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Release of lead from Renaissance lead-glazed ceramics from southern Denmark and northern Germany: implications from acetic acid etching experiments

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Abstract

Lead-glazed potsherds from archaeological excavations at six Renaissance (1536–1660 CE) sites in southern Denmark and northern Germany have been subjected to etching experiments using 4 wt% acetic acid. The extracts of 45 sherds were analysed by Inductively Coupled Plasma Mass Spectrometry. At one site, the ducal hunting castle of Grøngaard, Pb levels in acid extracts from glazed dishes were so high (up to 29,000 µg Pb cm^{-2} day^{-1}) that acute toxic effects likely occurred if the dishes were used for serving food containing vinegar. More moderate acid-etching Pb levels were found in dishes from other sites, but they still exceed the WHO critical level if used daily. Acetic acid etching experiments performed on pipkins (three-legged cooking pots with a handle) yielded somewhat lower Pb extract values, averaging ca. 25 µg Pb cm^{-2} day^{-1}. Taking into account the widespread use of pipkins for cooking, they might easily have led to a higher weekly Pb intake than the use of the moderate-level dishes. The question remains whether such high levels of Pb exposure during meals led to injurious Pb intake. Prior skeletal analyses have shown that medieval to early modern individuals from the area, especially in towns, were exposed to Pb. While exposure could have come from various sources other than lead-glazed ceramics, such as cosmetics, paint, antibacterial ointments, and lead water pipes, widely distributed lead-glazed ceramics had the potential of being a main source of Pb. How the pottery was actually used is uncertain, and it certainly was not evenly distributed across all segments of society, but the etching experiment results suggest that severe poisonous effects could have resulted from the use of lead-glazed Renaissance ceramics.

Keywords: Renaissance, Ceramics, Glazing, Lead, Etching, Northern Europe

Introduction

We examine the extent to which Renaissance lead glazed utilitarian ceramics in southern Denmark and Northern Germany were a source of Pb exposure on a regular basis. This type of pottery had a great potential to contaminate food when glazed surfaces were in contact with acids with a pH equivalent to vinegar.

The first evidence of lead-glazed ceramics production dates to the first century BCE during the Late Hellenistic period in Anatolia [1, 2]. Lead-glazed ceramic surfaces are slick and impervious to liquids and fats, amongst other substances, making them easy to clean. The glaze adds mechanical strength to pottery, so it is less likely to break and chip during daily use. Attractive colours produced by adding transition metal oxides enhance the visual appeal of both utilitarian and decorative items. Using

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such ceramics, however, comes at a biological cost. It has long been known that Pb exposure, which can originate from lead-glazes, exerts a severe toll on human health, including adverse effects of a cognitive nature, affecting intelligence and behaviour [3–6].

Lead glazing is still used today. Such pottery sufficiently contaminates food and liquids to represent a significant health hazard, especially in some ethnic groups and regional distribution networks [7–17]. Much of the problem in recent decades comes from everyday pottery made for relatively limited and poorly regulated markets; therefore, this sort of Pb-exposure has an uneven geographical distribution. In the not-so-distant past, however, utilitarian lead glazed pottery vessels saw widespread use in many countries, including those in northern Europe.

The present work complements recent analyses of human skeletons where it was found that medieval to early modern period Pb exposure varied according to social position and residential location in the study area [18, 19]. At that time, a stark difference in Pb exposure was related to where people lived, with those in rural communities having skeletons remarkably free of Pb, whereas the Pb burden was high in urban environments. There was also a tendency for greater Pb exposure in the higher social strata. The Pb concentrations in cortical femoral tissue ranged from ca. 1 $\mu g\ g^{-1}$ in rural Tirup to ca. 100 $\mu g\ g^{-1}$ in urban Ribe. One likely difference between rural and urban life was the extent to which households had access to lead-glazed ceramics typically obtained in urban markets or shops. Analysing pottery from the immediate post-medieval period establishes whether an appreciable amount of Pb could have been released from lead-glazed ceramic vessels used to cook, serve, and store food. This is of importance to archaeological studies of community life in the region because locally made and widely exchanged lead-glazed ceramics were common throughout Scandinavia and the Baltic at that time [20–24].

Materials and methods

Ceramic samples

Samples of lead-glazed redware pottery, dishes and pipkins, were obtained from six sites in southern Denmark and northern Germany (Fig. 1). Glazed ceramics during the Renaissance were so ubiquitous in the region that almost any excavation yields such pottery, although its representation in ceramic assemblages varies considerably from site to site, especially between rural and urban settlements [25]. The sherds analysed here came from different socioeconomic contexts: two town-based production sites, two ducal castles, one manor, and one rural settlement. One site is located in northern Germany. Five sites are located in Jutland (southern Denmark, Fig. 2), while the rural site is on the adjacent island of Funen. During the Renaissance, the southern part of Jutland included the Duchy of Schleswig, which was then part of the Kingdom of Denmark. The duchy, along with the Duchy of Holstein, was divided into parts governed either by representatives of the Danish King or dukes related to him. Although the ducal hunting castle and the manor are situated in rural settings, the inhabitants were far from country folk, as they were among the richest in Denmark at that time.

Husum

An excavation conducted by Hans Joachim Kühn and Frauke Witte from 1996 to 1998 revealed the remnants

Fig. 1 Typical examples of whole vessels from the Danish and German Renaissance: to the left a dish; and to the right a pipkin (neither pot is a part of this investigation) Examples of sherds included in the present study can be found in the Additional file 1

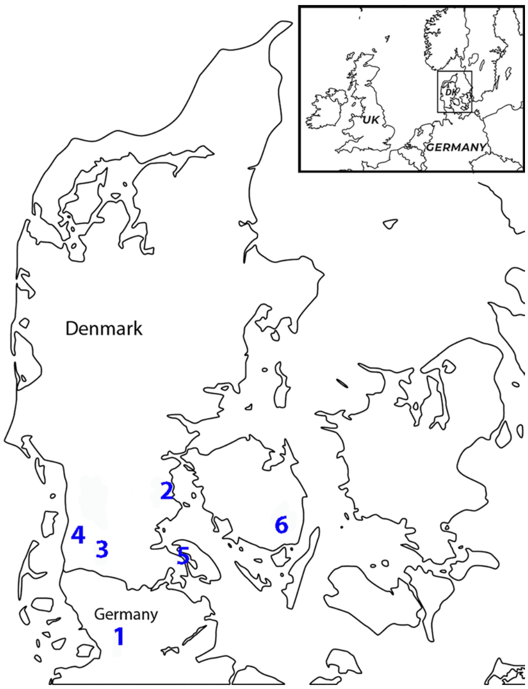


Fig. 2 Sampled sites in Germany (1) and Denmark (2–6): 1, Husum; 2, Haderslev; 3, Grøngaard; 4, Trøjborg; 5, Sønderborg; and 6, Rødskebølle

of a potter's workshop on the grounds of Süderstrasse 11 in Husum, a small provincial town in northern Germany [26, 27]. The form and decoration of the pottery, along with written sources, indicate the workshop was run by three generations of potters, beginning in 1613 with Thomas Meyer and lasting to the second half of the 17th century. The workshop was near St. Nicolai Church, which at that time was close to the town centre. Several hundred objects were found, many of which were intact because they were incorrectly fired, hence immediately discarded. They included numerous oven tiles and various kinds of glazed pots. There were also large amounts of slip-painted glazed dishes. Prior to the workshop's discovery, it was thought that the glazed dishes unearthed in Husum were imported from the Netherlands or from further south in Germany.

With only a few exceptions, all dishes had a transparent Pb glaze on their upper surfaces, and the interiors of the pipkins were glazed. Sometimes white clay and a green colourant can be seen beneath the transparent, but not always clear, glaze on the dishes. Pipkin exteriors were occasionally decorated with a rolling stamp, but otherwise only the fine surface striations characteristic of wheel-thrown pottery are present. Potters at the workshop apparently specialized in making flat dishes. While being turned on the potter's wheel, a spiral of light clay was applied to the rim. Other decorative elements were added later, including various abstract designs, leaves, flowers, pomegranates, thistles, birds, and deer. Several of the slip-painted dishes are decorated with the year 1629; it probably does not indicate the year of production but commemorates the peace treaty that ended the Danish involvement in the Thirty Years War [28]. The workshop presumably sold its ceramics to the town's citizens, as well as to dukes and nobility. Previous analyses have indicated that ceramics from Husum were also used in the Trøjborg manor 85 km to the north across the present-day Danish-German border [27].

Haderslev

Haderslev is a large provincial town in southern Denmark. In 1942 during construction work at Jomfrugang, a brick wall was encountered ca. 2 m below the surface. An excavation in 1949 by Hans Neumann showed that the wall was part of an oven originally located in the cellar of a house near the town centre [29]. Remnants of the red-brick kiln were as much as 0.71 m high and included an arched opening and two air vents. The excavation uncovered thick layers of sherds, which had been discarded as garbage. The pottery forms and decorative elements indicate the material dates to the end of the 16th or beginning of the 17th centuries.

