Report: Marine shell export Farm Boplaas, Erf 15387 and portion Erf 2001

Archaeological: Temporary export, for destructive analysis

Permit number: 1835

SAHRIS Case ID: 5504

Author of report: Cindy Nelson-Viljoen

Date of report: 11 October 2016

SAHRA permit officer: Mariagrazia Galimberti

Date of permit issue: 27 May 2014

Report due date: 30 June 2016

Expiry date of permit: 30 June 2015

Permit Holder: Cindy Nelson-Viljoen. PhD candidate. School of History, Classics and Archaeology. University of Edinburgh.

Permit to:

- Cindy Nelson-Viljoen. PhD candidate. School of History, Classics and Archaeology. University of Edinburgh.
- Dr. Curtis Marean. Arizona State University. Foundation Professor and associate director, Institute of Human Origins, School of Human Evolution and Social Change. Honorary Professor, Centre for Coastal Palaeoscience, Nelson Mandela Metropolitan University, Port Elizabeth.

Name of Locality/sites(s): Farm Boplaas, Erf 15387 and portion Erf 2001

Object ID's (batch ID): PP-SHELL-BATCH-CASEID5504

B. Executive summary:

This report outlines current progress on the sampling and analysis of archaeological shell from the Later Stone Age site identified as PPSMC (Pinnacle Point Shell Midden Complex [Farm Boplaas, Erf 15387 and portion of Erf 2001]). 301 Archaeological shell specimens were exported from the Mossel Bay Archaeology Project to the School of History, Classic, and Archaeology for destructive analysis as identified and described in section I. These analyses form part of a PhD research project on the seasonal shellfish use of Later Stone Age inhabitants of the Pinnacle Point site. Due to significant delays in funding, the sampling and analysis of the materials has not yet been completed. Preliminary results on the oxygen isotope pilot study of one modern and archaeological *O. sinensis* shell is described in section I (summary of results).

C. SAHARIS Object or Site links:

http://www.sahra.org.za/sahris/cases/marine-shell-export-farm-boplaas-erf-15387-and-portion-erf-2001

D. Location details:

- **Location name(s)**: Farm Boplaas, Erf 15387 and portion of Erf 2001
- **GPS coordinates**: S 34° 12.31 E 22° 05.40
- **Adequate mapping**: Yes
- **Nearest town**: Mossel Bay
- **Local district**: Mossel Bay
- **Magisterial district**: Mossel Bay
- **Province**: Western Cape
- **Formation/Subgroup/Group (for paleontological specimens)**: N/A
- **Approximate age of materials**: ~1533 to 3000 BP

E. List of all participating researchers:

- Cindy Nelson-Viljoen (PhD researcher). School of History, Classics and Archaeology. University of Edinburgh

F. Curation of materials:

- **Name of institution**: Mossel Bay Archaeology Project
- **Name of Curator**: Dr. Curtis Marean
- **Contact details of curator**: Curtis.Marean@asu.edu. USA Office Phone: 480-965-7796
- **Institutional address**: Munro Cottages, Dias Museum Complex, Mossel Bay, 6500, South Africa

- **How materials are being curated**: Specimens to be curated in clear re-sealable bags with tag including site name, sample number, and species identification and stored in cardboard boxes at the Mossel Bay Archaeology Project storing facility.

Specific information

G. Paleontological collections and Excavations: N/A

H. Archaeological Research Collections and Excavations: N/A

I. Destructive analysis:

- **Detailed description:**
    - **Acetate peels**

As shellfish grow, calcium carbonate ($CaCO_3$) and conchiolin is deposited via the mantle in successive increments. Each shellfish species has its own optimal growth conditions (Hallmann *et al.*, 2009; Galimberti, 2010; Burchell *et al.*, 2013). Changes in the aquatic environment, such as sea surface temperature, salinity, nutrition, disease, pollution, predation, and water turbidity result in metabolic responses by the organism that in turn affects shell growth patterns, structure, colour and its chemical composition. These consecutive growth lines (used to determine growth increments) are used to calculate calendar dates and distinguish between tide controlled growth such as daily and fortnightly patterns, aiding in the establishment of seasonal collection patterns (Lutz and Rhoads, 1980; Deith, 1983; Kent, 1992; Jones and Quitmyer, 1996; Milner, 2001; Schöne and Giere, 2005; Schöne and Surge, 2005; Hallmann *et al.*, 2009). To view internal increments shell specimens are embedded in epoxy resin for sectioning, before producing acetate peels.

