COMMENTARY

Untangling complex organic mixture in prehistoric hearths

Alexandre Lucquin[a,1]

In the last decades, organic residue analysis of ceramic artifacts has advanced our understanding of culinary practices and economies in the past. Current approaches, deploying lipid residue analysis, have allowed a wide range of prehistoric commodities processed in pottery to be identified (1, 2). Recently, organic residues analysis has allowed us to gain a new perspective on the emergence and adoption of pottery by prehistoric hunter-gatherers. These data have shown a strong reliance on the exploitation of aquatic resources (e.g., refs. 3, 4). However, this approach is limited by the fact that not all hunter-gatherer societies used pottery and that use of pots seems specialized in comparison to the existing broader spectrum economies (4). Thus, looking at organic residues contained in fire structure remains would provide an extended testimony of diet and cooking practices complementary to the study of vegetal and faunal remains. Although organic residue analysis of prehistoric hearths began in the late 1980s (5–7), such analyses are still an underestimated source of information and only a few studies have explored their potential. In PNAS, Choy et al. (8) use isotopic and molecular analysis of organic residues from hearths to obtain new insights into salmonid exploitation and processing by Alaskan hunter-gatherers of the end of the Pleistocene.

Hearth Organic Matter Complexity

The main objective of Choy et al.'s paper (8) is to resolve the complex mixture of organic matter (OM) found within hearths and to obtain quantifiable data of the contribution of the various sources considered (regrouped as terrestrial, freshwater, and marine food) to allow a comparison of the content of the fire structures from the Upward Sun River (USR) occupations. This is a relevant issue because OM preserved in hearths may unlock archaeological information, although complex to deconvolute. Indeed, preserved OM is a mixture resulting from the potential input of sedimentary OM initially present or coming from postdepositional processes (e.g., deposition and migration of sediment) and plant or animal tissues used as fuel (e.g., wood, bones, dung) or processed during cooking activities (e.g., roasting or grilling of animal resources) as well as other domestic activities. Moreover, the OM has been subject to a natural oxidation and to heat, conducive to a partial or total removal of compounds and to molecular transformations.

Biomolecular Analysis of Hearths

Choy et al. (8) have followed analytical procedures previously used. OM studies in hearths have focused on the molecular characterization of lipids from archaeological or experimental replicates using gas chromatography mass spectrometry (GC-MS) (e.g., refs. 6, 9–12), associated more recently with stable isotopic analysis of bulk organic matter [elemental analyzer coupled to a continuous flow isotope ratio spectrometer [isotope ratio mass spectrometry (IRMS)] (13) or of individual molecular compounds obtained by GC combustion combined with IRMS (14, 15). By combining those biomolecular techniques, Choy et al. (8) address the mixing issues.

The presence of anthropogenic OM is demonstrated by a higher $\delta^{15}N$ compared with the control samples. The $\delta^{15}N$ values also indicate a contribution of aquatic resources, and the variability observed reflects the diversity of the composition of the OM. Because the bulk $\delta^{13}C$ possibly reflects an input of wood fuel, and because no specific biomarkers have been recovered, further insights are obtained with the compound-specific $\delta^{13}C$ value of individual fatty acids. Finally, the composition of the mixture is resolved using stable isotope analysis in R (SIAR), a Bayesian isotopic mixing model, allowing one to calculate the relative contribution of the various sources (regrouped as terrestrial, freshwater, and marine food). Importantly, the good bone preservation of the component 3 of the USR allows Choy et al. (8) to validate the result by obtaining a positive correlation between the calculated contribution of salmonids by SIAR and the frequency index of salmonids in the faunal assemblages. Thus, Choy et al. (8) can distinguish certain patterns of activity within component 3 but also can infer the exploitation of anadromous salmon as early as in component 2, showing that hunter-gatherers living in Alaska relied heavily for their

[a]BioArCh, Department of Archaeology, University of York, York YO10 5DD, United Kingdom

Author contributions: A.L. wrote the paper.

The author declares no conflict of interest.

See companion article on page 9757 in issue 35 of volume 113.

[1]Email: alexandre.lucquin@york.ac.uk.

diet on aquatic resources, and notably anadromous fishes, since the end of Pleistocene.