Grøngaard

Grøngaard was a ducal hunting castle of Duke Hans "the Elder" (1521–1580). This Italian inspired villa in *Poggio Reale* style was erected in 1570, and it was rarely used after 1580 [30]. The castle was designed to impress guests who joined the duke for hunts [31]. By 1634 it was completely abandoned, and it was torn down in 1656. An inventory list from 1580, the year the duke died, sheds light on the utensils available in ducal hunting castles. Besides objects fashioned from silver and pewter, there were also chalices of "marmelstene" (of marble stones?). The list does not mention glazed ceramics, but that is probably because the value of pottery was insignificant when compared to metal objects. Metal items had the further advantage that they could be melted down and re-used for other purposes when necessary. The ceramics, excavated by Hans Stiesdal [30] in the 1950s, date to 1570–1656, with most of it from Grøngaard's heyday from 1570 to 1580.

Trøjborg

Trøjborg's ruins are on a moated site near southern Jutland's western coast. In 1580, the medieval castle was donated by the Danish King Frederik II to the nobleman Peter Rantzau who replaced it with a then-modern Renaissance manor. Partly demolished in 1851, it exists today as a picturesque ruin. Renaissance ceramics were among the many objects found in a moat that surrounded the manor when excavated by Johannes Hertz from 1959 to 1976 [32]. All the objects were tossed into the moat as garbage, and the sherds of typical Renaissance ceramics can be roughly dated to the century following the manor's construction in 1580. Some of the lead glazed redware sherds have been identified as products from the potter's workshop in Husum's Süderstrasse 11.

Sønderborg slot

Sønderborg Slot is a castle that guarded access by sea to the major Danish provincial town of the same name. The castle was established around 1200, but it was almost constantly refurbished up until the 20th century. It was modernized in Renaissance style by the Danish King Christian III and Queen Dorothea, but from 1571 to 1667 it belonged to a succession of local dukes. The glazed ceramics from Sønderborg Slot were unearthed during a lengthy restoration from 1964 to 1973 [33]. Glazed redware ceramics, both pipkins and slip-painted dishes, were found inside the towers and in the courtyard, and they date to the castle's use in the 16th and 17th centuries.

Rødskebølle

When a new motorway was built on Funen between Odense and Svendborg, ca. 3800 m^2 of a village about 3 km north of Svendborg's present-day city limits were excavated by Svendborg Museum [34]. The site, Rødskebølle, was once a small rural community. Among the excavated features were the remnants of five houses, fences, a furnace, and two wells dating between 1100 and 1600. Most of the finds, however, were from 1500 to 1600. Of the many sherds, six lead-glazed sherds from the Renaissance deposits were selected for analysis. Four were from different sized dishes and two were too small to classify. Three sherds were decorated with yellow paint beneath the glaze.

All together, 45 samples were investigated, out which 29 were dishes, 14 pipkins, and 2 of undetermined type. There were 6 samples from Husum, 5 from Haderslev, 15 from Grøngaard, 7 from Trøjborg, and 6 each from Sønderbog Slot and Rødskebølle.

Analytical procedures

Laboratory etching experiments

Some of the glazing has a rather regular appearance and a fairly uniform thickness of between 100 and 400 µm. The variation is most likely attributable to an unequal application of glaze in different workshops. Glaze on the sherds used in the experiments was for the most part intact, but in some cases there were small traces of wear. Sometimes otherwise rather smooth and slick surfaces exhibit crazing where angular segments of intact glaze 10–100 µm in diameter are separated by tiny cracks. Figure 3 shows optical images of such surfaces, as well as the same samples after prolonged etching with 4 wt% acetic acid. Completely intact surfaces are seen on sherd rims. They might have originated from pottery that was broken shortly after production or while being transported; that is, they were damaged and discarded before being used. Other sherds have worn surfaces, often on vessel rims, indicating the dishes and pipkins had been used for extended periods.

Sherds were washed in MilliQ water and dried. Each sherd was then lacquered with shellac, except on the glazed surfaces, and left to dry for 24 h. If the shellac was absorbed by the exposed ceramic, the lacquering process was repeated and the sample was left to dry for another 24 h. That process ensured the broken edges were sealed so they were impervious to the etching effects of acid added later in the experiment. Doing so eliminated the possibility of contamination from the sherd if it held dissolvable Pb-rich compounds. Adding impervious shellac similarly avoided any effect from the exposed edges of the glaze, and it prevented the ceramic paste from absorbing the acid. Glazed surfaces were photographed and measured. The exposed areas varied from 0.24 to 1.44 cm^2.

Each shellac-treated sherd was placed in a sealed plastic container, and 5 mL or 10 mL ICP-MS grade 4 wt% acetic acid was added; the volume depended on the sherd's size. A concentration of 4 wt% acetic acid was used because it is similar to what can be found in present-day food, such as pickles and vinegar bought in a supermarket (ca. 4–8 wt % acetic acid), and closely approximates the test methods for the release of Pb and Cd according to ISO 7086-1

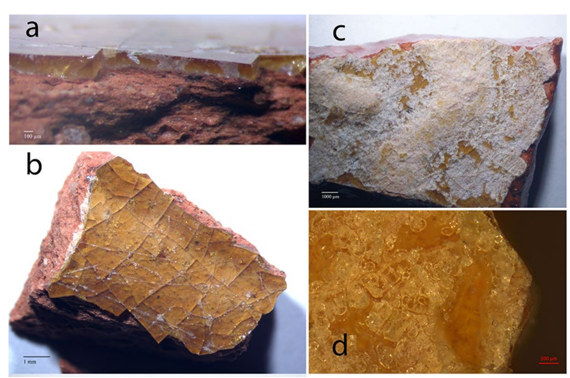


Fig. 3 Optical images of a surface of a piece of glazed pottery. **a** Side view of unetched surface showing the glaze (top) and paste (bottom) (KLR-2282). **b** Top view of unetched surface with crazed glaze (KLR-2282). **c** top view of experimentally etched surface (KLR-2278); and d, high magnification with crossed polars of experimentally etched surface (KLR-2278)

for glass hollowware in contact with food. It is a concentration high enough to be effective in preserving food, while low enough to taste good. This concentration has previously been used in an analysis of traditional pottery manufactured just over a century ago [14] and in several studies of commercially and locally made ceramics where Pb ingestion poses a potentially significant threat to public health [7–9, 11, 13, 16].

Once the acetic acid was introduced, the plastic containers were sealed and placed on a shaking table with a velocity of 275 movements min^{-1} for 24 h at room temperature (ca. 21 ºC). All etching experiments were done on duplicate samples prepared separately. The values reported here are averages of the two.

Lead analyses by ICP-MS

Lead was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The samples from acetic acid treatment were diluted to 10 mL with Milli-Q water and filtered through 0.45 µm PVDF Q-Max disposable filters. The resulting solution was stored at + 4 °C until analyses were performed a day or two later. Analyses were carried out on a Bruker ICP-MS 820 equipped with a frequency-matching RF generator and a Collision Reaction Interface (CRI) operating with either helium or hydrogen as skimmer gas. Radiofrequency power was 1.40 kW; plasma gas flow was 15.50 L min^{-1}; auxiliary gas flow was 1.65 L min^{-1}; sheath gas flow was 0.12 L min^{-1}; and nebulizer gas flow was 1.00 L min^{-1}. The CRI reaction system was activated for Fe and Cu because of interferences with polyatomic species produced by a combination of isotopes from the argon plasma, reagents, or the matrix. A mixture of ^{45}Sc, ^{89}Y, and ^{159} Tb was used as an internal standard added to all analyses. Three Pb isotopes were measured without skimmer gas, ^{206}Pb, ^{207}Pb and ^{208}Pb, and an average was calculated by the Bruker Software. The contribution from each mass was corrected according to their natural abundances. Individual Pb isotopes were not treated separately, neither were they used for calculating isotopic ratios. They were only used to calculate the weighted average of the three isotopes intended for quantification. The dwell time was 20 ms for each isotope. Five replicate analyses of each sample were made, with each replicate consisting of 30 mass scans.

Prior to analysis the samples were diluted 1:20 with 1% acetic acid. Multi-element calibration standards were prepared in 1% acetic acid concentrations (0, 1, 10, 20, 100, and 200 µg L^{-1}), but for each element only 3 standards were selected to fit the appropriate concentration range found in the sample. Each day an in-house standard sample made from a homogenized medieval bone was analysed along with the samples to monitor overall performance. The Limit of Quantification (LOQ) for Pb was 0.98 µg L^{-1}. However, no readings were below the LOQ. The results are listed in Table 1.

