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The chemical composition of medieval wood ash glass from Central Europe

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ABSTRACT

Medieval wood ash glass classified as 6 early medieval wood ash glasses, 17 wood ash glasses, 5 early wood ash lime glasses, 7 wood ash lime glasses and 9 mixed alkali glasses has been analyzed by microprobe and ICP-mass spectrometry on 61 elements. Their calcium oxide to potassium oxide ratio (CaO/K_2O) increases from early to late medieval glasses according to an increase of the proportion of twigs in the bulk amount of wood (logs plus twigs). Twigs because of their relatively large proportion of bark contain more calcium than wood logs. The ratio CaO/K_2O of the glasses from not yet evaluated excavations can be used for dating. The observation that the 25 minor elements Be, Sc, V, Cr, Ge, Y, Nb, REE (La to Lu), Ta, W and Bi occur in almost equal concentrations in the five subtypes of wood ash glass makes it highly probable that these elements were introduced into the starting mixtures of the glasses by means of quartz from quartz-rich sand with heavy minerals. The majorities of the wood ash glasses contain so-called europium anomalies within the group of rare-earth elements (REE). Their Eu concentrations normalized to those of the Continental Earth's Crust are lower than the normalized samarium and gadolinium concentrations. These Eu anomalies are apparently inherited from the granitic source of quartz in the upper Continental Earth's Crust. Soda ash and soda lime glass as the other major types in the history of glass contain no Eu anomaly. Therefore a different source of quartz has caused this important element constellation for these glass types. The elements K, Cu, Rb and S are physiologically separated from Ca, P, Mn, Sr and B during the growth of the wood and bark, respectively, in the trees. Different sources of the metals Cu and Co were used for colouring the glasses of our report.
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1. Introduction

Glass is usually formed from quartz (silica) and sodium or potassium rich flux plus a calcium compound as stabilizer at temperatures above 1000 °C (Morey et al., 1930). In the early medieval period the import of sodium carbonate from Egypt to Europe to produce high-quality soda lime glass decreased. Therefore at about 800 AC several glass-houses probably in the western part of the Carolingian Empire started to use the ash of wood logs as a major flux for the production of glass. Before this use they had burnt these wood logs only for heating of the glass furnaces. The common tree at that time was beech. The major metal oxides in their ash are calcium, potassium and magnesium oxide (Wedepohl, 1998, Table A). The average CaO/K_2O ratio in the beech trunks ranges from about 1 to 2 and in beech bark is close to 16. The average CaO/MgO ratio in beech trunks is close to 4. The CaO/K_2O ratio in the final beech ash depends on the proportion of twigs and branches to trunks in the wood to be fired in the furnace. In our studies of the composition of the medieval wood ash glass we detected a systematic increase of the CaO/K_2O ratios in these glasses with younger age. Subtypes of wood ash glass with increasing CaO/K_2O ratios are early wood ash glass, wood ash glass (in the fullest sense of the word), wood ash lime glass and mixed alkali glass. The samples used for this investigation are listed in Table 1 and plotted in the map of Fig. 1.

2. Samples and analytical techniques

The lowest CaO/K_2O ratio indicates the highest quality of wood with a large proportion of beech trunks in the starting materials. We know a contemporary glass recipe of the beginning 12th century published by the monk Theophilus Presbyter in his "Diversarum Artium Schedula" (Theobald, 1933). He suggested to melt two parts ash of beech trunks with one part of quartz sand for making wood ash glass.

The large proportion of potassium in wood ash glass causes a relatively low melting temperature of about 1200 °C (Morey et al., 1930) that was favoured at the time of minor technical progress. These conditions when wood ash glass with a relatively low melting temperature was easily available were gone when the population increased at 1200–1300 AC. The increasing population required a larger production of glass, which to a major extent was used for church windows.

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Table 1
List of samples of wood ash glass separated into 5 subtypes (A early wood ash glass, B wood ash glass, C early wood ash lime glass, D wood ash lime glass and E mixed alkali glass).