The embedding process consisted of pouring 200 ml MetPrep kleer set polyester casting resin into a cardboard cup and adding 120 drops of MetPrep kleer set hardener whilst stirring the mixture continuously with a wooden stirrer. Once the liquid turns clear, a thin layer of resin is poured into the bottom of the moulds and left to harden for approximately 40 minutes. Labels (indicating sample number) are prepared and placed face down and in opposite corners of the mould, on top of the hardened resin layer. The shell samples are then positioned in the mould and a second layer of resin is poured to cover the shell completely. Samples are left to harden for no less than 12 hours, the timing varies depending on the thickness of the resin layer (Aramac, 2014).The embedded samples are sectioned with an IsoMet® 1000 Precision cutter, using a 30HC IsoMet Wafering diamond blade, perpendicular to the growth lines of the shell along the axis of maximum growth (Figure 1). *P. perna* are sectioned from the umbo to the ventral margin, to the right of the tooth of the left valve (Aramac, 2014). The limpets *Scutellastra longicosta* and *Cymbula oculus* are sectioned from back to front along the longest axis. For the top shell *Oxystele sinensis* and whelk *Burnupena cincta* the samples are sectioned along the whorls following the natural spiral growth trajectory from apex to the posterior end of the aperture, similar to methods described by Bigatti *et al.* (2007).

The sectioned surfaces of the samples to be used for growth increment analyses are ground on the MetaServ® 3000 Grinder/Polisher, starting with the coarse P120-grit grinding disk and moving up to the finer P400, P1200, P2500 and P4000 git size grinding disks until a mirror like surface is created (Butler, 2014, pers. comm.). Samples are then polished on the Buehler Polisher with Mecaprex diamond polishing paste solution in preparation for the acetate peels. Acetate peels are produced by etching the polished shell surface in a 2% hydrochloric acid (HCl) solution for a set period, depending on species, to create the relief necessary to preserve surface details. Best results are achieved by submerging *P. perna* for three minutes. *C. oculus*, *S. Longicosta*, *B. cincta* and *O. sinensis* are etched for two minutes. Thereafter the shells are immediately rinsed with deionised water to stop the etching process, and left to dry at room temperature. Once dry, the etched surfaces are flooded with 100% acetone [$(CH_3)_2CO$]. A thin (35 µm) Agar Scientific cellulose acetate sheet is then applied before the acetone evaporates, thus allowing the acetate to melt (dissolve) onto the etched surface. Samples are left to dry for approximately 20 minutes, depending on sample size (Aramac, 2014). The acetate sheets are then carefully peeled and mounted on glass slides to be examined under 4x and 10x magnification with a Leica DM750P polarizing microscope and photographed with a 5 megapixel Leica MC170 HD microscope camera.