Multi element mapping by LA-ICP-MS

Magnesium, Al, Si, Ca, Fe, and Pb were mapped in a polished cross section of one sherd (KLR-2276) using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Laser ablation was performed with a CETAC LXS-213 G2 equipped with a NdYAG laser operating at a wavelength of 213 nm. A 10 µm circular aperture was used. The shot frequency was 20 Hz. The helium flow was 600 mL min^{-1}. The laser operations were controlled by the DigiLaz G2 software provided by CETAC. The ICP-MS analyses were carried out using a Bruker Aurora M90 equipped with a frequency matching RF-generator. Radio frequency power was 1.30 kW, plasma argon gas flow rate was 16.5 L min^{-1}, auxiliary gas flow rate was 1.65 L min^{-1}, and sheath gas flow rate was 0.18 L min^{-1}. The following isotopes were measured without skimmer gas: ^{24}Mg, ^{27}Al, ^{29}Si, ^{44}Ca, ^{57}Fe, and ^{208}Pb. No interference corrections were applied to the selected isotopes. The analysis mode used was peak hopping using 3 points per peak, and the dwell time on each peak was 1 ms.

SEM-EDS

A subset of 11 samples was analysed in detail using a Zeiss Evo-15 Scanning Electron Microscope with an Oxford Instrument AZtec EDS system, using polished cross sections that included the glaze, the underlying transitional zone from glaze to ceramic body. Analyses of the glaze were done separately for three areas ca. 30 µm deep and ca. 200 µm wide near the top surface and near the contact with the ceramic body, respectively, avoiding areas with inclusions or visible damage. Ten elements were consistently found at concentrations at or above ca. 0.1 wt% of their oxides: Na, Mg, Al, Si, P, K, Ca, Ti, Fe, and Pb. An accelerating voltage of 20 kV and beam current of around 2.5 nA were used to optimise detection limits for transition metals. Data are reported following ZAF correction procedure, assuming oxygen content by stoichiometry and normalised to 100 wt% total sum (Table 2). The data quality was monitored through repeat analysis of Corning glass standards, reported in the Additional file 1).

Results

The acetic-acid etching results are provided in Table 1 and shown in Figs. 4 and 5 for dishes and pipkins, respectively. Six dishes from Grøngaard yielded extremely high Pb values, from 10,300 to 29,100 µg Pb cm^{-2} day^{-1}, relative to the other vessels. The latter include three dishes from Grøngaard that have more moderate values

Table 1 Results of the etching experiments using 4 wt% acetic acid

Site	Lab No.	Type	Description	Pb leaching µg Pb cm^{-2} day^{-1}	SD µg Pb cm^{-2} day^{-1}
Grøngaard	KLR-2276	Dish	RW, WP, GP	3.69	0.52
Grøngaard	KLR-2277	Dish	RW, WP, GP	4.45	0.62
Grøngaard	KLR-2278	Dish	RW, WP	11,1	1556
Grøngaard	KLR-2279	Dish	RW, WP	5969	836
Grøngaard	KLR-2280	Dish	RW, WP	7822	1095
Grøngaard	KLR-2281	Dish	RW, WP	3714	520
Grøngaard	KLR-2282	Dish	RW, WP	29,2	4082
Grøngaard	KLR-2283	Dish	RW, WP	10,3	1436
Grøngaard	KLR-2284	Dish	RW, WP	43.7	6.12
Husum	KLR-2301	Dish	RW, WP, GP	2.55	0.36
Husum	KLR-2302	Dish	RW, WP, GP	2.60	0.36
Husum	KLR-2304	Dish	RW, WP, GP	33.9	4.7
Husum	KLR-2305	Dish	RW, WP, GP	61.8	8.7
Husum	KLR-2306	Dish	RW, WP, GP	7.64	1.07
Husum	KLR-2307	Dish	RW, WP, GP	3.45	0.48
Sønderborg	KLR-2308	Dish	RW, WP, GP	26.1	3.7
Sønderborg	KLR-2309	Dish	RW, WP, GP	16.3	2.3
Sønderborg	KLR-2310	Dish	RW, WP, GP	14.3	2.00
Sønderborg	KLR-2311	Dish	RW, WP, GP	16.3	2.30
Sønderborg	KLR-2312	Dish	RW, WP, GP	24.1	3.40
Sønderborg	KLR-2314	Dish	RW, WP, GP	6.79	0.95
Trøjborg	KLR-2285	Dish	RW, WP, GP	142	20.0
Trøjborg	KLR-2286	Dish	RW, WP, GP	20.3	2.8
Trøjborg	KLR-2287	Dish	RW, WP, GP	12.7	1.80
Trøjborg	KLR-2288	Dish	RW, WP, GP	58.3	8.20
Rødskebølle	KLR-6839	Dish	RW, WP	1.62	0.23
Rødskebølle	KLR-6840	Dish	RW, WP, GP	13.1	1.80
Rødskebølle	KLR-6841	Dish	RW, WP, GP	6.88	0.96
Rødskebølle	KLR-6842	Unknown	RW	17.2	2.40
Rødskebølle	KLR-6843	Unknown	RW, WP	4.45	0.62
Rødskebølle	KLR-6844	Dish	RW, WP, GP	0.63	0.09
Haderslev	KLR-2291	Pipkin	RW	2.99	0.42
Haderslev	KLR-2295	Pipkin	RW	0.301	0.04
Haderslev	KLR-2296	Pipkin	RW	3.22	0.45
Haderslev	KLR-2298	Pipkin	RW	4.38	0.61
Haderslev	KLR-2299	Pipkin	RW	1.11	0.15
Trøjborg	KLR-6626	Pipkin	RW	26.6	3.70
Trøjborg	KLR-6627	Pipkin	RW	25.2	3.50
Trøjborg	KLR-6628	Pipkin	RW	1.04	0.15
Grøngaard	KLR-6629	Pipkin	RW	948	133
Grøngaard	KLR-6630	Pipkin	RW	21.7	3.0
Grøngaard	KLR-6631	Pipkin	RW	11.0	1.50
Grøngaard	KLR-6632	Pipkin	RW	4.47	0.63
Grøngaard	KLR-6633	Pipkin	RW	17.0	2.40
Grøngaard	KLR-6634	Pipkin	RW	2.87	0.40

The columns contain information about the site, sample laboratory number, pottery type, type of decoration beneath the glaze (RW, redware; WP, white paint; GP, green paint), Pb etching rate given in µg Pb cm^{-2} day^{-1}, and standard deviation of the etching rate in µg Pb cm^{-2} day^{-1}

Table 2 Results of SEM-EDS analyses of the glazes of 11 selected samples

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	FeO	PbO	Leach rate
2276 top	0.11	0.42	6.1	29.8	0.12	0.56	0.34	0.47	1.3	60.6	3.70
2276 bot	0.10	0.44	6.8	29.9	0.13	0.54	0.38	0.49	1.3	59.9	
2278 top	0.11	0.34	4.2	20.4	0.09	0.35	0.16	0.28	1.1	72.9	11116
2278 bot	0.15	0.39	4.2	21.4	0.08	0.33	0.16	0.27	1.2	71.9	
2279 top	0.06	0.36	4.1	20.0	0.09	0.33	0.16	0.28	1.4	73.1	5969
2279 bot	0.07	0.40	4.0	21.4	0.10	0.37	0.18	0.25	1.3	71.9	
2280 top	0.09	0.30	4.0	20.5	0.08	0.29	0.13	0.28	1.1	73.2	7822
2280 bot	0.09	0.29	4.0	22.3	0.08	0.36	0.14	0.28	0.8	71.7	
2281 top	0.07	0.39	4.6	20.5	0.09	0.32	0.17	0.33	1.6	71.9	3714
2281 bot	0.07	0.39	4.6	21.2	0.11	0.36	0.18	0.33	1.5	71.2	
2283 top	0.01	0.34	4.1	20.8	0.17	0.31	0.15	0.26	0.9	72.9	10258
2283 bot	0.02	0.32	4.3	22.0	0.13	0.30	0.17	0.29	1.0	71.5	
2287 top	0.01	0.11	2.1	30.0	0.12	0.42	0.13	0.32	0.5	66.3	12.7
2287 bot	0.13	0.29	3.0	30.6	0.10	0.50	0.18	0.26	0.7	64.2	
2288 top	0.07	0.18	2.0	30.4	0.07	0.43	0.14	0.20	0.4	66.1	58.3
2288 bot	0.12	0.17	3.3	29.9	0.03	0.51	0.16	0.34	0.5	64.9	
2301 top	0.10	0.41	3.5	34.4	0.11	0.65	0.33	0.35	1.0	59.2	2.60
2301 bot	0.09	0.45	4.6	34.3	0.09	0.72	0.33	0.34	1.1	58.0	
2305 top	0.00	0.25	2.1	28.4	0.08	0.43	0.19	0.26	0.5	67.8	61.8
2305 bot	0.02	0.61	3.1	31.6	0.08	0.74	0.27	0.20	1.0	62.4	
2306 top	0.00	0.42	2.3	30.9	0.06	0.62	0.46	0.24	0.6	64.3	7.60
2306 bot	0.01	0.69	3.5	31.7	0.07	0.84	0.60	0.23	1.1	61.3	

