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Oxygen Isotope Analysis and Tooth Enamel Phosphate and Its Application to Archaeology

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1.0 INTRODUCTION TO OXYGEN ISOTOPE ANALYSIS

Oxygen is the most abundant element on earth (Hoefs 1987). It occurs in everything that is familiar to us: the atmosphere, land, plants, animals and, most importantly, water. To learn more about past and present environmental, climatic, and biological conditions, scientists analyse the oxygen in sea and meteoric waters (Fricke and O'Neil 1996). In particular, they analyse the isotopes of oxygen. Isotopes of an element are atoms that have a different number of neutrons, but the same number of protons (Plummer and McGeary 1996). Oxygen has three stable isotopes: ^{16}O, ^{17}O, ^{18}O, each occurring in different abundances: $^{16}O = 99.763\%$, $^{17}O = 0.0375\%$, $^{18}O = 0.1995\%$. The $^{18}O/^{16}O$ ratio is usually determined because of the higher quantity and greater mass difference (Hoefs 1987; Garlick 1969). Isotope ratio values are expressed as δ-values (given in per mill (‰) units). The standard used for oxygen is Standard Mean Ocean Water (SMOW) because ocean water is the most suitable standard for oxygen (Taylor 1997; White, *et al.* 1998).

Figure 1: The Hydrological Cycle (http://www.iaea.or.at/ 1998)

The δ-value is defined as:

$$\delta = \left(\frac{R_{SAMPLE}}{R_{STANDARD}} - 1 \right) \times 1000$$

where R_{SAMPLE} is the ratio of $^{18}O/^{16}O$ in the sample and $R_{STANDARD}$ is the ratio of $^{18}O/^{16}O$ in the standard (Taylor 1997). Ocean waters and meteoric waters have distinct oxygen isotope compositions which usually allow scientists to differentiate between the two (Sheppard 1986). Figure 1 represents the hydrological cycle, showing the movement of water both above and below the earth's surface. The figure indicates approximate $\delta^{18}O$ values. These values change through environmental processes and can be used to trace the pathway and history of water (http://www.iaea.or.at/ 1998). The value of $\delta^{18}O$ in meteoric water is a function of geography and climate (Figure 2). Values will decrease with higher latitudes and elevation, as well as lower temperatures. Relative humidity also plays an important part in determining $\delta^{18}O$ values. If there is low humidity, water will evaporate and ^{16}O is preferentially lost during evaporation, thus increasing the amount of ^{18}O in the water and, therefore, the $\delta^{18}O$ value (White, *et al.* 1998; Taylor 1997; Yurtsever and Gat 1981).

FIGURE 2: Contours of the average $\delta^{18}O$ values of meteoric waters falling as rain and snow for the month of January for the entire Earth (Taylor 1997).

This paper discusses the scientific validity of using oxygen isotope analysis of tooth enamel phosphate for archaeological studies. The conventional technique (Tudge 1960) used in the analysis of oxygen isotopes is extremely complex and time consuming. In 1994, O'Neil, *et al.* devised what they believed was a simpler, more precise method of analysis. Part of my research for this paper included testing this method in the laboratory in order to determine if this was in fact the case. The University of Waterloo was interested in developing the O'Neil, *et al.* method for their Environmental Isotope Laboratory, and I was given the opportunity to assist them. Therefore, this paper also discusses my own

work using the O'Neil, *et al.* method, along with a critical evaluation of this technique and a logistical evaluation discussing the appropriateness of oxygen isotope analysis to archaeology.

2.0   STRUCTURE OF TEETH

Various scientific disciplines, such as geology, hydrogeology and geochemistry, have recognized the enormous potential that teeth have for numerous areas of study, and archaeology is no exception. Teeth represent some of the most common finds on archaeological sites (Hillson 1986). They are constructed of very hard materials and are, therefore, little affected by the processes of decomposition (White, *et al.* 1998; Wright and Schwarcz 1998). The fact that they are abundant and durable makes them ideal for various types of archaeological analyses. Archaeologists primarily use teeth for purposes of human evolution, species identification, determination of age at death, and the health and hygiene of an individual or group. Large numbers of teeth found at sites can also aid in reconstructing the demography, diet, husbandry, and hunting practices of a specific culture (Hillson 1986). However, a largely untapped area of study is the isotopic analysis of teeth.

