AN INVESTIGATION OF STABLE SULPHUR ISOTOPES AS A PALAEODIETARY INDICATOR IN SOUTH AFRICA

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DECLARATION

I know the meaning of plagiarism and declare that all the work in the document, save for that which is properly acknowledged, is my own.

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ABSTRACT

The purpose of this thesis is to assess the use of stable sulphur isotope analysis as a tool for studying the diet and mobility of Later Stone Age people in the Western Cape Province of South Africa. Stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios have long been analyzed for palaeodietary studies. Only recently have technological advances made the routine analysis of sulphur isotopes ($\delta^{34}S$) in small samples possible, enabling measurement of valuable archaeological specimens without undue destruction. For this study 33 archaeological animal bones and 37 archaeological human skeletons were analyzed, as well as 7 modern faunal specimens from areas where it was difficult to obtain suitable archaeological material. Samples were selected from a number of coastal localities on both the southern (Indian Ocean) and western (Atlantic Ocean) coastlines, as well as from several inland sites. This is the first archaeologically oriented sulphur isotope study to attempt to map $\delta^{34}S$ values across a landscape on this scale. $\delta^{34}S$ values of marine animals ranged from 15.2 to 17.6‰ (n=12), in good agreement with previous studies. Coastal terrestrial animals varied from 8.5 to 20.2‰ (n=18), reflecting the "sea spray effect" but also (in some areas) the influence of local geology and/or estuarine and marshland environments. Animals from the Fold Belt Mountains had high $\delta^{34}S$, and only inland of these mountains were values distinctly lower. Values for humans tended to cluster with those for animals from the same site, except humans from sites with a significant brackish water source had low $\delta^{34}S$, while browsing animals from the same sites did not. $\delta^{34}S$ measurements therefore have the potential to identify distinct feeding habitats within coastal environments. Further analysis of animal and plant samples is required to fully understand the patterning in $\delta^{34}S$ values.

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CHAPTER I: INTRODUCTION

This thesis attempts to explore the contribution of sulphur stable isotope ratios to the understanding of subsistence behavior of prehistoric people in the Western Cape Province of South Africa. Emphasis is placed on the period between 4500 and 2000 BP, when the main economy was foraging (hunting and gathering). Numerous changes occurred during the mid-Holocene concerning group dynamics and population, possibly as a reaction to climatic shifts (Deacon & Deacon 1999; Miller et al. 1995; Mitchell 2002; Sampson 1974). This time span was chosen primarily because of the large quantity of archaeological remains, including human skeletons, which are available for analysis. In addition, there are long-standing questions about the degree of mobility at that time, to which sulphur stable isotope analysis may be able to make a contribution. This region has been intensely studied for several decades, and a large set of stable carbon and nitrogen isotope values have been accumulated from archaeological faunal and human remains, as well as modern plants and animals that were common prehistoric food sources (Lee-Thorp et al. 1989; Sealy 1984, 1996, 2006; Sealy & Pfeiffer 2000; Sealy & van der Merwe 1986, 1988; Sealy et al. 1987, 1992). Two problems were encountered in these studies: first, a terrestrial C_4 plant component on the southern coast can result in elevated $\delta^{13}C$ values in terrestrial animals, blurring the distinction between terrestrial and marine signatures (Sealy 1997, 2010); and second, in arid parts of the west coast north of Saldanha Bay, terrestrial animals show elevated $\delta^{15}N$ values, which also reduces the usual marine/terrestrial difference in nitrogen isotope values (Sealy et al. 1987). Nitrogen values increase with aridity, and terrestrial animals from areas receiving less than 400mm of rain per year can have high $\delta^{15}N$ values (>10‰) due to the effects of water stress (Ambrose & DeNiro 1986; Heaton et al. 1986). Two studies (Corr et al. 2005; Styring et al. 2010) have sought to address this problem using compound-specific stable isotope analysis of individual bone

collagen amino acids on a limited number of samples from the Western Cape Province. Results have been compelling for both $\delta^{13}C$ and $\delta^{15}N$, and further study may help provide clarification between marine and terrestrial animals and high marine protein consumption in humans. The addition of sulphur isotope analysis could help to clarify and interpret the results in these areas. Faunal and human samples were therefore obtained throughout the Western Cape Province in order to explore variation in $\delta^{34}S$ in areas with differing geology and proximity to the coast.

Conventional archaeological approaches based on food remains found in sites frequently struggle to reconstruct ancient diets (see Schwarcz & Schoeninger 1991 for a comprehensive description). Analyses are typically based on scant plant and animal remains, essentially waste, some of which might have been deposited by animals rather than humans. Foods consumed entirely leave no trace, and smaller debris, such as plant seeds and fish bone, may not be preserved or may be missed during excavation. Animals too large to carry would have been butchered at the kill site, and only edible parts brought back to camp, leaving little trace of items that might have been a significant component of the diet. Many foods leave no processing or inedible waste, so they would be completely invisible to modern excavators. Chemical techniques that look at the composition of bones, such as isotope analysis, enable direct tracing of dietary contributions in a particular individual.

Stable carbon and nitrogen isotope ratios have long been used to determine past diets (see Katzenberg 2000; Sealy 2001; and Lee-Thorp 2008 for overviews). During metabolic processes the lighter isotope reacts more rapidly than the heavy isotope, resulting in an enrichment of the heavy isotope in the remaining reactant pool. Carbon isotope analysis can determine the consumption of marine (^{13}C enriched) or terrestrial foods (depleted in ^{13}C), and distinguish between plants depending on their photosynthetic

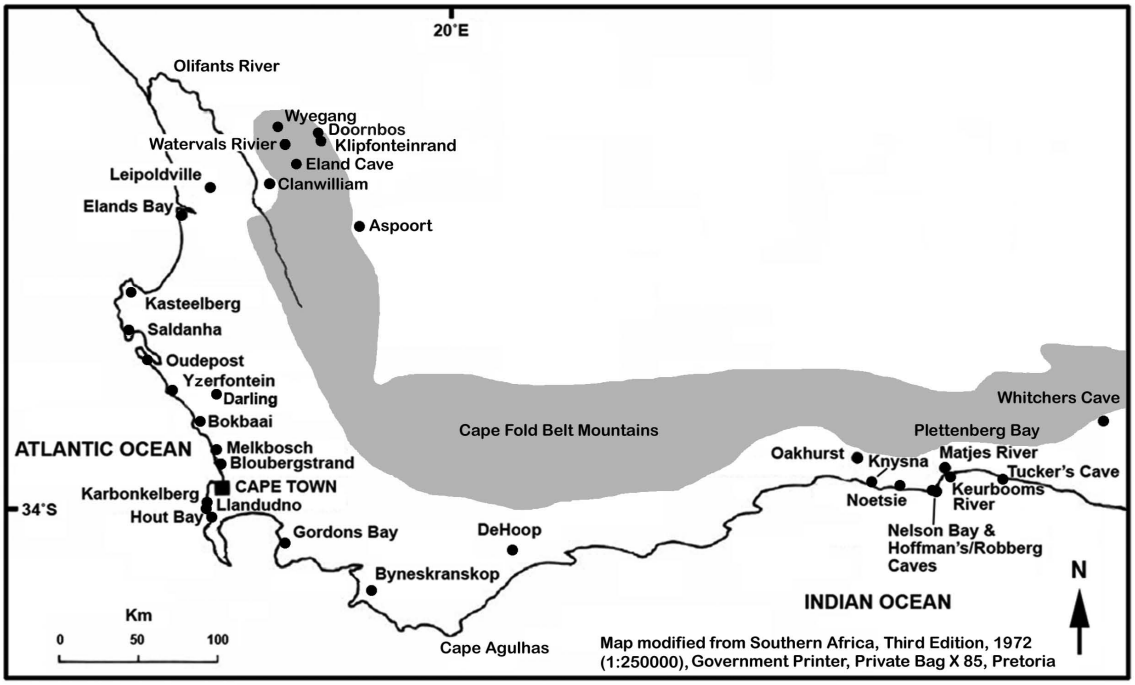
pathway (C_4 are ^{13}C enriched, C_3 are ^{13}C depleted) (Heaton 1999; Smith & Epstein 1971); with $\delta^{13}C$ values typically enriched by ~1‰ from herbivores to carnivores in a food web (Bocherens & Drucker 2003; DeNiro & Epstein 1978). Carbon in bone collagen is obtained primarily from dietary protein, but can also be incorporated from carbohydrates and lipids (Ambrose & Norr 1993; Howland et al. 2003; Jim et al. 2006). Nitrogen in collagen is obtained only from dietary protein, and values increase by 3-5‰ per trophic level (DeNiro & Epstein 1981; Hedges & Reynard 2007; Schoeninger & DeNiro 1984). Nitrogen isotope analysis can indicate consumption of high trophic level marine food and freshwater fish, as well as distinguish between diets that were plant or animal-rich (Schoeninger & DeNiro 1983). Sulphur is also incorporated into collagen only from dietary protein, and all sulphur in collagen occurs as the essential amino acid methionine. Unlike nitrogen isotopes, there is little fractionation of sulphur isotopes with increasing trophic levels, so the $\delta^{34}S$ measurements of organisms reflect the values of the local ecosystem (Peterson & Fry 1987). This makes sulphur isotope measurements a good indicator of the geographic localities of foods selected by consumers.