Average data of 5 individual measurements of area scans, normalised to 100 wt%. Sample codes and site names are as in Table 1; pairs of data give the surface glaze near the top and the lower glaze near the bottom but close to the ceramic body

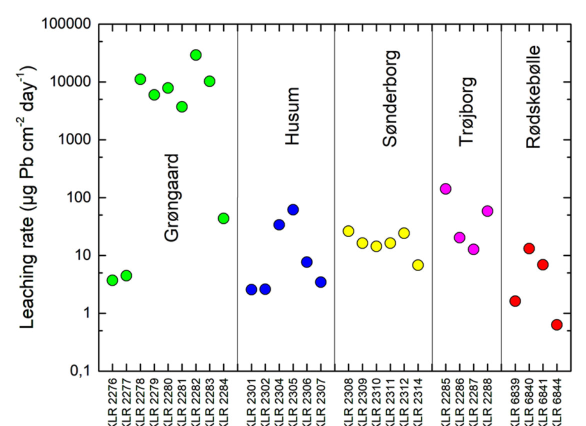
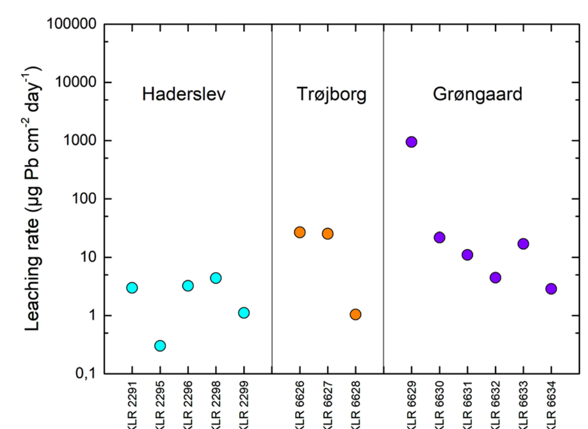


Fig. 4 Experimentally determined Pb-etching rates on dishes; Grøngaard (green), Husum (blue), Sønderborg (yellow), Trøjborg (magenta), and Rødskebølle (red). Error bars of ± 1σ based on three repeated independent measurements of each sherd are smaller than or comparable to the point size and are therefore left out



Figs. 5 Acetic-acid leaching results from pipkins; Haderslev (cyan), Trøjborg (magenta), and Grøngaard (green). Error bars of ± 1σ based on three repeated independent measurements of each sherd are smaller than, or comparable to, the point size and are therefore left out

between 1.60 and 142 µg Pb cm^{-2} day^{-1} (Fig. 4). In contrast, five of the six pipkins from this site have leaching rates below 25, and only one pipkin from Grøngaard reaches a remarkably high value of 948 ± 133 µg Pb cm^{-2} day^{-1} (KLR-6629). The more moderate values that characterize most of the pottery might be separated into two groups: one with values above 50 µg Pb cm^{-2} day^{-1} (average of 11,300 µg Pb cm^{-2} day^{-1}), and the other with values below 50 µg Pb cm^{-2} day^{-1} (average of 22 µg Pb cm^{-2} day^{-1}); see Fig. 5. Overall, the Pb levels for pipkins are consistent with dishes exhibiting lower etching values.

The dishes are mostly decorated with a yellow paint often overlaid by green paint, which is part of a decoration beneath the glaze. Occasionally, no green paint is observed. This can be because of a sherd's small size, although sometimes the green paint seems to be missing altogether, as in six of the eight dishes from Grøngaard. The pipkins are all glazed redware. Detailed observations are given in Table 1. The ceramic bodies were made from ferruginous clay, consistent with the red colour of the pastes.

Here, we focus on the glaze, the material in contact with the food and potentially subject to Pb leaching. The glaze compositions (Table 2) are dominated by lead oxide (58 to 73 wt%) and silica (20 to 34 wt%) as main compounds, with minor amounts of alumina (2 to 7 wt%) and iron oxide (ca. 1 wt%). No other compounds in the glazes were discovered exceeding 0.5 wt%, except for CuO at around 1 wt% in samples KLR 2287, 2305 and 2306, related to the decoration.

The glazes are quite homogeneous as can be seen in Fig. 6. Another example of the homogeneity is the LA-ICP-MS mapping of a cross section made of a single sherd which can be seen in Fig. 7 (KLR-2276). No variation of any element is visible. In particular, no Pb is detected in the ceramic paste (lowest frame in Fig. 7). A detailed analysis of the compositions near the top surface (top) and near the contact to the ceramic body (bottom), but without including any of the interaction or transition layer, shows a slight systematic gradient with higher alumina and silica concentrations in the bottom part compared to the top, balanced by lower lead oxide values. The differences in concentrations do not exceed 2 to 3 wt% in absolute values (Table 2).

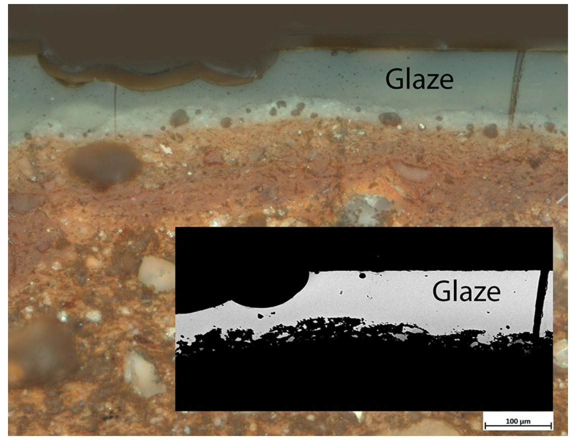


Fig. 6 An example of the layered structure of a glazed sherd (KLR 2279) seen in cross section under the OM with crossed polarisers. The glaze appears light grey, with a crack (right) and some surface pitting (left). A thin white interaction zone overlays the ceramic body. The body is relatively coarse with numerous mineral inclusions. Inset is a high-contrast SEM image of the upper right part, showing only slight Pb enrichment in the glaze near the surface and a limited penetration of PbO into the underlying ceramic material; the ceramic body appears dark in this extreme contrast

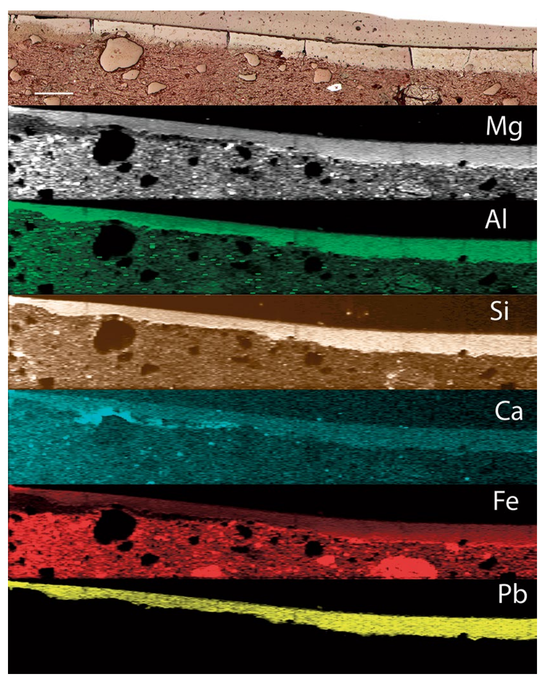


Fig. 7 LA-ICP-MS multi-element mapping of a polished cross section of sample KLR-2276, with elements indicated. Scale bar of 200 µm in the top panel, an optical image

Discussion

The nature of the glaze and the mechanism of pb release

Relatively pure lead-silica glazes were common since at least the Roman period [35], and their use continued through the Ottoman period and the Renaissance into modern times. Typically, the PbO content in these glazes rarely exceeded 65 wt% and was often as low as 50 to 60 wt%. Higher PbO values have been documented, for instance in the Hellenistic Group 1 in Walton and Tite [2] with around 70 wt% PbO and in some similarly high Pb glazes from 14th to 15th century Belgrade [36]. The most common Pb glaze recipes are the application of a pure lead oxide or lead carbonate compound which during firing reacts with the ceramic body to form the glaze, and the application of a mixture of lead oxide and silica onto the ceramic surface. According to experimental work done by Molera et al. [37], the latter leads to a glaze with higher concentrations of typical ceramic oxides (alumina, iron oxide) near the ceramic-glaze interface, decreasing to the surface, where a nearly pure lead silicate prevails. In contrast, the application of pure lead oxide leads to a more homogenous glaze composition throughout, with the ratio between silica and other main ceramic oxides broadly unchanged in the glaze [2, 35]. The main parameters determining the glaze composition, specifically its lead oxide content, and the basic recipe, the firing temperature, and duration of firing.

Figure 8 shows the systematic increase in alumina and decrease in lead oxide in the lower part of the glazes compared to the upper parts. The difference is much larger for the glazes with less than 70 wt% PbO, and barely noticeable for those with higher PbO concentrations. Sufficient firing time to reach near equilibrium or higher temperatures should lead to increased uptake of silica and alumina up to their limit of solubility in lead oxide, and therefore reduced lead oxide concentrations in the glaze. Generally slow diffusion rates in the viscous melt result in a gradient of decreasing ceramic components away from the glaze-ceramic interface (e.g. [2]:Fig. 6).