Teeth are made up of organic and inorganic compounds. The enamel contains the least amount of organic material, being comprised mainly of calcium phosphate (Ca_2PO_4) in the form of apatite, which takes the form of hydroxylcarbonic apatite in humans and other mammals (Hillson 1986; White, *et al.* 1998). The oxygen component from teeth comes from body water. The isotopic composition of body water ($\delta^{18}O_{bw}$) in mammals is a function of the isotopic composition of the water in their environment ($\delta^{18}O_w$), and is largely determined by the $\delta^{18}O$ value of local precipitation (White, *et al.* 1998). Body water determines the

composition of body phosphate ($\delta^{18}O_p$), which is a structural component of teeth and bone (White, *et al.* 1998; Tortora and Grabowski 1996). If there is any change in $\delta^{18}O_p$ values over time this will reflect a change in $\delta^{18}O_w$ (Fricke, *et al.* 1995).

The apatite crystals of enamel are larger than those found in dentine and bone and are more densely packed. In addition enamel's lower organic content makes it virtually resistant to physical and chemical change. As a result, enamel is usually well preserved at archaeological sites. These features give enamel a significant advantage over the more organic compositions of dentine and bone for scientific research, and it is the preferred material in O^{18} analysis (Hillson 1986; Fricke and O'Neil 1996). Enamel is formed by a process called mineralization. Mineralization begins at the crown, forming what are called domes, and then continues downward in a layered sequence, called sleeves, forming last at the cervical margin where the crown meets the root (Hillson 1986). Figure 3 illustrates the layered sequence of the formation of tooth enamel.

FIGURE 3:   Layering of Enamel (Hillson 1986)

Mineralization occurs in intervals at various ages and lasts for a certain period of time with each interval. The age and length of intervals depends on the species, as well as the individual. Figures 4 and 5 show deciduous and permanent crown formation in humans.

FIGURE 4: Deciduous Crown Formation in Humans (Massler, *et al.* 1941)

FIGURE 5: Permanent Crown Formation in Humans (Massler, *et al.* 1941)

Mineralization can also be influenced by biological and environmental factors such as the sex, size, health, and diet of an individual (Hillson 1986; Smith 1991). The oxygen isotopic signature of local precipitation is incorporated into tooth enamel phosphate, via drinking water and the water that is in food, at the time of mineralization during the early years of a mammal (White, *et al.* 1998; Luz, *et al.* 1984). Any changes in the isotopic composition of water that is consumed by an individual during an interval of mineralization will be expressed in that layer of enamel (Fricke and O'Neil 1996).

Enamel is not continuously dissolved and precipitated like bone and, therefore, $\delta^{18}O$ values in local precipitation, and any change in these values, will be retained in the enamel when an individual reaches maturity (Fricke, *et al.* 1995). As a result, every individual has their own personal record of water consumption changes from childhood, which makes the use of enamel O^{18} analysis particularly beneficial, especially since the rate of tooth development is known (Wright and Schwarcz 1998).

When water is ingested, the isotopic signature of oxygen changes (fractionates) between water and tooth enamel, depending on temperature. Thus, because a mammal's body temperature is constant (~ 37°C), the signature of the ingested water can be calculated using the measured $\delta^{18}O_p$ in tooth enamel and the fractionation factor. The amount that the water isotopic signature is fractionated is also dependent on the size and metabolic rate of the mammal. These fractionation factors have been empirically determined for several species including pigs, cattle, sheep, deer, horses, and humans. (Fricke and O'Neil 1996).

3.0 ARCHAEOLOGICAL APPLICATION OF OXYGEN ISOTOPE ANALYSIS IN TEETH

The study of oxygen isotopes in tooth enamel phosphate for archaeological research is a relatively new and untapped area of study (Fricke, pers. comm 1999). However, in a moderately short period of time, oxygen isotope analysis has provided archaeologists with a number of ways to probe even further into past human behaviour and cultural change.

The weather is an important aspect of our modern society. However, the impact it had on the lives of ancient peoples is probably greater than many of us can imagine. When environmental or climatic change took place, depending on its severity, people may have been forced to move from an area or change their subsistence strategies in order to adapt. Archaeologists need this kind of information in order to understand how people responded to these situations. Oxygen isotope analysis can provide archaeologists with records of climate change spanning years, decades or longer. These changes can be linked to ancient civilizations. Archaeologists can use this data to investigate how groups responded individually to climate change, and they can compare the rate and extent of change between groups of varying sizes and complexity (Fricke, *et al.* 1995).

