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**FINAL REPORT FOR PERMIT No. 2005-12-002**

For the project:
HWC application No. 2005/12/APM 002
HWC Ref. No. C13/3/6/2/1/1/1/1/C16
Permit No. 2005-12-002

The following final report is prevailing for my research on 79 *Turbo sarmaticus* opercula from Garcia State Forest (GSF) 2, GSF 3, GSF 6, GSF 7, GSF 8 (Blombos Cave) and GSF 9 in the Riversdale Magisterial District, Western Cape Province.

My supervisor for the project is Professor C.S. Henshilwood at the African Heritage Research Institute, 167 Buitenkant Street, Gardens, Cape Town, 8001. The analyses for the project have been undertaken at the Department of Earth Science at the University of Oslo, Norway and the Institute for Energy Techniques at Kjeller, Norway.

If there are any questions or additional information you might need, please do not hesitate to contact me.

Yours sincerely

Lena J. Brune

# Introduction

One method used to reconstruct the palaeoenvironmental fluctuations, which is applied to various kinds of archaeological material, is stable isotope analysis. Marine molluscs excavated from archaeological sites worldwide are commonly used in this methodology. The hard shells and opercula of molluscs are mostly waste from food consumption. This particular waste is composed of a biologically produced mineral, calcium carbonate ($CaCO_3$). These calcium carbonates can be used to reconstruct past climates, because biologically produced minerals contain information that reflects the environment at the time of growth in an organism. The stable oxygen isotope component of $CaCO_3$ of certain species of marine shellfish displays in part the temperature of the water in which they lived, while the stable carbon isotope component can reflect other environmental factors of the ocean, such as seasonal variation in upwelling. This is because $CaCO_3$ absorbed during growth is precipitated in isotopic equilibrium with the ambient seawater (Urey *et al.* 1951; Anderson & Arthur 1983: 1.65; Weiner & Dove 2003: 18). Thus, marine molluscs found in an archaeological site are thought to be valuable in reconstructing the environment, and additionally reflecting the season of occupation.

However, the factors controlling the carbon isotope composition in $CaCO_3$ from marine molluscs are more complex and less understood than for oxygen isotopes (Richardson 2001: 130). In addition, the stable oxygen isotopes are the isotopes that reflect temperatures, which usually is the focus of palaeoenvironmental reconstructions. Therefore, the stable carbon isotopes will not be given a similar amount of attention as the stable oxygen isotopes in this study.

For almost 60 years, it has been assumed that the method used to determine temperatures by stable oxygen isotopes is completely reliable; the method has remained virtually unchanged and unchallenged. In the late 1970s and 1980s, oxygen isotope analysis became particularly popular in archaeology and palaeoenvironmental reconstructions.

However, parallel to the method of stable isotope analysis, used on marine molluscs, gradually becoming a more common tool in archaeology and palaeoenvironmental reconstructions, the archaeological and modern molluscan calcium carbonate material became subjects for closer investigations. Consequently, the knowledge on growth in marine molluscs and influences to the isotopic composition of biogenic marine minerals has constantly expanded over the last 30 years (Hoefs 1980: 147-151; Lutz & Rhoads 1980; McConnaughey 1989a;

Mount *et al.* 1994; Cohen & McConnaughey 2003; Weiner & Dove 2003; Meibom *et al.* 2004). Several factors are now thought to have disarranging effects on the stable isotope results used to determine palaeoenvironmental fluctuations.

It is now known that calcium carbonates and isotopic content of the marine molluscs can have altered while the animal was still alive, after deposition in archaeological sites and/or during laboratory procedures. In the first instance, the control possessed by the animal over the precipitation processes can alter or eliminate the isotopic signals. Therefore, not all biologically produced calcium carbonates are in isotopic equilibrium with the ambient seawater (Epstein *et al.* 1951:422; Anderson & Arthur 1983: 1.66; Bemis *et al.* 1998). In addition, the stable oxygen isotopes of the molluscan $CaCO_3$ can be affected by factors such as seawater salinity, evaporation and trace elemental composition, meaning that temperature is not the only circumstance causing fluctuations in the oxygen isotopes of $CaCO_3$ precipitated from the ocean. Diagenesis, the changes that occur after a shell or operculum is deposited at a site, can also affect the isotopic results. The calcium carbonates precipitated from seawater can be dissolved and new calcium carbonates or other materials can recrystallise. The stable isotopes in a case of recrystallisation will represent a completely different event than $CaCO_3$ precipitated from seawater, and the oxygen isotopes will therefore not represent the temperatures of the ocean while the molluscan animal was alive. Finally, during the cleaning and sampling procedures changes in the stable isotopes of the $CaCO_3$ can occur. Careful control in assessing the degree of preservation for each molluscan specimen is required to ensure the results accurately reflect past climates (Tripati *et al.* 2001: 105-106; Weiner & Dove 2003: 17-18).

Therefore, the mentioned factors, which can disarrange the stable isotopic content of molluscan calcium carbonates, are causing the palaeoenvironmental reconstructions based on stable isotope analysis to no longer be seen as a straightforward task. Thus, it is essential to re-examine different variables of the methodology. A fundamental place to start is the examination of the procedural techniques of the method, because procedures are needed that will recognise molluscan calcium carbonates that are chemically and physically unaltered. The procedures themselves must not alter the calcium carbonates and their isotopic composition before samples have been collected for stable isotope analysis.

Several procedural stages performed to analyse the calcium carbonates of archaeological specimens of marine molluscs experienced few varieties or changes between the 1970s and the late 1990s. During this time, the samples would be cleaned with pure distilled water, a hydrogen peroxide and lye solution and/or roasted under vacuum to remove cementation, clay minerals and organic material. However, each of these cleaning procedures can alter the calcium carbonates and/or their isotopic composition.

External and internal changes of the physicality and/or chemical composition on a micro-scale were rarely thoroughly studied. X-ray Diffractometry was the common procedure performed to control that the calcium carbonates had not been altered before stable isotope analysis was conducted using a mass spectrometer. The samples for X-ray Diffractometry would be grinded to a powder, but often the powder would be collected from a large area of the shell, or even from the whole shell, studied. This would create a sample with mixed material, instead of determining the chemical composition of smaller, confined areas to know exactly where an unaltered sample can be collected.

Over the last three decades, progress in procedural techniques of the methodology has been made possible based on technological advances, such as the Scanning Electron Microscopy with Energy Dispersive X-ray System, and/or scientific progress. In the case of scientific progress, one example is Harald & Stipp's (2006) research indicating that pure distilled water, which have been used for years to clean samples, will in fact dissolve calcium carbonate upon contact. Another example is the recent identification of a transient amorphous calcium carbonate. It is likely that the crystalline calcium carbonates forms from the amorphous calcium carbonate in the marine molluscan shells and opercula. This amorphous calcium carbonate phase is unstable. Thus, the stable isotope results, and their information on the ambient environment, from this initial stage of formation will be lost during roasting under vacuum at high temperatures, which has been another commonly used method to clean samples (Weiner & Dove 2003; Meibom *et al.* 2004).

Therefore, one anticipated contribution of the present study is to use the technological and scientific advances to create procedural stages that can act as criteria to find physically and chemically unaltered calcium carbonates in marine molluscan shells and opercula: Calcium carbonates that can confidently be sampled for stable isotope analysis. A new method of cleaning the samples will be presented; this method of cleaning with ethanol will be evaluated against previous cleaning procedures to assure it is not destructive to the $CaCO_3$ or its isotopes.

Microscopy and Scanning Electron Microscopy with Energy Dispersive X-ray System will be used to study the physical surface and the chemical composition of the selected marine molluscan specimens. These two procedures have previously not been commonly applied to study the $CaCO_3$ prior to sampling for isotopic analysis. However, they are valuable tools in determining if dissolution and/or recrystallisation have taken place. In the case of Scanning Electron Microscopy with Energy Dispersive X-ray System, growth processes, alterations and/or trace elemental composition can be identified on a micro-scale, and even down to a nano-scale (Treble *et al.* 2005). Buchardt (1977) used an early version of the Scanning Electron Microscopy to identify traces of recrystallisation and secondary crystal growth in fossilised aragonitic shells. However, this did not become a commonplace technique to study the ancient biogenic calcium carbonates.

In addition, X-ray Diffractometry will be used to determine the chemical composition. However, instead of examining the entire specimen of shell or operculum, small powder samples will be drilled from confined areas and examined to identify the most unbiased and unaltered calcium carbonate.

Microscopy, Scanning Electron Microscopy with Energy Dispersive X-ray System and X-ray Diffractometry were chosen for this study as the most favourable methods to determine unaltered and uncontaminated $CaCO_3$-material, which then can be used for stable isotope analysis. The stable isotope analyses will be performed on a mass spectrometer.

The palaeotemperature equation is another variable of the methodology that will be examined; its difficulties and possibilities will be addressed. A palaeotemperature equation is a formula that measures the relationship between seawater temperature and isotopic fractionation between molluscan calcium carbonates and seawater. Thus, three factors are important in a palaeotemperature equation: Seawater temperature, the composition of stable oxygen isotopes in seawater and in calcium carbonates. If two of the three factors are known, the third can be calculated. Thus, the palaeotemperature equation calculates the oxygen isotopes from calcium carbonates into temperatures, when the oxygen isotopic composition of the seawater is known.

When wanting to sample calcium carbonates for isotope analysis from archaeological specimens of marine molluscs, it is essential to first sample modern specimens of the same shellfish species as the archaeological one to be used. The procedure of all palaeoenvironmental studies on marine molluscs is to start by collecting modern specimens regularly, and at the same time measure the actual temperatures and isotopic component in the seawater at the site of collection. The modern specimens of the molluscan species will then be measured for stable isotopes. Knowledge of the actual seawater temperature, isotopic composition of both seawater and modern molluscan $CaCO_3$ makes it possible to choose the palaeotemperature equation that provides values closest to the accurately measured temperatures when calculating oxygen isotopes from the modern $CaCO_3$ into temperatures. This same palaeotemperature equation will then be used to calculate the stable oxygen isotopes from archaeological specimens of the same molluscan species into ancient seawater temperatures. However, when using the same palaeotemperature equation to calculate the oxygen isotopes from archaeological specimens into temperatures, it is assumed that the seawater has had a constant isotopic composition over time. Meanwhile, it is known that for example ocean salinity, evaporation and dilution by freshwater will change the isotopic composition of the seawater (Cohen 1993: 40-41). However, corrections for possible changes diluting or enriching isotopic values of seawater are difficult to make, and become equally uncertain as the modern values.

Several palaeotemperature equations have been created over the 60 years the stable isotope methodology has been in existence, and a variety exist for both biogenic and inorganic versions of calcitic and aragonitic calcium carbonates. The large variation of palaeotemperature equations in existence can produce any temperature range for any material in a study. In addition, with this considerable number of palaeotemperature equations available, it will create difficulties to confidently choose one that determines accurate temperatures from ancient calcium carbonates. However, good precision for the temperatures calculated from isotopes can be possible by choosing one palaeotemperature equation and using it for all samples in a study. This makes, at least, the isotopic results and temperatures found in the archaeological shells compatible with each other, and thus creates a relative temperature scale.

In the present study, calcium carbonate samples taken from the opercula of the marine gastropod *Turbo sarmaticus* were chosen for the examination of the method. Human inhabitants of the southern Cape coastal regions, South Africa, have collected *Turbo sarmaticus* as a staple food resource for at least 125 000 years; its shell and operculum have been found in several archaeological sites in this area (Voigt 1975: 89-90; Foster 1997: 2).

The operculum, which is a calcified plate attached to the foot of the animal, fills the aperture of the shell when the animal withdraws into the shell (Claassen 1998: 16 & 18). Ten archaeological opercula specimens chosen for this study are from four Later Stone Age (LSA) sites of Garcia State Forest (GSF) nature reserve situated on the southern Cape coast of the Western Cape Province, South Africa. The four sites chosen from Garcia State Forest nature reserve are GSF 2, GSF 3, GSF 8 (Blombos Cave) and GSF 9. Hunter-gatherer groups occupied all of these sites during the Holocene. Modern opercula were also included in this study, as a comparative control collection.

Ten opercula can seem like a small sample collection. However, the cuts of number of opercula had to do with the emphasis on examining the method used for reconstructing the palaeoclimate. The time limitations of this study could only allow for thorough examinations of only a few opercula in a variety of procedures. None the less, the careful study of a few opercula could give indications to the reliability of the methodology of using stable isotope analysis to determine palaeotemperature fluctuations. The procedural examinations proved valuable, because six out of the ten opercula had to be discarded from being used in stable isotope analysis. Their physical and/or chemical appearances proved to be altered.