The presence of the ceramic body, acting as a buffer or reservoir providing further silica and alumina as the reaction proceeds, is essential for this gradient to occur. Chen et al. [38] have published the liquidus surface and phase equilibria in the system PbO-SiO_2-Al_2O_3. In Fig. 9, the glaze compositions are plotted onto the PbO-rich corner of the diagram (the entire ternary diagram is offered in the Additional file 1).

The estimated firing temperatures for the glazes from Grøngaard are about 800 °C, similar to those from Trøjborg and Husum. However, the two groups differ in their position within the liquidus surface.

The position of the glazes from Trøjborg and Husum (grouped together as Husum in Fig. 9) within the cotectic trough leading towards the silica-rich corner (top of the diagram) at the foot of the steep slope towards increasing silica contents is significant. This is the equilibrium melt composition at the firing temperature in the presence of an unlimited silica reservoir relative to the small amount of lead oxide—silica mixture applied as glaze. At this composition, the melt volume is maximised by incorporating as much material from the ceramic as the firing temperature will permit. In contrast, most of the Grøngaard glazes fall into the more lead-rich part of the diagram at a similar liquidus temperature, but they did not yet absorb their maximum possible amount of ceramic material, resulting in a higher PbO content in the glaze and the lack of an alumina gradient in the glaze (Fig. 9). Thus, it appears that the firing duration for the

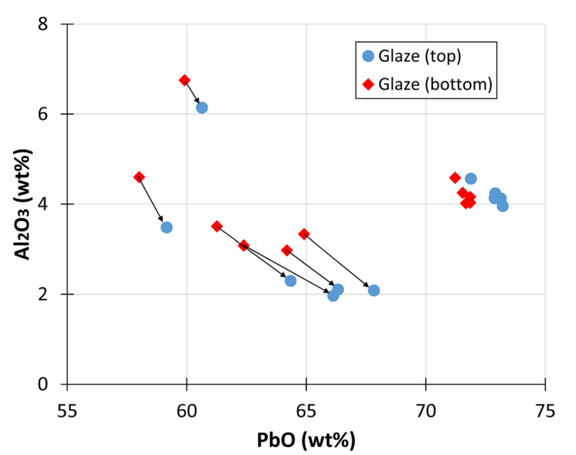


Fig. 8 The alumina content in the bottom of the glazes, near the ceramic body, is systematically higher than near the top of the glaze. The arrows connect pairs of data (bottom and top) for individual glazes. The effect is barely noticeable for the high-lead glazes from Grøngaard (right, no arrows), indicating no significant absorption of ceramic material into the glaze compositions

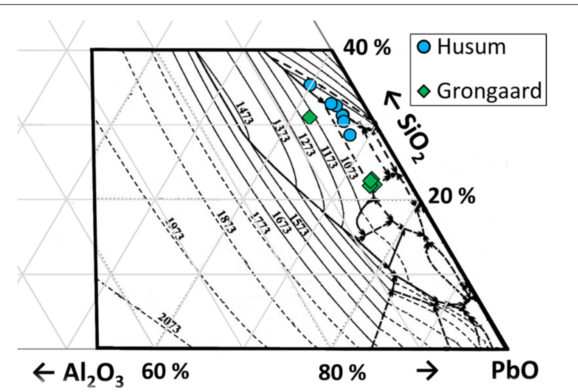


Fig. 9 Projection of glaze compositions onto the lead-rich corner of the phase diagram Al_2O_3-SiO_2-PbO. The Husum glazes fall close to the eutectic trough towards higher silica concentrations, while the Grøngaard glazes are in an intermediate region closer to the lead-rich corner. The projected liquidus temperature for most compositions is around 1073 K (800 °C) or below. See OSM Additional file 1: Fig. S1 for the full phase diagram. Temperatures are given in Kelvin. Modified after Chen et al. [38]

Grøngaard dishes was insufficient to allow maximum diffusion of silica and alumina from the ceramic body into the viscous melt. Therefore, the glaze remained higher in PbO than in the other vessels, particularly in the surface area away from the ceramic body—the area in direct contact with the liquids and foodstuffs served on these vessels. The analysed dishes from Husum and Trøjborg have overall lower PbO concentrations, possibly reflecting a firing duration sufficient to reach near equilibrium and maximum absorption of silica and alumina across the glaze thickness.

During the use of these glazed wares, increased temperature and decreased pH increase the amount of Pb that can be released by acetic acid [39]. So too does the amount of time a surface is in contact with acid [40]. Two different mechanisms can be proposed through which Pb is released from glazed surfaces in the presence of acids. One is leaching as proposed by Gould et al. [40] and Escardino et al. [41]. The Pb atoms on the glaze react with the acid and leave vacant sites that are then filled by Pb atoms from deeper in the glaze. That leads to a diffusive transport of Pb from the interior of the glaze. At the same time, H^+ is transported inwards. The other mechanism is simple etching, during which acid removes the glaze surface leaving the rest of it intact. In the investigated sherds, it seems that simple etching is dominant, as can be seen from Fig. 10 where optical micrographs show the glazed surface before and after the laboratory etching experiments. The etching takes place in circular bays and with seemingly uneven speeds. These bays can also be seen in sherd surfaces (Fig. 3d) and in cross-sections (Fig. 6).

The possibility that all the Pb can be extracted from a glazed dish through daily use has been investigated [42]. For dishes etched in acetic acid 3 times in a single day, there was a substantial decline in the amount of released Pb. When such a dish was washed and left for the next day's use, the released Pb approximately equalled the amount detected on the previous day. This finding was explained as a surface reaction between the glazed surface and carbon dioxide dissolved in a thin water film.

The present results (Table 1) exhibit some cases of extremely high etching rates, the maximum at about 29,100 µg Pb day^{-1} cm^{-2}, a soaring value. At this rate a 200 µm thick glaze will disappear after only 24 h had the vessel been continuously exposed to 4 wt% acetic acid. Other vessels with more moderate etching rates of 10 µg Pb day^{-1} cm^{-2} would take daily exposures to such acid concentrations an entire year for a 200 µm glaze to disappear.

Apart from acidity, temperature, and duration of the solvent, the leaching rate for lead glazes is strongly affected by the concentration of lead oxide in the glaze. Modern regulations accordingly limit permissible PbO content in glass vessels and glazes used for food preparation or serving. The PbO content of the glazes analysed here is more than twice the currently accepted levels of 24 to 32 wt% PbO in lead glass for hollowwares (European Council Directive 1969/493/EEC). A ten-fold higher leaching rate has been found for glasses with 66 wt% PbO than for those with only 47 wt% PbO [43, 44]. They link the difference to more easily leachable Pb acting as network former in high-lead glasses (Pb-O-Pb bonds) compared to the more stable PbO bonded as network modifier (Si-O-Pb bonds) in lower Pb glasses [45]. This strong correlation between leaching rates and PbO content in the glaze is also evident from the data in the present study (Fig. 11), which show an exponential increase in the leaching rate with increasing PbO content.

The exponential increase in leaching rates for glazes with PbO content beyond ca. 65 wt% is remarkable but limited to the Grøngaard dishes. All other dishes, and all but one of the Grøngaard pipkins, show much lower leaching rates and, where analysed, PbO content. Future

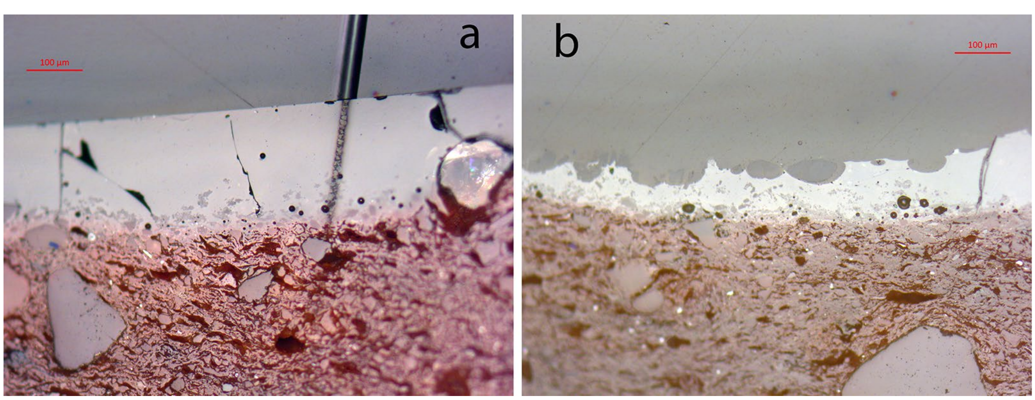


Fig. 10 Optical images showing the glazed layer before (**a**, KLR-2276) and after (**b**, KLR-2278) the laboratory etching experiment