Another important application, discussed in more detail below, uses oxygen isotope analysis in conjunction with carbon isotope analysis to help determine when children were weaned from their mother's milk. The health and development of children from a population have important implications to the growth and success of the entire population, and determining when children were weaned can give archaeologists insights in to the success of the entire society (Wright and Schwarcz 1998).

4.0 SIMILAR STUDIES

As a result of improved techniques (O'Neil, *et al.* 1994), several oxygen isotope analyses

have been conducted in the past decade. The majority of them have been done by professionals in the field of geology relating to, among other things, long term paleoclimatic change. However, their results have important implications for archaeologists studying prehistoric human behaviour and culture change (Fricke and O'Neil 1996).

Geologists are not the only professionals using oxygen isotope analysis. A handful of physical anthropologists and archaeologists have also taken advantage of this fascinating area of study to help shed light on issues such as the cultural practise of weaning, locational stability, and movement (Wright and Schwarcz 1998; White, *et al.* 1998). This section summarizes several oxygen isotope studies conducted by geologists, physical anthropologists, and archaeologists to demonstrate that oxygen isotope analysis has scientific validity for archaeology.

4.1 Inter- and Intra-tooth Variation in the Oxygen Isotope Composition of Mammalian Tooth Enamel Phosphate: Implications for Palaeoclimatological and Palaeobiological Research

Drs. Henry Fricke and James O'Neil (1996) studied the oxygen isotope composition of tooth enamel phosphate ($\delta^{18}O_p$) from a fossil adult bison (~500 B.P.) and a modern sheep.

Each animal lived in very different conditions during its lifetime. The bison was assumed as having an unlimited range, thus having access to many possible water sources. The sheep, on the other hand, was raised on a farm where it had limited access to open land and water sources.

Samples of enamel were taken from various molars and from incrementally layered growth bands from the same molar. The method of phosphate analysis used by

Fricke and O'Neil (1996) is the focus of this paper and will be described in detail in the following section. When the samples were introduced to the mass spectrometer, the values were used to make inter- and intra-tooth comparisons. It was discovered that the $\delta^{18}O_p$ values for the bison and sheep teeth varied, and there were also variations between the layers of a single bison tooth. This intra-tooth variation is a function of the time of year the enamel was mineralized, the main source of ingested water, as well as the behavioural habits of the animal itself (Fricke and O'Neil 1996).

Because the oxygen isotope composition of $\delta^{18}O_p$ is a reflection of the local precipitation ($\delta^{18}O_w$) ingested by a mammal, Fricke and O'Neil (1996) stated that the tooth remains of mammals at different geological or archaeological layers from a single site can be used to reconstruct relatively long term climate change as well as the rate of change. They also stated that in order to better understand $\delta^{18}O_p$ change in relation to climate change, researchers should examine the implications biological factors and behavioural habits have on $\delta^{18}O_p$ values by looking at modern populations to help describe archaeological and geological deposits (Fricke and O'Neil 1996).

Drs. Fricke and O'Neil have not limited their research to animals, and the next section briefly describes their analysis of $\delta^{18}O_p$ from medieval Greenland in order to show the relationship between climate and human society.

4.2 Oxygen Isotope Composition of Human Tooth Enamel from Medieval Greenland: Linking Climate and Society

Drs. Fricke and O'Neil used the same analytical technique to examine how the

temperature changed in medieval Greenland during and after Norse settlement. They obtained teeth from three sample areas that represented both Norse and Inuit groups living in these areas at different times (around A.D. 1000). The $\delta^{18}O_p$ values of the teeth they sampled allowed them to document past $\delta^{18}O_w$ values, which were used to chronicle past latitudinal temperature differences and climate change (Fricke, *et al.* 1995). One sample in particular was lower than the average $\delta^{18}O_p$ value. Interestingly, these lower values indicated a cooling trend which coincided with the historically documented Little Ice Age. Intra-population variation was also identified, and it was determined that these values could very well relate to various types of human behaviour. For example, several different water sources were available to the residents of a particular area including streams, snow melt, and glacial runoff. These people may very well have used any number of water sources because of stress on the environment or for cultural reasons. It was also postulated that the variation of $\delta^{18}O_p$ values within a population could have been the result of migration. This hypothesis has validity because many of those who lived and were buried on Greenland were European settlers. The isotopic composition of the water they ingested as children and adolescents remained in their enamel throughout life, thus there would be a variation in $\delta^{18}O_p$ values within a given area (Fricke, *et al.* 1995).

