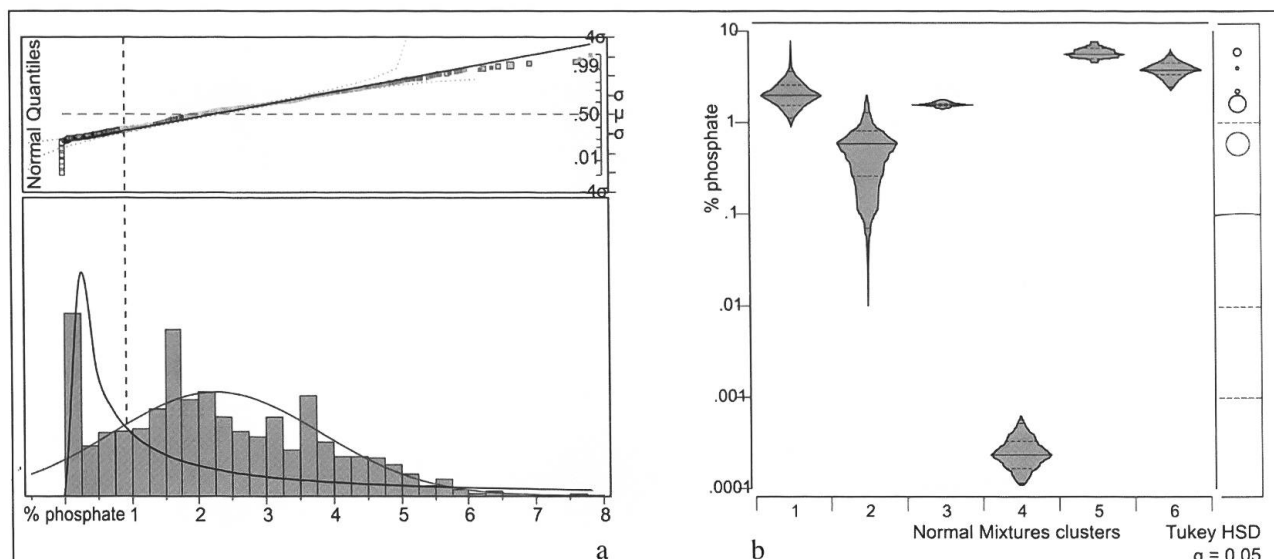


**Fig. 2:** Scatterplot with  $P_2O_5$ , CaO and  $K_2O$  of plant ash and K-Ca glass taken from literature ( $n=340$ , symbols as in fig. 1b). The «one-percent-phosphate criterion» and the logistic regression confidence interval is represented by a thin line, and dotted lines respectively, reflecting the fact that the phosphate content of whole-ash varies. And so does also any mixture of ash with sand. Potash extract on the other hand may contain a small amount of phosphate, which may be elevated when cullet is applied for glass-making (see also text for further discussion). The horizontal line close to 0.7 CaO/ $K_2O$  separates the compositional fields of beech ash from fern ash.

**Tab. 2:** Chemical analyses, wt.-%, volatile free (codes: CH = Switzerland, GB = Great Britain, D = Germany, I = Italy, n = numbers; F = fern ash, L = fern glass, M = mixtures, B = beech ash, P = potash, LOI = loss on ignition, nd = not determined, f = fairchildite, q = quartz).

