## Shell-tempered American Indian prehistoric (900-1500 A.D.) pottery from the Mississippi Valley

### Robert B. Heimann, Ph.D. Professor emeritus of Technical Mineralogy and Materials Science D-02826 Görlitz, Germany. Email: <u>robert.heimann@ocean-gate.de</u>

During the late prehistoric time in North America (800-1500 A.D.) in the Mississippi Valley an important cultural tradition flourished that is characterized by burial mounds in the shape of truncated pyramids, ceramics tempered with shells instead of sand, and strongly increased use, transport and trade of salt. This culture replaced the older, technologically less inclined Woodland culture. Today the Mississippian culture is subdivided into basically two groups: a group with a high technological development thriving in the area of the confluence of the Mississippi and the Missouri rivers (Cahokia) and what is today the state of Illinois (Angel), and a group with lower technological skills existing upstream (Oneota culture) without burial mounds and with less involved ceramics in the area of today's Wisconsin (Aztalan, Armstrong and Mero).

Relatively thin-walled pottery was produced in the bottomlands of the Mississippi Valley by members of the First Nations from pronounced smectite-type clays that were to 95% tempered with mussel shells instead of sand or grog. The technological implications of addition of carbonatic shells will be discussed in terms of

- Improvement of workability of the smectite-rich 'fat' clays available as raw materials
- Reduction of the shrink-swelling ratio by converting Na-loaded into Ca-loaded smectite
- Increase of lime popping that however, was limited by intentional addition of rock salt
- Shift of pore size distribution of calcite by forming a ternary eutectic melt with NaCl and Na<sub>2</sub>CO3 during firing
- Improvement of plain strain fracture toughness, work of fracture, and critical energy release rate by replacing sand by shell temper thus creating a reinforced ceramic microstructure.

What was essentially produced was a ceramic-ceramic reinforced composite material with superior mechanical and thermal strengths compared to previous solutions using sand temper.

The study shows that Mississippian ceramics is an excellent example how by synergistic interaction originally insufficient raw materials could be turned into functionally sufficient ceramic end products. Catalysts for such a development was the ingenuity of crafts people that created a superior ceramic by cleverly combining natural factors (raw materials), intellectual factors (knowledge and experience), and socio-cultural factors (need). The result was a ceramic ware treasured and admired by many early European settlers as a testimony to the technological talent of the 'noble savages'.

## Geochemistry and mineralogy of prehistoric tin smelting slags from Rooiberg, Limpopo Province, South Africa

### <u>Robert B. Heimann<sup>1</sup></u>, Shadreck Chirikure<sup>2</sup> and David Killick<sup>3</sup>

<sup>1</sup>D-02826 Görlitz, Germany, <sup>2</sup>Department of Archaeology, University of Cape Town, South Africa, <sup>3</sup>Department of Anthropology, University of Arizona, Tucson, AZ, USA

During two excavation campaigns in 2006 and 2007 prehistoric tin-smelting slags from Rooiberg, northwestern Limpopo Province, South Africa were recovered and investigated by light and electron optical microscopy in conjunction with energy dispersive x-ray spectroscopy (EDX). To determine the origin of the different elements present in the slags a search for the source of the major element was undertaken using the technique of chemical fingerprinting by studying elemental trends and correlations by x-ray fluorescence (XRF) and inductively-coupled plasma mass spectrometry (ICP-MS).

The Rooiberg cassiterite ore bodies were formed by replacement within a stratigraphically defined, orthoclase-rich arkosite horizon. A system of shear and tension fractures served as channelways for epithermal stanniferous solutions emanating from granites associated spatially and genetically with the Bushveld Igneous Complex (BIC). These fractures as well as ore-bearing pockets were exploited by ancient miners of ancestral Sotho-Tswana origin. The mineral paragenesis of the pockets is dominated by tourmaline, cassiterite, carbonates (ankerite, magnesian siderite), and a variety of sulfides (pyrrhotite, pyrite, chalcopyrite, bismuthinite, sphalerite, galena). Their structure is generally concentric with an outermost zone of reddish orthoclase, an inner zone of strongly sericiticized quartzite ('greisen') impregnated with cassiterite, and a center consisting of iron-rich tourmaline (schörl) partly embedded in cassiterite. Carbonates are found ubiquitously as a late formation, replacing all earlier minerals.