As previously mentioned, oxygen isotope analysis is also being used by physical anthropologists and archaeologists to better understand past human behaviour and culture change. The next section summarizes an interesting contribution to this research in which both oxygen and carbon isotopes were analysed in order to learn something about the patterns of breastfeeding and weaning in prehistoric Guatemalan society.

4.3 Stable Carbon and Oxygen Isotopes in Human Tooth Enamel: Identifying Breastfeeding and Weaning in Prehistory

Early childhood nutrition is recognized as being an important factor in the overall growth, development, and demographic structure of a population (Wright and Schwarcz 1998). Drs. Wright and Schwarcz, in an attempt to determine the pattern of breastfeeding and weaning in prehistoric Guatemalan society, analysed the changes in $\delta^{13}C$ to determine at what stage in a child's life solid foods were introduced. They also analysed the changes in $\delta^{18}O$ to determine when breastfeeding was replaced with another source of water. The breast milk of a nursing mother is heavier in $\delta^{18}O$ than the water she ingests, so it was hypothesized that $\delta^{18}O$ values would be able to indicate the presence or absence of breastfeeding in the enamel of a human tooth (Wright and Schwarcz 1998).

Wright and Schwarcz (1998) conducted their analysis by comparing different adult teeth from 35 burials at Kaminaljuyú, a prehistoric archaeological site located beneath modern Guatemala City. Because they used adult enamel, they were also able to study dietary changes of one individual throughout their lifetime (Wright and Schwarcz 1998). The $\delta^{13}C$ and $\delta^{18}O$ values showed that solid foods were introduced to the children of Kaminaljuyú at a young age, but that breast milk continued to be an important source of nutrition for a long time. Weaning a child completely off of breast milk was a long and gradual process (Wright and Schwarcz 1998).

5.0 A DETAILED DESCRIPTION AND CRITICAL EVALUATION OF OXYGEN ISOTOPE ANALYSIS USING THE O'NEIL, *et al.* METHOD

Oxygen isotope analysis of phosphates has been explored off and on since the 1960's (Fricke, pers. comm. 1999). The first analyses were made by Tudge (1960), whose technique isolated PO_4 as $BiPO_4$ (bismuth phosphate) from which the oxygen could be withdrawn using a fluorinating reagent, BrF_5 (bromine pentafloride). Fluorination releases all extrinsic oxygen from the precipitate (O'Neil, *et al.* 1994). The oxygen is then converted to CO_2 for isotopic analysis (Tudge 1960). Although useful for the analysis of phosphorites, conodonts, fish, and mammals (O'Neil, *et al.* 1994), the Tudge method is very complex and time consuming because of the fluorination process. In addition, it is problematic in that $BiPO_4$ absorbs water from the air which must be removed before fluorination. As a result, the process of volatilization may change the isotopic signature of the phosphate (Karhu and Epstein 1986). In 1994, O'Neil, *et al.* developed a much simpler and more precise method for oxygen isotope analysis of phosphate. The following describes in more detail the O'Neil, *et al.* method, which I had the opportunity to work with at the University of Waterloo's Environmental Isotope Laboratory (EIL).

5.1   Description of the Technique

5.1.1   Dissolution of Phosphate and Reprecipitation as Ag_3PO_4 (Trisilver Phosphate)

The sample types used at the EIL consisted of the molars of a wolf and the molars, premolars, and canines of a cat. They were ground up with a mortar and pestle, although a dental drill is preferred when only the enamel used. Our samples were organically rich so they had to be oxidized in 30% H_2O_2 (hydrogen peroxide) to destroy the organic material, rinsed with distilled water, and put into a drying oven. Then they were dissolved in 2 ml of 2M HNO_3 (nitric acid). The pH

was raised to about 5 with 2 ml of 2M KOH (potassium hydroxide), and 2 ml of 2M HF (hydrofluoric acid) was added to the solution to dissolve the calcium. The samples sat for 24 hours to allow the calcium to precipitate out of solution as CaF_2 (calcium fluoride). The solutions were placed in plastic centrifuge tubes and centrifuged for about 10 minutes to separate the CaF_2 and any insoluble residues from the solution. The samples were rinsed three times with distilled water and transferred to 100 ml beakers. Fifteen millilitres of buffered silver ammine solution was added to the beakers, which were placed on a hotplate set to a temperature of about 55°C to 60°C to slowly evolve ammonia. After about an hour, Ag_3PO_4 (trisilver phosphate) began to precipitate as yellow dendritic crystals that enlarged and fell to the bottom of the beakers. When the crystals were completely formed, the beakers were removed from the hotplate and cooled at room temperature. The Ag_3PO_4 crystals were filtered, rinsed with distilled water, placed in a drying oven for several hours, and weighed (O'Neil, *et al.* 1994).