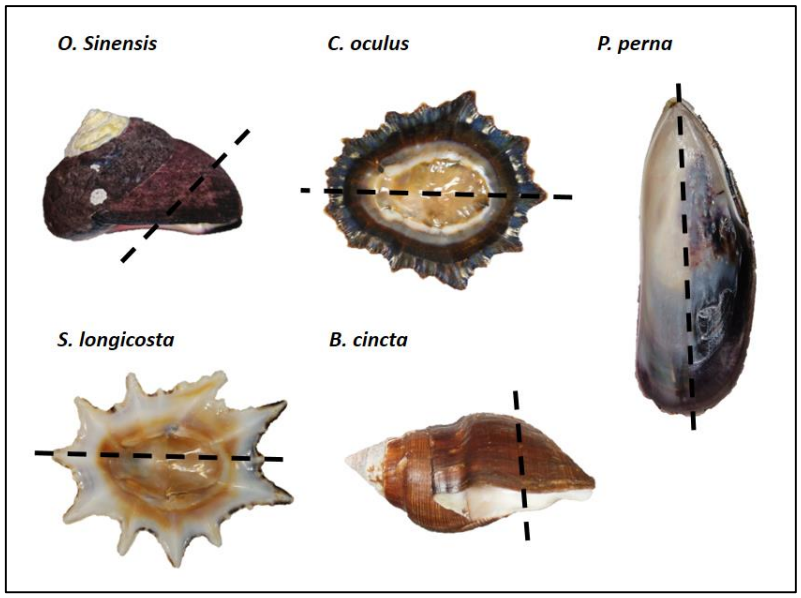

Figure 1. Location and direction of section through shells (molluscs not according to scale).

- **Oxygen Isotopes ($\delta^{18}O$) analysis**

As shellfish grow, their shells record information about the temperature and salinity of the seawater in which the organism lives. By analysing the O-isotope composition of a shell along the direction of growth, seasonal changes in seawater conditions can be quantified and the season of death of the animal (hence the time of collection) determined (Jones and Quitmyer, 1996; Schöne *et al.*, 2004; Galimberti, 2010). Various methods have been described to sample shells for analysis but all follow the same basic steps of removing sequential samples by micro-drilling along the direction of growth from individual shells to yield µg quantities of calcium carbonate ($CaCO_3$) for analysis. A pilot study was undertaken in 2015 to establish whether $\delta^{18}O$ analysis of *O. sinensis* can indicate seasonality of shellfish harvesting, i.e. whether seasonal variation in $\delta^{18}O$ was sufficient to indicate season of death. 72 samples of powdered $CaCO_3$ from one complete modern *O. sinensis* shell were sampled by manual

drilling at approximately 2 mm intervals in reverse ontogenetic order i.e. from the aperture (outer lip) to the apex in the direction of growth (Figure 2) at the British Geological Survey (BGS) facilities, in Nottingham, under the supervision of Prof. Melanie Leng and Miss. Carol Arrowsmith. Care was taken to remove the outer layer of periostracum before taking between 60 and 300 µg of $CaCO_3$ from the outer purple layer. The samples were drilled with a handheld Dremel 200 series with 0.9 mm NTI diamond drill bit, mounted on a Dremel workstation 220 to convert into a table top drill press. The powder was collected on non-absorbent weighing paper and transferred to 0.5 mm Eppendorf vials.

Due to financial constraints, the entire shell surface of the remaining shell specimens were not sampled. Instead, 77 samples from one archaeological shell (sample number 165) were drilled from the aperture to apex, the data was then compared with the full isotopic profile of the modern pilot study. Ten samples from each of the remaining nine modern and five archaeological shells are sampled to allow for the reconstruction of the temperature and seasonality range (Leng, 2016, pers. comm.). Specimen 165 and the five archaeological shells (specimen numbers 152, 154, 157, 163 and 164) are sampled as described above from the aperture. As aragonite material is preferred for isotopic temperature reconstruction (Schöne and Gillikin, 2013) (Leng, 2016, pers. comm.), the outer calcitic purple layer is removed by careful drilling and discarded, before drilling into the white-grey aragonite layer, recovering approximately 60 to 300 µg $CaCO_3$. The modern shells for this study's comparative sample are sampled at the School of History, Classics and Archaeology, University of Edinburgh, with a handheld Dremel 3000 multi-tool with 0.8 mm engraver drill bit, mounted on a Dremel workstation 220 to convert it into a table top drill press.