Christopher Henshilwood (1995) has previously studied the Garcia State Forest sites, and has conducted stable isotope analysis on *Turbo sarmaticus* opercula from these sites. The isotopic results have been used to determine palaeoenvironmental conditions and seasonality of occupation on the southern Cape coast. However, 11 years have past since these investigations were completed. It is now known that $CaCO_3$ easily dissolve and recrystallise, even during laboratory procedures, and thus new procedural techniques and thorough investigations of the calcium carbonates were required before sampling for stable isotope analysis in this study. Thus, *Turbo sarmaticus* opercula from the Later Stone Age sites of Garcia State Forest nature reserve were chosen for a re-examination of the method used to determine palaeotemperatures from stable isotopes.

However, the relevance of the re-examination of *Turbo sarmaticus* opercula from the Garcia State Forest sites is not restricted to only these exact sites. The main aim and anticipated largest contribution of this study is to consider the potential pitfalls at all stages of the application of the method, and demonstrate how the potential dangers of the pitfalls can be identified, solved and/or avoided through a variety of carefully selected procedures. The results will be relevant for calcium carbonates collected from archaeological specimens of molluscs worldwide. It is anticipated this study will reveal if the method used to gain information on past climates through oxygen isotope studies of calcium carbonates from marine molluscs should be discarded or whether it might still be used with reliability in future archaeological research. In addition, this study can disclose a need for re-evaluating the applicability of results gained from earlier stable isotope analysis on archaeological specimens of marine molluscs. Thus, results gained on palaeoenvironmental fluctuations and seasonality, without a thorough investigation of the archaeological calcium carbonates before sampling for isotope analysis, might not be as trustworthy as previously imagined. In other words, the study might reveal that palaeotemperatures previously used in archaeology can be faulty. By association, the hypotheses drawn from these palaeotemperature fluctuations may need scrutiny as well.

## Conditions affecting the marine calcium carbonates

Various influential factors are decisive for how, and in what ways, marine calcium carbonates may precipitate, dissolve and recrystallise. In addition, various factors that may cause $CaCO_3$ precipitation in isotopic disequilibrium with the ambient seawater, overly depleted or enriched isotope results and varying elemental composition will be discussed. Most of the conditions presented can cause alterations in physicality and/or chemistry of the archaeological opercula studied. These alterations can cause the isotopic composition of the calcium carbonates to diverge from isotopic equilibrium with seawater.

It is essential to know the circumstances that cause alterations in the marine calcium carbonates to be able to understand the results achieved in the methodological procedures. After all, these results are the foundation for determining if the individual archaeological specimens of *Turbo sarmaticus* opercula are reliable for palaeoenvironmental reconstructions. If certain conditions alter the isotopic signal of *Turbo sarmaticus* opercula to be independent of temperature and isotopic composition of ambient seawater, calcium carbonates of all species of marine molluscs, exposed to similar circumstances, will probably experience isotopic alterations. Thus, material in certain specimens or whole specimens altogether may have to be avoided when sampling for stable isotope analysis.

When considering stable oxygen isotopes, temperature is thought to be the main factor causing their fluctuation. In fact, the reconstructions of palaeoenvironments from archaeological marine carbonates depend on it. However, various other conditions may cause slight variations in the isotopic record of the marine organisms. The conditions that can have an effect on the stable isotopes of calcium carbonates are for example kinetic, metabolic and taxonomic effects; evaporation, humidity and precipitation; Salinity, salt effects and strontium-effects; melting of the polar ice caps; pH and meteoric waters. Certain changes and exchange processes may be physically noticeable in the marine shells and opercula. However, chemical changes and alterations in microstructure may not be revealed by physicality, but will be disclosed when the isotopic results are presented.

Stable carbon isotopes will not be influenced much by the ambient water temperatures, but may produce information on other influences of the environment in which the organisms live: For example, seasonal upwelling activity, salinity and input of biological carbon in the seawater. However, metabolic activity in the organism can affect the stable carbon isotopes, and cause environmental signals to be disguised. The information on carbon isotopes can help in understanding if the stable isotope results are a product of the inorganic nature of the ambient oceanic environment or are caused by the control the animal has over its precipitation of $CaCO_3$.

## Methodology – laboratory procedures

In this section, the procedural processes used to conduct the study of the calcium carbonates will be presented. *Turbo sarmaticus* opercula selected for the present study were subjected to a variety of laboratory procedures to make sure that the calcium carbonates sampled for isotope analyses would be aragonite precipitated by the organism in isotopic equilibrium with the seawater in which it was growing. These calcium carbonates will yield the most accurate oxygen isotopes to be calculated into temperature with a carefully selected palaeotemperature equation.

After careful consideration of different cleaning procedures used in other projects the samples were cleaned with pure ethanol. All of the opercula had cementation or other types of unfavourable materials, such as ash patches, sand and organic material, covering the surface. Therefore, before the opercula could be sampled they had to be cleaned. Ethanol cleaning was chosen, because it was the least destructive for the calcium carbonates. Ethanol evaporates fast, and gives little exposure time for a possible reaction between the ethanol and the $CaCO_3$. The ethanol is not reactive with calcium carbonates in any case. In addition, any unwanted material was manually removed from each sample, while studying it under the microscope.

Microscopy, X-ray Diffractometry and Scanning Electron Microscopy with Energy Dispersive X-ray System were laboratory procedures performed to evaluate the physical and chemical appearance of calcium carbonates found in the archaeological *Turbo sarmaticus* opercula. The physical appearance and chemical structure of the opercula can reveal if they are composed of calcium carbonates originally precipitated by the organism during its lifespan in the ocean, or if they are products of recrystallisation after deposition in the archaeological context. In addition, trace elemental composition may disclose information on the oceanic environment in which *Turbo sarmaticus* lived, and thus if the oxygen isotope results fluctuate due to something other than temperature.

Microscopy, X-ray Diffractometry and Scanning Electron Microscopy with Energy Dispersive X-ray System will prevent that carbonate material unsuitable for stable isotope analysis is sampled. These new and/or improved procedures will determine if stable isotope analysis can be conducted with reliable results, or if the isotope results should be discarded.

Mass spectrometry was conducted to disclose stable isotope ratios for both carbon and oxygen of the calcium carbonates in *Turbo sarmaticus* opercula. The isotopic results will reveal if the carbonates have been deposited in equilibrium with the ambient seawater, because only a limited range of isotopic results achieve equilibrium. This range is between 0.0‰ and +2.0‰ on the $\delta^{18}O_{PDB}$ scale.

Temperature will have some effect on the fractionation of carbon isotopes between aqueous carbonate and solid $CaCO_3$, but not to the same extent as the oxygen isotopes between water and solid $CaCO_3$. The $\delta^{13}C$ will only be affected by temperature about one tenth of what $\delta^{18}O$ is (Anderson & Arthur 1983: 1.80). However, they are influenced by other factors of the oceans, such as the content of dissolved inorganic carbon, and may help to give a more complete picture of the surrounding environment in which the shellfish lived (Andreasson *et al.* 1999: 278-279; Carré *et al.* 2005: 5). If the $\delta^{13}C$ of biogenic aragonitic calcium carbonates are in equilibrium with the $\delta^{13}C$ of dissolved inorganic carbon, the $\delta^{13}C$ of $CaCO_3$ can be used as a proxy to provide information about for example seasonal variation in upwelling activity, salinity, biological carbon input and productivity (Carré *et al.* 2005: 13; Gillikin *et al.* 2005: 71). However, the factors controlling the $\delta^{13}C$ composition for marine calcium carbonates are more complex and less well understood than for $\delta^{18}O$ (Richardson 2001:130). It does seem like metabolic activity can affect the $\delta^{13}C$ causing the environmental signals to be disguised (Geist *et* *al*. 2005). Therefore, the carbon isotopes have been given less attention than the oxygen isotopes in this study. The $\delta^{13}C_{PDB}$ should be 3‰ in inorganically precipitated $CaCO_3$-compounds in equilibrium with seawater. If temperature was the only factor that influences the isotopic composition and everything else was constant, which means an inorganic equilibrium, the carbon isotopes would not fluctuate much in this system.

Only four opercula, S 1.1, S 1.2, S 1.3 and S 26.1 were used for stable isotope analysis. During the preliminary research, the other six opercula were discovered to not be preferable for isotope analyses due to various taphonomic processes, and changes and exchanges in chemical composition and physical appearance. The stable isotopic values could in these six opercula not be guaranteed to be from originally precipitated calcium carbonates.

However, having to reject so many opercula from use in stable isotope analyses is regarded as an interesting development for this project. The dismissal of some opercula after the preliminary research indicates that there is a need for scrutiny, and possibly alterations, of the procedural phases of the methodology.

The archaeological opercula were scanned at the initial phase of the project and after each new procedure of invasive research technique, meaning when the opercular surface was cleaned, scraped or drilled. This was done to document each specimen at all stages of the investigations. Images of all opercula were photographically scanned into a computer at a scale of about 5:1 cm.

***Palaeotemperature equations:*** The palaeotemperature equation describes the relationship between sea surface temperature and the isotopic fractionation between $CaCO_3$ and seawater (Cohen 1993: 39). The original form of palaeotemperature equation was derived using living molluscs grown under controlled conditions (Epstein *et al*. 1951, 1953). In previously published literature, it is difficult to find consistency of palaeotemperature equations used to calculate the oxygen isotope results into temperatures (Anderson & Arthur 1983; McConnaughey 1989a; Dettman *et al*. 1999). Authors operate with large differences on similar material: Varieties on isotopic values of seawater; several differences between the isotopic component of oceans now and in the past; and research is conducted on varying standard scales, even within the same palaeotemperature equation.

A species dependence on oxygen isotope fractionation can exist. Therefore, as an example, a palaeotemperature equation made for aragonitic bivalve shells may not describe the oxygen isotope fractionation of all aragonitic bivalves (Carré *et al.* 2005: 22). Thus, due to the difficulty in discovering correlations between the different equations, it is difficult to get good accuracy of the temperature calculations. However, good precision may be achieved by choosing one equation for use throughout all the samples. This creates an opportunity to compare the different specimens' isotopic results with each other and a relative scale of temperature fluctuations can be made.

In Figure 1, different palaeotemperature equations can be seen creating a great diversity of temperature possibilities based on isotopic data collected from similar type of material. Most of the equations presented in this figure are based on inorganic calcium carbonates. As can be seen, the fractionations between $\delta^{18}O$ for $CaCO_3$ and $\delta^{18}O$ for water give a large variety of isotopic results that further creates large variations in temperatures. More ranges of temperature results found in oxygen isotope fractionation in organic biominerals may be seen in Bemis *et al.* (1998: 155 (Figure 2)). The oxygen isotope results of the organically formed carbonates are even more difficult, because the organism's own control on the precipitation will be an additional factor influencing the stable isotope results.

The palaeotemperature equations calculated for both organic and inorganic carbonates are found by controlled experiments and measurements, so it is difficult to tell why they end up so differently. In addition, it is impossible to say which are reliable or not, and this can make calculations of the environment at and around archaeological sites, based on carbonate material, difficult. Therefore, even if discovering and sampling pure aragonitic $CaCO_3$ precipitated in isotopic equilibrium with the ambient seawater for stable isotope analysis, it is difficult to calculate oxygen isotopes into accurate temperatures for the past oceanic environment. The best possibility is, as mentioned, a relative temperature range from the archaeological $CaCO_3$, where it is possible to evaluate warmer or colder results, in relation to each other, as shifting seasons.