5.1.2   Combustion of Ag_3PO_4 and Formation of CO_2

At the time this paper was being researched, the EIL was still developing this technique for its lab. As a result, combustion of Ag_3PO_4 and formation of CO_2 did not proceed until after this paper was written. However, the procedure according to O'Neil, *et al.* (1994) is as follows.

The Ag_3PO_4 is placed into silica tubes with a stoichiometric quantity of graphite. The tubes are attached to a vacuum line, heated to 550°C, pumped to remove any water, and sealed off. The tubes are then placed in a tube furnace at 1200°C for three minutes to combust the samples and form CO_2 (O'Neil, *et al.* 1994). After reaction, the tubes are quickly immersed in water. If this is not

done, and the tubes are allowed to cool slowly, O'Neil, *et al.* (1994) claim that back reaction and isotopic exchange will occur. After quenching, the tubes are attached to a mass spectrometer for isotopic analysis.

5.1.3   Critical Evaluation

According to O'Neil, *et al.* (1994), this new method has several advantages:

1. The chemical procedures are a lot simpler.
2. A fluorination step is not used.
3. The method is quick.
4. The method is precise with reproducibility comparable to or better than similar methods.
5. It is less expensive than similar methods.
6. It can be easily set up in any stable isotope laboratory.

After assisting the EIL in setting up this method, it is clear that most of the advantages listed above are valid. The chemical procedures are relatively simple. Several people at the EIL, who are familiar with fluorination, stated that the omission of this step would make the procedure less complicated and time consuming. O'Neil, *et al.* (1994) also state that their method is easily set up in any stable isotope laboratory. However, working with organic material did complicate things a bit, and it took time to work out some of the kinks associated with trying to dissolve the organic material. Nevertheless, once the preparation techniques are mastered, this method will be fairly quick and inexpensive to employ. Because the samples were not combusted until after this paper was initially written, δO^{18} values have not been included. Nonetheless, O'Neil, *et al.* (1994) claim reproducibility is usually better than ± 0.2‰. Fricke, *et al.* (1995) claim reproducibility of better than ± 0.3‰.

Some problems were encountered at the EIL, most of which pertained to organic material present in the tooth samples. Organic material does not allow phosphate to be fully recovered from the sample, and a slight isotopic offset occurs between the amount of sample recovered and that which is not (Stuart-Williams, pers. comm. 1999). It was soon realized that H_2O_2 was not successful in destroying the organic material in the tooth samples, although this apparently worked for O'Neil, *et al.* (1994). As a result, instead of nice yellow Ag_3PO_4 crystals, we ended up with a black residue at the bottom of the beaker. Soaking the samples in Clorox bleach for 24 hours is more likely to work (Fricke, pers. comm. 1999). It was at this point when we realized grinding up the whole tooth was a bad idea because of the organic material in dentine. It was agreed that only tooth enamel should be used from that point on.

There may also be a problem with the high temperature reaction of Ag_3PO_4/graphite. According to O'Neil, *et al.* (1994) there has to be a ratio of approximately 0.3 mg of C to 22.0 mg Ag_3PO_4. If there is too much carbon, CO is produced and the measured $\delta^{18}O$ value of the CO_2 can increase. As well, if there are any organic remnants left in the Ag_3PO_4 crystals the carbon in the organic material would compete with the carbon in the graphite to react with the oxygen. They also state that with a bit of experience the proper ratios can be maintained (O'Neil, *et al.* 1994). However, one definitely would need a great deal of precision and standardization of method when handling and preparing samples (Stuart-Williams, pers. comm. 1999).

This paper has attempted to demonstrate how oxygen isotope analysis of tooth enamel phosphate can help archaeologists in learning more about past human societies. Several studies have been presented that document this technique's usefulness. However, as with all scientific

analyses, it has its limits. As mentioned throughout this paper, $\delta^{18}O_p$ values reflect the mean value of $\delta^{18}O_w$ for a particular period of enamel growth. Subsequently, any change in climate that has an effect on $\delta^{18}O_w$ values has to last long enough for those changes to be incorporated into the new enamel. As a result, oxygen isotope analysis of tooth enamel phosphate cannot be used to examine seasonal changes in the climate, annual averages, or short periods of climate change (Johnsen, *et al.* 1992; Meese, *et al.* 1994). Its strength lies in examining climate changes that took place over a number of years, decades, or even longer (Fricke and O'Neil 1996).