Sulphur isotope ratios are commonly used in ecology, wildlife migration, geographical provenance, and pollution monitoring studies. Only recently have they made a significant impact on archaeology with the advancement of analytical technology. Mammalian bone collagen contains very little sulphur, roughly 0.16 to 0.18 wt%, calculated from amino acid composition (Privat et al. 2007; Richards et al. 2001); methionine occurs with a frequency of five residues per 1000 (Eastoe 1955). Early studies therefore required large sample sizes, resulting in significant damage to archaeological specimens. Only recently have technological developments allowed analysis of samples as small as 10 mg. of collagen (Giesemann et al. 1994; Morrison et al. 2000).

To date, the few archaeological studies analyzing sulphur isotopes were mainly concerned with European/Eurasian archaeological material and focused on multiple samples from few sites. Sulphur isotopes are used in archaeology to differentiate between marine, freshwater, and terrestrial resources, as well as to identify immigrant individuals among a burial population.

For this study, Cape Agulhas is used as an arbitrary divider of the Western Cape Province (Figure 1); all sites north and west of the Cape, with an Atlantic Ocean coastline, are considered "western coast," and all sites east of the Cape, with a coastline along the Indian Ocean, are classified "southern coast." Sites in the Cederberg Mountains (at least 70 km from the sea, and a part of the Cape Fold Belt Mountains) and the Karoo are termed "inland." The study area encompasses three biomes, or distinct ecological communities consisting of similar plant and animal species that are suited to the geology and climate of the region. The fynbos biome vegetation extends throughout the western coast, the Cederberg Mountain inland regions, and most of the southern coast. Some of the southern coast sites in this study are in the forest biome. A few of the samples are from the succulent karoo biome, found in the north coast and over the Fold Belt Mountains inland. This region provides an ideal backdrop for a study of a new isotopic technique. The period between 4500-2000 BP has been closely studied and is characterized by greater reliance on smaller prey sources and shellfish (Deacon & Deacon 1999; Mitchell 2002; Parkington et al. 1987) and a decrease in mobility (Binneman 1996; Hall 1990). Archaeological evidence suggests greater interpersonal conflict (Bahn 2003; Morris & Parkington 1982; Morris et al. 1987; Pfeiffer et al. 1999; Pfeiffer & van der Merwe 2004) and an overall reduction in body size (Pfeiffer & Sealy 2006; Sealy & Pfeiffer 2000; Sealy et al. 2000). These factors suggest an increase in population size and more restricted territories. Climatic shifts and a minor regression of the sea could have instigated these

Figure 1: Map of Sites and Sampling Locations, Western Cape Province, South Africa



changes by exposing productive mussel colonies (Miller et al. 1995; Yates et al. 1986). Most of the excavated archaeological sites in the Western Cape Province are shallow caves or large rock shelters, which provided transient people with a temporary place to stay and bury their dead. Many of these shelters offered relatively dry microenvironments and provided excellent organic preservation. The majority of skeletons from the southern coast were found in multiple burials while those from the western coast were most often isolated or from small groupings from coastal dunes or rock shelters (Pfeiffer & Sealy 2006).

The two major proteins making up the organic fraction of bone are type 1 collagen and osteocalcin. Collagen is frequently the material of choice in stable isotope studies, due to the abundance (22% by weight, 36% by volume of compact bone) and turnover rate (Hedges & Law 1989; Collins et al. 2002). It is a highly repetitive insoluble protein which is easy to isolate and remove contaminants with careful sample preparation. During life, collagen is constantly reworked so the collagen isotopic signature represents the average diet of an individual over a minimum of 10-15 years prior to death (Hedges et al. 2007).

In six chapters this thesis attempts to determine the sulphur isotope values of a variety of animals (including humans) in the Western Cape Province of South Africa. This broad region includes several diverse habitats, and samples were selected from multiple environments to determine if $\delta^{34}S$ values distinguish between locations, particularly differentiating between coastal and inland localities. This is the first analysis of stable sulphur isotopes on archaeological specimens in South Africa, and it is important to "map" $\delta^{34}S$ values of faunal species known to have restricted habitats before applying any interpretation to human values. The aim of this thesis is to develop a preliminary $\delta^{34}S$ "baseline map" of the region to assess if $\delta^{34}S$ values vary sufficiently to warrant further

exploration. The broad sampling design resulted in limited material from individual sites so site-specific statistical testing was not performed.

The remainder of this thesis is laid out as follows: Chapter 2 provides a general introduction to the peoples and lifestyles of the Western Cape Province of South Africa during the Later Stone Age, particularly the period between 4500 to 2000 BP. A discussion of the geology, geography, fauna and flora for each area is presented to provide a framework for interpreting the sulphur isotope values. This chapter also gives an account of previous stable light isotope work done in the Western Cape Province. A review of sulphur isotope literature is presented in Chapter 3. The metabolism of sulphur in plants and animals is discussed briefly, as well as the laboratory methods involved in sulphur isotope analysis and quality control guidelines. The "sea spray effect" is also discussed. The emphasis of this section is, however, placed on the limited body of work concerning sulphur isotopes applied to archaeological questions. Chapter 4 describes the methodology of the laboratory work conducted at the University of Cape Town and the Max Planck Institute for Evolutionary Anthropology, in order to extract and analyze the bone collagen of the 37 archaeological human, 33 archaeological faunal, and 7 recent faunal samples presented in this thesis. Also, criteria for assessment of sample quality and preservation are outlined. The results of this laboratory work are presented in Chapter 5, and Chapter 6 discusses these results in the context of the Western Cape Province and provides a comparison with archaeological literature. The chapter concludes with summary and final remarks.

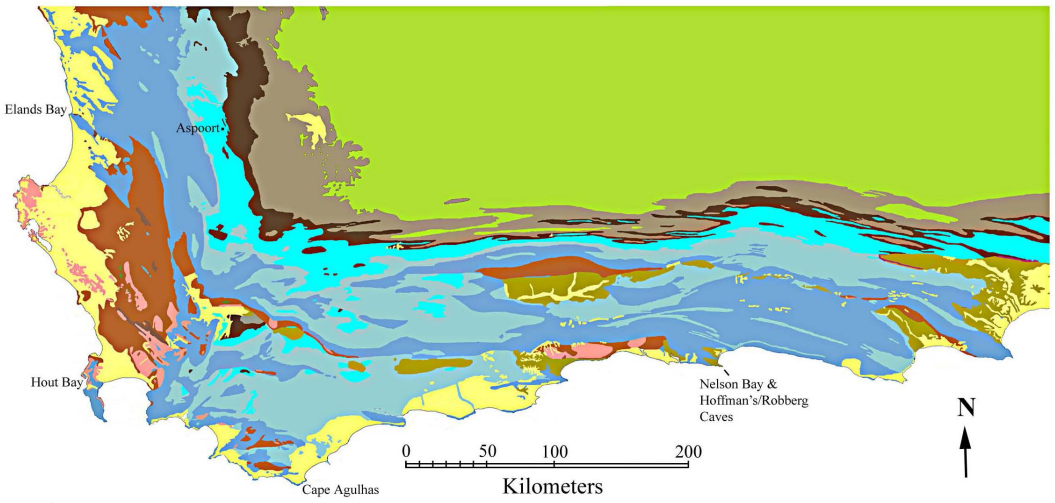
CHAPTER 2: ARCHAEOLOGY IN THE WESTERN CAPE PROVINCE, SOUTH AFRICA

Climate and Food Resources of the Later Stone Age Western Cape Province

This section introduces the three geographic regions in this study: western coast, southern coast, and inland. These three areas fall within the Cape Ecozone (Deacon & Lancaster 1988) and include the Fold Belt Mountains inland. Cape Agulhas is recognized by the International Hydrographic Organization as the dividing point between the Atlantic and Indian Oceans and is used as the arbitrary divider between the western and southern regions for this study. The climate in the western part of the study area is Mediterranean with wet winters (rainy season is between May and October), and the terrestrial vegetation predominately follows a C_3 photosynthetic pathway. The average annual rainfall varies from less than 200mm in the northern region to slightly more than 1,000mm/year (Deacon & Lancaster 1988; Pfeiffer & Sealy 2006). Moving eastwards, the proportion of summer rainfall increases and the forested areas of the south coast (Knysna-Tsitsikamma area, including Robberg) receive rain year-round (Chase & Meadows 2007). Within this region the geology is primarily Table Mountain Group (Cape Supergroup) with older Malmesbury Group sedimentary rocks and Cape Granite intrusions, and clastic grain sizes vary from clays to pebbles (Figure 2). The coastal lowlands are coated with recent marine aeolian sands, with periodic Paleozoic clastic rock exposures, primarily Table Mountain quartzite (Butzer 2004).