		A Fern														Source			
	Code	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3t</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	sum	H <sub>2</sub> O	CO <sub>2</sub>	LoI		
<b>Ash</b>																			
	F	20.80	0.02	0.54	0.23	0.22	7.90	10.50	2.10	38.50	12.6	5.0	1.5	99.9	12.3	5.5		This paper	
	F	24.50	0.02	0.29	0.20	0.21	6.40	10.20	2.10	38.70	10.8	4.5	1.6	99.6	21.6	57.1		This paper	
	F	31.70	0.00	0.09	0.07	0.15	2.95	5.37	3.16	44.40	6.5	2.2	3.8	100.4	16.2	12.7		This paper	
	F	17.99	0.01	0.55	4.21	0.60	5.79	10.70	2.66	44.21	9.0	4.4	nd	100.0			nd	Jackson et al. 2005, 791	
	F	21.07	0.02	0.35	0.35	0.68	5.40	10.49	0.26	42.52	9.3	9.6	nd	100.0			nd	Jackson et al. 2005, 786	
	F	14.70	nd	0.22	0.22	0.11	7.70	9.40	0.11	54.70	8.4	nd	4.7	100.3			6.8	Wedepohl 2003, 184	
	F	11.99	nd	2.10	1.01	0.75	12.11	26.71	0.61	37.45	5.9	nd	4.9	98.6			nd	Ashtor & Ceviddali 1983, table V	
	F	6.10	nd	nd	nd	nd	7.60	14.10	4.60	42.80	9.7	5.1	10.2	100.2			nd	Turner 1956, 289	
	F	6.00	nd	nd	1.00	nd	7.40	8.80	2.00	48.30	15.6	4.1	8.6	101.8			7.9	Wolff 1871, 136	
	F	13.90	nd	nd	0.33	nd	8.03	13.50	0.00	46.20	7.0	1.4	10.7	101.0			5.1	Wolff 1871, 136	
	F	4.39	nd	nd	0.97	nd	8.28	18.70	5.31	39.80	2.6	5.4	14.7	100.1			7.6	Wolff 1871, 136	
	F	3.83	nd	nd	0.40	nd	7.67	21.40	8.70	35.61	3.3	6.6	12.6	100.1			6.8	Wolff 1871, 136	
	F	14.75	0.01	0.59	0.82	0.39	7.27	13.32	2.63	42.77	8.37	4.82	7.33	100.16					
	Std deviation	8.44	0.01	0.63	1.12	0.25	2.06	5.81	2.45	5.10	3.54	2.13	4.42						
	n	12	5	7	11	7	12	12	12	12	12	10	10						
<b>Glass</b>																			
	L	58.30	0.02	0.29	0.15	0.15	4.90	6.30	1.40	19.90	7.70	0.20	0.00	99.3			nd	This paper	
	L	72.60	0.03	0.33	0.11	0.09	3.10	4.30	0.82	13.60	4.30	0.20	0.10	99.6			nd	This paper	
	L	62.03	0.01	0.59	0.26	0.35	3.58	6.38	0.83	21.33	4.00	0.00	nd	99.4			nd	Jackson et al. 2005, 789	
Compounds		Calculated compositions : fresh/with volatiles vs calcined/dry ash without volatiles																	
	KHCO <sub>3</sub>	0.0						0.00		47.00				47.0	9.0	44.0		Kalcanite	
	K <sub>2</sub> CO <sub>3</sub>	0.0						0.00		68.20				68.2		31.2		Potash	
	CaCO <sub>3</sub>	0.0						56.00		0.00				56.0		44.0		Calcite	
	K <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub>	0.0						28.00		34.00				62.0		38.0		Fairchildite = f	
	SiO <sub>2</sub>	100.0						0.00		0.00				100.0		0.0		Quartz = q	
	KHCO <sub>3</sub> Calc:Q	66.0						18.50		15.60				100.1	2.3	22.0		f+q=1:1, ash with volatiles	
	KHCO <sub>3</sub> Calc:Q	50.0						27.20		22.80				100.0	0.0	0.0		f+q=1:1, ash without volatiles	
	KHCO <sub>3</sub> Calc:Q	33.3						36.20		30.50				100.0	3.0	29.3		f+q=2:1, ash with volatiles	
	KHCO <sub>3</sub> Calc:Q	33.3						36.20		30.40				99.9	0.0	0.0		f+q=2:1, ash without volatiles	
	K <sub>2</sub> CO <sub>3</sub> Calc:Q	61.7						17.30		21.00				100.0		19.0		f+q=1:1, ash with volatiles	
	K <sub>2</sub> CO <sub>3</sub> Calc:Q	50.0						22.60		27.40				100.0		0.0		f+q=1:1, ash without volatiles	
	K <sub>2</sub> CO <sub>3</sub> Calc:Q	44.6						25.00		30.40				100.0		25.0		f+q=2:1, ash with volatiles	
	K <sub>2</sub> CO <sub>3</sub> Calc:Q	33.3						30.20		36.60				100.1		0.0		f+q=2:1, ash without volatiles	