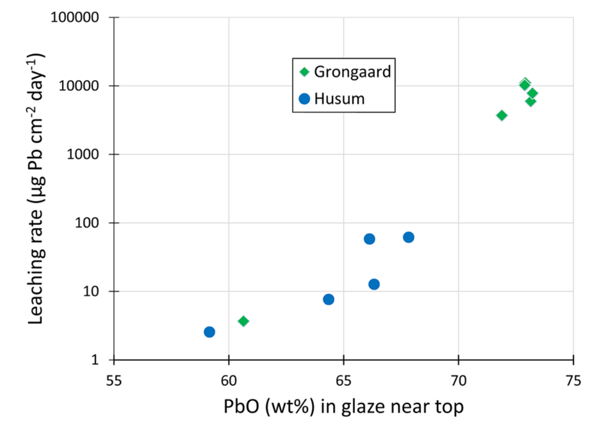


Fig. 11 Leaching rate (in µg Pb cm^{-2} day^{-1}) versus PbO content of the glaze of dishes. Blue circles are from Trøjborg (KLR-2287, 2288) and Husum (KLR-2301, 2305, and 2306). The green diamonds are from Grøngaard (KLR-2276, 2278, 2279, 2280, 2281 and 2283). Note the logarithmic scale of the Y-axis and the strong correlation between leaching rate and PbO contents. The five high-lead glazes are all dishes from Grøngaard

research will have to assess whether the dishes with high-lead glazes were intended for food use or to decorate the ducal hunting castle, although it seems unlikely that the high PbO pipkin from Grøngaard could have had any decorative value. Their high Pb leaching rates would have made acidic food served in them highly toxic.

Vinegar in Renaissance food

The widespread use of vinegar in Danish Renaissance food is indicated by recipes from the period. No Danish cookbooks are known from the 16th century, but one of the oldest handwritten medieval recipe collections from Europe exists in two Danish versions dating to around 1300. Both show a common use of vinegar in marinades and sauces. The first Danish cookbook in print appeared in 1616, and it was a translation of a hundred recipes from a more comprehensive Alsatian recipe collection attributed to Anna Wecker [46]. Three decades later in 1648 all Anna Wecker's recipes were published in a Danish translation [47]. Vinegar was recommended for fish and meat marinades, fish stock and bouillon, and various sauces, or just drizzled over cooked meat, fish, and vegetables.

Vinegar, like salt, was also used to preserve food. This was especially true of marinades [48]. Vinegar does not appear in contemporary account books as often as one might expect considering the amounts supposedly used. But vinegar, much like beer and juices from apples and pears, were often produced at home, hence would not have been listed in the accounts of big households. The lengthiest of the late medieval accounts from Denmark is from the court of King Hans' queen, Christine, dating from 1497 to 1521 [49]. A considerable amount of vinegar was bought for dinners and banquets when the queen was travelling, but not when the court was residing at home or at one of the royal residences. However, it is mentioned once that a cooper made six barrels for vinegar, showing that large quantities of vinegar were readily at hand in the court's pantry [49]:161.

In addition to vinegar, other components of the diet contributed to the acidic content of what was routinely consumed by many people. They include fruit, mustard, and honey used when cooking food or to accompany it [50, 51]. Some of them, such as cider, were presumably stored or served in ceramic vessels with surfaces covered by a Pb glaze.

While recipes from cookbooks reflect the aspirations of well-to-do households, such meals were not prepared on a daily basis in ordinary homes [50]. Two different traditions of cooking existed using different forms of ceramics. In urban and manorial contexts, an internationally inspired food culture, as described in cookbooks, had made inroads into the diet, and it was prepared, stored, and served in glazed vessels produced in pottery workshops and sold in town markets [52]. It coexisted with a traditional agrarian tradition that focused mostly on boiled food and used locally produced pottery, including an unglazed black ware. The food consumed by poor townsfolk was likely similar to what people in the countryside ate. One can expect, therefore, that Pb exposure varied by where people lived and their station in life.

Renaissance kitchenware and tableware

While it is reasonable to believe that acidic food was often served to well-to-do people during the Renaissance, there remains a question about the extent to which it came into contact with glazed ceramic surfaces. Especially in large households where many people were served at one time, big copper kettles were the backbone of cooking. They are documented in written sources, such as wills and estate inventories, but rarely found in archaeological contexts because the metal could be melted down and reused [52]. The most common and cheapest cooking pot, at least in urban settings, was the pipkin with a glazed interior. The limited size of pipkins meant they were best suited for boiling food such as porridges and stews for individual households Stews could have been cooked for hours, and they often contained vinegar. Pipkins could also have been used to prepare sauces and dressings, typically including vinegar.

Glazed slip-painted dishes were prestigious and decorative household utensils used to serve food. Among the nobility and other wealthy people, a meal might consist of several servings, usually three to four of them, each consisting of various kinds of food [48]. Everything for one serving was put on the table at once, and people helped themselves to their liking. It was considered important to have an abundance of food since it was embarrassing if any dish was entirely emptied. Food was either eaten directly from serving dishes or transferred to individual plates made of wood, pewter, or pottery. If food was served on pottery, it could have been in contact with glazed surfaces for lengthy periods, starting when the kitchen help ladled food onto a dish, followed by its presentation and consumption.

Poorer people in towns and outlying rural areas had fewer glazed dishes, although when compared to earlier centuries they were more commonly available to all segments of society during the early modern period [23]. When used, these dishes were probably emptied quicker than they would have been in a noble or wealthy person's house where meals tended to be protracted affairs. The poorer segments of society would have often used a wooden platter or a bread trencher to hold stews and the like. Unglazed wares were also in widespread use as containers, although pipkins were probably used to prepare and serve food. That meant food stayed in contact with the glazed surface of a pipkin from hearth to table.

Health consequences

The most interesting question, of course, is whether repeated exposure to lead-glazed ceramics was sufficient to affect the health of people in Renaissance Denmark and Germany. The potential for Pb contamination is estimated separately for dishes and pipkins under various conditions. While the specific circumstances of use are unknown, and glaze recipes presumably varied from one workshop to another, the range of estimated values from this study provides some appreciation of Pb exposure at that time.

Calculations of exposure from acidic food on dishes

When estimating what people might have experienced, the dish diameter is irrelevant. What matters is the size of the serving. For this exercise, three different food servings with diameters of 10, 15 and 20 cm, corresponding to areas of 79, 177, and 314 cm^2, were used. The time that food stayed on a dish presumably varied as well, and it is, in fact, unknowable. For present purposes, it is conservatively assumed that food was in contact with a serving dish for 30 min; that is, a half hour passed from the time food was placed on a dish until it was eaten. It is further assumed that one meal a day was eaten from glazed dishes that held food prepared with vinegar. These assumptions permit the calculation of the weekly intake of Pb.

Estimates for selected dishes from five sites using a 15 cm diameter food serving are provided in Table 3. The selection of sherds spanned the range of Pb leaching rates observed in this study. To illustrate how the amount of food influenced the weekly Pb intake, estimates for one of the moderate-level Pb leaching vessels, a Sønderborg dish (KLR-2308), are plotted according to the three

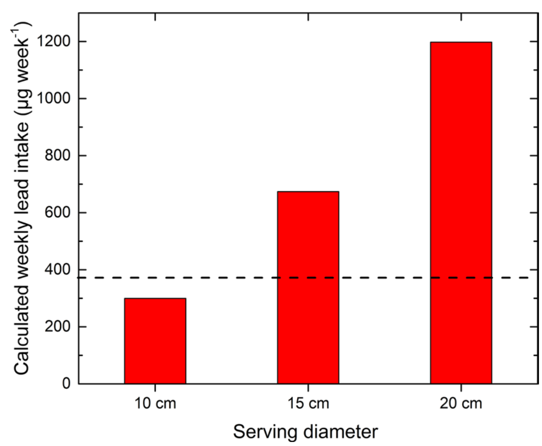


Fig. 12 Weekly Pb intake for a Sønderborg dish (KLR-2308) based on 30 min of contact with the glazed surface and one serving per day. The dashed line represents the WHO threshold limit for Pb exposure for a child weighing 15 kg (370 µg Pb week^{-1})

Table 3 Lead intake for five sherds representative of experimentally measured Pb etching rates: acid etched Pb in µg Pb cm^{-2} day^{-1}; acid etched Pb in µg per 30 min; and weekly consumption of Pb in µg per week^{-1}

Site	Type	Lab No.	Acid etched Pb µg Pb cm^{-2} d^{-1}	Acid etched Pb µg Pb per 30 min	Weekly intake Pb µg Pb week^{-1}
Rødskebølle	Dish	KLR-6839	1.62	6.0	42
Trøjborg	Dish	KLR-2287	12.7	46.9	328
Sønderborg	Dish	KLR-2308	26.1	96.3	674
Husum	Dish	KLR-2305	61.8	228	1596
Grøngaard	Dish	KLR-2281	3714	13,698	95,888

Calculations are based on food with a 15 cm diameter served once a day that remained on the dish for 30 min serving sizes (Fig. 12). As expected, the amount of food consumed has a big effect on Pb exposure.