Fynbos, a fine-leaved fire resistant shrub, is the dominant vegetation type for most of the study area. It can grow in fairly nutrient-depleted, mostly sandstone-derived acidic soils, and typically in areas of winter rainfall (Cowling 1992). It is one of the richest and most diverse plant communities in the world in terms of plant species per unit area (Goldblatt 1997). Primary species include sclerophyllous (evergreen, hard-leaved),

Figure 2: Geological Map of Project Area, Western Cape Province, South Africa



Geological Legend

Quaternary to Tertiary Unconsolidated Deposits, Conglomerate, Sandstone, Limestone, Marl

Cretaceous Conglomerate, Sandstone, Shale, Limestone

Karoo System (Triassic to Jurassic):

Basalt, Pyroclasts, Minor Sandstone
Sandstone, Shale, Mudstone, Marl, Coal
Beaufort Series, Shale, Mudstone, Coal, Limestone, Sandstone

Ecca Series, Shale, Sandstone, Coal
Dwyka Series, Tillite, Sandstone, Shale

Cape Supergroup System
(Ordovician to Lower Carboniferous):

Witteberg Series, Quartzite, Shale
Bokkeveld Series, Quartzite, Sandstone
Table Mountain Series, Quartzite, Shale, Tillite

Klipheuwel Formation, Conglomerate, Shale, Greywacke

Precambrian System:

Precambrian Syenite

Cape Granite, Kuboos Plutons, etc., Granite, Syenitic rocks, Quartz Porphyry

Nama System (Malmesbury, Cango, Numees, Ntingwe, Franschoek Beds), Quartzite, Arkose, Limestone, Shale, Tillite, Lava, Tuff

After: Department of Mines, 1970. Geological Map of the Republic of South Africa and the Kingdoms of Lesotho and Swaziland (1:1,000,000)

flowering shrubs and geophytes (bulbed plants) (Charters 2003-2008). Soil type and parent rock appear to determine the varieties of fynbos to grow in a particular area (Ojeda et al. 2001). According to Charters, "Lowland fynbos" is most often found in sandy, clay, or limestone soils. The other broad type, "Mountain fynbos," is found in sandstone-derived soils or soils leached from granite or shale, and in areas of greater rainfall (Charters 2003-2008). An additional vegetation type found within the fynbos biome is renosterveld (Acocks' vegetation type No. 46; Acocks 1953), currently the most endangered vegetation type within the Cape Floral Kingdom (Walton 2006). Prior to the introduction of large-scale agriculture, this veld type would have provided some of the richest plant resources for humans and animals, as it grows in more nutrient-rich soils (derived primarily from metamorphosed shale from the Precambrian Malmesbury Group). Generally speaking, in areas where rainfall is 25-60 cm/year renosterveld vegetation is found (Walton 2006). Fynbos is dominant in areas with higher rainfall; and where there is little rainfall, succulent karoo vegetation is found. For the most part, species diversity of fynbos appears to be consistent throughout the Cape Floristic Region, regardless of the local environment (Cowling 1990).

The northern portion of the western coast region (around Elands Bay) is classified as succulent karoo, with many succulents and few grasses (which follow a C_3 photosynthetic pathway) and very low rainfall (Butchart 1995; Rutherford & Westfall 1986). Vegetation around all Fold Belt Mountain sites was predominantly mountain fynbos dominated by a variety of shrubs (Acocks' vegetation type No. 69, Acocks 1953).

The southern coast is characterized by fynbos biome and the rich forest biome, which is located in the east of the area studied for this thesis, and consists of afromontane forest, with patches of closed-canopy evergreen trees (Mucina & Rutherford 2006). The area around Plettenberg Bay is a mosaic of different vegetation types, with patches of

more open vegetation interspersed among forested ravines. Temperatures are mild and temperate in the forest biome, with rainfall around 800mm per annum (Schulze 1965). Marine and terrestrial dietary resources are abundant year-round. Terrestrial vegetation is a mixture of C_3 and C_4 species (Vogel 1978). Forest, bush, and grassland are all represented, although humans would have eaten predominantly C_3 plant foods and any C_4 input to the human diet would have been through consumption of grazing animals. The southern coastal region consists of predominantly rocky shoreline and a coastal platform with an elevation of approximately 200m, which ranges in width from 2-20km and meets the Fold Belt Mountains to the north. The Fold Belt Mountains separate the Cape Ecozone from the Karoo. There are numerous forested river valleys, with streams bringing nutrients from the interior. Soils are generally well developed and can be deep (Charters 2003-2008). Throughout the Holocene the forest likely stretched from Knysna to Tsitsikamma, and perhaps farther (Mucina & Rutherford 2006).

Numerous observations have been made concerning food sources available to and selected by foragers between 4500-2000 BP. There are several indications that the Western Cape Province experienced a period of population growth after 4000 BP. 'Smaller package' food items, such as geophytes, fruits, nuts and small, predictable animals became stable features of archaeological site contents and along the coast fish and shellfish dominate middens (Deacon & Deacon 1999; Jerardino 1998; Jerardino & Yates 1996; Mitchell 2002; Parkington 1977; Parkington & Poggenpoel 1968; Parkington et al. 1988; Sealy & van der Merwe 1985). Available terrestrial plant foods throughout the study area included geophytes and berries, along with starchy underground corms of members of the iris family (Deacon 1984; Hall 1990; Mitchell 2002; Parkington et al. 1988; Sealy & van der Merwe 1985, 1986).

Small browsing species were the dominant terrestrial fauna and included steenbok and/or grysbok (*Raphicerus* spp.), grey duiker (*Sylvicapra grimmia*), bushbuck (*Tragelaphus scriptus*), and vaalribbok (*Pelea capreolus*) (Klein 1981; Skead 1980). Some grazers and larger ungulates, such as eland (*Taurotragus oryx*), Cape hartebeest (*Alcelaphus buselaphus*), Cape buffalo (*Syncerus caffer*), blue antelope (*Hippotragus leucophaeus*), and reedbuck (*Redunca fulvorufula, R. arundinum*) were also present (Klein 1981; Stock & Pfeiffer 2004). Other terrestrial mammals commonly exploited were the Cape hare (*Lepus capensis*), scrub hare (*L. saxatilis*), mole rat (*Bathyergus suillus*), porcupine (*Hystrix africaeaustralis*), rock hyrax (*Procavia capensis*), and aardvark (*Orycteropus afer*) (Klein & Cruz-Uribe 1983). Angulate tortoise (*Chersina angulata*) was also abundant in the arid regions of the western coast and the Fold Belt Mountains, and emphasis on tortoise seems to have gradually increased, even becoming the dominant terrestrial animal food source at many west coast sites between roughly 2700 and 2200 BP (Klein & Cruz-Uribe 1983; Jerardino 2010). Tortoise size in archaeological assemblages decreased due to greater collecting pressure (Klein & Cruz-Uribe 1983). One burial from the Namaqualand coast (dating to 2700 BP) revealed rodent remains within the body cavity, suggesting micro fauna were also a part of the diet (Jerardino et al. 1992). Marine mammals, particularly the Cape fur seal (*Arctocephalus pusillus*), sea birds, fish, crayfish and shellfish were also numerous (Klein & Cruz-Uribe 1983). Dominant marine fish species along the west coast were hottentot (*Pachymetopon blochii*), white steenbras (*Lithognathus lithognathus*), white stumpnose (*Rhabdosargus globiceps*) and haarders (*Mugil* and *Liza* species) (Poggenpoel 1987b, 1996). Common fish species along the south coast included red steenbras (*Petrus rupestris*), carpenter (*Argyrozona argyrozona*), and poenskop (*Cymatoceps nasutus*) (Poggenpoel 1987a).

The appearance of "megamiddens" along the west coast around 3000 BP indicates a shift in resource exploitation (Jerardino 1995). Marine productivity seems to have improved as the climate became cooler and wetter around 3000 BP (Mitchell 2002). Several hundred years prior, around 3800±50 BP, a high stand of the ocean caused sea levels to rise roughly two meters above what they are today; a subsequent drop in sea level exposed low-lying reef around Elands Bay and allowed access to the productive mussel colonies that were exploited around 3000 BP (Miller et al. 1995; Yates et al. 1986). Similar events have been documented along the southern coast as well, although mostly earlier (Marker & Miller 1993, 1995; Miller 1990; Miller et al. 1993; Reddering 1988). Climatic conditions and sudden resource availability appears to have instigated a move from rock shelters to large, open air sites, and "megamiddens" become a major archaeological feature along the western coast (Miller et al. 1995; Parkington et al. 1988). While dominated by shell, primarily the black mussel (*Choromytilus meridionalis*), density studies have shown that the "megamiddens" often included a substantial quantity of bone and some lithic artifacts, indicating that these were multi-purpose sites, not just shell processing stations (Jerardino & Yates 1997). Black mussels, limpets, and Cape rock lobster appear to have been harvested in such quantities that an overall decrease in body size was observed (Buchanan et al. 1978; Jerardino 2010; Parkington et al. 1988). After 2800 BP, sea level rose again (Miller et al. 1995). Environmental conditions in the mid-Holocene at Elands Bay were probably more saline and tidal than today (Yates et al. 1986). Very few cave sites show occupation, and those that do (such as Steenbokfontein and Pancho's Kitchen Midden) indicate increasing numbers of occupants (Jerardino 1998; Jerardino 2010; Jerardino & Yates 1996).

