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Residues in Medieval Pottery from Basel

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Pottery; 15th century; Basel; archaeometry; bone-ash; cast printing type

Archaeometric investigations started in the Basel Geochemical Laboratory (Institute for Mineralogy and Petrography MPI, Department of Earth-Sciences, Basel University) in 1969 when colours of early prints and incunabulae were analysed chemically and mineralogically (Stern 1971). These first analyses were destructive in the sense that either micro- or macroscale sub-samples had to be taken. In the following years, experience with non-destructive techniques was gathered and applied on forensic and archaeological matter like alloys, ceramics, coins, gem stones, glass, precious metals and pigments. An overview over these activities is given by Stern 2001.

The present study concerns residues in medieval pottery which was excavated by the Archäologische Bodenforschung in Basel (Keller 1999; Keller/Gerber/Stern 1999; Tschudin 2000). One group of residues consists of a greyish layer on the inside of cooking pots from the 13th to 15th century (St. Alban-Vorstadt 30/32); the other group consists of an enamel like covering on ceramic vessels dated to the late 15th century from St. Alban-Vorstadt 28 in Basel.

The Greyish Residues in Cooking Pots from the 1996-Excavation, St. Alban-Vorstadt 30/32

Greyish-yellowish residues in cooking pots are a relatively widespread phenomenon among household pottery of the 13th to 15th century in Basel and elsewhere.

First considered to be some kind of carbonaceous sinter, these residues were puzzling since they only occur on the inner part of cooking pots and never on the outside, and since they did not react with acetic or hydrochloric acid and hence did not consist of calcite. A chemical surface analysis with energy-dispersive X-ray fluorescence spectrometry (ED-XFA) revealed soon that besides calcium the element phosphorous was present as a main component, and hence some kind of „bone“ matter seemed to be present (Keller/Gerber/Stern 1999).

Bone consists of biominerals like apatite s.l., which are wrapped in fibrilles of collagen and fat. The respective amounts of these compounds vary not only in spongiosa and corticalis, but possibly also from one animal species to another, and with bone type (cranium, spondylus, femur etc.).

When bone matter is „thermally treated“, a gradual transformation takes place (*schematic*):

- 100 to 200 °C: boiling in water, acids or lye extracts collagen which can be used as *size/glue*;
- 200 to 300 °C: fat is extracted which can be used for making soap and tallow (*candles*);
- 300 to 400 °C: dried and powdered bone with its incinerated remaining organic matter can be used as a *black* pigment (*Ivory black*);
- 600 to 800 °C: powdered bone may be used as *white pigment* or engobe;
- 800 to 1100 °C: bone ash, consisting of transformed biominerals (apatite -> whitlockite) may be used as a base material for making glass and ceramics (*bone china*), but also in metallurgical procedures like cupellation.

It is evident that bone and its derivatives are essential base materials available since millen-