Archaeology of Cooking

Control of fire is one of the exclusive and typical traits of humanity, as reflected in numerous myths where fire is the element that allows humanity to "get out" of the natural kingdom (16). However, the fire in question is not any fire to heat or light; it is the fire that allows cooking (17), transforming a natural resource in cultural food. Once adopted, fire was never abandoned, and as a consequence, there is no society that does not process by heat at least a part of its food (18, 19). Organic residues analysis of archaeological hearths provides a direct testimony on the evolution of diet and subsistence practices in human societies.

1 Regert M (2011) Analytical strategies for discriminating archeological fatty substances from animal origin. *Mass Spectrom Rev* 30(2):177–220.
2 Evershed RP (2008) Organic residue analysis in archaeology: The archaeological biomarker revolution. *Archaeometry* 50(6):895–924.
3 Craig OE, et al. (2013) Earliest evidence for the use of pottery. *Nature* 496(7445):351–354.
4 Lucquin A, et al. (2016) Ancient lipids document continuity in the use of early hunter–gatherer pottery through 9,000 years of Japanese prehistory. *Proc Natl Acad Sci USA* 113(15):3991–3996.
5 Rottländer RCA (1989) Chemische untersuchungen an sedimenten der Höhle Geissenklösterle bei Blaubeuren. *Fundberichte Aus Baden-Württemberg* 14:23–32. German.
6 March RJ, Baldessari A, Gross EG (1989) Determinacion de compuestos orgánicos en estructuras de combustión arqueológicas. Nature et Fonction Des Foyers Préhistoriques, Actes Du Colloque International de Nemours, eds Olive M, Taborin Y (APRAIF, Nemours, France), pp 47–58. Spanish.
7 Cliquet D, et al. (1989) Approches d'une étude comparative des matières organiques de foyers préhistoriques et de foyers expérimentaux: l'exemple du gisement moustérien de Saint-Germain-des-Vaux, Manche. Nature et Fonction Des Foyers Préhistoriques, *Mémoires du Musée de préhistoire d'Ile de France*, eds Olive M, Taborin Y (APRAIF, Nemours, France), pp 29–36. French.
8 Choy K, et al. Chemical profiling of ancient hearths reveals recurrent salmon use in Ice Age Beringia. *Proc Natl Acad Sci USA* 113(35):9757–9762.
9 March RJ (1999) Chimie organique appliquée à l'étude des structures de combustion du site de Tunel I (Terre de Feu, Argentine). *Revue d'Archéométrie* 23:127–156. French.
10 Kedrowski BL, et al. (2009) GC/MS analysis of fatty acids from ancient hearth residues at the Swan Point archaeological site. *Archaeometry* 51(1):110–122.
11 March RJ, Dumarçay G, Lucquin A, Joly D (2006) Les activités liées à l'utilisation du feu: Un dernier hiver à Pincevent: les Magdaléniens du niveau IV0 (Pincevent, La Grande Paroisse, Seine-et-Marne). *Gallia Préhistoire* 48(1):89–108. French.
12 Lejay M, Alexis M, Quénéa K, Sellami F, Bon F (2016) Organic signatures of fireplaces: Experimental references for archaeological interpretations. *Org Geochem* 99:67–77.
13 Heron C, Nilsen G, Stern B, Craig O, Nordby C (2010) Application of lipid biomarker analysis to evaluate the function of "slab-lined pits" in Arctic Norway. *J Archaeol Sci* 37(9):2188–2197.
14 Buonasera TY, Tremayne AH, Darwent CM, Eerkens JW, Mason OK (2015) Lipid biomarkers and compound specific δ13C analysis indicate early development of a dual-economic system for the Arctic Small Tool tradition in northern Alaska. *J Archaeol Sci* 61:129–138.
15 March RJ (2013) Searching for the functions of fire structures in Eynan (Mallaha) and their formation processes: A geochemical approach. *Natufian Foragers in the Levant: Terminal Pleistocene Social Changes in Western Asia, Archaeological Series*, eds Bar-Yosef O, Valla FR (International Monographs in Prehistory, Ann Arbor, MI), pp 227–283.
16 Frazer JG (1967) *Mythes sur l'origine du feu* (Payot, Paris). French.
17 Barrau J (1983) Les hommes et leurs aliments: esquisse d'une histoire écologique et ethnologique de l'alimentation humaine (Messidor/Temps actuels, Paris). French.
18 Lévi-Strauss C (1968) *L'origine des manières de table* (Plon, Paris). French.
19 Goody J (1982) *Cooking, Cuisine and Class. A Study in Comparative Sociology* (Cambridge Univ Press, Cambridge, UK).