Large shell middens are also found along the south coast, such as Matjes River Rock Shelter (Döckel 1998; Louw 1960). Inskeep (1987), on the basis of material from

Nelson Bay Cave, suggested that shellfish became a consistent part of the diet after 4500 BP, and that exploitation of immediately local food sources intensified around 3300 BP. At inland sites further to the east, Hall (1990) observed storage pits and an increase in quantity of riverine mussels and fish starting around 4300 BP.

Later Stone Age People in the Western Cape Province

The first detailed ecologically based study of Holocene Later Stone Age hunter-gatherers in the Western Cape Province was by John Parkington (Parkington 1972, 1976a, 1976b, Parkington et al. 1988). After excavating sites on the coast (Elands Bay Cave) and in the Fold Belt Mountains, he developed a Seasonal Mobility Hypothesis, proposing that Later Stone Age populations migrated in an annual cycle between the western coast and the Fold Belt Mountains, with movement based upon the seasonal availability of dietary resources in each environment (Parkington 1972, 1976a, 1976b; Parkington et al. 1988). Subsequent analysis of stable carbon isotopes in foodstuffs and in human skeletal remains indicated that Later Stone Age skeletons discovered on the coast had $\delta^{13}C$ values suggesting predominantly marine-based diets, while those discovered inland consumed diets primarily focused on terrestrial foods. The conclusion was that these were in fact two separate groups, as opposed to the same highly migratory population (Sealy & van der Merwe 1985, 1986, 1992; Sealy 1989b; Sealy et al. 2000; but see also Parkington 1991). Both archaeological and bone chemistry data suggests that settlement along the west coast during this period was coastally oriented.

Between 4500 and 3500 BP mean body size decreased (in linear and mass dimensions) in humans along both south and west coast regions, accompanied by an increased diversity in body size (Pfeiffer & Sealy 2006; Sealy & Pfeiffer 2000). The climate, topography, and resources vary greatly between the fynbos vegetation of the west

and the forest of the south, yet people living in these regions seem to have faced similar challenges simultaneously. Carbon and nitrogen isotope data did not elucidate any dietary reason behind this reduction in body size (Pfeiffer & Sealy 2006), and skeletal remains do not reveal chronic stress or signs of infectious diseases (Pfeiffer 2002, 2005), but may indicate poorer nutrition as territories became increasingly smaller and food more scarce. The most likely cause of this reduction in body size is diminished availability of good quality protein sources, which would not necessarily show up in the archaeological or biochemical record. Body size again increased around 3000 BP throughout the region, around 1,000 years before the adoption of pastoralism (Pfeiffer & Sealy 2006).

In the late Holocene, occasional instances of interpersonal violence are indicated in the archaeological record (Bahn 2003; Morris & Parkington 1982; Morris et al. 1987; Pfeiffer & van der Merwe 2004; Pfeiffer et al. 1999). These may reflect community stress. Reduced mobility is indicated during this period along the south coast (Binneman 1996; Hall 1990; Sealy 2006), and possibly along the west coast (Sealy & van der Merwe 1985, 1986). Repeated burials at the same locations (south coast) and the frequency of grave goods, especially in the graves of children, also attest to changing social dynamics (Hall 1990; Hall & Binneman 1987; Inskeep 1986). As would be expected with increasing population, the number of burials dating to 4000-2000 BP is far greater than during previous times, and nearly 40% of the skeletons found in the region date to this time (Jerardino 2003).

Stone tool assemblages concur with the reduced mobility concept throughout the Western Cape Province during this period (Deacon & Deacon 1999; Deacon 1984; Sampson 1974). The widespread mid-Holocene microlithic Wilton Industrial Complex was replaced by more regionally variable assemblages. On the south coast, informal Post-Wilton macrolithic assemblages utilized locally available materials and consisted mostly

of large crude pieces, although in the west, backed microliths similar to Wilton technology continued to occur (Inskeep 1987; Manhire 1993; Mitchell 2002; Orton 2002, 2006). Various wood, shell, and bone implements, scrapers, and bored stones were also common components of the tool assemblage (Deacon 1984; Deacon & Deacon 1999; Ouzman 1997; Sampson 1974). A distinctive difference in lithic technology is the near disappearance of "exotic" raw materials (Jerardino 2007; Jerardino et al. 2009; Parkington et al. 1988; Smith & Ripp 1978). The best documented sequence comes from Nelson Bay Cave, around 3300 BP, as non-local chalcedony disappears from the record and large indigenous crude quartzite pieces appear, alongside a significant increase in fish and young seal remains and terrestrial forest dwelling animals (Inskeep 1987). A similar shift appeared along much of the south coast concurrently (Binneman 1996; Sampson 1974; Van Noten 1974). Sites in the fynbos biome, along the west coast and in the Olifants River Valley, show an increased frequency of adzes (up to 50% or more of retouched artifacts) which may have been used to form digging sticks, suggesting a greater emphasis was placed on underground plant resources (Jerardino 1998; Jerardino & Yates 1996; Mitchell 2002; Schweitzer & Wilson 1982). The higher frequency of adzes corresponds to an increase of plant food residues in the archaeological record (Mazel & Parkington 1981). In the forest biome adzes do not seem as common, although at Oakhurst, a site roughly 14km inland from Knysna, scrapers that may be adzes do appear more frequently at this time (Deacon 1984). Bows and arrows, spears, and digging sticks were of prime importance during the Later Stone Age. A long bone robusticity study (Stock & Pfeiffer 2004) indicates that Later Stone Age people in the fynbos biome likely used a bow and arrow to hunt, while people in the forest biome may have used spears more often. Lower limb robusticity indicates people in the forest biome were somewhat more mobile than

those in the fynbos biome (ibid.). Women along the west coast appear to have consumed more terrestrial plant foods than men (Sealy 1989).

Around 2000 BP, domesticated animals (sheep and cattle) were introduced to the Western Cape Province by pastoralists from further north in Africa. By the 15th century AD early travelers describe specialized pastoralist societies as dominating the coastal plain, although there are references to groups of people who continued to live primarily by hunting and gathering. Skeletons that post-date 2000 BP may therefore be the remains of hunter-gatherers or herders. This is usually difficult to determine from burial context, although individuals buried in caves and rock shelters are more likely to have been hunter-gatherers. Agriculture was not practiced in this region until after European colonization in the seventeenth century.

Geology of the Western Coast Region and Site Details

Wide sandy coastal lowlands are characteristic of the coastline. Aeolian sands are a result of two seasonal weather patterns: during the winter, constant westerly storms bring strong northwesterly winds to the western coast, and during the summer months the South Atlantic high pressure frequently shifts southeastward, directing strong southeasterly winds to False Bay (Butzer 2004). Franceschini et al. (2003) traced the modern transport pattern of sand from False Bay, south of Cape Town, to St. Helena Bay, 32 km north of Saldanha. The authors discovered that the beaches are a mixture of terrigenous and carbonate material along the coast between Cape Town and Saldanha Bay, where there is little river output; carbonate rich between Saldanha Bay and St. Helena Bay, due to the high biogenic $CaCO_3$; and terrigenous-rich north of St. Helena Bay due to riverine contributions. The article concludes that the terrigenous input by rivers into False Bay and Table Bay is moved northwards by longshore drift and mixed with carbonate shell

fragments. Dune formations have changed dramatically in response to variations in climate and sea level (Compton & Franceschini 2005). Dominant vegetation types along the fine-grained coastal marine sands are coastal fynbos (Acocks' vegetation type No. 47, Acocks 1953) and strandveld (Acocks' vegetation type No. 34, Acocks 1953), both with many grasses.

Elands Bay and Leipoldville represent the arid northern extent of the research area and the end of winter rainfall, receiving between 150 and 250 mm of rain annually (Parkington et al. 1988). Table Mountain Series sandstones are the primary geologic feature, with some quartzite and shale, and soils are typically weakly developed and sandy (Anonymous 1965; Anonymous 1970). The Verlorenvlei River and coastal lake at Elands Bay would have provided a source of freshwater, and sandstone outcrops around the bank offered several rock shelters and caves (Parkington et al. 1988). Shellfish was easily available along the rocky shores, and nutrients brought up by the Benguela Current upwelling supported a rich marine ecosystem including whales, fish, crayfish, seals and sea birds (ibid.).

The basement rock from Yzerfontein to Saldanha and Kasteelberg (including Darling and Oudepost) is Late Precambrian Malmesbury Group metasediments with Precambrian to Cambrian gabbro and diorite intrusions around Yzerfontein, and Cape Granite Suite intrusions around Oudepost and Darling (Theron et al. 1992; Norman & Whitfield 2006). Traces of Pleistocene dune deposits sit under Holocene calcareous sand dunes of the Witsand Formation (Tankard & Rogers 1978). Small limestone and conglomerate components are present, and soils are typically weakly developed on loose sediments, although around Saldanha and Kasteelberg solonetzic soils are common (Anonymous 1965; Anonymous 1970; Anonymous 1973). Unique features of the region are the Saldanha and Darling batholiths which are comprised of granodiorite, biotite

granite, and granite that are cut by meta-volcanics (this formation is much older than the other rock types in the area) (Scheepers & Schoch 2006). Vegetation around Kasteelberg was probably dominated by renosterveld (Klein & Cruz-Uribe 1983).