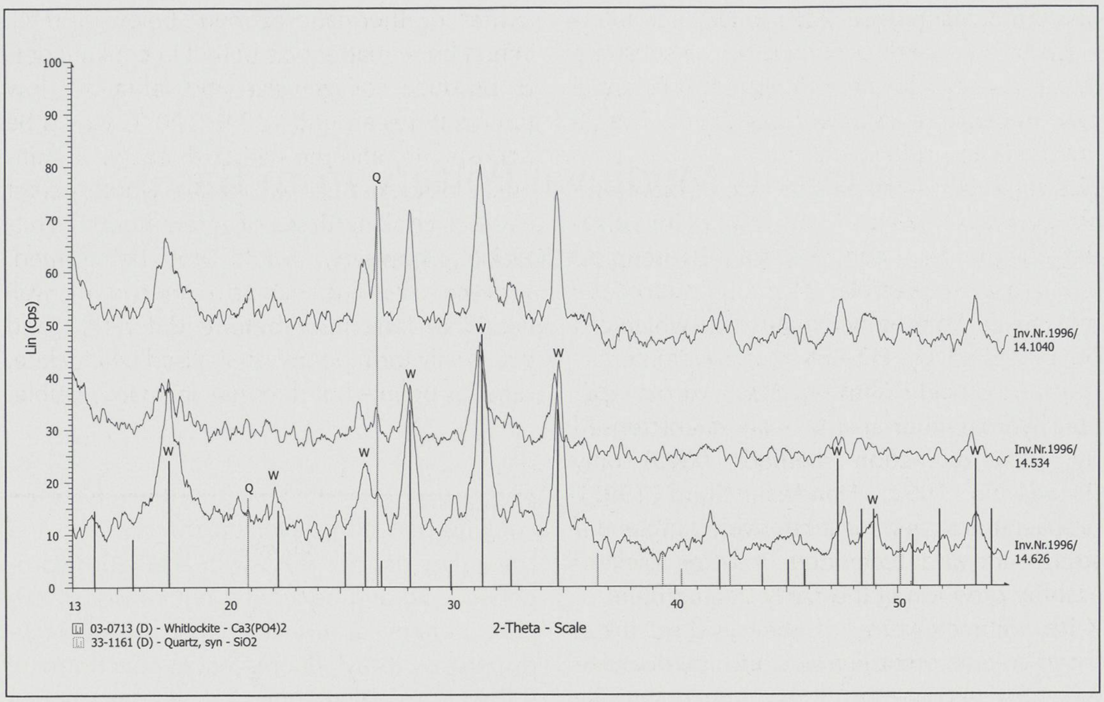

Fig. 1: X-ray diffractograms of greyish residues on pottery of the 15th century from the 1996 excavation St. Alban-Vorstadt 30/32, Basel. The residues contain neither calcite nor apatite, but the mineral whitlockite (tricalcium phosphate). One specimen contains some quartz, probably introduced from the ceramic substrate. Note the form of the reflections with small height, broad shape reflecting a low crystallinity/ordering of whitlockite.

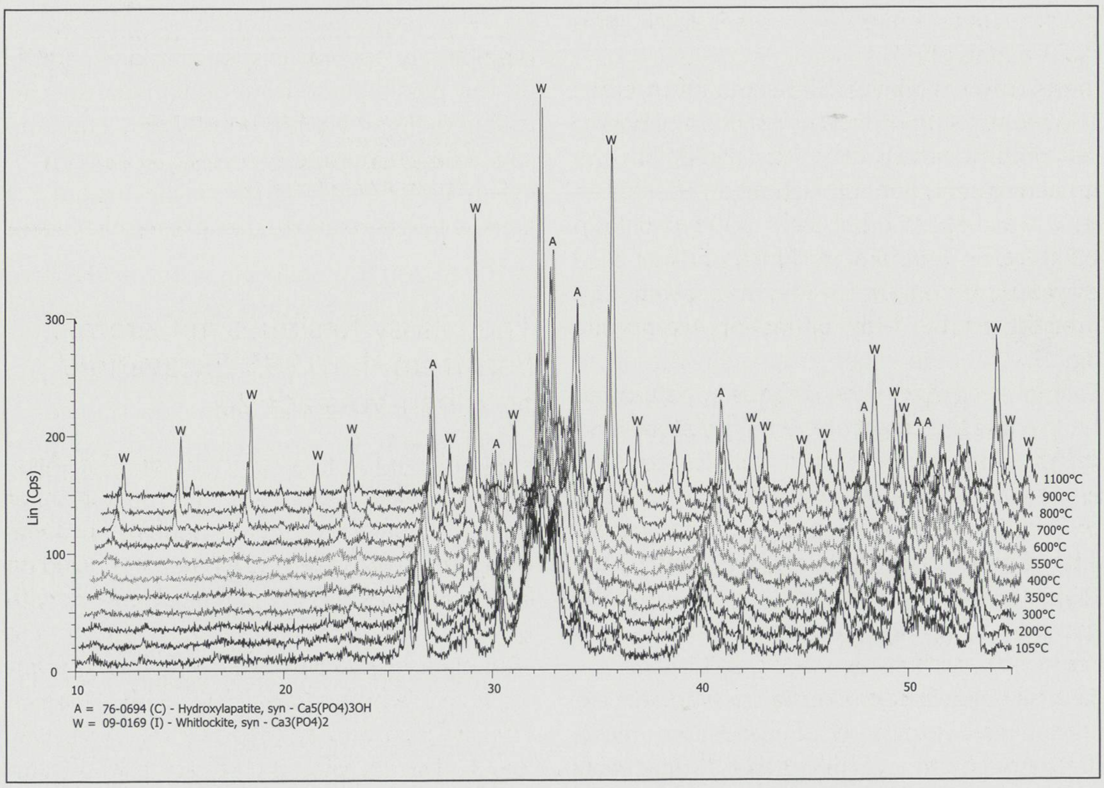

Fig. 2: Tempering experiments with bovine bone. At low temperatures (black, 105 to 400°C) all reflections are broad and low. Above 500°C (grey) the apatite reflections become narrower and higher. Above 600°C whitlockite begins to build up at the expense of apatite. Above 900°C all reflections are sharp indicating a high degree of crystalline ordering.

nia. But archaeologists have so far been interested in bone and ivory merely as a substrate for art and handicraft, and not as an essential base material for various technologies. The literature is accordingly scarce.

The extremely small particle size of biominerals (typically 2 x 5 x 17 nm) makes investigations by means of conventional microscopical techniques impossible. Electron microscopy may prove the presence of plateles, which can be identified by ED-XFA, but the mineralic species – apatite (fluor-apatite, hydroxy-apatite, hydroxy-fluor-apatite) – are characterised by X-ray diffraction methods (XRD) only (Handschin 1992; Handschin/Stern 1995). Since diffractometry is a relatively simple and straight-forward technique, it lends itself to identify products of thermally treated bone.