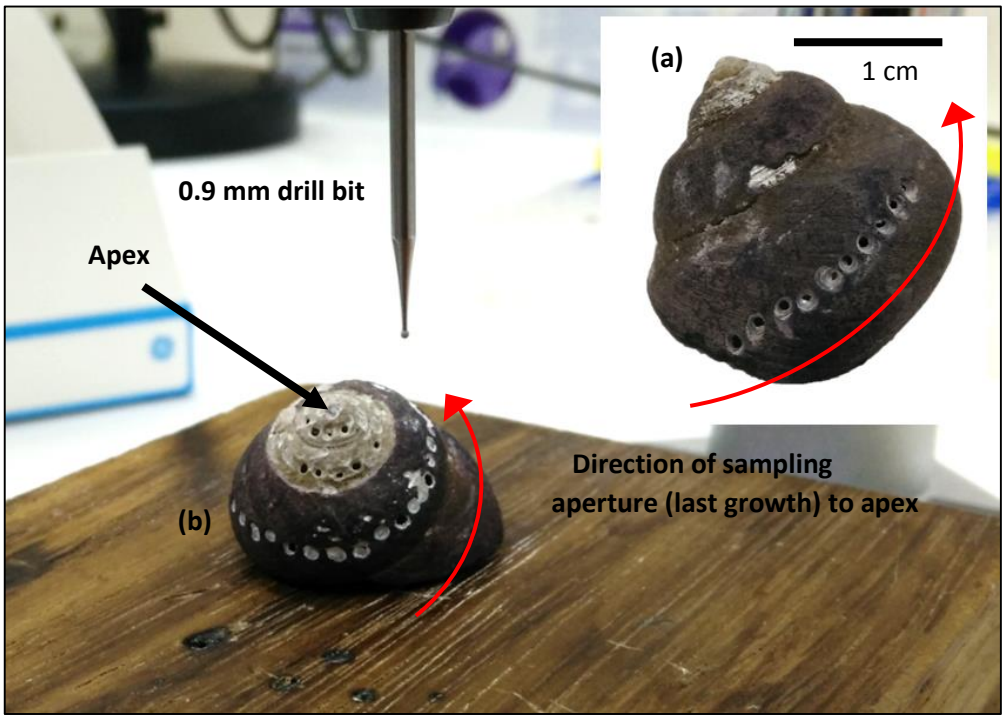

Figure 2. Example of isotope sampling locations and direction from aperture to apex; on (a) modern and (b) archaeological *O. sinensis* samples.

- **Photos before and after**: not yet compiled, sampling and analysis not completed
- **Description of analytical techniques**:
    - **Acetate peels:**

Sampling and analysis not yet complete (see section I; Acetate peels)

- **Oxygen isotopes**

Powdered $CaCO_3$ samples are analysed using an Isoprime dual inlet mass spectrometer with attached Multiprep for the analysis of $^{13}C/^{12}C$ and $^{18}O/^{16}O$, at the BGS facilities under the supervision of Miss Hilary Sloane. Approximately 50 to 100 µg of the $CaCO_3$ samples are loaded into glass vials and sealed with septa. Anhydrous phosphoric acid (H_3O_4P) is added to the carbonate at 90°C. After 15 minutes reaction the evolved CO_2 is passed through to the mass spectrometer. Within the mass spectrometer the gas is firstly ionised and the positively charged molecules are then focussed and passed through a magnetic field. The three most common molecule masses i.e. 44 (^{12}C ^{16}O ^{16}O), 45 (^{13}C ^{16}O ^{16}O) and 46 (^{12}C ^{16}O ^{18}O) are sorted according to mass/charge ratio and collected separately in the detectors. The isotope values ($\delta^{13}C$ and $\delta^{18}O$) are reported as per mille (‰) i.e. part per thousand, deviations of the isotopic ratios ($^{13}C/^{12}C$ and $^{18}O/^{16}O$) and calculated to the VPDB (Vienna Pee Dee Belemnite) scale using a within-run laboratory standard, calibrated against NBS-19 (VPDB). The Calcite-acid fractionation factor applied to the gas values is 1.00798. A drift correction is applied across the run, due to the long run time of 21 hours, and calculated using the standards that bracket the samples. The Craig (1957) correction is also applied to account for $\delta^{17}O$. The average analytical reproducibility of the standard calcite (KCM) is 0.05‰ for $\delta^{13}C$ and $\delta^{18}O$ (Mccrea, 1950; Craig, 1957; Shackleton, 1973; Friedman and O'neil, 1977; Kim *et al.*, 2007). The Palaeotemperature reconstruction is achieved by converting the shell $\delta^{18}O$ values into sea surface temperatures (SST) using six palaeotemperature equations:

$$T = 16.5 - 4.3 (\delta^{18}O \text{ carbonate} - \delta^{18}O \text{ water}) + 0.14 (\delta^{18}O \text{ carbonate} - \delta^{18}O \text{ water})^2$$ (Epstein and Mayeda, 1953)

$$T = 16.9 - 4.38 (\delta^{18}O \text{ carbonate} - \delta^{18}O \text{ water}) + 0.18 (\delta^{18}O \text{ carbonate} - \delta^{18}O \text{ water})^2$$ (Shackleton, 1974)

$$T = 21.8 - 4.69 (\delta^{18}O \text{ aragonite} - \delta^{18}O \text{ water})$$ (Grossman and Ku, 1986)

$$T = 20.6 - 4.34 (\delta^{18}O \text{ aragonite} - \delta^{18}O \text{ water})$$ (Grossman and Ku, 1986)

$$T = 19.7 - 4.34 (\delta^{18}O \text{ aragonite} - \delta^{18}O \text{ water})$$ (Hudson and Anderson, 1989)

$$T = (20 \pm 0.2) - (4.42 \pm 0.1) (\delta^{18}O \text{ aragonite} - \delta^{18}O \text{ water})$$ (Böhm *et al.*, 2000)

T is the reconstructed sea surface temperature. The results are compared with the SST measured at the time of modern shellfish collection, to determine which of these palaeotemperature equations most closely resemble the measured SST. The chosen palaeotemperature equations are then applied to the archaeological shell $\delta^{18}O$ values to determine the SST of last shell growth, i.e. when the shell was collected.

- **Discussion on efficacy of technique**: N/A (sampling and analysis not yet completed)
- **Summary of results**:
  - **Acetate peels:** Sampling and analysis not yet completed

Looking at the sectioned shell under microscope, very few shells showed clear growth increments. Current experimentation of the cutting angels and grinding methods are underway to resolve the inconsistencies with the acetate peels.

  - **Oxygen isotopes:** Sampling and analysis not yet completed

Comparison of recorded sea surface temperatures measured at Pinnacle Point, and the calculated temperature curve from the pilot study indicated that varying water temperatures are recorded in *O. sinensis* shells, and that Shackleton and Epstein equation most closely resemble SST values recorded at time of shellfish collection during 2013/14 (Figure 3). However, the isotope values of the pilot study shell collected in May 2013 does not correspond with the recorded sea surface temperatures for the month of May. Accurate isotope analysis of archaeological shell is dependent on the preservation of the original shell crystalline structure. As shell carbonate consists of aragonite and calcite attention must be paid to metastable aragonite that converts into stable calcite polymorph during post-depositional recrystallization. This process distorts the original isotopes recorded in shell carbonate. To clarify the mineralogical complexities of *O. sinensis,* Scanning Electron Microscopy and Backscatter Diffraction (SEM-EBSD), in addition to Raman spectroscopy analysis on modern shell is underway to identify the precise location of the aragonite:calcite crystals and detect possible post-depositional recrystallization. Sampling of the remaining archaeological *O. sinensis* shell will commence on completion of these analyses. The archaeological pilot study (shell 165 [Figure 4]) indicated that the archaeological specimen recorded at least 4 possibly annual cycles, as indicated by summer temperature peaks. Further analysis of the reaming modern and archaeological shell isotope values are required to make meaningful interpretations on the seasonality of shellfish collection during the Later Stone Age at PPSMC.