**Fig. 3:** a) Histogram of overall  $P_2O_5$  distribution ( $n=828$ ; data from literature and from own analyses – Court Chaluet, Swiss Jura); normal and lognormal distribution fit curves. Superposed: normal quantiles, distribution confidence intervals ( $\alpha=0.05$ ). (Vertical dotted line: resulting mean phosphate threshold = 0.9268 %  $P_2O_5$ ). b) Distribution shape plots of Normal Mixtures clusters 1-6.  $P_2O_5$  range scale logarithmic. Note: highly skewed Cluster 2 features the largest spread and range. Very compact Cluster 3: Court-Chaluet whole-ash glass data. Right margin: Tukey HSD comparison circles for means overlap,  $\alpha=0.05$ .

$P_2O_5$ , and about 8 % of variance on Principal Component 2 (PC2) is explained by MgO; phosphate and magnesia together account for 95.741 % of the total variance (table 3).

Hence we may reduce the multidimensional variable space to Principal Components 1 and 2 instead of the actual chemical compounds  $P_2O_5$ , MgO, CaO,  $K_2O$ , trading very little loss of information for a considerably simpler and more robust 2-dimensional mixture model.

The optimal group segmentation with the Normal Mixtures procedure was obtained, by empirical iteration, with six clusters (fig. 3b).

Weighted Recursive Partition of Principal Components with Normal Mixtures clusters as identity categories identifies a primary split threshold on PC1 at 0.0417425. This value translates into a mean phosphate threshold value of 0.92684569 % (fig. 4).

Logistic regression validates this split threshold with a  $\chi^2$  of 1755.966 for a  $R^2$  (U) coefficient of exactly 1.0. The threshold C.I. at  $\alpha=0.01$  describes a very steep interval, between 0.89970778 and 1.03086505 %  $P_2O_5$ .

(Unweighted Recursive Partition on log phosphate and magnesia alone achieves a primary split mean threshold value of exactly 1 %).

Technical Note: Data Analysis was performed using SAS JMP version 7.0.1, the Normal Mixtures module on previous versions 6.0.3 and 7.0 having variously failed. Additional statistical graphing was performed using Aabel version 2.3. Computing platform: Mac OS X 10.4.10 on PPC G5 and Intel Core 2 Duo processors.

#### 4. The phosphate treshold as a screening criterion

In an early paper based on a detailed analytical study on French hollow and flat glass of the 13<sup>th</sup> to 17<sup>th</sup> century, Barrera and Velde (1989) stated,

PC	Eigenvalue	Percent	Cumulative
1	7.1309	87.467	87.467
2	0.6745	8.274	95.741
3	0.2708	3.321	99.062
4	0.0765	0.938	100.000

**Tab. 3:** Principal Components on covariances of  $P_2O_5$ , MgO, CaO,  $K_2O$ .

«that potassic glass was made using either fern-ash *leachings* or those of beech trees» (p. 93, *italics* by the authors of this contribution). In a recent internet publication Velde (2003) mentions that French potassium glass was made with the **ash** of forest plants (Velde's **emphasis**), and confirmed implicitly that not necessarily only potash (ash leachings/extract) was used.

By using the phosphate criterion as a discriminant, interesting regional differences in Medieval and modern potassium glass of Continental Europe emerge (data from Barrera and Velde 1989, Maus 1997/98, Gerber et al. forthcoming; table 4).

In conclusion does potash glass indeed occur among Central European K-Ca glass, but is predominant only in certain regions. No obvious correlation with time or with typology is found. Potash glass found in the debris of an excavated glass kiln operating between 1699 and 1714 near Chaluet in the Swiss Jura Mountains, is predominantly colourless, whereas whole-ash glass is tinted from greenish to yellowish or bluish (Gerber et al. forthcoming).

The prevailing potassium glass between the 13<sup>th</sup> and 19<sup>th</sup> century in Continental Europe is whole-ash glass, not potash glass when the phosphate content is used as a criterion.