The shoreline at Bokbaai consists of sandy beaches alternating with Malmesbury Series dark shale and slate, with a limestone coastal plateau 50m above sea level (Mabbutt 1955). There are two major areas of ferricrete, one of which forms the base of a large shell midden (Rudner, I & J 1955). Two seasonal streams, the Bok and Buffels Rivers, provide fresh water and resources.

The geology around Cape Town, Bloubergstrand and Melkbosch is primarily granite of the Cape Granite Suite and/or sedimentary rocks of the Malmesbury Group (Norman & Whitfield 2006), with some quartzite and limestone (Anonymous 1970). Soil development is weak and sands blanket the coastal areas (Anonymous 1973). Gordon's Bay, situated on the eastern edge of the Cape Flats, has similar geology and soil development (Anonymous 1970; Anonymous 1973). The site is located near two streams with mountains to the east and south (van Noten 1974).

The geology of Karbonkelberg, Hout Bay and Llandudno is primarily Table Mountain Group (quartzitic sandstone) with some shale, resulting in a high surface runoff of low-salinity, acidic water (River Health Programme 2003). Mean annual precipitation is 923mm (ibid.). Hout Bay is set in a narrow valley with one river and was the only site along the west coast study area that was dominated by forest rather than fynbos in antiquity ("Hout" means "wood" in Afrikaans). This area has undergone dramatic deforestation in the last 200 years, and is now almost devoid of the heavy forests that dominated the landscape 2000 years ago (Buchanan 1977). In his diary (July 1653) Van Riebeeck wrote "They were the finest forests in the world and contained as long and thick spars as one would wish to have. It is amazing to see the fine forests that lie scattered all

about the mountain-side" (Thom 1952). He also mentions that the forest started about 5,500m from the sea (ibid.). Mountain fynbos is the dominant vegetation today, with patches of afromontane forest in the valley and renosterveld along the coast (River Health Programme 2003). The upper catchment of the Hout Bay (or Disa) River is in Table Mountain National Park at an altitude of 720m amsl, and is about 12km long (River Health Programme 2003). Before development the river was wide enough in the valley to accommodate rowing boats. The Hout Bay estuary is about 500m long and varies seasonally; in the summer little water flows in creating a closed, brackish system, while in winter the system is more saline (River Health Programme 2003). Old photographs show a significant estuary with an impounded brackish to freshwater lake situated in marsh flats towards the central portion of the valley. Soil formation is usually well developed, with soils around the main archaeological site belonging to the Fernwood and Warrington soil series (Anonymous 1976).

Byneskranskop is located near the boundary between the western and southern coasts. The cave site is situated about 10km from the sea and near the top of a limestone ridge at the junction of the coastal plain and the foothills of the southern Cape Fold Mountains (Schweitzer & Wilson 1982).

Geology of the Southern Coast Region and Site Details

Precambrian Malmesbury sediments and sandstones, quartzites, and shale of the Table Mountain, Witteberg, and Bokkeveld series dominate the geology of the southern coast (Norman & Whitfield 2006; Thamm & Johnson 2006). The Robberg Peninsula, which forms the western boundary of Plettenberg Bay, is composed of late Cretaceous - Jurassic sediments (known as the Robberg Formation) and includes a variety of intertidal sediments, primarily various sandstones, beach conglomerates and estuarine mudstones,

lying above the quartzite (Norman & Whitfield 2006; Shone 2006). A unique feature of the Robberg Peninsula is the presence of a seal colony, a resource found at no other site in the study.

Matjes River Rock Shelter, a rocky overhang on the western side of the mouth of Matjes River, about 15km east of Robberg Peninsula, contains a massive shell midden with abundant shellfish, animal bone and stone artifacts, and few plant remains (Döckel 1998; Louw 1960). This site has a long east-facing sandstone wall for shelter, and has yielded the largest number of Later Stone Age skeletons recovered from a single site in South Africa (Morris 1992; Sealy 2006). Just east of Matjes River Rock Shelter, the Tsitsikamma National Park (stretching along the coast, between the Bloukrans and the Storms River) is another archaeologically rich area within the forest biome and includes Tucker's and Whitcher's Caves.

Around Knysna, several coastal lakes were formed during a long series of marine regressions and transgressions which carved valleys and subsequently filled them with water and sediments (Norman & Whitfield 2006). Enon Formation (dominantly a Mesozoic conglomerate) is common in Knysna, indicating alluvial fan deposition (Shone 2006). Often, Bredasdorp Group (on-shore coastal Cenozoic) deposits are found on top of the Enon Formation (Roberts et al. 2006). The only other areas near Plettenberg Bay with Enon conglomerate are the Keurbooms River valley and Noetsie (ibid.). Noetsie is located roughly five kilometers east of Knysna, and is one of few excavated open air sites (Orton & Halkett 2007).

Previous $\delta^{13}C$ and $\delta^{15}N$ studies have indicated that the inhabitants of Robberg Peninsula/Plettenberg Bay and the area around Matjes River consumed different diets (Sealy 2006), although separated by only 14km. People buried at Robberg consumed large quantities of high-trophic level marine protein ($\delta^{15}N$ values above 13‰, up to 17-

18‰), while those from the Tsitsikamma forest and Matjes River ate more mixed diets (Sealy 2006). Such a dietary separation implies both groups were living in clearly demarcated territories, perhaps divided by the estuary of the Bietou/Keurbooms River (Sealy 2006). Stable isotope evidence also indicates that inhabitants of Whitcher's Cave, only 14km from the sea and still within the same geographic region (FitzSimons 1926), had nearly exclusively terrestrial diets, with low $\delta^{15}N$ values, most under 10‰ (Sealy & Pfeiffer 2000). This area is rugged and the cave is located approximately 100 meters from the mountain summit at an elevation of nearly 700m, with a tributary of the Elandsbos River in the deep valley beneath (Schauder 1963), so it is reasonable to assume sufficient food resources were located in the vicinity and although the inhabitants may have visited the coast, marine food did not make a substantial contribution to diet. The isotopic differentiation between these three localities, all within the same region, indicates that between 4500-2000 BP groups were more sedentary and living within territories defined either geographically or socially, or, most likely, both.

Geology of the Inland Region and Site Details

The Fold Belt Mountains are mainly quartzitic sandstones of the Table Mountain Group which were uplifted and folded around 250mya (Norman & Whitfield 2006). Weathering is slow, and soils poorly developed, acidic, low in nutrients, and easily erodible (Lambrechts 1979). Stream sediments are derived almost solely from the weathering of mountain sandstones, and the sand-sized quartz is continually being reworked and recycled, which keeps the sedimentary debris contained within this area (ibid.). Malmesbury shale and quartzite are also prevalent (Norman & Whitfield 2006). The Olifants River flows year-round and the river valley consists mainly of underlying sandstone or shale. The shale in the region was formed in shallow marine conditions, with

the exception of the Cederberg formation, which was formed under deeper ocean (Thamm & Johnson 2006).

Clanwilliam receives on average only 213mm of rain per annum (Weather Bureau 1954), so that animals from this area and the adjoining Pakhuis region have high nitrogen isotope values (Sealy et al. 1987). Caves are numerous in this region as well as freshwater fish provided by rivers (Parkington & Poggenpoel 1968; Parkington 1977). Archaeological remains of freshwater fish are rare, although *Labeo seeberi* (sand or mud-fish) have been found at Klipfonteinrand (Hall 1977) and an unidentified fish was recovered from the archaeological assemblage at Aspoort (Smith & Ripp 1978).

Few human skeletons have been found from inland localities compared with large numbers from the coastal areas of the Western Cape Province (Morris 1992). Stable carbon and nitrogen isotope values from the few skeletons found at sites in the Clanwilliam district are very consistent ($\delta^{13}C$ values from -19.0‰ to -17.3‰ for seven Later Stone Age individuals; unfortunately $\delta^{15}N$ measurements may be compromised by aridity), and indicate terrestrial based diets (Parkington & Poggenpoel 1971; Sealy et al. 2000).

The sites of Klipfonteinrand, Wyegang, Eland Cave, and Watervals Rivier are all caves in Table Mountain sandstone/quartzite, with shale and some tillite occurring nearby (Anonymous 1970; Thamm & Johnson 2006). Soils in the area are weakly developed on rocks with K-horizons (calcium carbonate calcrete soil deposits) (Anonymous 1973). Klipfonteinrand is the largest site, with an occupational sequence that spans the Middle and Later Stone Ages (Parkington 1976a). Watervals Rivier is a medium-sized overhang with rock paintings, located on the southeast bank of the river of the same name (Sealy et al. 2000). Eland Cave is named for the large panels of eland painted on the back wall; this is one of the greatest concentrations of rock art in the area. It contained the double burial

of two children in a shallow grave lined and covered with grass, and the bodies were placed on leather, some of which is still preserved (Sealy et al. 2000).