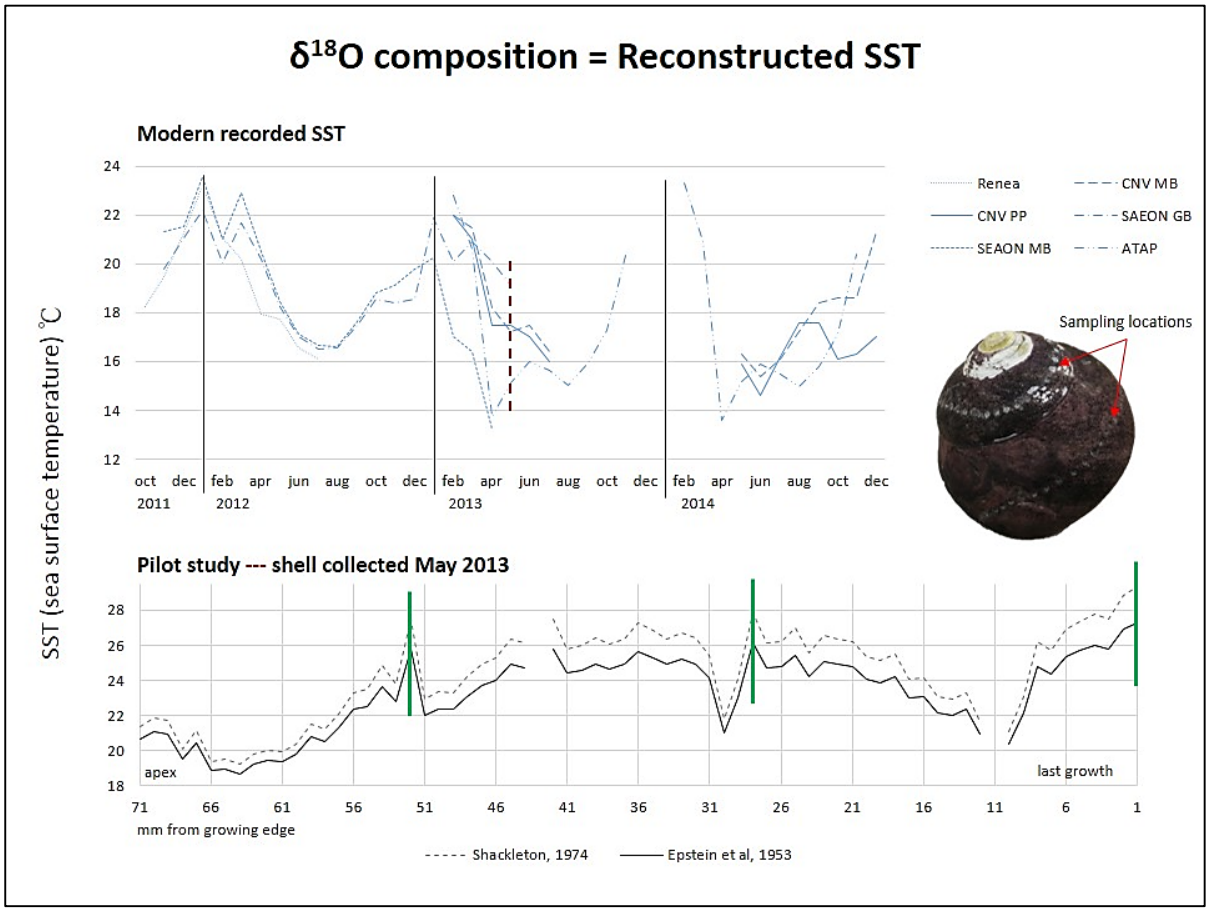

Figure 3. Isotope pilot study on one modern *O. sinensis* specimen. Results indicate 3 possible summer peaks.