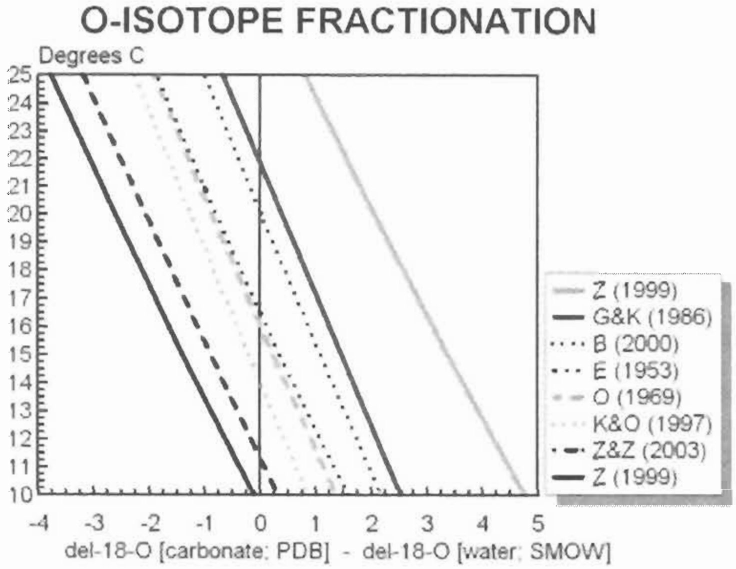

Figure 1 Temperature fluctuations dependent on oxygen isotope fractionation between calcium carbonate and water. The same isotopic values can translate into different temperatures with varying palaeotemperature equations. Author names are abbreviated in the figure: Z = Zheng (1999); G&K = Grossman & Ku (1986); B =Böhm *et al*. (2000); E = Epstein *et al*. (1953); O =O'Neil *et al*. (1969); K&O = Kim & O'Neil (1997); Z&Z = Zhou & Zeng (2003). Kim & O'Neil (1997) has been extrapolated for under 25° The blue lines represent palaeotemperature equations for aragonite, while green are for calcite. The red line represent the equation for this study, while the black stapled line is the earliest palaeoclimatic equations calculated. Due to computer technical reasons in the software of the program the figures were made in, it is not possible to write the delta-notation, superscript, subscript or degrees. Therefore, °C is written as degrees C and $\delta^{18}O$ is written as del-18-O.

# Results and discussion

## *Microscopy*

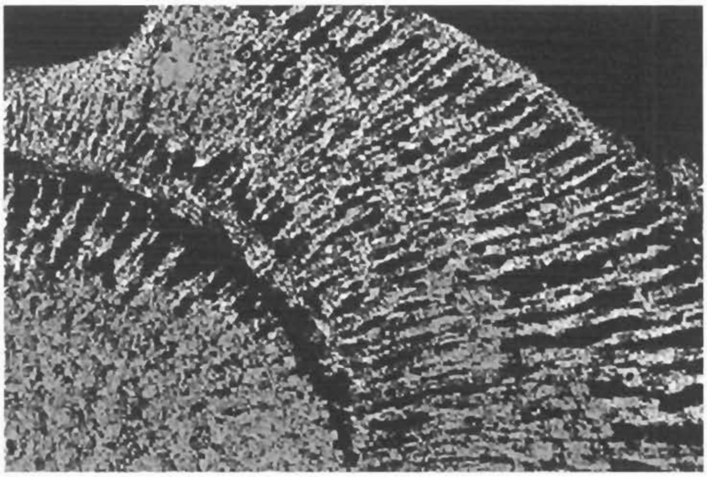

Figure 2 The aragonitic palisade growth pattern from a section of S 1.5. Photograph taken with technique of reflected light microscopy. The colours have been adjusted to better show the contrasts between the lighter, green areas showing the reflection pattern of $CaCO_3$, and the darker hollows possibly representing areas where recrystallisation of other material, for example quartz, has happened.

In reflected light, all the brightly reflected, here false green, palisades probably consist of originally precipitated $CaCO_3$ (Figure 2). Along the longest axis of the palisades, there are dark areas where light is not well reflected. These dark regions could be dissolution cavities in the original material created by meteoric water or represent where the organic macromolecular matrix of original precipitation were located in the structure. Over time, these organics may have perished, leaving open hollows in between the mineralogical carbonates. The dissolution cavities and hollows were most likely refilled at a later stage.

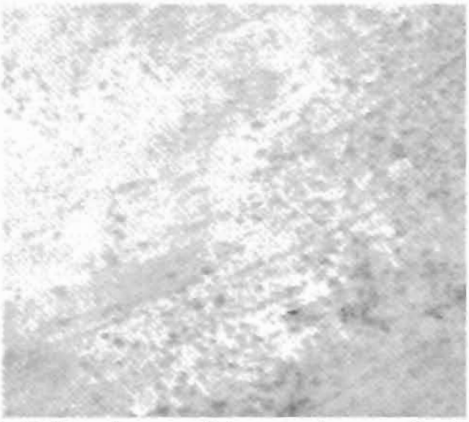

Figure 3 Hollows from possible meteoric water dissolution. Section from S 1.3.

At some stage after deposition, it seems likely that the opercula have been exposed to freshwater, for example groundwater or rainwater, which have caused etch marks, cracks and hollows to form (Figure 3). These type of etch marks are present in several of the opercula, but are more distinguishable in some of the specimens.

A starting phase of diagenesis is obvious on close inspections of the opercula. Diageneses are the different processes of dissolution and recrystallisation that can happen to the calcium carbonates after deposition in an archaeological site. One example is when shell fragments, small animals and varying small particles are deposited and cemented together to form a mineral. It is most striking in all cracks and hollows, especially prevailing in the spiral trench closest to the vortex. This trench seems most vulnerable for recrystallisation. Some of the recrystallised material can be identified to mineral species, but most cannot. The crystals/particles are too small to discover mineralogical distinguishable hallmarks and have too little material to sample for X-ray diffractometry. Some particles were lying loose on the opercular surface. However, after blowing compressed air onto the opercular surface, many of the crystals were still deeply embedded in the material.

The microscopy revealed some disturbing results along the outer edge of some of the archaeological opercula. Some of the growth lines appear to undulate along the edge. A growth line may be present at a stretch of the edge, disappear and re-materialise somewhere else. Other growth lines seem to have dissolved completely, causing the next growth line to be influenced by etchings. This is expected, because the outer edge is most exposed to weathering and has the thinnest width of the opercula. Close examinations of the terminal growth edge are needed before sampling it for stable isotope analysis. This must be conducted on each separate specimen to determine that the outer growth edge actually represents the last season of growth.

### *X-ray Diffractometry (XRD)*

X-ray Diffractometry results show that the largest constituents of *Turbo sarmaticus* opercula are aragonite and magnesian calcite. In addition, calcite, quartz and a strontium-compound are present. Background disturbances are visible on the resulting diffractographs, which can be from the uncrystalline amorphous calcium carbonates or organic materials.

The variation between quantity of aragonite and magnesian calcite in the opercula seem to fluctuate through the years, and even seasons, of the animals' life. The X-ray Diffractometry show that most samples taken of apparently original material contain aragonite; for example growth lines, palisades, vortex and outside nodules. This indicates that originally precipitated calcium carbonates are intact.

The aragonitic content dominates in the opercula from the younger sites, Garcia State Forest sites 8 (Blombos Cave) and 9. In fact, magnesian calcite is completely absent, while calcite is present in only two samples. This can indicate a Mg-content of over 0.11 mol in the ocean (Figure 2): At least from about 2000 B.P. to around 480 B.P., which is the time period Garcia State Forest sites 8 and 9 represent in this study. Aragonite will then have had a lower solubility and been more stable in near surface conditions of the earth and ocean than other versions of the calcium carbonates, even after completed precipitation. However, the dates of the opercula collected from Garcia State Forest sites 8 and 9 will mean that they have been buried in an archaeological context for a much shorter period than the opercula collected from older sites. Thus, being less exposed to weathering and taphonomic processes causing alterations to the calcium carbonates. In addition, the Garcia State Forest site 8 and 9 are covered sites, and will be less exposed to weathering than the open sites.

The operculum from Garcia State Forest site 9 revealed ambiguous results. As was to be expected, the burning of the specimen has had an effect. However, the effect has not presented itself in the fashion anticipated. The effect of burning is physically detectable on the surface of the operculum. Hollows with recrystallisations and collapsed indentations are visible all over the surface. In this regard, the conclusion would be that burnt material could not be used for isotope analysis. However, the chemical results indicate that the originally precipitated aragonite in the operculum is still intact. This goes against previous notions that exposure to high temperatures will change the biomineral composition of the $CaCO_3$ from aragonite to calcite. This may either indicate that the temperatures in the hearth were not high enough to change the carbonate material, or prove an actual stage of high-Mg content in seawater, and consequently low aragonite solubility, around 480 B.P.

In the samples of original material from the opercula of Garcia State Forest site 2, there are many samples reflecting high magnesian calcite content in addition to the aragonite. This may be interpreted as a period where the Mg-content in the ocean water is below 0.11 mol. Consequently, calcite has a lower solubility than aragonite. From the stage of 0.11 mol downwards, *T.sarmaticus* will still precipitate aragonite, but the aragonite will be metastable and more prone to inclusions of magnesian calcite. However, in the opercula from Garcia State Forest site 2 it might be argued that the presence of magnesian calcite represent an evolved process of dissolution and recrystallisation, because of the age of this site. However, the samples mostly contain aragonite and magnesian calcite together, while calcite is virtually non-existent. If the original material had gone through a complete process of dissolution and recrystallisation, it could be expected to find less aragonite and more calcite. In comparison, samples of original material from the modern operculum also contain a mixture of aragonite and magnesian calcite. This indicates that the magnesian calcite content can have more to do with natural inclusion from the ocean rather than a change in original material.

Strontium seems to be present in trace amounts and/or have been precipitated with the aragonitic calcium carbonates. The presence of strontium, in any amount and combination, may signify that seawater, where *Turbo sarmaticus* lived, evaporated to some extent to cause strontium-precipitation. If the precipitation of strontium-compounds really has happened through seawater evaporation, this event had changed the $\delta^{18}O$-value of seawater as much as 10 ‰ on the SMOW-scale. This is because strontium will first be precipitated into the calcium carbonates when 90% of the original seawater has evaporated. This granted that the organism does not control the precipitation of strontium.

It is a possible for evaporation to have happened in the environment where *Turbo sarmaticus* live. In the author's experience, it is at times possible to collect large *Turbo sarmaticus* without diving; at least on certain parts of the stretch of coast near the Garcia State Forest sites. At low tides, some of *Turbo sarmaticus*' living spaces can be turned into rock pools of varying size and depths, where they may easily be collected. In these rock pools, evaporation may happen and influence the strontium- and salt-intake of *Turbo sarmaticus*. Evaporation is a likely event to explain the strontium-content, especially since strontium is not present in all of the opercula. This indicates that the different individuals may have lived in different environments with variable conditions.

### *Scanning Electron Microscopy with Energy Dispersive X-ray System*

Images were taken in the Scanning Electron Microscopy of the operculum from Garcia State Forest site 3, because this operculum had been cleaned with freshwater. The images show the opercular surface on a micro-scale. In some of these images, there is a presence of etch pits (Figure 4a). The etchings visible in the operculum can have been created when this operculum was exposed to freshwater. Other findings in the operculum are varying recrystallisations in the deep trenches, possibly imprints of small organisms, and bacteria and algae growth (Figure 4b). These features can be found in all calcium carbonates of biogenic shells and opercula, if they have been exposed to weathering and taphonomic processes after deposition in archaeological contexts. If any of these features are included in the samples used for stable isotope analysis, the isotope results will have been contaminated. Temperatures calculated from contaminated isotope results will yield wrong conclusions on the palaeoenvironment.

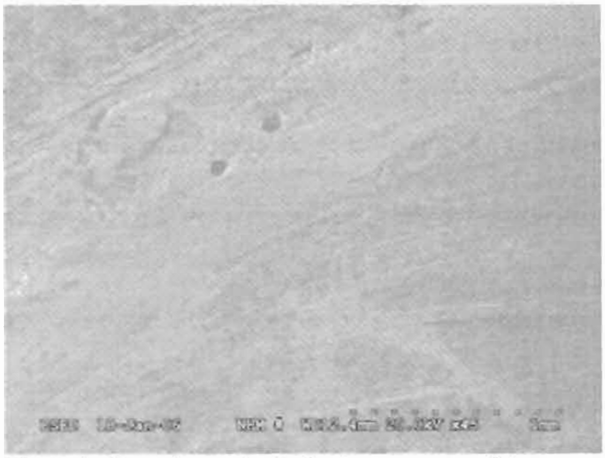

Figure 4a Two clear etch pits in the top-centre of the frame. The area presented in the figure is 1 mm across in width.