X-Ray diffractograms of the residue, taken from three different shards, show that not minerals of the apatite species are present, but the mineral whitlockite, chemically $Ca_3(PO_4)_2$ (fig. 1). The reflections are low and broad, as is typical for poorly crystallised matter. The first pattern displays also some quartz, probably stemming from the shard/substrate. The question arises, whether whitlockite is the product of some kind of intended or incidental „thermal treatment".

In order to examine the influence of „thermal treatment" on bone matter, a section of bovine femur was crushed, boiled at 100 °C with water as a solvent, but also with acid and alkaline fluids, and ignited gradually at defined temperatures in a laboratory furnace. After each thermal step a sub-sample was taken and investigated by X-ray diffraction (composite fig. 2).

Each run represents the diffraction pattern after thermal treatment at the temperature indicated on the right side. Increasing temperature above 500 °C induces progressive ordering of the apatite lattice as is expressed by narrower and sharper reflections. Above 600 °C the mineral whitlockite begins to crystallise at the expense of apatite, which is, however, still present after (short) tempering at 1100 °C.

The outcome is controversial to a certain extent: under experimental conditions, whitlockite begins to form above 600°C only. High and narrow reflections indicate a well developed crystallinity, i.e. ordering. The greyish residue consists of whitlockite, but displays broad reflections as is typical for native bone matter or thermal treatment below 500 °C. When bone matter was boiled in cooking pots to produce collagen/size and fat/tallow, low temperatures around 100 to 300 °C would be appropriate, and the native character of mineralic bone matter, i.e. apatite, would persist at short cooking times of a few hours. Whitlockite, however, would not be formed. Whether a residue sticking to the ceramic wall would at long term behave differently, and eventually form poorly crystallised whitlockite, remains open – but does not seem impossible.

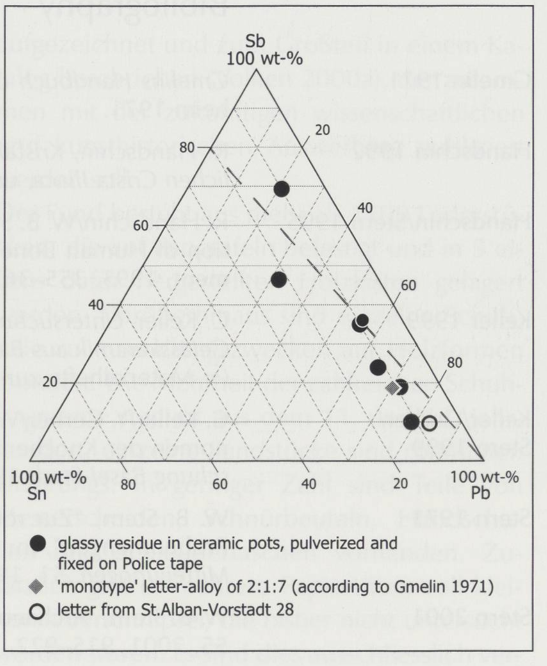

Fig. 3: The metals antimony, lead and tin of glassy residues plotted in a ternary diagram; the glass forming elements Si, Al, Mg, Ca and alkalies are disregarded.

The Glassy Residues in Ceramic Pots from the 1995-Excavation/ St. Alban-Vorstadt 28

From a large lot of ceramic shards with glassy or enamel-like residues mainly on the inner side, 119 specimens were sampled, i.e. some milligrams were taken, pulverised and fixed on Police tape (Cellux[R]) for chemical analysis with ED-XFA. The same complex, dated to the 15th century, had also delivered a metal printing type (Tschudin 2000, 154, Abb. 2) which was sampled and analysed in the same way (fig. 3). Disregarding the silicate part of samples, three metals prevail, namely lead, antimony and tin, whilst iron, copper and arsenic are present as a trace element or minor component only. Bismuth is missing entirely.

Although quite a wide variation of the three components is observed, one may conclude that the projection points represent an antimony-tin compound of 4 parts antimony to 1 part tin (see dotted line) with addition of 20 to over 90 wt-% lead. Certain samples plot very close to the so-called ‚monotype'-alloy of 2 : 1 : 7 (Sb : Sn : Pb), known to be the hardest of all printing type metals with a low melting point between 200 and 260 °C, and a hardness H_B around 28 (Gmelin 1971).

The ceramic matter itself consists of a common fired clay, quite different from refractory matter as used for glass making, where high temperatures above 900 to 1100 °C are applied. The conclusion hence is, that the present residues dating from the late15th century are connected with early printing, or more precisely with early production of printing types. The alloys used – inasmuch as they are documented by the analysed residues – reveal a quite experienced early technology at least in certain cases.

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