Sub-type	Site of origin	Symbol	Object	Age	Colour	Reference
A	Drudewenshusen (Goettingen)	Dru1	Vessel	800	?	Wedepohl (2003)
A	Paderborn (Palace)	Pad10	Pane	about 780	Light green	Wedepohl et al. (1997)
A	Paderborn (Palace)	Pad11	Pane	1000 (?)	Light green	Wedepohl et al. (1997)
A	Lorsch (Monastery)	Lor36	Vessel	800	Light green	Sanke et al. (2002)
A	Staré Město (Moravia)	Sady4	Vessel	800–900	Blue	Galuška et al. (2009)
A	Staré Město (Moravia)	Sady5	Bottle	800–900	Light green	Galuška et al. (2009)
B	Brunshausen (Kreiensen)	Bru1	Ring	12 Century	Green	Stephan et al. (1994)
B	Brunshausen (Kreiensen)	Bru3	Vessel	12 Century	Green	Stephan et al. (1994)
B	Brunshausen (Kreiensen)	Bru5	Vessel	12 Century	Colourless	Stephan et al. (1994)
B	Corvey (Church)	Corv24	Tile	12 Century	Red	Stephan et al. (1997)
B	Corvey (Church)	Corv25	Tile	12 Century	Green	Stephan et al. (1997)
B	Lorsch (Monastery)	Lor15	Vessel	12 Century	Blue green	Sanke et al. (2002)
B	Lorsch (Monastery)	Lor21	Vessel	12 Century	Green	Sanke et al. (2002)
B	Brunshausen (Kreiensen)	Bru15	Pane	12 Century	Red	Stephan et al. (1997)
B	Brunshausen (Kreiensen)	Bru16	Pane	12 Century	Brown	Stephan et al. (1997)
B	Brunshausen (Kreiensen)	Bru19	Pane	12 Century	Blue	Stephan et al. (1997)
B	Hoexter (source Bohemia?)	Höx22	Beaker	15 Century	Light green	König et al. (2002)
B	Hoexter	Höx42	Bowl	13/14 Century	Light green	König et al. (2002)
B	Hoexter	Höx19	Smoother	13 Century	Brown green	König et al. (2002)
B	Hoexter	Höx16	Beaker	12/13 Century	Green	König et al. (2002)
B	Steimcke (Bramwald)	Steim1	Raw glass	13 Century	Green	Stephan et al. (1992)
B	Steimcke (Bramwald)	Steim2	Raw glass	13 Century	Green	Stephan et al. (1992)
B	Steimcke (Bramwald)	Steim3	Raw glass	13 Century	Green	Stephan et al. (1992)
C	Laudengrund (Spessart)	Spe1	Vessel	1300	Colourless	Schmid et al. (1996)
C	Laudengrund (Spessart)	Spe2	Bottle	1300	Green	Schmid et al. (1996)
C	Laudengrund (Spessart)	Spe3	Vessel	1300	Green	Schmid et al. (1996)
C	Laudengrund (Spessart)	Spe4	Thread	1300	Yellow	Schmid et al. (1996)
C	Laudengrund (Spessart)	Spe5	Beaker	1300	Blue	Schmid et al. (1996)
D	Hoexter	Höx24	Beaker	15 Century	Green	König et al. (2002)
D	Hoexter	Höx25	Beaker	15 Century	Green	König et al. (2002)
D	Hoexter	Höx26	Beaker	15 Century	Green	König et al. (2002)
D	Hoexter	Höx29	Beaker	15 Century	Green	König et al. (2002)
D	Hoexter	Höx50	Pane	13 Century	Light green	König et al. (2002)
D	Hoexter	Höx49	Pane	14 Century	Green	König et al. (2002)
D	Hoexter	Höx35	Bottle	13–15 Century	Green	König et al. (2002)
E	Glashuetten (Emsbach)	Ta3	Fragments	1450–1490	Green	Wedepohl and Kronz (2009)
E	Glashuetten (Emsbach)	Ta4	from	1450–1490	Green	Wedepohl and Kronz (2009)
E	Glashuetten (Emsbach)	Ta7	glass	1450–1490	Green	Wedepohl and Kronz (2009)
E	Glashuetten (Buchholzweg)	B1	production	1450–1490	Red	Wedepohl and Kronz (2009)
E	Glashuetten (Buchholzweg)	B3		1450–1490	Green	Wedepohl and Kronz (2009)
E	Glashuetten (Buchholzweg)	B9		1450–1490	Blue	Wedepohl and Kronz (2009)
E	Glashuetten (Dornsweg)	D1		1450–1490	Red	Wedepohl and Kronz (2009)
E	Glashuetten (Dornsweg)	D2		1450–1490	Green	Wedepohl and Kronz (2009)
E	Glashuetten (Dornsweg)	D14		1450–1490	Blue	Wedepohl and Kronz (2009)

In the 14th century the forest administration in some regions began to control the wood consumption for the glass production. The production of 1 ton of glass requires the consumption of 250 tons of wood. Regulations in the forest of the Spessart Mountains at 1331 and 1406 AC limited the masses of production of glass vessels and glass panes. Parallel to these regulations limiting the size of the production of certain glass-houses the quality of wood for glass making decreased. It is recorded that in Central Europe large areas had lost their forests.

A larger CaO/K_2O ratio of about two (instead of one) in glass from the Laudengrund glass-house in the Spessart Mountains reflects a larger proportion of twigs beside trunks in the wood used for the ash. The glass-house was active at about 1300 AC and has been detected as a pilot site for this glass type by Wedepohl in Schmid et al. (1996). Because of the relatively large proportion of calcium we called this type early wood ash lime glass. In the later produced wood ash lime glass potassium decreases to 7.5% K_2O and the CaO/K_2O ratio is on average as large as 3.4. In this subtype the low potassium as alkali flux was supplemented by some sodium added as NaCl to the starting mixture of the glass. The change in chemical composition from wood ash to wood ash lime glass caused an increase of the melting temperature of the glass from 1200 to 1350 °C. In the present investigation we calculated the average composition of 7 wood ash lime glasses from Hoexter (Westphalia) based on the original investigation by König et al. (2002). They were used in the 14th to 16th century and later.

For the final glass subtype of the medieval period only twigs and branches of beech trees were used resulting in high calcium and low potassium concentrations. The CaO/K_2O ratio of this mixed alkali glass is close to nine. The low potassium (close to 3% K_2O) is supplemented by about 2.5% Na_2O added as NaCl. Gerth et al. (1998) explored experimentally the maximum concentration of sodium chloride soluble in wood ash glass melts being close to 2.3% NaCl.

The nine mixed alkali glasses analyzed for this investigation came from 3 glass-houses of late medieval age (about 1450 AC) in the Taunus Mountains (Wedepohl and Kronz, 2009) excavated by Steppuhn (2006).

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