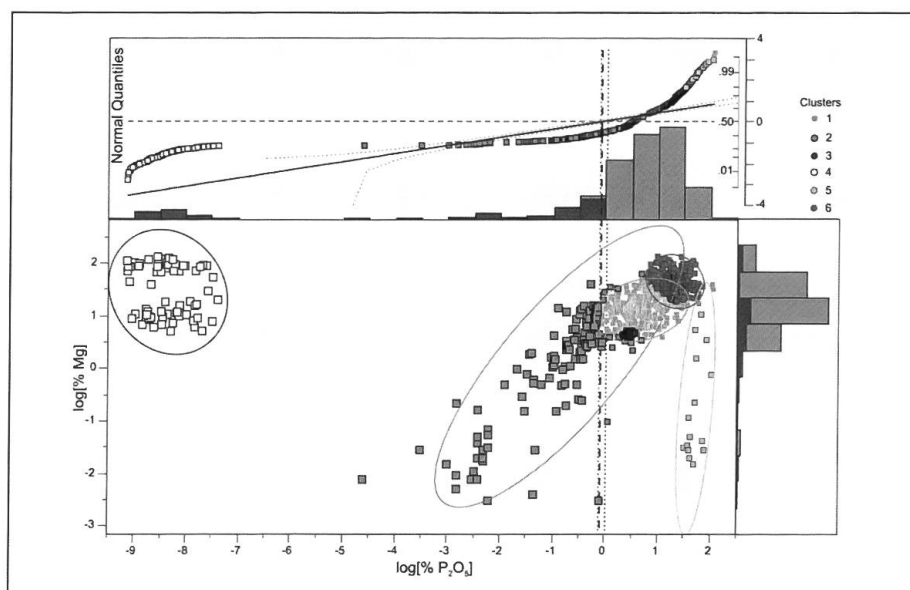
The question, however, remains whether this plant-ash glass is made with wood ash (e.g. from beech) or with fern ash, e.g. from ubiquitous

bracken, as is stated in literature. Occasional addition of fern ash to wood ash might have been practised at all times.

## 5. Wood consumption for forest glass-making: old reports and new calculations

There are several, quite controversial statements as to the devastating effect of wood consumption for forest glass-making in Central Europe, ranging from 0.45 ha wood (figure derived from Maus 1997/98), 3 ha wood (derived from Wikipedia, German version, 26<sup>th</sup> of September 2007), 4.5 ha wood (derived from Schuler 2000) to 5.5 ha (derived from citation in Maus 1997/98) for one ton of K-Ca glass. Assuming an annual production of 4 to 10 ton forest glass per production unit (Wedepohl 2003), the calculated forest consumption ranges from 2 ha to roughly 50 ha or 0.5 km<sup>2</sup> per annum. Assuming a life-span of 20 years for one glass hut, the harvested wood area would equal a surface of 0.4 to 10 km<sup>2</sup>, which results in quite a long transport distance of timber from forest to glass hut (nearly 2 km in a circular cleared woodland).

This suggests either moving the glass hut to virgin wood after a certain period in order to keep the transport distance of timber to the glass hut short. Or else to establish a decentralised «ashing system», where wood is burnt «in the forest», and from where the resulting ash (the



**Fig. 4:** Normal Mixtures clusters and their 95 % density ellipses on log [% P<sub>2</sub>O<sub>5</sub>] and log [% MgO] axes, corresponding to Principal Components 1 and 2. Marginal distribution histograms; dark grey: primary segmentation below threshold. Normal Quantiles superposed. Vertical dotted line: primary mean phosphate threshold = 0.92684569 %. Note: Cluster 4 data are mostly coded for assigned detection limit values; lognormal random jitter added. Cluster 3: very compact group of Court-Chaluet whole-ash glass data.

	Sodium glass		Potassium glass			
	total	total	ash glass		potash glass	
	n	n	n	%	n	%
France, 13th-17th c.:						
Cour Napoléon, Paris	47	119	117	98	2	2
Rouen	10	31	30	97	1	3
Argonne Pairu	0	42	42	100	0	0
Châlons sur Marne	4	38	8	21	30	79
Orléans	28	40	0	0	40	100
Black Forest, 13th-19th c.	67	205	135	65	70	35
Swiss Jura, 1699-1714 (cullet)	0	106	78	74	28	26

**Tab. 4:** Whole-ash glass vs. potash glass among Central European K-Ca glass.

ash being roughly 1 % only from the mass of wood) was transported to the distant glass hut; this in analogy to charcoal-burning. The system of such ashing places, however, is not known so far from literature.

