Dr Jayson Orton
ASHA Consulting (Pty) Ltd
6A Scarborough Road
Muizenberg 7945

Cc South African Heritage Resources Agency
111 Harrington Street
Cape Town 8001
Republic of South Africa

29 November 2016

Dear Jayson,

UPDATE: REFINING SOUTHERN AFRICAN CHRONOLOGY THROUGH RADIOCARBON DATING OF LIPIDS EXTRACTED FROM ARCHAEOLOGICAL CERAMICS USING SUPERCRITICAL FLUIDS

Dr Vincent Hare
Department of Earth and Environmental Sciences, University of Rochester, NY, USA.

Dr Thibaut Devièse
Research Laboratory for Archaeology and the History of Art, University of Oxford, UK.

We write to update you about the progress being made on this project, and to outline our plans for future work, depending on the outcome of various funding applications currently being made.

Project aims and background

This project concerns samples of archaeological pottery from the site of Bobartia Road Midden (BRM), southwestern Cape, sent by you to the Research Lab for Archaeology and the History of Art (RLAHA) in 2016. Our project was aimed at extracting lipids from the pottery using new methods recently developed at the lab with hopes to refine the pre-colonial chronology of southern Africa by radiocarbon dating the extracted lipids. We are confident such approach will enable a more robust site chronology, potentially.

The extraction and characterisation of organic residues in ceramics is routine in archaeological science (Smyth *et al*., 2014). Conventionally, organic materials are extracted by wet chemistry methods, i.e. using combinations of solvents after grinding up the ceramic material. The residue is then characterised by gas chromatography – mass spectrometry (GC-MS). This is a time-consuming process which requires toxic solvents, and is also destructive. Additionally, the quantities of organic residues extracted are usually not sufficient for radiocarbon dating.

Over the last few decades, substantial developments in analytical chemistry have been achieved with new instrumentation allowing for faster analyses and more sensitive results. Instruments using supercritical fluids for extraction and chromatographic separation (SFE and SFC, respectively) have been part of this revolution. Ongoing research at the Oxford Radiocarbon Accelerator Unit seeks to explore the use of supercritical fluids to extract and isolate residues from ceramic sherds. Preliminary experiments with SFE (Van Ham-Meert, 2015) have shown order of magnitude increases in the yields of lipids from pottery relative to conventional methods. The significant increase in yield, together with appropriate characterization by GC-MS, now makes AMS dating of

lipids from single sherds feasible. SFE possesses another clear advantage when applied to valuable cultural material, since supercritical fluids do not cause alteration of the ceramic matrix and the technique is largely non-destructive. The material obtained from BRM is suitable for several reasons:

- The site has a sequence of pottery from several well-defined stratigraphic layers, as well as existing chronological constraints on the top and bottom of the sequence, which can be used to constrain a Bayesian model.
- We expect high yields of lipids from this type of pottery. Coarse earthenwares are commonly used in this region for the processing of foodstuffs (Bollong *et al*., 1997; Copley *et al*., 2004).

Current progress at RLAHA

We have applied this new technique to extract and characterise lipids from Bobartia Road shell midden pottery. An MSc student, Jasmine Lundy, successfully completed her research dissertation on this material, and a summary of her findings can be found in her recent report (3 January 2017). She found significant quantities of lipids, but the scope of her project was limited to a relatively small fraction of the material sent (25 sherds, ~40 g out of a total mass of 3.5 kg). Her project focused on methodological aspects of extraction, which we have now managed to refine. We have not yet managed to date the extract, since (a) both more extractions would be necessary on more material in order to get enough organic substances to date and (b) we have not secured funding for the radiocarbon dates. Although the technique is very promising, machine time is very expensive, and we have currently submitted several grants which would allow us to increase our manpower and experimental capabilities. It is our intention to pursue the dating of the extracts, but this is dependent on the outcome of several funding applications.

Future plans

Since the technique is largely non-destructive, and has shown that extraction is feasible with respect to the material from BRM, it would be advantageous for all if the material could be kept for sometime longer; at least until we have heard the outcome of our funding applications. If money can be secured for 14C dating of the extracted material, this project has the potential to answer important questions about the chronology of pre-colonial herding peoples of the southwestern Cape. Alternatively, if you prefer the samples to be returned, we will send them by courier as soon as requested.

We are very grateful for your support and collaboration, and will certainly keep you informed about any developments.

Yours sincerely,

Vincent Hare and Thibaut Devièse

V. J. Hare BSc Hons MSc DPhil (Oxon)
Postdoctoral Associate
Department of Earth and Environmental Sciences
University of Rochester, NY, USA

T. Devièse MEng, MSc, PhD, MRSC
Postdoctoral Research Assistant
Research Laboratory for Archaeology and the History of Art
University of Oxford
Dyson Perrins Building, South Parks Road,
Oxford, OX1 3QY (United Kingdom)

References

Bollong, C.A., Sampson, C.G. and Smith, A.B. (1997) Khoikhoi and Bushman pottery in the Cape Colony: ethnohistory and Later Stone Age ceramics of the South African interior. *Journal of Anthropological Archaeology*, 16(3), pp. 269-299.

Copley, M.S., Hansel, F.A., Sadr, K. and Evershed, R.P. (2004) Organic residue evidence for the processing of marine animal products in pottery vessels from the pre-colonial archaeological site of Kasteelberg D east, South Africa. *South African Journal of Science*, 100.

Orton, J. (2014) Archaeological excavations at Bobartia road midden, ERF 4492 Betty's Bay, Caledon Magisterial district, Western Cape: Interim report. Available from: http://www.sahra.org.za/sahris/sites/default/files/heritagereports/Bettys%20Bay%20erf%204292%20arch%20mitigation%20interim%20report.pdf *Accessed 18 Feb. 16*

Rowe, M. W., Phomakay, J., *et al.* (2013) Application of supercritical carbon dioxide-co-solvent mixtures for removal of organic material from archaeological artifacts for radiocarbon dating. *J. of* Supercritical Fluids, 79, pp. 314-323.

Van Ham-Meert, A. (2015) Supercritical fluid extraction of organics from ceramics. *MSc Dissertation*, Research Laboratory for Archaeology and the History of Art, University of Oxford.