A 1991 study (Sealy et al.) analyzed $^{87}Sr/^{86}Sr$ in several inland skeletons from the Olifants River Valley and found them to be enriched in ^{87}Sr, indicating that they had lived in areas with underlying sandstone or shale. Skeletons found at the coast, on the other hand, had lower $^{87}Sr/^{86}Sr$, similar to the value for the ocean. There are, however, possible problems of post-depositional contamination, especially for bones from shell middens where percolating groundwater contains high levels of strontium from the shells.

Unfortunately, scant archaeological data exists from the succulent karoo biome, and Aspoort is the only excavated site inland of the Cederberg. The environment today is very arid, but the small rock shelter is next to a perennial river. This area is flat and dry, with rains falling mostly in the winter and an annual rainfall of 2-25cm (Deacon & Lancaster 1988). The local geology is primarily of the Witteberg Series, with quartzite and shale (Anonymous 1970; Lane 1978). Soils are generally lime-rich and slow to develop, as rock decomposition is slow due to the aridity of the area (Charters 2003-2008; Smith & Ripp 1978). The main veld type is Succulent Karoo (Acocks' vegetation type No. 31, Acocks 1953), with plant species adapted to arid conditions (Acocks 1975; Smith & Ripp 1978). Vegetation is far more limited in this biome than in the others discussed previously, and consists primarily of small, succulent-leaved shrubs. For the majority of the year most available vegetation is unpalatable to animals (Smith & Ripp 1978). Soil formation at Doornbos in the Karoo is similar, with poorly formed desert soils (Anonymous 1965). The geology is primarily Beaufort Series, with shale, mudstone, sandstone and some limestone (Anonymous 1970).

Summary

Changes occurred in the environment and landscape throughout the Cape Ecozone around 4500 BP. In reaction, populations apparently increased and became more sedentary and territorial. The faunal assemblages at various archaeological sites document a greater reliance on small animals such as tortoise and hyrax, which can be obtained more regularly and reliably than large game. At the population level peak, after 3000 BP, "megamiddens" indicate a shift to greater exploitation of marine resources. By 2000 BP the focus of occupation had shifted away from the coast with the introduction of pastoralism. Dietary stress between 4500 to 2000 BP is indicated by the increase in diet breadth and focus on lower-ranked food sources, which may have led to a decrease in body size. There is also evidence for an increase in interpersonal violence, consistent with the hypothesis that more people were competing for resources within a smaller area.

CHAPTER 3: LITERATURE REVIEW OF STABLE SULPHUR ISOTOPES

Sulphur has four stable isotopes, of which ^{32}S is the most abundant (95.0%) and ^{34}S the second most abundant (4.2%: MacNamara & Thode 1950). Sulphur isotope measurements are expressed as $\delta^{34}S$ values, defined as the ratio of ^{34}S to ^{32}S in a sample, relative to the same ratio in the Canyon Diablo Troilite meteorite standard (Vienna CDT): $\delta^{34}S = (R_{sample}/R_{standard} - 1) \times 1000$, where $R = {}^{34}S/{}^{32}S$. Values are expressed as per mil (‰). Sulphur has several valance states in nature (-2 to +6).

Sulphur isotope research is far more limited than stable carbon and nitrogen isotope studies, primarily due to the difficulty (until recently) in obtaining measurements. Routine measurements of $\delta^{34}S$ are now possible due to advances in continuous flow-isotope ratio mass spectrometry (CF-IRMS), which allows measurements of sulphur in 10 mg collagen samples (Giesemann et al. 1994; Morrison et al. 2000). One of the main problems with sulphur isotope analysis is the production of SO_2 gas in the elemental analyzers, which contaminates surfaces and could interfere with future measurements (Fry 2007). To compensate, laboratories have often dedicated one mass spectrometer solely to sulphur isotope analysis, which is costly. Recent developments allow the addition of a second gas chromatography (GC) column to measure sulphur (%S, $\delta^{34}S$) from the same sample and simultaneously with carbon and nitrogen (ibid.).

As with strontium isotopes (Bentley 2006), $\delta^{34}S$ values have much potential for aiding migration studies. Sulphur is ubiquitous in the environment, and a large range of $\delta^{34}S$ values is possible depending on oxidation state, regional geology, bacterial activity, metabolic process, and proximity to the ocean. Sulphur is essential to plant and animal survival, is present throughout the body, and is passed from source to consumer with little fractionation (Arneson & MacAvoy 2005; Richards et al. 2003). As sulphur isotope ratios

in plants ultimately indicate the soil sulphur, which is most often derived from bedrock, $\delta^{34}S$ values can be used as geographic indicators when there is sufficient difference between geologic substrates in the study area. Isotopes in bone collagen potentially indicate several aspects of the environment in which an individual resided during the last several years of life, including rock types, soil, plant species, proximity to the ocean, atmospheric composition, and redox potential.

Sulphur Isotopes in the Environment

The four major forms of sulphur in the environment are sulphur dioxide [SO_2], sulphate [SO_4]$^{2-}$, sulphite [SO_3], and sulphide [H_2S], with a wide range of $\delta^{34}S$ values. Figures 3 and 4 present simplified illustrations of potential sources of sulphur in both marine and freshwater/terrestrial ecosystems. Different areas of bedrock can have $\delta^{34}S$ values ranging between -19‰ and +30‰, found in uplifted marine sediments, pyrite and evaporites (Krouse et al. 1987; Peterson & Fry 1987). Sulphur occurs in the atmosphere as SO_2 and H_2S, as [SO_4]$^{2-}$ in evaporites (with $\delta^{34}S$ values of ~10 to 30‰), in igneous and metamorphic rocks (-20 to 20‰), in sedimentary rocks (-40 to 50‰), in marine sediments as both sulphate and sulphide, as sulphate in the ocean, sulphide in ore deposits, and sulphur in the earth's core (Hoefs 1997; Krouse 1989).

Sulphur compounds in the atmosphere have a wide range of isotopic values (see Nielsen 1974 for full discussion); occurring as ionic sulphate and in gaseous state as H_2S and SO_2, and can originate naturally through bacterial action and dimethylsulfide (DMS, with $\delta^{34}S$ values ranging from -30 to +10‰, as H_2S or oxidized to SO_2), volcanism (~ -5 to +10‰), and as aeolian sediment particles (Hoefs 1997). Anthropogenic sources include combustion and refining of fossil fuels (~ -10 to +30‰), ore smelting (-30 to +30‰), and gypsum mining and processing (+10 to +30‰) (Hoefs 1997). Measured anthropogenic