6.0   THE LOGISTICS OF OXYGEN ISOTOPE ANALYSIS OF PHOSPHATE

Dr. Henry Fricke, Ph.D., from the Geophysical Laboratory, Carnegie Institute of Washington, Washington, D.C., has conducted extensive research on oxygen isotope analysis using the method outlined in this paper. A lot of his research has far reaching implications for archaeology. He was contacted regarding the appropriateness of this technique to archaeology, its strengths and weaknesses, and the logistics of conducting this kind of analysis. His advise was very useful to the aims of this paper, and he raised an important issue regarding oxygen isotope analysis that had not been encountered during research for this project.

Dr. Fricke stated that most scientists who are familiar with oxygen isotope analysis of tooth enamel phosphate, as well as the O'Neil, *et al.* (1994) method, would say that it has a lot of potential for archaeology. He confirmed the claim made by O'Neil, *et al.* (1994) that this technique is simple, precise, and cost effective. He stated that samples can be run relatively quickly at very little cost (approximately US $15 per sample at his lab).

However, he then mentioned that archaeologists do not need to examine phosphates in most cases. It all depends on how far back in time one wants to investigate. In his opinion, carbonates are better for archaeological analysis of periods during the Late Pleistocene and Holocene. The analysis of carbonates provides two values, an oxygen value and a carbon value because, as mentioned earlier, teeth are composed of hydroxylcarbonic apatite (White, *et al.* 1998). As a result, information about diet, as well as climate, can be obtained for the study area. The analysis of carbonates is also very simple and cost effective, as long as there is a lab with the proper equipment and line set up. By comparison, the analysis of phosphates will yield only one value, that of oxygen (Fricke, pers. comm. 1999).

The advantage of examining phosphates is that they are more resistant to exchange during diagenisis, whereas carbonates are more susceptible. As a result, phosphate techniques are appropriate for very old samples, including those older than 20,000 years. Those interested in research during the Miocene, Pliocene, and Upper Pleistocene would benefit from phosphate analysis (Fricke, pers. comm. 1999).

7.0   CONCLUSION

Oxygen isotope analysis of tooth enamel phosphate is a scientifically valid area of study for archaeology. The isotopic composition of body water ($\delta^{18}O_{bw}$) is a function of the isotopic composition of water in the environment ($\delta^{18}O_w$), largely determined by the $\delta^{18}O$ value of local precipitation. The water in a mammal's body, in turn, determines the composition of phosphate ($\delta^{18}O_p$) in teeth and bones. Any change in $\delta^{18}O_p$ values over time will ultimately reflect a change in $\delta^{18}O_w$ (Fricke and O'Neil 1996). Oxygen isotope analysis of phosphate can measure these changes since

they are recorded in the growth layers of enamel. The $\delta^{18}O_p$ values can be used to record climate change over relatively long periods of time. These records can help archaeologists make inferences about how different societies responded to this kind of change (Fricke and O'Neil 1996).

Although oxygen isotope analysis is a relatively new technique, professionals from many fields have applied it to their research. Physical anthropologists and archaeologists have used this technique to study the links between climate and society as well as the cultural practice of weaning to gain insights into the growth and development of prehistoric societies (Wright and Schwarcz 1998).

There are several methods used to analyse oxygen isotopes in teeth and the O'Neil, *et al.* (1994) method has proven to be a relatively simple, precise, and cost effective means of analysing phosphate. However, no method is without its problems, and this one requires a great deal of precision and standardization of methods when handling and preparing samples (Stuart-Williams, pers. comm. 1999). Oxygen isotope analysis in general also has its advantages and disadvantages. This technique is not always recommended because carbonates can be used instead. Carbonates provide archaeologists with values for carbon as well as oxygen isotopes, whereas phosphates provide only a value for oxygen isotopes. On the other hand, phosphates are more resistant to exchange during diagenisis than carbonates are, and this makes them very useful to archaeological and paleoanthropological studies of great age (Fricke, pers. comm. 1999). However, the limitations of oxygen isotope analysis are relatively inconsequential. This is a fascinating area of study that should be included on the list of analytical techniques used by archaeologists.

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