Our own calculations on wood consumption for making one ton of K-Ca glass show 0.2 to 0.3 ha for a 1:1 recipe (ash:sand) to 2:1 recipe respectively, in the case of beech wood in Germany (data taken from Meyers Konversationslexikon 1888). According to forest density, plant habitat, wood species, and glass-making recipe the calculated wood surface needed for one ton of forest glass varies widely in different countries (mixed forest of beech, fir and pine unless otherwise stated; table 5).

## 6. Fern and its use in ancient glass-making

According to earlier authors and ancient sources has fern/bracken been in wide use for making glass (Turner 1956). This has also been stated of lichen (Biringuccio 1540, quoted in Frank 1982, p. 75), but lichen is nowadays not seriously discussed as a raw material for glass-making.

The discussion on the topic of fern as a main «potassium supplier» in Medieval glass production has intensified in recent years (e.g. Frank 1982, Ashtor and Cavidalli 1983, Barrera and Velde 1989, Wegstein 1996, Wedepohl 2003, Jackson et al. 2005). The availability of bracken, where forest had disappeared, suggests its use

for K-Ca glass-making, although its annual availability begins only in summer, implying a late and short season for glass-making, if a glass hut would have relied exclusively on fern.

Historical and ethnobotanical records report of diverse use of bracken in Medieval and recent times (Rymer 1976; McGlone et al. 2005). However, the toxicity of fresh and dry bracken (Fenwick 1989; Yamada et al. 2007 for a comprehensive review) raises questions about its prolonged large-scale use, harvesting or contact (even for our own experiments!). One may consider nevertheless its suitability in technological terms.

The possibility may be considered that potash extract from fern ash might have been used on a larger scale, because potash extracted from wood ash and from fern ash is largely identical. There is hardly an argument, based on the main chemical composition of glass, for deciding which of the two potash types was preferentially used. Considering the small proportion of potash glass among potassium glass in general, one may conclude that potash extract from fern ash only has been relatively rare and not common practice in Central European potassium glass-making between the 13<sup>th</sup> to the 19<sup>th</sup> century.

The likelihood that fern ash exclusively was used for glass-making is further lowered given the yield of fern per harvested surface unit vs. the corresponding yield of wood. This aspect has not been discussed in literature so far.

## 7. Experimental investigation on fern, fern ash and fern-ash glass

No data for Central Europe seem to exist in literature on bracken availability per surface unit. In order to obtain at least approximate informations on bracken availability per surface unit in Central Europe, the following experiment was carried out. In July 2005 bracken (*Pteridium aquilinum*) growing densely on a surface of 100 by 100 cm was harvested by cutting the whole plants (n=30) 5 cm above the soil at Alpe Mergugno/Ticino, Switzerland, GPS coordinates Swiss grid 696.050 E/109.450 N, elevation 1050 m above sea level. The general plant output per surface unit is estimated to be lower, i.e. one third to two thirds = 10 to 20 fern plants growing per m<sup>2</sup>.

The fresh plants weighed 1.82 kg after harvesting. The fronds were sun-dried. Dry stalks and dry fronds were separately burnt on an open fire, and later ignited at 500°C in a laboratory muffle oven. The total fern ash obtained was 17.9 g (= 1 % ash yield) of which 86 % were ex-fronds, and 14 % ex-stalks.

The ash of fronds and stalks was analysed by XRD (X-ray diffraction) for mineralogical examination (in analogy to Stern and Gerber 2004) and subsequently analysed by WD-XFA for chemical main components (table 2).

The chlorine content of fern ash is high, but analytical data obtained by WD-XF (classical wavelength-dispersive X-ray fluorescence on Li<sub>2</sub>BO<sub>4</sub>-beads) tend to be too low due to evaporation of Cl during sample preparation. The X-ray diffraction pattern of the same fern ash dis-

plays sylvite (KCl, JCPDS 41-1476) as a main mineral constituent. The high potassium content of fern ash is obviously not entirely due to potassium carbonate, which is the flux needed for glass-making. Estimated 10 to 20 wt.-% of the present potassium belong to sylvite which will partially or entirely be lost during the fritting and melting process. The high SO<sub>3</sub> content of fern ash is due to arcanite (K<sub>2</sub>SO<sub>4</sub>, JCPDS 44-1414) which forms a separate phase («gall») during glass-melting and does not act as a network modifier either. The potassium content of the final glass, therefore, need not be directly correlated with the original high potassium content of the fern itself.