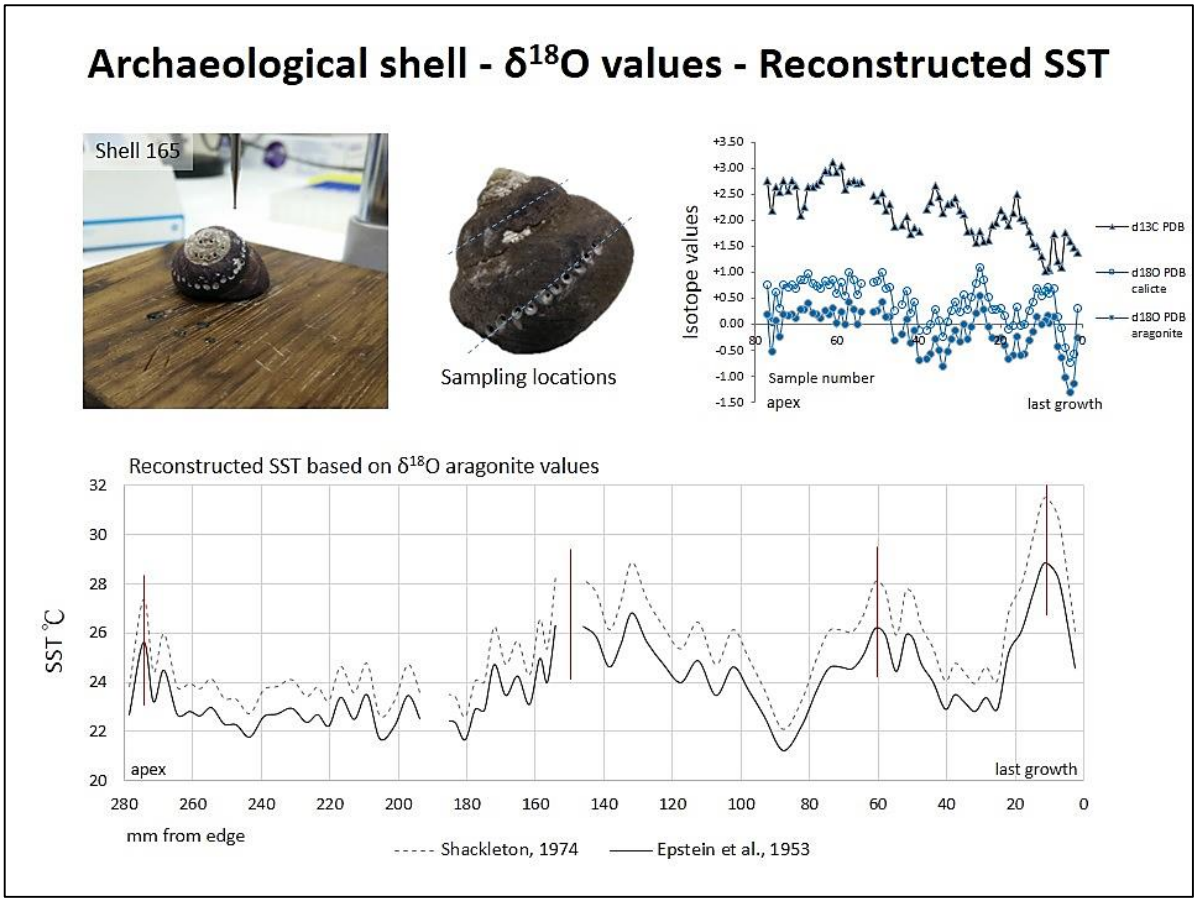

Figure 4. Isotope pilot study one archaeological shell specimen. Result in indicate 4 possible summer peaks.

- **Copies of publications**: N/A

J. Temporary Export: Travel log

- 5 March 2015 – from Mossel Bay Archaeology Project to the School of History, Classics and Archaeology, University of Edinburgh (sent via Federal Express Europe, arrived on 12 March 2015).
- 25 March 2015 – from University of Edinburgh to the British Geological Survey (BGS), Nicker Hill, Keyworth, Nottingham NG12 5GG, and returned to University of Edinburgh on the same day (carried by Cindy Nelson-Viljoen)
- Stored at the School of History, Classic and Archaeology's finds processing and thin section laboratory at the University of Edinburgh whilst awaiting Isotope NERC funding application outcome.
- 8 March 2016 – from University of Edinburgh to the British Geological Survey (BGS), Nicker Hill, Keyworth, Nottingham NG12 5GG, United Kingdom (carried by Cindy Nelson-Viljoen)
- 10 March 2016 – from British Geological Survey (BGS), Nicker Hill, Keyworth, Nottingham NG12 5GG to the University of Edinburgh (carried by Cindy Nelson-Viljoen).

K. Conservation/Maintenance: N/A

L. Filming Permit: N/A

M. Phase II Mitigation: N/A

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