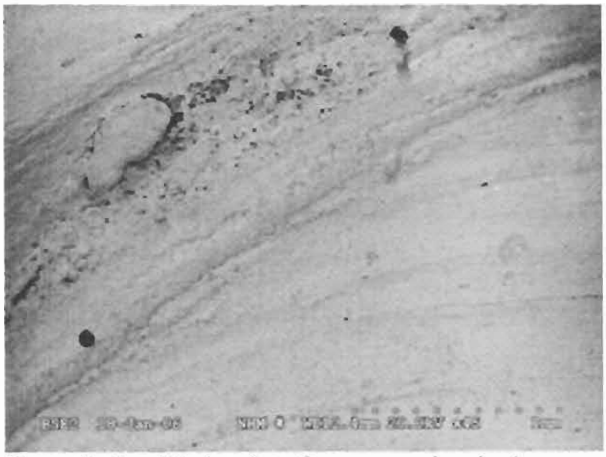

Figure 4b Possible imprint after an organism in the top-left corner of the frame. Small blotches that may be bacteria or algae growth are also present. The whole area presented in the figure is 1 mm across in width

*Energy Dispersive X-ray System: Results and discussion:* The Energy Dispersive X-ray System results are difficult concerning ratio between the organic materials and the biogenic minerals. Hydrogen from the organic inclusions is too light to be measured by the Energy Dispersive X-ray System, so the weight percentage is expressed without all factors being considered. However, if all elemental components in each sample are normalised in accordance with the calcium (Ca) present, the difficulties with organic presence in the samples will be minimal. This normalisation is based on the individual element's atom percentage divided by the Ca atom percentage present in the opercula (atom%/Ca) (Figure 5a-b), because the Ca-content is stable in all the samples analysed.

Looking at the chemical element analyses taken along the holes of the drilled samples of S 26.1 from Garcia State Forest site 8 (Blombos Cave) (Figure 5a) and S 1.2 from Garcia State Forest site 2 (Figure 5b) they are quite different. The operculum S 26.1 (growth A; Figure 5a) has greater differences between the chemical elements than what operculum S 1.2 does (growth B; Figure 5b). Some of the points, as aluminium (Al) in Figure 7a and Al and chloride (Cl) in Figure 5b, are underneath the detection line of atom%/Ca content in this project.

The results of the elemental analyses were compared with the $\delta^{18}O$ variations (Figure 7a-d). The elements magnesium and strontium, in Mg/Ca and Sr/Ca ratios, should correlate inversely with the calculated temperatures, if ambient sea surface temperatures are recorded in the magnesium and strontium values of the aragonite (Richardson 2001: 142; Gaetani & Cohen 2006: 4632). However, in the corals studied by Gaetani and Cohen (2006), contents of magnesium and strontium in the skeletal calcium carbonates were proven not to be in equilibrium with contents of magnesium and strontium in seawater, and therefore did not reflect sea surface temperatures. The temperature information indicated by the ratios of Mg/Ca and Sr/Ca in the aragonitic coral skeletons originated from the control the organisms have over precipitation or from other factors of the ambient oceanic environment, for example evaporation. Support for this is found in Carré *et al.* (2006: 4911) and Freitas *et al.* (2006), where studies on aragonitic and calcitic bivalves prove no significant correlation with Mg/Ca or Sr/Ca in calcium carbonates and measured sea surface temperature.

In this study, the ratios of both Sr/Ca and Mg/Ca do not fluctuate in an inverse relationship with temperatures. Therefore, the magnesium and strontium in *Turbo sarmaticus* opercula are not in equilibrium with the magnesium and strontium content of seawater, and not representative as indicators for sea surface temperatures. Thus, the Mg/Ca and Sr/Ca ratios from *Turbo sarmaticus* shell and operculum cannot be used as indicators of palaeoclimatic fluctuations.

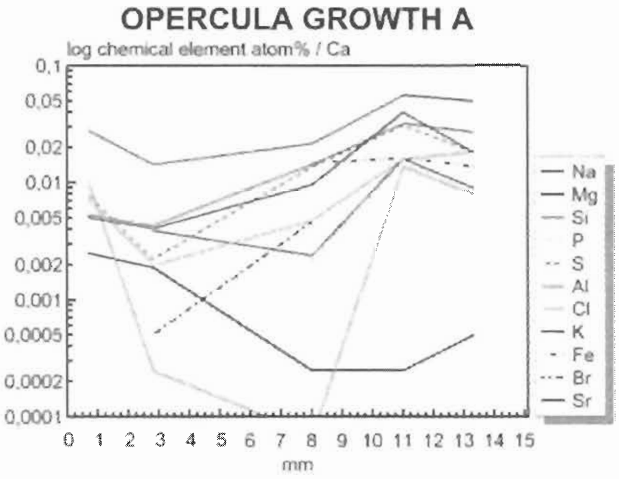

Figure 5a The chemical element analyses (log scale) of operculum S 26.1. Ca-normalised

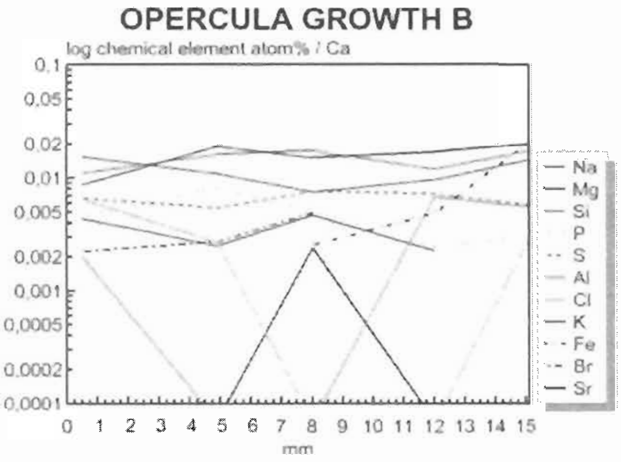

Figure 5b The chemical element analyses (log scale) of operculum S 1.2, Ca-normalised

However, the presence of magnesium and strontium in the opercular calcium carbonates can still indicate stages of evaporation. Therefore, it should be assessed if evaporation, rather than temperature, can have been influential in the variations of the oxygen isotopic results and elemental composition. The elements precipitated during evaporation will be magnesium (Mg), sulphur (S), sodium (Na), chloride (Cl) and strontium (Sr); the concentration of all these elements will increase in accordance with the oxygen isotopic content increasing. This will happen as the event of evaporation progresses. Magnesium will be precipitated at the first phase of the evaporation process, sulphur will precipitate next, then sodium and chloride as the evaporation process progresses and lastly strontium will be precipitated. If no evaporation can be proven to have happened, the presence and fluctuation of the mentioned elements may come from another source of origin, for example cementation, freshwater washing, burning, humidity, sea spray and/or groundwater.

In operculum S 1.2 (growth B; Figure 5b), all of the elements have quite a flat pattern with little fluctuations, except for strontium. This shows that the pattern visible cannot be due to evaporation. However, in the operculum S 26.1 (growth A; Figure 5a), it can be seen that the magnesium, sulphur, sodium and chloride have similar patterns, indicating evaporation. The strontium-pattern does not follow in the same extent. However, evaporation may still have happened, as strontium is the last element to be precipitated in the calcium carbonates through evaporation of seawater. Meanwhile, the content of magnesium, sulphur, sodium and chloride in the operculum do not fluctuate in accordance with the oxygen isotopes. What is left is a likely isotopic temperature-series that does not appear to be altered by seawater evaporation-effects.

However, the elemental composition of magnesium, sulphur, sodium and chloride present in the opercula, in patterns fluctuating in accordance with one another, seem to represent some type of evaporation. Two explanations are possible. On one side, evaporation may have happened, but the animal is able to control and compensate for the effect evaporation has in its carbonate material. The other possibility is that the elements represent a phase of sea spray or sea humidity after the operculum was deposited in an archaeological site on land. A thin film of seawater may have been deposited on the operculum before evaporating away again. The process of re-evaporation of the humidity film seems to have happened rather rapidly, because no obvious exchange of isotopes between the opercula and water vapour/humidity is visible.

### *Mass Spectrometry*

Palaeotemperature equations and modern temperatures: First, it was important to decide on which palaeotemperature equation to use for calculating the oxygen isotopic results. The equation developed for aragonitic bivalves by Grossman and Ku (1986) was chosen for this project:

$$T\ (^{\circ}C) = 21.8 - 4.69\ (\delta^{18}O_{ar} - \delta^{18}O_{w}),$$

where $\delta^{18}O_{ar}$ is the oxygen isotopic result from aragonite (PDB) and the $\delta^{18}O_{w}$ is the isotopic value of the ambient water (SMOW) the opercula were collected from. The latter was not available for direct measurements, but was calculated to be 0.0‰.

Grossman and Ku's (1986) palaeotemperature equation seemed the most promising choice. The material of their work and the material used in this thesis are similar; aragonitic marine gastropods. In addition, Grossman and Ku (1986) examined specimens of aragonitic foraminifera and scaphopods to have a better foundation for their palaeotemperature equation for biogenic aragonite. Additionally, it seems that other authors have found the equation of Grossman and Ku reliable; either using it was originally calculated (Krantz *et al.* 1987; Jones & Allmon 1995; Richardson 2001; Adkins *et al.* 2003; Jones *et al.* 2005) or have used it with just minor adjustments (Dettman *et al.* 1999; Wurster & Patterson 2001; Carré *et al.* 2005).

When investigating the accuracy of the correlation between temperatures calculated from oxygen isotopes and measured temperatures, it will be of significance to explore this aspect with modern opercula before using archaeological specimens. Henshilwood provided the isotopic measurements taken during his PhD from modern *Turbo sarmaticus* opercula, and these were calculated into temperatures using Grossman and Ku's (1986) palaeotemperature equation. When comparing the total temperature range from his six modern opercula with that of the measured sea surface temperatures, the comparativeness seems relatively good. With the isotopic results for the modern opercula, the highest temperature is 23.1°C and the lowest is 13.7°C, while the modern measured range lies between 22.6 and 11.5°C. The highest temperatures correlate quite well, while the lowest temperature values are divided by as much as 2.2°C. Therefore, the temperatures calculated based on isotopes should be regarded as a relative guide and not the absolute temperatures experienced by the animal. However, the two ranges have such a good correspondence that they indicate that temperatures are fairly well represented by Grossman and Ku's (1986) palaeotemperature equation.

However, it must be remembered that there exist a large variety of palaeotemperature equations (see Figure 1). All of these palaeotemperature equations can be used to calculate oxygen isotopes into temperature, and will present largely varying temperature ranges for the same isotopic values. In using modern measured temperatures and comparing those to the isotopes drawn from modern shellfish species, basic presuppositions are made for the method to work. The assumption has to be made, and believed in, that Holocene oceanic conditions did not change enough over the last 10 000 years to have an effect on the temperatures calculated from oxygen isotopic composition in marine calcium carbonates. In addition, it is assumed that the aragonitic $CaCO_3$ of the modern specimens of molluscan species have not been altered between collection and testing. If the calcium carbonates have been altered by dissolution and/ recrystallisation, the isotopic component will have changed from the one precipitated in isotopic equilibrium with the seawater. Thus, in the event of using altered material to choose a palaeotemperature equation, the equation will be representative to flawed material. Therefore, it is equally important to process and handle the modern specimens in a careful fashion with similar procedural stages as the archaeological ones.

When temperatures were calculated from oxygen isotopes from archaeological opercula, these results also seemed compatible to the measured sea surface temperatures of Stilbaai. The temperatures of the archaeological opercula are approximately 1-2°C lower than the modern measured sea surface temperatures. The temperature range from the archaeological opercula is between 10.9 and 20.1 °C, while the temperature range of the measured sea surface temperatures is between 11.5 and 22.6 °C. However, here it is the lowest temperatures that are representative, while the highest temperatures are far apart. The total variability for the ten years of sea surface temperatures measurements from Stilbaai is 11.1°C. For the opercula, the total variability is 9.2°C. Thus, the two ranges are very similar. It is assumed that the Holocene sea surface temperatures have not changed much from the start of the epoch to today, and 1-2°C difference is not a big change in the marine environment.

Thus, the palaeotemperature equation of Grossman and Ku (1986) seems to represent the temperatures of isotopic content in archaeological opercula fairly well, and is the equation best suited for use in the context of this thesis. However, even if the palaeotemperature equation does not calculate the exact temperatures indicated by oxygen isotope results, it will at least provide relative temperature ranges in each specimen of opercula with low temperatures representing winter and high temperatures representing summer. These relative temperature ranges can be compared from specimens within the same context and with specimens collected from other archaeological sites, as long as the same palaeotemperature equation is used for all the samples.

*Oxygen isotope results and equilibrium:* The $\delta^{18}$O for aragonite in isotopic equilibrium with the ambient seawater lies between 0.0 and + 2 ‰ on the PDB-scale. The isotopic results from this study show that oxygen isotopes are within the limits of equilibrium, even if *Turbo sarmaticus* seems to grow approximately 5 mm per year. This is in spite of the maximum equilibrial growth rate having been claimed to be less than 2 mm a year (McConnaughey 1989a: 156). The maximum equilibrial growth rate therefore seems to be varying for different taxa of marine organisms. Figure 6 shows that the molluscan *Turbo sarmaticus* is deviant from other taxa of marine life: *Turbo sarmaticus* represent stable isotopes precipitated into its calcium carbonates in equilibrium with ambient seawater. Therefore, *Turbo sarmaticus* are one of the molluscan species that can theoretically be used in palaeoenvironmental reconstructions. The other marine taxa in Figure 6 will not be suited for studying palaeoclimatic fluctuations. These marine taxa can have an even faster growth rate than *Turbo sarmaticus*, and therefore be out of equilibrium.