Figure 3: Potential Sulphur Sources in the Marine Ecosystem

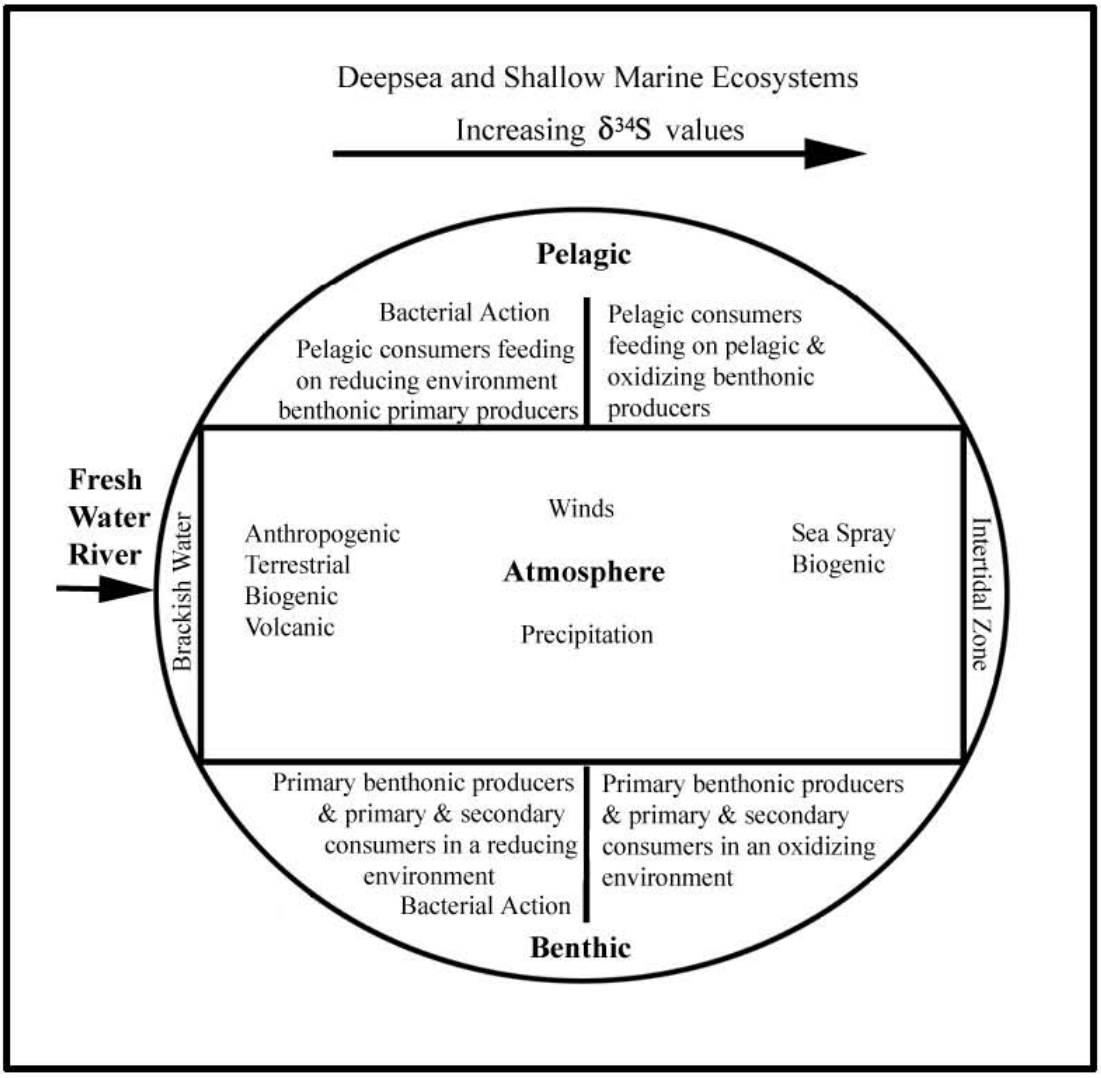
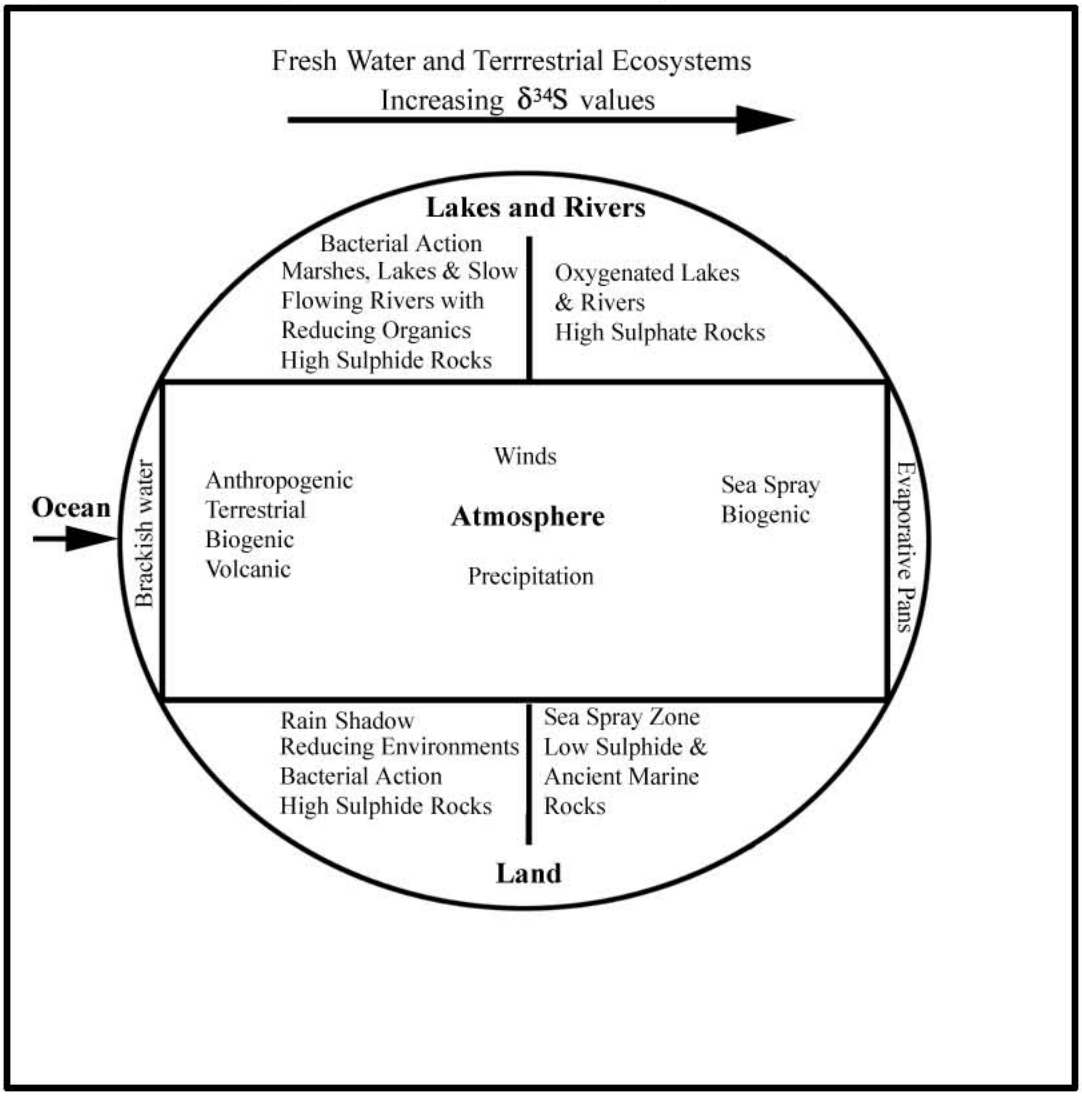


Figure 4: Potential Sulphur Sources in Terrestrial Ecosystems



sulphur in Europe has values around +4‰ (McArdle et al. 1999), although the value appears to vary greatly elsewhere (Krouse & Case 1983). Seasonal differences have been observed for sulphur in precipitation and aerosols, varying depending upon location in the world (Nriagu & Coker 1978; Nriagu et al. 1991).

All modern seawater sulphate $[SO_4]^{2-}$ has a fairly uniform value of around +20‰ (Peterson et al. 1985; Rees et al. 1978). Analysis of marine sulphate minerals indicates that marine sulphate values fluctuated throughout time; from +30‰ in the Cambrian to a low of +10‰ during the Permian (Faure 1977; Holser & Kaplan 1966; Thode & Monster 1965). The difference in $\delta^{34}S$ between freshwater and marine has been used to distinguish lake dwelling from migratory ocean fish found in the same bodies of water in Canada (Hesslein et al. 1991).

Freshwater and terrestrial ecosystems exhibit a wide range of sulphate values (ca. -20‰ to +20‰: Peterson & Fry 1987), with lower values mainly due to reduction of sulphate to hydrogen sulphide by anaerobic bacteria. This bacterial fractionation of sulphur in freshwater ecosystems often results in lower $\delta^{34}S$ values and allows lake and sluggish riverine environments to be distinguished from the surrounding terrestrial environment (Faure 1977; Hesslein et al. 1991). Terrestrial animals typically have $\delta^{34}S$ values ranging from -5 to 10‰ (Krouse 1980; Peterson & Fry 1987), with a slight ($\leq$1‰) fractionation between dietary methionine and human bone collagen (Richards et al. 2003).

Arikawa et al. (1991) suggest that $\delta^{34}S$ values in plants, marine and terrestrial animals and humans are typically higher in the southern hemisphere than in the northern hemisphere, with $\delta^{34}S$ values of all materials sampled highest in those from Oceania. The authors conclude this pattern is attributable to anthropogenic sulphur in the northern hemisphere (which typically has low $\delta^{34}S$ values) and the greater proportion of sea to land in the southern hemisphere.

Sulphur Isotopes in Plants

Sulphur is available to plants in four forms: weathering from bedrock (sedimentary sulphate and igneous and sedimentary sulphide minerals), wet atmospheric deposition (sea spray, acid rain), dry atmospheric deposition (SO_2 gas), and as organosulphur (microbial generation in soils and degradation of dead plant and animal matter) (Brady & Weil 1999; Hedges et al. 2005; Krouse 1989). Dissolved sulphate is the primary source from which microorganisms and plants draw, and soil texture controls the permeation of sulphur compounds, as travel is much more efficient in sand than in clay (Krouse 1989). A few plant species, such as those growing in marshes, utilize sedimentary sulphides and have $\delta^{34}S$ values around -10 to +5‰ (Thode 1991).

Fractionation of sulphur within marine, freshwater, and terrestrial plant ecosystems is small, with plant $\delta^{34}S$ values typically 1.5‰ lower than their sulphate sources (Trust & Fry 1992). A wide range of $\delta^{34}S$ values have been observed in vegetation, ranging from -30 to +30‰ (Krouse & Tabatabai 1986; or -22 to +22‰ as reported in Peterson & Fry 1987), although in areas with little atmospheric sulphur contribution foliage over a broad area can have very similar $\delta^{34}S$ measurements (Krouse 1989). The sulphur content in plants varies from 0.1% to more than 1.5% by dry weight (ibid.).