The harvested fern ash was also taken for producing genuine fern-ash glass on a laboratory scale. Fern ash and commercially available pure quartz sand (B-100 of Sihelco & Co, CH-4127 Birsfelden) were mixed by applying two different blendings, one with two parts ash and three parts sand, and one with three parts ash and two parts sand (table 2). The analyses of these two glasses were also incorporated in fig. 1b and table 2. Its chemical composition is predicted by ash composition and the mixture ratio of ash and quartz sand. It corroborates to a certain extent the findings of Jackson et al. (2005). The projection points are on the tie-lines between the previously analysed fern ash and quartz sand («L» in fig. 1b).

Stalks and fronds of bracken are chemically different, stalks being poorer in earth alkalis. Taking fronds only, not stalks, for making fern-ash glass would be useful.

Country	m <sup>3</sup> per km <sup>2</sup>	t per km <sup>2</sup>	t ash	forest per ton glass	source
CH	36 100	26 930	94	0.6 ha to *) 1.0 ha	
D	27 100	20 210	71	0.8	1.3
A	26 600	19 840	69	0.9	1.3 Jahrbuch Wald und Holz 2002ff
F	11 600	8 550	30	2.0	3.0
S	10 500	7 830	27	2.2	3.3
D	60 000	52 140	261	0.2	0.3 beech, Meyers Konversationslex. 1888
CH	1 m <sup>3</sup> = 1t potash			3.0	to 4.5 Schuler 2000

\*) forest use for 1 ton K-Ca glass for 1:1 and 2:1 recipes (ash : sand)

**Tab. 5:** Wood consumption per surface unit in European countries, calculated after various sources.

From the observed harvested fern ash per square meter the extrapolated figures of fern consumption for fern-ash glass-making were taken: To produce 1 ton of fern-ash glass (with a mixture ratio of 1:1 ash:sand) over 3 hectare (33000 m<sup>2</sup>) densely growing bracken has to be harvested. The needed surface of loosely growing bracken would amount to 6 to 9 ha and accordingly more in case of a mixture ratio of 2:1 (ash:sand) K-Ca glass recipe. When beech ash is used, a needed surface of only 0.2 to 0.3 ha results according to the glass-making recipe (see above).

Fern can be harvested once per year, starting in June/July depending on habitat. A glass hut relying solely on bracken would have a brief annual production span.

If an annual potassium-glass production of 4 ton in a small glass hut, and of 10 ton in a larger glass hut are assumed (Wedepohl 2003), the average bracken consumption would amount to 12 to 90 ha, i.e. 0.1 to 0.9 km<sup>2</sup> per year (1:1 mixture recipe). These large areas to be harvested suggest that bracken might have been used as a substitute where the forest had disappeared due to wood cutting, or where a forest with mixed populations of trees and fern existed. The exclusive use of fern ash for making K-Ca glass on a large scale over longer periods, however, seems rather improbable in Central Europe. The toxicity of bracken might be another argument against its regular use on a large scale.

## 8. Summary

Plant ash as an organic provider of alkali carbonates for making glass has been a main raw material until the 19<sup>th</sup> century, with ash of halophile plants such as *Salicornia* for making sodic glass, and of terrestrial plants for making potassic glass in Medieval and modern time. Plant ash is easily processed/washed for extracting either soda from ash of halophile plants, or potash from ash of terrestrial plants like beech or bracken. When ash extract of wood or bracken is used, the resulting glass is virtually free from phosphate, whereas the use of the whole-ash leads to alkali-calcium glass containing usually 1.3 to 10.4 wt.-% P<sub>2</sub>O<sub>5</sub>.

When studying K-Ca glass of Central European origin of the 13<sup>th</sup> to 19<sup>th</sup> century AD, it seems useful to consider the phosphate content (tentative 1 wt.-% P<sub>2</sub>O<sub>5</sub>) as a discriminating criterion between whole-ash glass and potash glass.