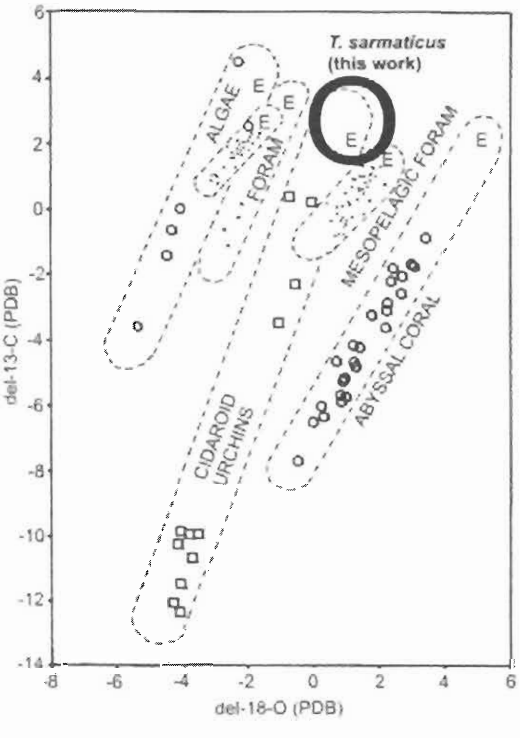

Figure 6 Carbon (C) and oxygen (O) isotopic delta variations (both vs. PDB) reported for biological carbonates from different species, modified after McConnaughey (1989a). Isotopic equilibrium (E) for calcite or aragonite was estimated using the best available data for seawater temperature and isotopic composition. Results from the present work are represented by the bold circle.

*Palaeoenvironmental reconstructions:* There are few conclusions that can be drawn for palaeoenvironmental reconstructions, when considering the small sample collection used in this project. Thus, the results cannot be used to draw large conclusions on palaeoclimate. It will rather be attempted to discover an agreement between the results from this study and previous results on palaeoenvironment on the southern Cape coast of South Africa.

Considering the operculum from Garcia State Forest site 8 (Blombos Cave), it has a temperature range of 12.0°C to 18.2°C. This creates a difference in temperature from minimum to maximum of 6.2°C. In comparison, the modern temperature range at Stilbaai for 1983 to 1992 is between 11.5°C and 22.6°C; creating a difference of as much as 11.1°C. The minimum temperatures of both ranges deviate by only 0.5°C. The maximum temperatures are a different story, however, as there is a difference of 4.4°C. The climate approximately 2000 B.P. was cooler and wetter than today at the coast of the southern Cape. The temperatures representing the warm season in the operculum definitely reflect a cooler environment. However, the results are conflicting, since the temperatures for the cold season are quite similar to the modern measured ones. Therefore, it is not possible to draw anything conclusive from this operculum to support or reject the theory on the palaeoenvironmental conditions of 2000 years ago.

Oxygen isotope studies on marine molluscs from Nelson Bay Cave determined that prior to 6300 B.P. the seasonal temperatures were lower on the southern Cape coast than those recorded today. The summer and winter sea surface temperatures supposedly only started getting higher than today between 6000 and 4000 years ago. The date on the square I3, from which the three opercula from Garcia State Forest site 2 were collected, is 6740 ± 70 B.P. According to the Nelson Bay Cave record, the Garcia State Forest site 2 opercula should reflect temperatures lower than those today. The collective range of the three opercula from this site lies between 10.9°C and 20.1°C. Compared to the modern measured sea surface temperatures, this could actually reflect a colder climate when this site was visited about 6800 years ago.

*Edge values: Terminal growth and season of collection:* The outer edge of the *Turbo sarmaticus* operculum represents the terminal growth. Thus, the oxygen isotopic values sampled from the outer edge should yield temperatures that represent the season the specimen was collected. The season the specimen was collected will be informative to when the hunter-gatherers visited the coast. In South African archaeology, seasonal movement and subsistence patterns of indigenous hunter-gatherer populations of the Cape during the Holocene have been a recurrent theme of archaeological research since the 1970s (Henshilwood 1995: 209; Jerardino 1996: 137). An ongoing debate has been whether hunter-gatherers moved between inland and coast to maximise their access to seasonally available and reliable staple food resources (Parkington 1972, 1987, 1991), or whether hunter-gatherers groups lived year-round at the coast Sealy & van der Merwe 1985, 1986, 1988, 1992; Lee-Thorp *et al.* 1989).

All the opercula from Garcia State Forest site 2 have similar values on the outer edge, which is thought to represent the final growth (Figure 7b-d). The values are taken between 0.0 mm and 0.5 mm from the edge, and they all lie between 16 and 17°C. The three opercula were all picked from the same square, and should therefore represent animals that were collected during the same occupation.

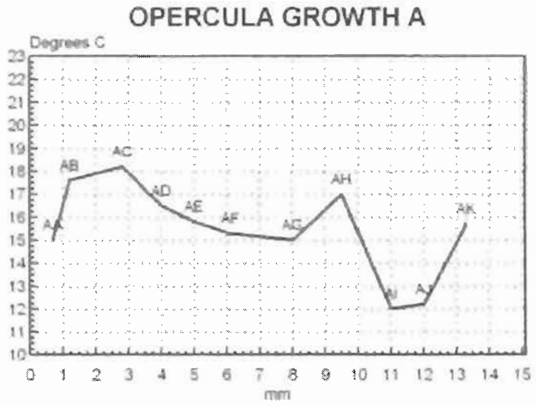

Figure 7a. Operculum S 26.1

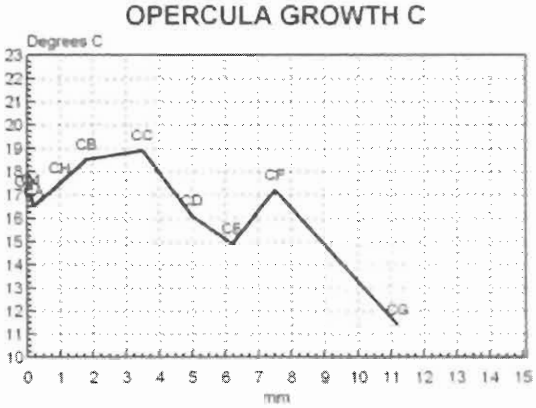

Figure 7c Operculum S 1.1

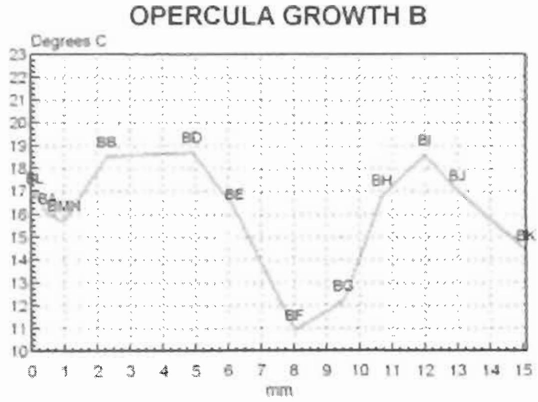

Figure 7b Operculum S 1.2

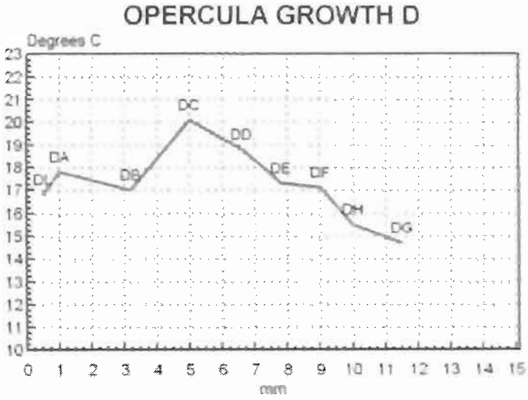

Figure 7d Operculum S 1.3

Figure 7a-d: The representation of temperature in relations to distance from the edge (mm). Due to computer technical reasons in the software of the program the figures were made in, it is not possible to write sign for degrees, so instead of °C, it has been written out as Degrees C.

The sample DA from operculum S 1.3 (Figure 7d) has a temperature value of 17.8°C, and is taken one mm from the outer edge. This sample indicates higher temperatures when moving from the outer edge and into earlier stages of the animal's life. However, at the same distance from the edge, sample DJ indicates a temperature of 15.3°C, which indicates lower temperatures. The latter is more in accordance with the samples BM and BN from operculum S 1.2, which also were taken one mm from the outer edge. These samples register temperatures of 15.5°C and 15.9°C, respectively (Figure 7b). This may indicate that the isotopic value, and consequently temperature, of sample DA is slightly too high.

However, sample DA could be representative of the correct values for this operculum, because the whole of the D-series (operculum S 1.3) generally give higher results than the B-series (operculum S 1.2). The difference may be explained by different growth pattern and pace for the different opercula. They are of similar size and age, but may have experienced different influences to their growth where they lived. For example, when adult *Turbo sarmaticus* are exposed to very high or low temperatures, they will stop growing. Therefore, one of the two opercula may have been exposed to extreme temperatures, for example by living in rock pools heated by the sun or being exposed to cold upwelling from the bottom of the ocean. This would have caused a break in the growth before the specimen was able to migrate into tidal zones with more preferable temperatures.

The last operculum from Garcia State Forest site 2, S 1.1, has temperatures increasing when moving inwards from the outer edge. However, the sample CB was taken as far from the outer edge as 1.8 mm, which can be a great leap from one mm in terms of seasons. The temperature calculated to 18.5 °C (Figure 7c). The most compatible measurement in the B-series (operculum S 1.2) would be the sample BB situated 2.3 mm from the edge. Here the temperature also has reached 18.5 °C (Figure 7b).

The operculum from Garcia State Forest site 8 (Blombos Cave) has similar edge values as the other opercula, but indicates somewhat colder temperatures in comparison. The outermost sample, AA, was taken 0.7 mm from the edge. It gives a temperature of 15.0°C (Figure 7a).

All of the temperatures from all samples taken at or near the outer edge of the opercula were compared to the ranges of modern sea surface temperatures measured at Stilbaai 1983-1992. Each month has a range of temperatures that have been achieved over the measured ten years. All of the isotopically measured edge temperatures were compared to each month's range to find if the specific temperature could appear in a particular month. None of the isotopically calculates temperatures from edge appears in January, February, November and December. Thus, none of the temperatures lies within the range of summer. Only sample AA from operculum S 26.1 lies within mid-winter. The rest of the samples lie within autumn and spring.

Therefore, it becomes important to look at the calculated temperatures just prior to the terminal growth edge to find out if there was movement towards a colder or warmer season when the sample was collected. In the operculum from Garcia State Forest site 8 (Blombos Cave), the A-series, the temperature just before the edge was the highest recorded in this operculum, so it seems probable that the shell was picked when moving out of a warm season and towards a colder one. The results of the other opercula were in accordance with the operculum from Garcia State Forest site 8 (Blombos Cave). They all had high temperature measurements just before the edge. Thus, with some reservations, it seems like all of these opercula were collected rather in autumn going towards winter than in spring going towards summer.

*The carbon isotopes and the dissolved inorganic carbon and* $\delta^{18}O_w$*:* A value of 0.0‰ of dissolved inorganic carbon in the ocean water was used for the temperature calculation for carbon isotopes on the PDB-scale. The value of 0.0‰ in this setting was chosen from Ohmoto and Rye (1979: 558-559), who found this value to statistically be the arithmetic mean of dissolved inorganic carbon from oceans. The seawater, $\delta^{18}O_w$, has also been given an oxygen isotope value of 0.0‰ on the SMOW-scale. The combined carbon and oxygen calculated temperatures are represented by the horizontal cross-line in the Figures 8a-e, calculated based on Grossman and Ku (1986) for the oxygen isotopes and Deines *et al.* (1974) for the carbon isotopes.