According to the WHO, the intake of Pb should not exceed 25 μg kg^{-1} $week^{-1}$ for children and 50 μg kg^{-1} $week^{-1}$ for adults [53]. According to the estimates of Bennike and Brade [54], women might often weigh somewhere around 52–53 kg, while the average man weighed 62–63 kg. For a Renaissance child of 15 kg and an adult 60 kg, the WHO threshold values are 370 and 3000 μg Pb $week^{-1}$, respectively.

As can be seen from the last column in Table 3, the Sønderborg dish was hazardous for children, but not adults according to WHO criteria. In fact, three pots listed in Table 3 were hazardous for children. The dish from Grøngaard is hazardous for everyone. Six of the nine Grøngaard dishes leached so much Pb that the WHO criteria are exceeded by, on average, 780 times for children and 98 times for adults, again assuming they consumed one 15 cm diameter serving each day. Acute toxic effects must have occurred if people ate regularly from vessels similar to the six from Grøngaard sampled here.

Even if the six extremely high Pb Grøngaard dishes are omitted from further consideration, an average etching rate of 100 μg Pb cm^{-2} day^{-1} resulted in an intake of 2500 μg $week^{-1}$ under the conservative assumptions adopted here. That exceeds by a factor of 7 the WHO value for Pb intake for children. For adults, the weekly Pb intake from the average dish was about 80% of the WHO weekly threshold. While the use of these vessels might not have been harmful for adults, it is still a substantial exposure because Pb from other environmental sources must also be taken into account.

Translating the Pb intake from food into what is absorbed into the body, hence its harmful effects, is not straightforward (see references in [55]). Nevertheless, it is instructive to look at children because their cognitive development is particularly susceptible to Pb exposure [3, 56–58]. Using software from the US EPA, children from 1 to 7 years will have a Pb blood level above 10 μg dL^{-1} if the WHO limit of 250 μg Pb $week^{-1}$ is exceeded. Children can lose up to 10 Intelligence Quotient (IQ) points if exposed to blood levels above 10 μg dL^{-1} [56].

Pipkins and acidic food

As shown experimentally, Pb leaching was lower for pipkins than for dishes. The average acid-leaching level for pipkins was 9.4 μg Pb cm^{-2} day^{-1}, excluding the anomalously high Pb pipkin from Grøngaard (KLR-6629). While perhaps looking relatively harmless, pipkins were used differently from dishes. The three legs and handle, along with scorched exteriors, indicate pipkins were placed within hearths or put over openings on the top of a stove. Cooking food likely took longer than the 30 min estimate for food and glaze contact. Once pipkins were removed from a heat source, they could have been used to serve the food or hold it for later. Doing so prolonged the time food had contact with the Pb glaze, perhaps for several hours up to a day or more. In our estimates, three different food and glaze contact periods were used: 2 h, 24 h, and 3 days.

Heat accelerates the etching of Pb, hence its potential deleterious effects on health. It has been estimated that ca. 25 times as much Pb is etched with acetic acid at 90 °C than at 30 °C [59]. In fact, acid etching at 100 °C for a half hour extracts the same amount of Pb as four days of leaching at 25 °C [60]. Regardless of the specific

Table 4 Calculated weekly Pb intake for five different pipkin cooking scenarios

Site	Lab. No.	4% acid leached Pb	Scenario 1 2 h @ 50°C	Scenario 2 2 h @ 60°C	Scenario 3 2 h @ 100°C	Scenario 4 2 h @ 100°C + 24 h @ 20°C	Scenario 5 2 h @ 100°C + 72 h @ 20°C
		μg cm^{-2} day^{-1}	μg Pb $week^{-1}$	μg Pb $week^{-1}$	μg Pb $week^{-1}$	μg Pb $week^{-1}$	μg Pb $week^{-1}$
Haderslev	KLR-2295	0.301	190	364	5063	5379	6012
Haderslev	KLR-2298	4.38	2760	5290	73,600	78,200	87,400
Grøngaard	KLR-6631	11.0	6932	13,287	184,857	196,411	219,518
Grøngaard	KLR-6633	17.0	10,711	20,530	285,638	303,491	339,195
Trøjborg	KLR-6626	26.6	16,734	32,074	446,240	474,130	529,910

The Pb intake has been calculated for 5 pipkins, selected to span the range of observed Pb leaching rates. Scenario 1 consists of 2 h of cooking at 50°C, Scenario 2 the same but at 60°C, and Scenario 3 at 100°C. Scenarios 4 and 5 are the same as Scenario 3, but the food is left in the pipkin for either 24 or 72 h. Other parameters as described in the text. Only three values are below the WHO limit of 3000 μg Pb per week for adults figures used for different combinations of temperatures, acid concentrations, and glaze compositions—and one can expect any such estimates to vary depending on the context of use – prolonged heating when cooking greatly increased Pb contamination.

Table 4 illustrates the effects of heat on Pb leaching from some of the pipkins in this study. For these estimates, it is assumed that food contained 4 wt% acetic acid, it was cooked in a pipkin with a contact diameter of ca. 20 cm (ca. 600 cm^2), and it was heated for 2 h. Calculations were done using three different temperatures, 50 °C, 60 °C, and 100 °C. The temperature range accommodates the adjustment of pipkins relative to a heat source to keep stews and porridges from boiling over. Following Engberg [60], the release of Pb upon acetic acid treatment was increased by a factor of 192 at 100 °C, by 13.8 at 60 °C, and by 7.2 at 50 °C compared to room temperature. It is further assumed that food from a pipkin was shared by four people. As seen in Table 4, the WHO criteria under such conditions would have been exceeded in 18 of the 25 pipkins in this study. Figure 13 shows the weekly Pb intake relative to the WHO limit for Scenario 1, where food was cooked for 2 h at 50 °C in selected pipkins from this study. Children always exceed the WHO value, and that is also often true for adults.

Beyond vinegar

Vinegar, as estimated here by 4 wt% acetic acid, was not the only acidic material that might have come in contact with these pots. Another possibility was fruit juice, such as cider with its low pH. Matte et al. [61], for example, reported an elevated Pb level in the blood of a 7-year old girl in Mexico City who was served fruit punch from a lead-glazed bowl. Her Pb blood level increased from 23 μg dL^{-1} before the party to 95 μg dL^{-1} afterwards. Other guests experienced smaller increases in blood Pb levels up to 6 weeks later. Food contaminated with Pb can still be a health risk today when lead-glazed pots are used for cooking, as shown by experimental work with Mexican pottery [62, 63].

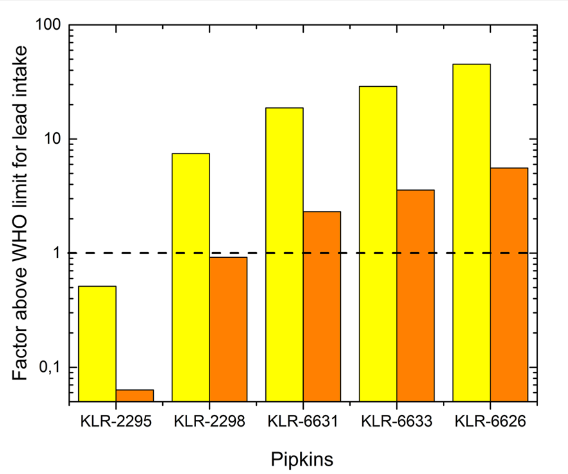


Fig. 13 Estimated Pb intake relative to the WHO threshold (horizontal dashed line; the threshold intake is 3000 μg Pb $week^{-1}$) for five pipkins where cooking conformed to Scenario 1; that is, 2 h at 50 °C. Yellow bars are for a child of 15 kg, and the orange bars are for an adult of 60 kg

As early as the mid-18th century in Great Britain, the consumption of food and liquids from glazed ceramics was recognized as a health hazard [64, 65]. Using pottery for "preserving sour fruits, or pickles with vinegar" could leave the "glazing of such vessels much corroded" [65]:228. Several decades earlier Pb exposure was considered enough of a hazard for the Massachusetts Bay Colony to ban the distillation of liquor with equipment made from Pb since it was so "unholsom (sic) and hurtful" [66]:302.

While Pb exposure must have been partly attributable to the use of glazed pottery to hold food and liquids in Renaissance Denmark, it was unlikely to be the entire story. In the late 18th century, Benjamin Franklin [67]:81 considered certain European occupations to be particularly susceptible to the "mischievous Effect from Lead", based in part on a Parisian hospital's (La Charité) tally of sufferers' occupations. That situation would have been common among laborers in other cities during earlier centuries who worked with lead, including those who applied glazes to pottery. Franklin also worried about the ill-effects of drinking rainwater collected from houses because he noticed that moss failed to grow where American buildings were painted with "white Lead". In both Germany and France, sugar of lead was added to wine to preserve and sweeten it, even though it was recognized by the 17th century that leaded wine had deleterious health consequences and should be banned [68]. For millennia, lead compounds were also used for cosmetics and for paint [68], as well as the active ingredient in antibacterial ointments [69]:496, [70–72].