The slags from two selected excavation sites (Smelterskop, Elandsberg Ledge) were found to contain high amounts of tin oxide up to 60 mass%. This suggests a very inefficient smelting technology applied by the ancient craftsmen. The scarcity of boron in the slags suggests that little if any tournaline was included as contamination in the cassiterite ore. Hence the ore appears to have been very carefully separated from surrounding tournaline, presumably by winnowing or elutriation of very finely ground ore of which evidence has been found at the Rooiberg site.

Spinels of variable compositions as well as hortonolitic olivine and calcic plagioclase occur as devitrification products of slags. The spinels belong to the ternary system normal 2-3 spinel (spinel *sensu strictu*, hercynite) – inverse 2-3 spinels (magnetite, chromite) – inverse 4-2 spinels (ulvöspinel, tin spinel). Since there is only limited solubility among the individual spinel members frequently exsolutions, overgrowth and zoning can be observed. In particular  $\operatorname{Sn}^{4+}$  species formed by disproportionation of  $\operatorname{Sn}^{2+}$  during freezing of the melt according to  $2\operatorname{Sn}^{2+} \rightarrow \operatorname{Sn}^{4+} + \operatorname{Sn}^{0}$  will be incorporated into the 4-2 spinel structure to form a hypothetical tin spinel  $\operatorname{Fe}^{2+}[\operatorname{Fe}^{2+}\operatorname{Sn}^{4+}]O_4$ . This is an indication of the high degree of compositional inhomogeneity that generates local microequilibria throughout areas small compared to the overall extension of the glassy slag sample. In particular the local oxygen fugacity  $f_{O2}$  established during reduction of the tin oxide will control the precipitation of the spinels and thus determine whether 'reduced' (hercynite, tin spinel) or 'oxidized' spinels (magnetite) will crystallize first.

# The workshop of M. Tullius Comitialis in Tabernum, Eastern Gaul: archaeometrical investigations into provincial Roman Terra Sigillata

### Robert B. Heimann, Ph.D. Professor emeritus of Technical Mineralogy and Materials Science D-02826 Görlitz, Germany. Email: <u>robert.heimann@ocean-gate.de</u>

Roman Terra Sigillata (TS) had been manufactured and traded in large quantities on a semiindustrial scale between the 1<sup>st</sup> century B.C. and the early 3<sup>rd</sup> century A.D. in all parts of the Roman Empire including Southern, Central and Eastern Gaul. This durable, esthetically pleasing, and for military usage highly standardized pottery originated around Arezzo in Tuscany, Italy ('Arretine' ware) and was predominately produced from calcareous illitic clays that were carefully collected, processed and classified by settling. The finest settling fraction (< 2 µm) with high potassium and iron contents was used as a slip into which the vessels were dipped before firing. During oxidizing firing at temperatures slightly above 1,000°C this slip turned into a partially vitrified, high glossy and bright red coating. Reducing firing of burnished ware produced shiny black surfaces (terra nigra).

Among superior examples of this ceramic tradition were bowls decorated with different designs produced by pressing or turning wet clay into a ceramic mould adorned with impressions of stamps thus converting the negative impression on the inside of the mould into its positive counterpart at the outside of the bowl. From these stamps or 'sigilla' the ware got its name. Since the figurative stamps were precious possessions that distinguished a Master potter of fame from a mediocre imitator they were sometimes copied or even stolen by less gifted competitors and counterfeiters. Evidence of such early 'industrial espionage' can frequently be observed.

The workshop of a potter was excavated in Tabernum, Eastern Gaul, today's Rheinzabern, Palatinate, Germany and the archaeological remains found were analyzed to answer a series of questions related to the technology of pottery production and organization of labor. Specific questions addressed include

- Where did the clay used to produce the pottery came from?
- Were the moulds discovered of local origin or imported?
- How was the technology of manufacturing TS ware?
- What are the technological differences between moulds and decorated TS ware?
- How was the organization of labor in a potter's workshop in the 1<sup>st</sup> century A.D.?

Technological experiments were conducted using a clay presumably identical to that utilized by the ancient potter M. Tullius Comitialis. Chemical and microstructural analyses were performed to characterize the ceramics, and discriminant analysis based on a  $D^2$ -Mahalanobis statistical approach was applied to determine distinguishing criteria between moulds and ware.