The modern opercula should reflect the dissolved inorganic carbon of the ocean best, because depositional processes have not affected these for thousands of years. Thus, the modern opercula give a certain indirect control of the dissolved inorganic carbon of the ocean, and the calibration of the carbon isotopes, when a direct measurement of the Indian Ocean outside

Stilbaai is not available. The value of dissolved inorganic carbon of 0.0‰ for carbon isotopes proved to not be a bad assumption, because the modern samples, SRO and MRO, from opercular nodules of two opercula plotted on each side of the horizontal line.

The prerequisite to use a chosen value of dissolved inorganic carbon is that this value has not changed too much during the course of the Holocene. However, the dissolved inorganic carbon will fluctuate according to atmospheric $CO_2$, dissolution of sedimentary carbonates and breakdown of organic compounds (Dettman *et al.* 1999: 1051).

The carbon isotopes can function as a control to see if the opercula are "untouched" by varying processes. If they are, the carbon isotopic value should lie on or close to the line for 0.0‰ dissolved inorganic carbon. However, it should be noted that a simple relationship between $\delta^{13}C$ in calcium carbonates of shells and $\delta^{13}C$ of the dissolved inorganic carbon might not exist in all marine organisms. The values are not always in equilibrium, and the offset can be caused by incorporation of freshwater dissolved inorganic carbon or metabolic carbon (Tanaka *et al.* 1986: 521; Geist *et al.* 2005). Changes in metabolism can affect the $\delta^{13}C$ of calcium carbonates more than changes in $\delta^{13}C$ of dissolved inorganic carbon (Andreasson *et al.* 1999: 279; Dettman *et al.* 1999: 1056). Therefore, the metabolic effects can make it difficult for carbon isotopes to be used in environmental interpretations, because they will disguise the environmental signals (Carré *et al.* 2005: 13; Geist *et al.* 2005).

In this study, the carbon isotopes prove to be different from sample to sample in the same operculum, and from operculum to operculum (Figure 8a-e). Almost all of them plot on the upper side of the temperature line in Figures 8a-d. The largest exception is the B-series (operculum S 1.2), where about half of the samples plot just underneath the line (Figure 8b). Some samples from the C-series (operculum S 1.1) also plot right underneath the line (Figure 8c), excluding sample CL taken of the cementation, which plots far from the other samples' values (Figure 8e). The cementation is created from meteoric water, and therefore the products of putrefaction in this meteoric water dominate the carbon isotopes in this sample. No other values come close to CL, and this means that none of the other calcium carbonates sampled are precipitated from any form of freshwater.

The results from the mass spectrometry show great variation in both carbon and oxygen isotopes. In S 26.1 from Garcia State Forest site 8 (Blombos Cave), the carbon isotopes fluctuate more than the oxygen isotopes (Figure 8a). The carbon isotopes in this operculum seem to get lighter and lighter the further from the leading growth edge the sample was taken. Lighter meaning of lower positive value and moving closer to the DIC-line. The oxygen isotopes fluctuate more randomly, which is positive in consideration of seasonal changes. A co-variation of the carbon and oxygen isotopes could prove kinetic effects, and calcium carbonates not precipitated in equilibrium with the ambient seawater.

The lightest $\delta^{13}$C-values recorded from calcium carbonate samples thought to be precipitated in equilibrium with the seawater are found in operculum S 1.2 and to some degree S 1.1 from Garcia State Forest site 2 (Figure 8b & c). The light $\delta^{13}$C-values can reflect upwelling currents, as upwelling currents are generally enriched in light carbon isotopes. Total dissolved inorganic carbon of the ocean contains more of the light $^{12}$C-isotope than the heavy $^{13}$C. Photosynthesis by various organisms in the surface waters will selectively remove $^{12}$C-isotopes, causing surface waters to be enriched in $^{13}$C compared to deeper waters. This makes the $\delta^{13}$C-value of dissolved inorganic carbon in the surface also enriched, and thus the marine molluscs precipitating calcium carbonates in the surface layers will indicate the heavier values of stable carbon isotopes. In deeper waters, the organic debris releases large amounts of $^{12}$C. Therefore, during upwelling, water whose carbon is isotopically light is brought to the surface, and included in the marine calcium carbonates (Richardson 2001: 136). Inclusions of warm surface water from the Agulhas Current will result in heavier $\delta^{13}$C being precipitated in the calcium carbonates of the opercula and shells of molluscs. This is because if the temperature is higher, more photosynthetic algae will thrive and remove $^{12}$C during the photosynthesis (Geary *et al.* 1992: 81; Richardson 2001: 136). This sort of event may be represented in the operculum from Garcia State Forest site 8 (Blombos Cave), which is enriched in $\delta^{13}$C (Figure 8a).

However, the carbon and oxygen isotopes do not correlate in the opercula to indicate upwelling or inclusion of warm Agulhas current water. If the $\delta^{13}$C is enriched, the $\delta^{18}$O-values should be lighter: inclusion of warm water should be reflected by higher temperatures. If the $\delta^{13}$C is depleted, the $\delta^{18}$O-values should be higher: upwelling of bottom waters should yield lower temperatures. Possibly, the carbon isotope results are neither enriched nor depleted enough to represent inclusions of warmer surface waters or upwelling, respectively, and lie in their normal range for reflecting the natural dissolved inorganic carbon content of the Indian Ocean near the southern Cape coast. The $\delta^{13}C_{PDB}$ should be +3‰ in inorganically precipitated $CaCO_3$-compounds in equilibrium with seawater, so the value is near the same for organically precipitated calcium carbonates. The main body of carbon isotope results are actually close to +3‰on the PDB-scale (Figure 8a-d).

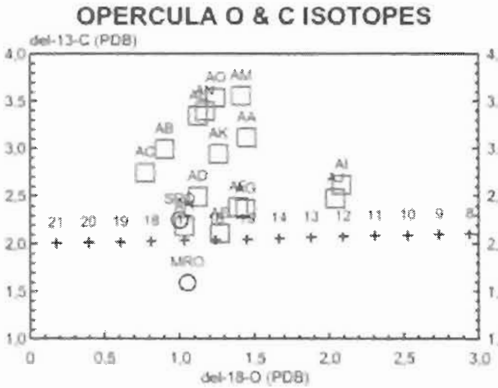

Figure 8a Operculum S 26.1

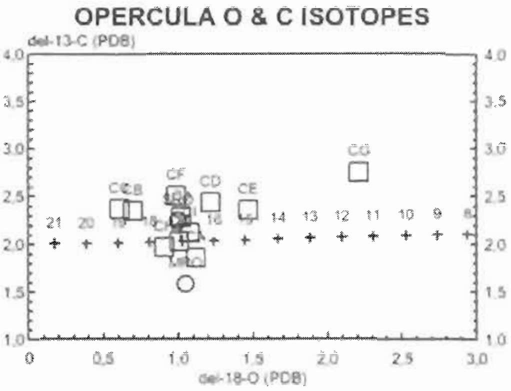

Figure 8c Operculum S 1.1

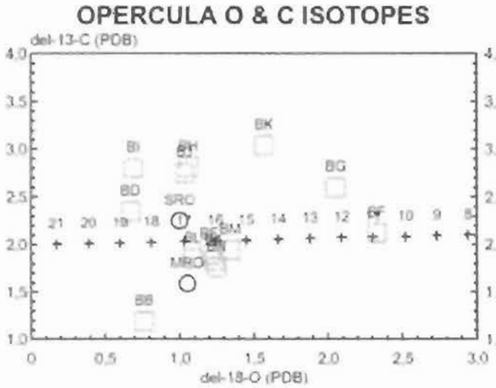

Figure 8b Operculum S 1.2

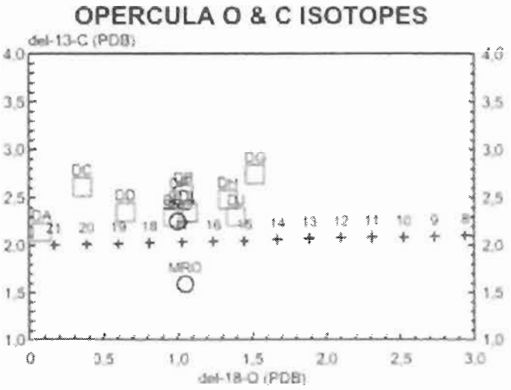

Figure 8d Operculum S 1.3

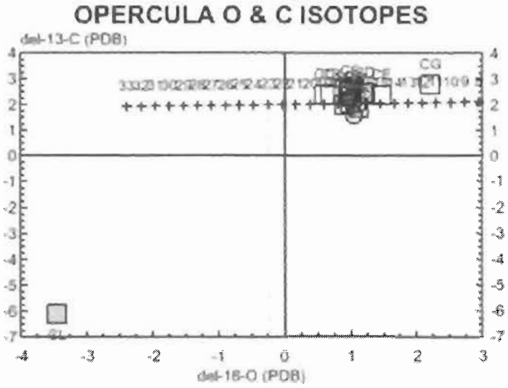

Figure 8e Operculum S 1.1

Figure 8a-e O and C stable isotope results. Due to computer technical reasons in the software of the program the figures were made in, it is not possible to write the delta-notation, superscript or subscript. Therefore $\delta^{18}O_{PDB}$ has been written as del-18-O (PDB) and $\delta^{13}C_{PDB}$ as del-13-C (PDB).

## Conclusions

In this study, the procedural stages of the stable isotope methodology have been examined. This method provides archaeological research with isotopically calculated palaeotemperature fluctuations at the time of occupation of sites, which further are used to draw conclusions on subsistence strategies, landscape use patters and social organisation of human groups. However, if any of the procedural stages of the method are faulted, the temperatures will be as well. Consequently, the archaeological deductions will be erroneous.

This study shows that *Turbo sarmaticus* can be a reliable recorder of the palaeoenvironment, albeit there are some reservations in using this molluscan species in palaeoclimatic reconstructions. In fact, these reservations prevail for using any marine calcareous species collected from archaeological sites in palaeoenvironmental reconstructions.

A variety of circumstances have been presented that can change the chemistry and physical properties of the original aragonitic calcium carbonates, and therefore causing the stable isotope component to be misrepresentative of past climates. It is therefore essential that the samples collected are original and representative of the events at which the research is directed. However, to be close to achieving this, procedural stages are needed that can determine if the calcium carbonates have been altered. In addition, none of the technical procedures must alter or affect the isotopic content of the calcium carbonates.

Cleaning the samples with ethanol to remove organic material, microscopy, X-ray Diffractometry and Scanning Electron Microscopy with Energy Dispersive X-ray System were found to be advantageous in this study. These investigative procedures made it clear that recrystallisations and alterations of the $CaCO_3$ is a pressing factor. In fact, six out of the ten opercula chosen to be part of this methodology study had to be discarded for stable isotope analysis. These six opercula had altered physical surfaces and chemical composition. However, this could not be seen with the naked eye when initially including the ten opercula for studies. If these six opercula had been included in stable isotope analysis, in all likelihood the isotopic results would have been biased. Therefore, close examinations of all samples were decisive for which materials to avoid and which to sample to obtain the calcium carbonates originally precipitated in equilibrium with the seawater; the correct reflector and representation of the ambient living environment of the organism.

The treatment of the modern comparative collection before stable isotope analysis must be equally punctilious as the one performed on the archaeological specimens. Thus, the modern specimens must be examined by the same procedural stages presented above. The modern specimens of *Turbo sarmaticus* opercula sampled by Henshilwood (1995) were probably rinsed and cleaned with water. This possible cleaning with water of the modern specimens of opercula does mean that a certain amount of care must be taken with the temperatures calculated, and the conclusions drawn from them, in this study. A new modern comparative collection should be made.

Rejecting calcium carbonates that obviously have gone through dissolution, recrystallisations and other taphonomic processes in the archaeological context will yield opercular samples that have their originally precipitated aragonitic calcium carbonates available for stable isotope sampling. However, this is only half the difficulty of the methodology of using stable isotope analysis from marine calcium carbonate to yield palaeotemperatures. The stable isotope results have to be made sure they are in equilibrium with the isotopic content of the seawater, before the oxygen isotopes can be calculated into temperature. Thereafter, it should be noted that oxygen isotopic results are not just a reflection of seawater temperature. Evaporation, upwelling events, melt water and salinity are amongst the factors that can change the oxygen isotopic content of seawater. In some cases, it can be virtually impossible to distinguish between oxygen isotope fluctuations due to temperature versus other natural events in the oceanic environment. However, if influences of non-temperature factors are likely to have happened or not, can be determined by careful studies of for example the trace elemental inclusions and fluctuations in the calcium carbonates. It is essential to do so in every study, so that the oxygen isotope results and calculated temperatures are not questionable. In this study, after careful investigations, it was found to be unlikely that melt water, salinity and evaporation had large influences on the isotopic results

A final aspect investigated in this study was that of the palaeoenvironmental equations used in palaeoclimatic studies. As has been presented in the thesis, there exist a large variety of palaeotemperature equations for both inorganic and biogenic versions of aragonitic and calcitic calcium carbonates. Most of the palaeotemperature equations have been calculated by carefully conducted experiments, so it is difficult to understand why many of them end up yielding largely varying temperatures from the same oxygen isotopic data.