All told – regardless of whether Pb was deliberately added to consumables or came from the vessels that held them – many people long ago were likely to have been exposed to worrisome amounts of Pb. Yet despite warnings voiced for centuries, lead-glazed pottery still represents a risk to health in some parts of the world today [73].

Differential effect on health

Use of lead-glazed ceramics

Human lead exposure would have been heavily affected by the availability of glazed ceramics and, when acquired, the frequency of their use. Although glazed ceramics are commonly found on 16th and 17th century Danish archaeological sites, they were not evenly distributed among people at that time.

An unequal distribution among households would have been particularly true of dishes, many of which were highly decorated. The highest rungs of society perhaps used dishes on a daily basis, while lesser folk did so mostly on special occasions. In fact, attractive dishes might have been intended primarily for display as status symbols in some households. Wealthy people would not only have had more dishes, but their meals also consisted of many courses that, in turn, required numerous serving dishes that held food for lengthy periods. For those who could afford them, many serving dishes were made from pewter, not pottery. Pewter serving dishes and individual plates in high-status households added to Pb exposure. It is not known, however, whether Renaissance pewter that contained a considerable amount of Pb was as vulnerable to acid as glazed pottery. The toxic effects of Sn and Sb should also be added to the hazards posed by the use of such utensils [74]. A full appreciation of heavy metal exposure during the Renaissance requires separate investigations.

European still life paintings from the 16th and 17th centuries offer a possible explanation why wealthy people and members of the nobility perhaps had less Pb exposure than otherwise might be expected from the data presented here. While pewter, or in some cases wooden bowls or baskets, were used for serving meat, pies, and large portions of food, pottery seems to have been used for serving smaller, delicate side dishes like nuts, fruit, vegetables, cakes, pastry, and the like [75]. This may be supported by the fact that only some of the sherds in the present analysis, all damaged and discarded, showed signs of acid degradation of glazed surfaces.

Pipkin use is hard to estimate, and it too undoubtedly varied among households. These pots were intended for cooking, and not for displays of wealth and social position. After all, pipkins were glazed on their interiors to form impervious surfaces, not on their more visible exteriors. Although these pots were presumably used by a broad cross-section of society, there would have been great variation in how frequently they were employed for the preparation of food. Wealthy families presumably had more Pb exposure from pipkins than poor people because they enjoyed more elaborate meals on a regular basis that featured a variety of food and sauces prepared in the pots.

Finally, the inhabitants of towns, regardless of their social rank, certainly had greater access to pottery, including pipkins, than the residents of outlying villages. Proximity to workshops and markets would have played a role in access to lead-glazed pottery, as did a household's economic capacity to acquire them. Although residence location and social position were important determinants of Pb exposure, this simple relationship was undoubtedly muddied by individual occupations. Servants for wealthy people, for example, were presumably exposed to lead-glazed pottery out of all proportion to their social position when they prepared, served, and occasionally consumed the food and drink left over in rich households.

Skeletons and lead

While social status and residence location affected Pb exposure, the extent to which it varied across different segments of Danish Renaissance society cannot be estimated from pottery alone. Recent work with human skeletons provides insights into this issue. Lead concentrations in the skeleton reflect habitual exposure because bone turnover is relatively slow, spanning a decade or more in the femoral cortical bone from Denmark that has been examined [18, 19]. Lead can be stored in human bones where divalent Pb^{2+} substitutes for Ca^{2+}. While situated in the mineral fraction of bone the Pb is inactive and harmless, but it can have adverse effects if released later in life when bone is remodelled or lost.

Although the influence of diagenetic Pb in archaeological bones cannot be entirely ruled out, recent studies based on mapping the elemental composition of bone show that contamination from the burial environment is typically located at a bone's outer edge [76–78]. Proper sample preparation and sampling strategies help to overcome this issue, and in so doing provide reliable results about biogenic Pb from lifetime exposure.

At the outset, it must be recognized that the skeletal evidence only indicates exposure to Pb, which could have arisen from sources other than glazed pottery. Nevertheless, as discussed above lead-glazed ceramics would have been an important—if not the major—source of regular Pb contamination for much of the Renaissance population [79, 80].

The Pb concentrations in medieval to early modern Danish and northern German skeletons vary greatly. In many skeletons, Pb concentrations are far less than what is typically found in modern bones. In others, they exceed what occurs today in people from notably contaminated settings [18]. Differences in both central tendencies and ranges of variation presumably reflect the dating and socioeconomic composition of the skeletal samples studied, as well as the nature of the towns themselves. Most importantly, there is a consistent distinction between Pb concentrations in the skeletons from towns and villages [18, 19]. Village inhabitants were exposed to far less Pb on a regular basis than townsfolk. That includes large and small settlements separated by only a handful of kilometres. This pattern, repeated throughout the study area, indicates the importance of residence location on Pb exposure. In addition, the range of variation in Pb exposure was much greater in towns. Although household wealth varied in both villages and towns, the latter included people who were, for the time, quite well off, hence had more contact with items containing Pb.

People who lived in towns had easy and frequent access to town markets where pottery from local producers, as well as imported ceramics, were readily available. Several other sources of Pb were also present in towns and manors, such as pewter tableware, waterpipes, paint, cosmetics, and lead-paned windows. The collection of rainwater from roofs partly or entirely sheathed in Pb was unlikely to have been a major source of lead in Renaissance Denmark because lead roofs were, as a rule, only found on churches.

Conclusions

Lead was leached from glazed ceramics using 4 wt% acetic acid to assess whether commonly used pottery posed a risk to the health of people in southern Denmark and northern Germany during the Renaissance period. Sherds from lead-glazed pottery came from six sites representing a cross-section of society. The leaching rate averaged ca. 100 µg Pb cm^{-2} day^{-1}, but at one location, Grøngaard, the rates ranged as high as 29,100 µg Pb cm^{-2} day^{-1}. The high leaching rates of most of the Grøngaard dishes appear to be attributable to a shorter firing time compared to the rest of the pottery, resulting in higher PbO concentrations and weaker bonds of PbO in the silicate glass.

Two types of pottery used for different purposes were examined: dishes for serving food and pipkins for cooking it. Individual vessels varied greatly in the amount of Pb released when their glazed surfaces were exposed to acidic food. Estimates of Pb exposure took into account the duration of food contact with glaze, as well as the use of pipkins for cooking, since heat accelerates chemical reactions.

Assuming dishes and pipkins were used frequently, they represented a major risk to health based on WHO criteria for preventing Pb poisoning. While glazed dishes, which were often nicely decorated, would have been used often by those who could afford them, their injurious potential was possibly moderated by their frequent use for low acidic side dishes. But regardless of their social standing, many households would have used pipkins in their kitchens. The composition of meals, which varied from the highest to lowest rungs of society, would also have had an effect on Pb exposure through the pottery that was used. Peasants and poor townsfolk typically consumed a humble diet, although the consumption of cider, for example, would have resulted in Pb exposure if it came in prolonged contact with lead-glazed storage vessels. Well-to-do households, in contrast, ate more elaborate meals where food was often prepared with vinegar that degraded the glaze of vessels used for cooking, serving, and storing it. Future studies might analyse well-preserved lead-glazed sherds through optical microscopy of residues and gas chromatography with mass spectrometry to identify the foodstuffs present. Doing so would clarify how the vessels were used, hence the Pb exposure people faced.

Given the variation that existed in diets and access to lead-glazed pottery, with the latter shown here to be a potential risk to health, actual exposure is best evaluated through skeletal remains. That work, reported elsewhere, shows that there was considerable variation in Pb exposure among medieval to early modern people [18, 19]. The residents of towns often had concentrations of Pb in their bones that were high by modern standards. Peasants from the countryside were in that respect better off because their Pb exposure was much lower than what people experienced in towns. Although the Pb might have come from various sources, this study shows that lead-glazed ceramics were a significant source of Pb for the inhabitants of Renaissance period southern Denmark and northern Germany.

Supplementary information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-022-00703-8.

Additional file 1. Photos of examples of samples analysed in the present work. Analyses of Corning glass standards for SEM-EDS. Full ternary phase diagram.

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Author contributions
KLR: Conceptualizing the experiments, writing. TD: Contributed to the writing. FW: Fieldwork and sample management. LKIJ: Made the etching experiments and performed the ICP-MS measurements. GRM: Contributed to the writing and historical information. ThR: Conceptualised, interpreted and visualised the SEM-EDS data and contributed to final draft writing. UK and PGH: historical and archaeological conceptualization and contribution to the writing. All authors read and approved the final manuscript.

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Availability of data and materials
Data are available upon request from the authors.

Declarations

Ethics approval and consent to participate
Not applicable.

Competing interests
The authors declare that they have no competing interests.

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