Chemical analyses of lipids preserved in Iron Age pottery from Bibracte, France

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Bibracte is a Late Iron Age *oppidum*, or fortified city, at the Mount Beuvray in Burgundy, France. Carbonized residues in recovered ceramic vessels suggest that they were used for cooking or storage of foodstuffs. Here we present the results of the first chemical investigation of organic residues from 11 potsherds. The lipids preserved in the interior of the vessels and those absorbed in the ceramic matrix were extracted with organic solvents, separated in fractions, derivatized and submitted to GC-MSD and GG-C-IRMS analyses.

The GC-traces of all samples show a series of straight chain fatty acids in the C_9 to C_{24} carbon number range, excluding C_{21} and C_{23}. The main saturated fatty acids are the $C_{12:0}$, $C_{14:0}$, $C_{15:0}$, $C_{16:0}$, $C_{17:0}$ and $C_{18:0}$ acids, maximizing at $C_{16:0}$ with generally clearly greater abundance of $C_{16:0}$ than $C_{18:0}$. These fatty acid distributions are typical of degraded fats, suggestive of animal origin. Small to trace amounts of $C_{10:0}$, $C_{11:0}$, $C_{13:0}$, $C_{20:0}$ and $C_{22:0}$ acids occur in all samples. The only unsaturated acids identified were $C_{16:1}$ and $C_{18:1}$. Terminally, branched iso and anteiso b-$C_{15:0}$ acids elute between $C_{14:0}$ and $C_{16:0}$. Apart from trace amounts of $C_{18:2}$, no polyunsaturated fatty acids were detected. The $\delta^{13}C$ values of the fatty acids for all samples ranged from –31.2 to –25.7‰ VPDB, which encompasses the range predicted for an ecosystem based on C_3-nutrition. The $\delta^{13}C$ values of the major fatty acids were compared with the isotopic fields of preindustrial animal and vegetable fats ($\delta^{13}C_{FA}$ value of modern material +1.6‰). Most samples plot in the $\delta^{13}C_{16:0}$ vs. $\delta^{13}C_{18:0}$ and $\delta^{13}C_{18:1}$ vs. $\delta^{13}C_{18:0}$ fields of preindustrial ruminant milk, and young suckling calf/lamb and pig adipose. The identification of plant and animal $C_{28\text{-}29}$ sterols (campesterol, ß-sitosterol, cholesterol, cholestanol) and plant epicuticular waxes (C_{25}, C_{27}, C_{29}, C_{31}, and C_{33} *n*-alkanes and C_{22}, C_{24}, C_{26}, C_{28}, C_{30}, C_{32} and C_{34} *n*-alkanols) in the TMS-derivatives indicate that the vessels contained both animal and plant material.

[1] Paunier *et al.* (2004) *Bibracte* **8**. [2] Spangenberg *et al.* (2006) *Jour. Arch. Sci.* **33,** 1-13.

Metal and isotope dispersion in an abandoned heavy metal mine: Callahan, Maine, USA

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The Callahan Cu-Zn-Pb mine produced ~800,000 tons of ore hosted by Cambrian volcanic and volcaniclastic rocks. The mine was sited in a marine estuary and is now a US-Environmental Protection Agency Superfund site [1]; ~5 million tons of sulfide-bearing waste and unprocessed ore remain on-site bordering ponds and tidal flats. Mineralogy, trace element, and Pb-Sr-Nd isotope geochemistry document metal redistribution among host rocks, ore, tailings and waste piles, stream and estuary sediments, and the aquatic biota.

Pyrite from waste piles is enriched in Cu, Pb, and As, and sphalerite is enriched in Cu, Pb and Cd. Sediment cores from open estuary ponds at the site contain <1-3% pyrite, and rare sphalerite; sediments vary in Zn (88-1590 ppm), Cu (14-268 ppm), Pb (4-1070 ppm), As (4-55 ppm), and Cd (up to 83 ppm). Bivalve shells from estuary sediments have variable contents of Cu (5-74 ppm), Zn (6-443 ppm), and Pb (1-76 ppm). Clam tissue at the site has 0.71 to 43 ppm Pb (US-EPA, 2008); some values exceed the US-FDA safety tolerance level (1.7 ppm Pb). Pb isotopes of estuary sediments ($^{208}Pb/^{207}Pb$ = 2.4223-2.4696; $^{206}Pb/^{207}Pb$ = 1.1544-1.1965) [2, this study] span a range from host volcanic rocks ($^{208}Pb/^{207}Pb$ = 2.4817-2.5466; $^{206}Pb/^{207}Pb$ = 1.2254-1.2537) to massive sulfide, and tailings ($^{208}Pb/^{207}Pb$ = 2.4224-2.4350; $^{206}Pb/^{207}Pb$ = 1.1566-1.1646). Pb isotope data analyses of bivalve shells ($^{208}Pb/^{207}Pb$ ~ 2.43-2.45, $^{206}Pb/^{207}Pb$ ~ 1.16-1.18) are within the range of the ores and tailings. Sr and Nd isotope compositions also link the host rocks, ore lenses and clam shells. The clams likely incorporated Pb and other metals by ingestion of fine sulfide and silicate particles in addition to dissolved metals. Within and immediately adjacent to the mine site the metals originated from sulfide weathering and metal mobilization. By contrast, at a distance of ~1 km from the mine site the impact of mining is essentially undistinguishable from the geogenic background.

[1] MACTEC Engineering & Consulting (2007) *Site Inspection Prioritization Report*, v. **1-3**. [2] Boeckeler & Gaudette (1996) *Geol. Soc. America*, *Abs*. **28**, 40.