A palaeotemperature equation will first be applied to modern specimens of a shellfish species. This is to make sure the equation calculates the oxygen isotopic values into accurate reflections of ambient seawater. By assumption, this same palaeotemperature equation is reliable for archaeological specimens of the same shellfish species throughout the Holocene. This presupposes that the isotopic component of the ocean has stayed virtually unaltered for the last 10 000 years, when it is clear that the oceanic environment has been prone to fluctuations causing variations in the isotopic content.

As has been shown in this thesis, the difficulties surrounding palaeotemperature equations cannot easily be solved. However, an awareness of the difficulties and possibilities surrounding these palaeotemperature equations are essential, so that the calculations and determination of palaeoclimatic fluctuations are not completely impossible. The method of calculating temperatures from stable oxygen isotopes still has a great deal of promise. As long as temperature can be proven to be the most influential factor on the oxygen isotopic results, palaeotemperature fluctuations can be decided. This is so even with a palaeotemperature equation that is not necessarily reliable. Each specimen of shell and operculum sampled for stable isotopes will reflect an internal fluctuating temperature scale. Even if the real temperatures are not revealed, the highest temperatures will indicate summer and the lowest temperatures indicate winter. If the same palaeotemperature equation is used for all specimen of a shellfish species, it is possible to compare the temperature fluctuations in the different specimens. The comparison can be employed within the same layer, within the same site and even between sites to see if there is a consistency or difference in different contexts. In addition, these results can be compared to other palaeoclimatic reconstructions in the same area to determine the reliability of palaeotemperatures calculated from stable isotopes collected from marine molluscan calcium carbonates.

In this study, only Garcia State Forest site 2 and Garcia State Forest site 8 (Blombos Cave), had opercula suitable for isotope analyses, and even within these two sites opercula had to be discarded from stable isotope analyse. The palaeotemperatures from Garcia State Forest site 2 were in agreement with other palaeoenvironmental reconstructions from the period under study, while the results from Garcia State Forest 8 (Blombos Cave) were inconclusive in respect of previous research. Meanwhile, the season the *Turbo sarmaticus* opercula were collected could be determined in the opercula from both sites. The relative temperature scale in each of the opercula specimens will peak temperatures indicating summer and low temperatures indicate winter. In such a fashion, the season of collection can be determined from the oxygen isotopically calculated temperature found at the terminal growth edge. In the present study, all of the opercula sampled for stable isotope analysis indicate collection during the colder seasons.

However, the sample size used for this study was considerably small. This was because the palaeotemperature reconstruction was a secondary aim; the main focus of this thesis was the examination of the method. Therefore, there are not many isotope results available, and the temperatures calculated from them must be carefully used.

Through the course of the present study, it was discovered that determining environmental changes by isotope analyses is not straightforward, because of complications at several stages, for example fluctuations in oceanic environment, unsatisfying preservation of opercula due to taphonomic processes, cleaning procedures, sampling procedures and palaeotemperature equations. However, the calcium carbonates from *Turbo sarmaticus* opercula seemed to be reliable and the isotopic results suitable for palaeoenvironmental research, if investigations and rigorous controls have been conducted on the calcium carbonates.

The method of using stable isotopes for determining palaeoenvironmental fluctuations and conclusions on seasonality in occupation patterns of archaeological sites can be used in future research, if the calcium carbonates samples are subjected to similar careful procedural stages as has been proposed in this study. In addition, archaeological marine molluscan species that have been sampled in the past without rigorous controls and punctilious examinations should be re-examined. The conclusions drawn from these palaeoenvironmental studies might also need to be reassessed until calcium carbonates subjected to careful investigations prove the same palaeoenvironmental fluctuations.

For the future use of the stable isotope palaeoenvironmental reconstructions, it is essential to remain aware of the limitations and possibilities of the methodology. It is not a straightforward task to reconstruct palaeoenvironment by stable isotope analysis, and therefore must neither the method be uncritically used on various archaeological material nor the results gained from this method be uncritically used to create hypotheses on the living conditions for past human groups at archaeological sites. Determining how representative the stable isotope methodology actually is, and with which reliability it can be use, is an ongoing field of discussion. Continuous advances on knowledge concerning precipitation and growth of calcium carbonates, detection of dissolution, recrystallisation and other events of calcium carbonate alterations, understanding and detection of non-temperature factors influencing the oxygen isotopes and further evolved palaeotemperature equations might render the palaeoenvironmental reconstructions from stable isotope analysis completely reliable or obsolete in the future. However, for now, pitfalls and complications are present in the stable isotope methodology, and hypotheses on palaeoenvironmental fluctuations and preferred seasons of visiting coastal and inland sites should be made and used with caution.

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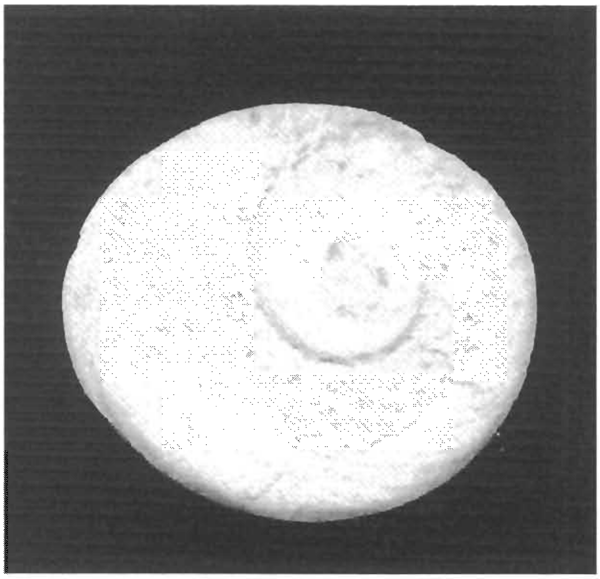
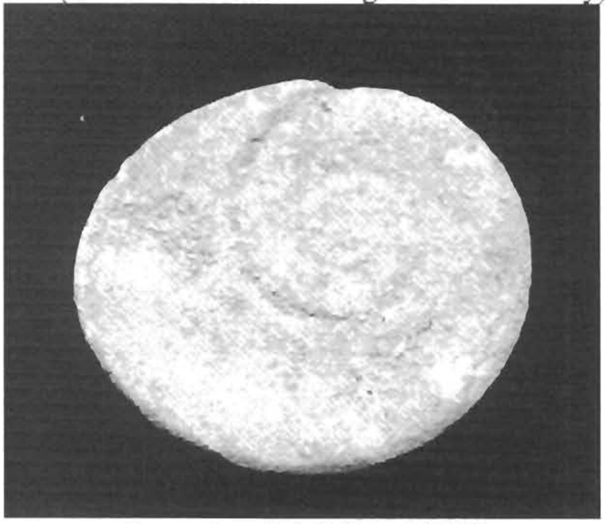
# Appendix

The ten *Turbo sarmaticus* opercula chosen for use in this study. These images are prior to any procedure performed.



Operculum S 1.1 (names and numbers are given for this study) from GSF 2



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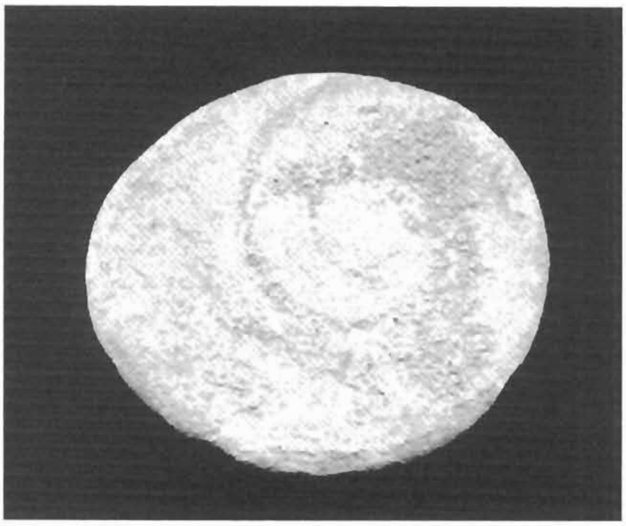
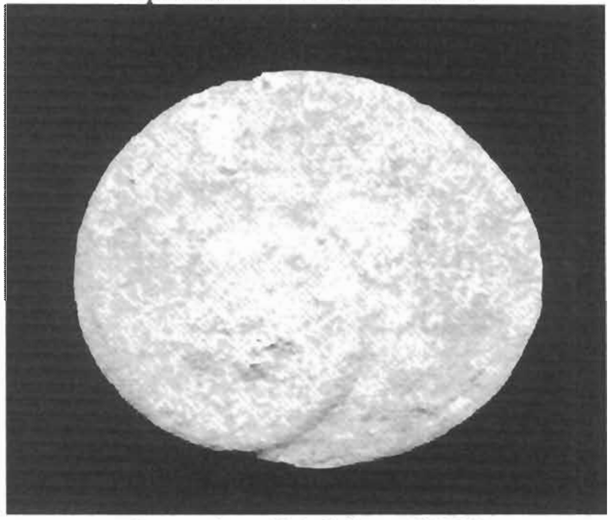


Operculum S 1.3 from GSF 2

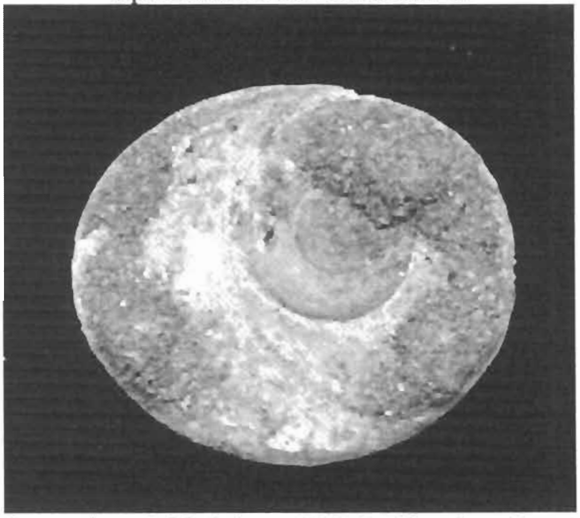
Operculum S 1.4 from GSF 2



Operculum S 1.5 from GSF 2

Operculum S 1.6 from GSF 2

Operculum S 9.3 from GSF 3

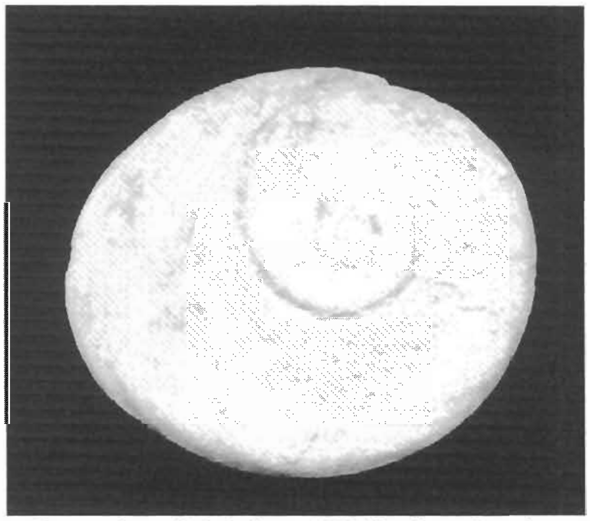


Operculum S 22.1 from GSF 8 (Blombos Cave)

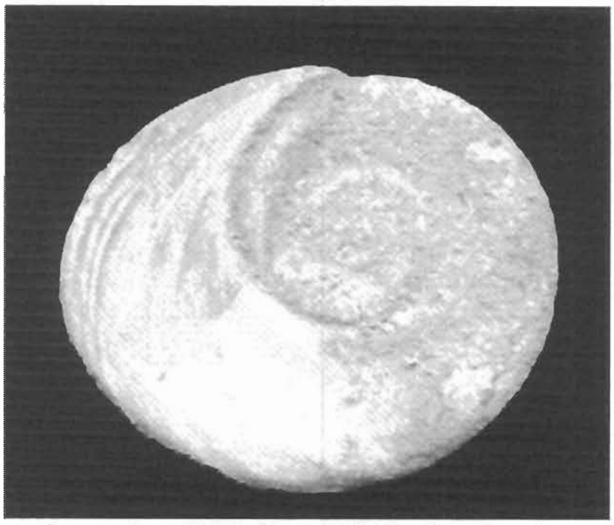
Operculum S 26.1 from GSF 8 (Blombos Cave)