For making potassium glass two plant types are mainly discussed in literature: wood ash (specifically beech, *Fagus sylvatica*) and fern ash (specifically bracken, *Pteridium aquilinum*), although the latter is highly toxic due to ptaquiloside. Own laboratory experiments demonstrate that also with beech, birch and pine ash glass can be produced (Stern and Gerber 2004), and with bracken as well (Jackson et al. 2005; and this study). All these glasses have their projection points on the tie-lines between the respective ashes and silica when plotted in a ternary graph based on SiO<sub>2</sub>-K<sub>2</sub>O-CaO (fig. 1b; birch and pine ashes are not plotted). Due to the high potassium and low lime content of whole-fern ash, the projection field of fern-ash glass is different from that of whole-wood ash glass. Screening 340 K-Ca glasses from literature, only a few plot in or near the fern-ash field, all originating from German glass huts. If potash is used for glass-making, no significant difference between fern-ash glass and wood-ash glass remains.

The few published analyses of fern ash show not only a high phosphate content, but also much SO<sub>3</sub> forming the separate phase «gall» which is not wanted in the glass production process. In order to avoid it, fern ash might have been processed, i.e. potash extracted and only that used for glass-making. Whether the high chlorine content of fern ash had an impact on the melting behaviour or on the glass quality is not known so far.

The initial questions (see p. 3/4) are answered as follows:

1. Whole-ash glass and potash glass represent two different technological procedures and may be differentiated by its phosphate content (1 wt.-% P<sub>2</sub>O<sub>5</sub> criterion). Whole-ash glass contains on average 7 wt.-% P<sub>2</sub>O<sub>5</sub> (typically 1.3 to 10.4 wt.-%), whereas potash glass, produced with the K<sub>2</sub>CO<sub>3</sub> extract of plant ash, contains usually less than 1 wt.-% P<sub>2</sub>O<sub>5</sub> (typically 0 to 0.3 wt.-%).
2. Both production techniques were used in ancient potassium glass-making, but whole-ash

glass was far more abundant than potash glass in most Central European production centres. Published K-Ca glass analyses from France (Barrera and Velde 1989) display regional preferences: in Paris (Cour Napoléon), Rouen and Argonne Pairu whole-ash glass prevails, whereas in Orléans and Châlons sur Marne potash glass is dominant.

3. K-Ca glass from France and the Black Forest shows no correlation between technological type and formal type so far. K-Ca glass from Court-Chaluet (Swiss Jura Mountains) contains 26 % potash glass, which is predominantly colourless. The interpretation is that potash extract was intentionally used for achieving a low content of colouring agents like iron, manganese, magnesia.
4. Whole-ash from trees may contain up to 5 wt.-% iron (as  $\text{Fe}_2\text{O}_3$ ), 13 wt.-% manganese (as MnO), 17 wt.-% magnesia (MgO) (table 2). When mixture ratios of either 1:1 or 2:1 of plant ash : quartz sand are applied, elevated percentages of these compounds enter the glass melt and still produce green, yellow or pink tints. Elevated MnO in glass (> 2 wt.-%) is hence not necessarily an indication of an intentionally added decolourant agent.
5. The high potassium and low lime content of fern ash may tentatively be used as discriminants to separate wood-ash glass from fern-ash glass (fig. 2). XRD studies on fern ash show, however, that part of the potassium is present as sylvite (chemically KCl), and does possibly not enter the final glass. The use of fern potash does possibly not cause a discernible chemical «fingerprint» in glass produced by it.
6. The calculated annual forest consumption for making K-Ca glass ranges widely from 0.2 to 0.3 ha (beech wood, 1:1 and 2:1 mixture ratios of ash : sand) to 2.2 to 3.2 ha in case of loosely growing mixed forest (Sweden). Considerable differences in land use exist also when fern-ash glass and wood-ash glass are compared: the production of one ton K-Ca glass needs 3 to 9 ha of bracken vs 0.2 to 0.3 ha of dense beech forest. It seems, therefore, reasonable to conclude that a medium size glass hut producing 4 to 10 ton K-Ca glass per year

may hardly have relied exclusively on fern ash. Rather, a combination of the two ash types seems plausible in cases where the forest had been harvested and the successor plant, bracken, began to prevail.

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