Operculum S 35.1 from GSF 9

The opercula were then cleaned with pure ethanol to remove cementations, ash and organic materials:



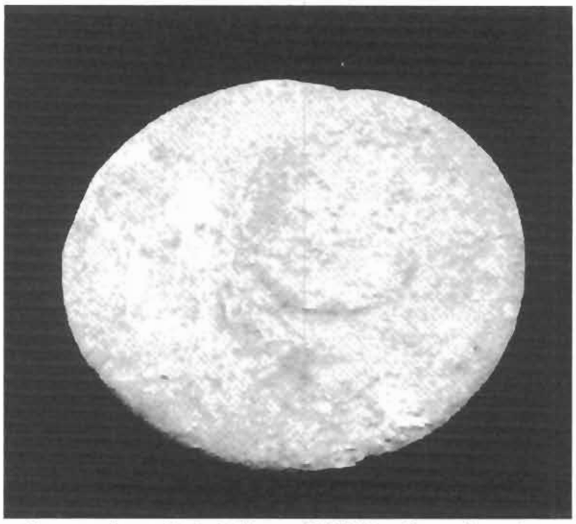
Operculum S 1.1 from GSF 2 after cleaning



Operculum S 1.2 from GSF 2 after cleaning

Operculum S 1.3 from GSF 2 after cleaning

Operculum S 1.4 from GSF 2 after cleaning



Operculum S 1.5 from GSF 2 after cleaning

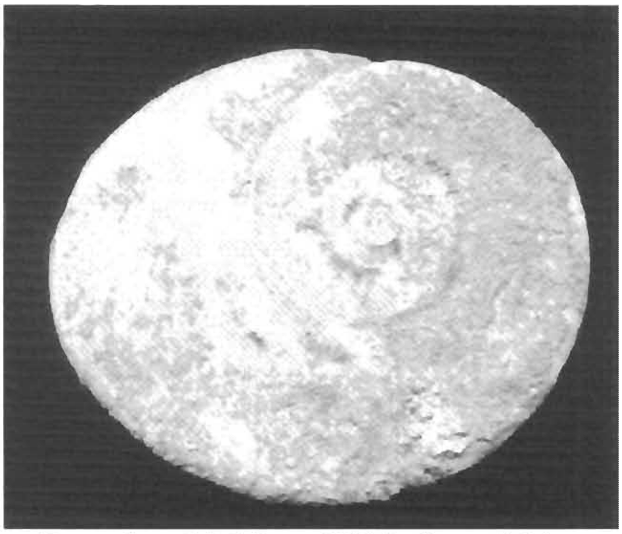
Operculum S 22.1 from GSF 8 (Blombos Cave) after cleaning.
In this image it is possible to see erosion and etch pits that were hidden by the sandy cementation. This operculum was discarded from further use in this study, because of these damages. Except for a sample was taken from the outside nodules for use in XRD to determine the chemical composition of these.

Operculum S 26.1 from GSF 8 (Blombos Cave) after cleaning

Operculum S 35.1 from GSF 9 after cleaning

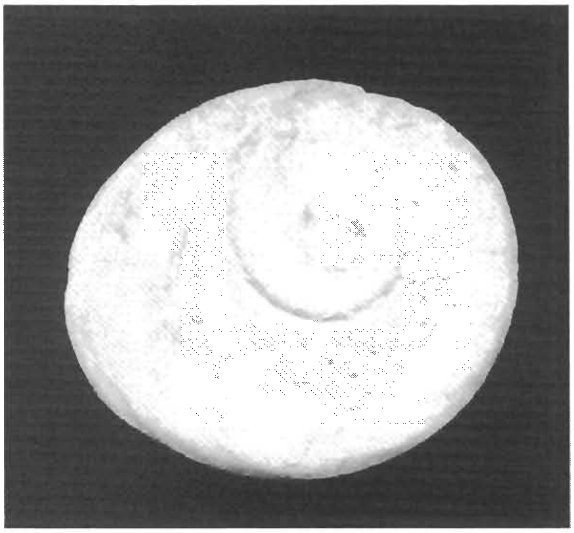
Operculum S 9.3 from GSF 3 was not cleaned with ethanol, as it had already been cleaned with pure water at Iziko: South African museum. This was of course before it was known of the damaging effects freshwater can have on calcium carbonates.

Operculum S 1.5 from GSF 2 was not possible to clean with just ethanol, so a light polish was performed to remove the cementation. However, the cementation was not spread in an equally dense layer across the entire surface and the opercular surface is not completely flat. Therefore, some of the surface layer of calcium carbonate was polished away too. This was an unfortunate accident, but lead to the possibility of studying the internal structure of the operculum.

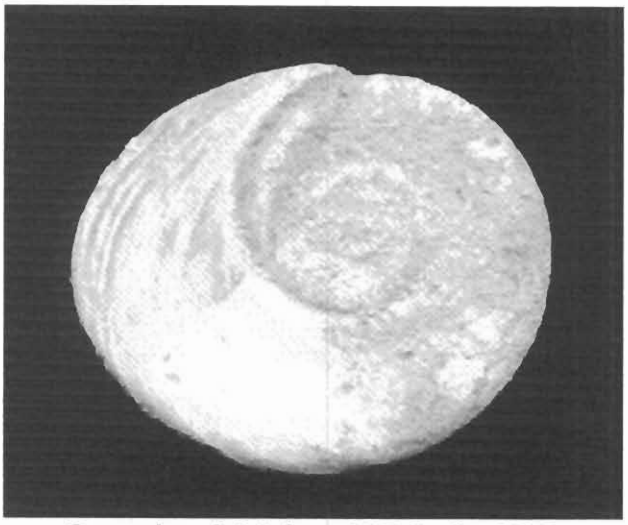


Operculum S 1.5 from GSF 2 after polishing.
The calcium carbonates in the areas around the vortex have been polished off. This is how the operculum looked at the end of the study. Except for a sample taken from its cementation for XRD, no further invasive procedures were performed on this operculum.

After the opercula had been cleaned, they were subjected to sampling for X-ray Diffractometry (XRD). Small samples were drilled, so that the best results possible could be obtained for their chemical composition. Only a few samples were drilled for each operculum.



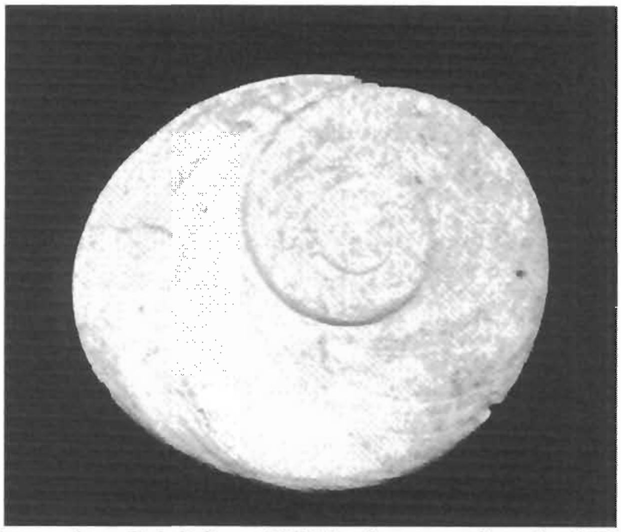
Operculum S 1.1 from GSF 2 after sampling for XRD



Operculum S 1.2 from GSF 2 after XRD

Operculum S 1.3 from GSF 2 after sampling for XRD

Operculum S 1.4 after sampling for XRD



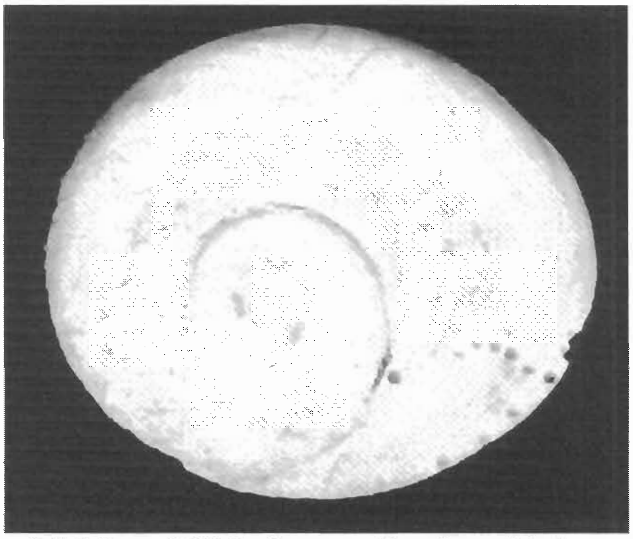
Operculum S 1.6 from GSF 2 after sampling for XRD

Operculum S 26.1 from GSF 8 (Blombos Cave) after sampling for XRD

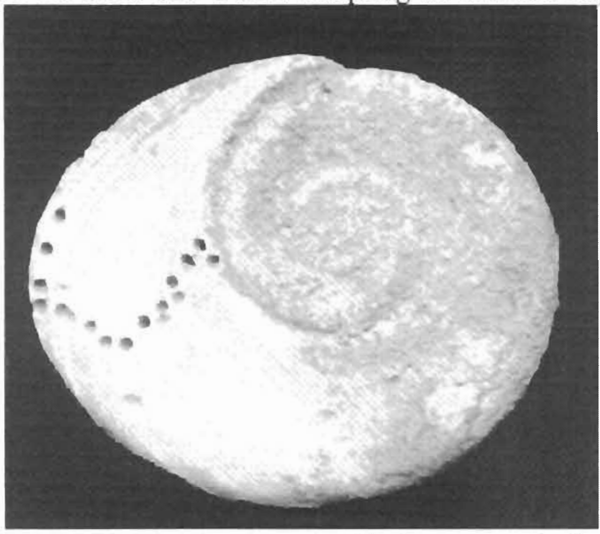
Operculum S 35.1 from GSF 9 after sampling for XRD

Operculum S 1.5 from GSF 2 had its cementation sampled for XRD, and therefore the surface of it was not drilled. The same is the case with S 22.1 from GSF 8 (Blombos Cave); after the removal of the cementation a sample was taken of the outside nodules for XRD. No other invasive procedures were performed on the opercular inner surface.

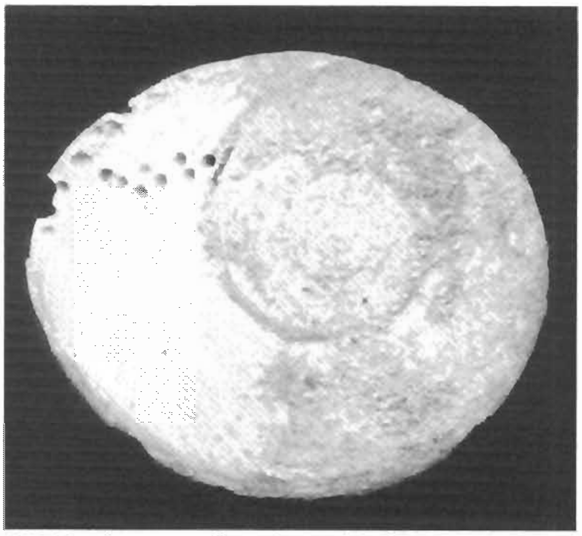
Only four opercula were chosen for sampling for stable isotope analysis. This was because the preliminary research had shown the calcium carbonates to have physical or chemical alterations to the calcium carbonates. The calcium carbonates seemed to have been exposed to diagenesis, dissolution and recrystallisation, after deposition in the sites. Therefore, the opercula not chosen for stable isotope analysis had no further invasive procedures performed than what is seen in the previous images.



Operculum S 1.1 from GSF 2 after sampling for stable isotope analysis



Operculum S 1.2 from GSF 2 after sampling for stable isotope analysis. In certain areas across the operculum there are parallel drilled holes. In these cases, the first sample was lost in the mass spectrometer and had to be sampled over again.



Operculum S 1.3 from GSF 2 after sampling for stable isotope analysis. In certain areas across the operculum there are parallel drilled holes. In these cases, the first sample was lost in the mass spectrometer and had to be sampled over again. In areas along the edge the material was thin, and unfortunately the drill-bit went right through the calcium carbonates.

Operculum S 26.1 from GSF 8 (Blombos Cave) after sampling for stable isotope analysis