Inorganic sulphur is absorbed from the soil through plant roots as the sulphate ion, and is transported to the leaves where sulphate is reduced to sulphite, then sulphide, before being converted into cysteine and sulpholipids (Lunde et al. 2006; Trust & Fry 1992). The cysteine is then further reduced to organic sulphur containing compounds including methionine (Rausch & Wachter 2005). Soluble inorganic sources of sulphur include rainwater (5-10‰), groundwater (-5 to 10‰) and stream water (-20 to 10‰) (Nriagu et al.

1991). Values reported for terrestrial plants range between approximately -7‰ to +8‰ (Nriagu & Coker 1978).

It is not currently known what proportions of plant sulphur are derived from atmospheric SO_2 (absorbed through foliage) and soil SO_4^{2-} (assimilated through the roots), and atmospheric, soil, climatic and botanical factors all have an influence (Krouse 1989). It has been reported (Brady & Weil 1999) that even when adequate amounts of soil sulphate are available, 25 to 35% of a plant's sulphur can be obtained from atmospheric sulphur dioxide.

Sulphur Metabolism and Sulphur Isotopes in Animals and Humans

Sulphur is essential for growth and survival in animals, although metabolism is complicated and poorly understood. Mammals, fish, and birds are unable to reduce sulphur so must consume sufficient levels of methionine and cysteine for protein synthesis and optimal growth (Griffith 1987). The human body cannot retain methionine and cysteine so sufficient quantities must be consumed daily (Ingenbleek 2006; Nimni et al. 2007). Any dietary excess is oxidized to sulphate then excreted in the urine (or reabsorbed), or converted to the metabolite glutathione (GSH) and stored in the liver (Nimni et al. 2007). There appears to be little variation in $\delta^{34}S$ values among tissues of the same individual; hair, nails, blood, urine, and kidney stones from humans had $\delta^{34}S$ values within 1 to 2‰ of one another (Krouse et al. 1987).

Several feeding studies have been conducted in agriculture and aquaculture, primarily on cattle, sheep, chickens (e.g. Abe et al. 2000; Kennedy et al. 1975; Schutte 1995), and many species of fish (e.g. Espe et al. 2008; Rumsey et al. 1983) to determine the effect of sulphur supplementation and sulphur starvation on growth. Nearly all other research has been limited to laboratory mice and rats. Few studies assess fractionation.

Most studies analyzing sulphur starvation in fish, other animals, and plants abruptly shift sulphur supply from abundance to severe limitation. The effects of sulphur deficiency in humans are not currently known. In plants, sulphur deficiency decreases yields, affects nitrogen uptake efficiency, and decreases protein content (Hawkesford & De Kok 2006). Rats fed a diet low in methionine showed arrested growth and developed a variety of deficiency symptoms (Young & Maw 1958). Methionine and protein deficiency during pregnancy in rats resulted in offspring that remained smaller for the rest of their lives (Rees et al. 2006). Commercial poultry diets are always supplemented with methionine/cysteine to enhance growth (Schutte 1995).

Mammals are dependent on plants to convert inorganic sulphur to organic, in a process similar to the accumulation of nitrogen in plant tissues, and both elements are closely interrelated. In the body, sulphur is found predominantly in the amino acids methionine, cysteine and taurine (Hesslein et al. 1991). Sulphur is distributed in the inorganic matrix of bone as calcium sulphate ($CaSO_4$) and within collagen as methionine with a frequency of five residues per 1000 (Eastoe 1955). Chondroitin sulphate connects the mineral phase and collagen fibers (Schneiders et al. 2008). As sulphur in bone collagen is present in only one amino acid, the amount of sulphur is low (~0.2%; Giesemann et al. 1994; Nehlich & Richards 2009; and 0.16% in Leach 2003 and Richards et al. 2001). Fish collagen contains more methionine (Eastoe & Leach 1958), so consumption of a small amount of fish will likely register in the $\delta^{34}S$ values of the consumer (Nehlich et al. 2010).

Most plants consumed by humans, apart from soy, do not contain enough sulphur amino acids (SAA) to fulfill human requirements (Ingenbleek 2006). High levels of methionine can be found in several nuts, seeds, fish, and meat. Poultry and red meat contain roughly the same amounts of cysteine and methionine, while the ratio of

cysteine/methionine in fish is 7/10 (with around 5% SAA for most animal protein) and in dairy products is 1/3 (with around 4% SAA) (Nimni et al. 2007). Starchy foods contain slightly more cysteine, while eggs contain significantly more cysteine (4/3) and are one of the most SAA-rich protein sources (egg whites contain 8% SAA) (ibid.). Most fruits and vegetables contain very little (less than 4%), although some, such as garlic, onions, and brussel sprouts, have a significant amount (Nimni et al. 2007). Most legumes contain very little.

The mean molar S:N of mammalian tissues is 1:14.5. Meat has S:N of 1:13 to 1:18 (egg white 1:10), while plants typically have S:N of 1:20 to 1:35 (Ingenbleek 2006). Over 90% of the methionine consumed in a day by healthy individuals is used to rebuild proteins that have broken down; only a small fraction undergoes oxidative degradation to sulphate and is excreted in urine, all within 24 hours (ibid.).

Controlled feeding studies in which sulphur isotopes were measured have found a small and consistent diet-tissue fractionation for a variety of animals: +1.3‰ for gypsy moth caterpillars and +1.2 to +1.4‰ for brook trout (Peterson et al. 1985). A study that fed pigs two isotopically known diets determined that the difference in $\delta^{34}S$ between diet and tissue (liver) was minimal (González-Martín et al. 2001). Katzenberg & Krouse (1989), after analyzing $\delta^{34}S$ values of a Hutterite community in Canada along with several dietary staples, established that fractionation is small in humans compared to $\delta^{34}S$ values of diet. The $\delta^{34}S$ of food items ranged from 0 to +5‰, while human hair had values around +3‰.

The controlled feeding study most often cited in archaeological research was conducted by Richards et al. (2003). Two horses were fed three different diets (two protein adequate C_3-based and one low protein C_4–based feed) over nine months to determine the fractionation of sulphur isotopes from food to tissue. On the nutritionally

adequate C_3 diet the fractionation between diet and hair was minimal (-1‰). On the low protein C_4 diet a fractionation of +4‰ was observed. This could be due to sulphur recycling from body proteins (endogenous synthesis of cysteine from methionine) during a time of lower digestible protein consumption, as both horses lost body mass on this diet.

Sulphur Stable Isotope Studies in Archaeology

Nehlich & Richards (2009) used modern samples from a variety of species in an attempt to establish criteria for collagen preservation for quality control of sulphur isotope measurements. Theoretical sulphur contents were calculated based on several published amino acid profiles and DNA/protein sequences. Amino acid sequences of Type 1 collagen were also discussed for three classes of modern animals (*Actinopterygii, Aves*, and *Mammalia*) and several Pleistocene species for comparison with the published profiles and the CF-IRMS data. Modern fish collagen was found to contain 0.63±0.08% sulphur and that of mammals and birds 0.28±0.07%, although there is considerable variation. The ranges are slightly greater for archaeological material (0.40% to 0.85% for fish and 0.15% to 0.35% for mammals and birds). Intact modern mammalian collagen has C:S of 313 to 696 and N:S of 111 to 216. Archaeological mammal collagen was found to be sufficiently well preserved to yield reliable sulphur isotope measurements if it had C:S of 600±300 and N:S of 200±100. Modern fish collagen typically has lower C:S ratios than mammalian collagen at 175±50 and N:S 60±20.

Only recently have $\delta^{34}S$ measurements become a common component of archaeological analysis, and little literature is available addressing the uptake and integration of sulphur into bone collagen in the human body. Amino acid analysis of collagen extracted from archaeological bones indicates usually about half of the methionine found in modern bone collagen remains, but can be much less (Richards et al.

2001). Collagen stable isotope values reflect the average diet of an individual a minimum of 10-15 years prior to death (Hedges et al. 2007).

The first major study to use CF-IRMS for measuring sulphur isotope ratios in archaeological bone collagen was that of Richards et al. (2001). This study measured $\delta^{34}S$ of 27 archaeological collagen samples from nine archaeological sites in Europe ranging in date from 6500 BC to 1300 AD. Seven modern samples were too contaminated by industrial pollutants to produce useful results. The authors suggested that C:S and N:S ratios should be used to verify the integrity of the collagen molecules. The study also used published amino acid sequences to determine that the amount of sulphur in bone collagen is 0.16%.

The authors compared $\delta^{13}C$ and $\delta^{34}S$ values and found the bone collagen samples from coastal sites (<20 km from the sea) all had marine $\delta^{34}S$ values (15.0‰ and above), but many did not have a $\delta^{13}C$ marine signature, indicating that $\delta^{34}S$ values can identify coastal inhabitants even if the individual did not consume significant amounts of marine protein. Their results indicate that dietary sources from different localities and the movement of humans or animals between regions could potentially be extrapolated. Of the samples from three inland sites in the study, both $\delta^{13}C$ and $\delta^{15}N$ values do not show marine signals, and the $\delta^{34}S$ values are consistent with bedrock values (around 6.0‰). Humans from one inland site (Bordesley) had $\delta^{34}S$ up to 13.7‰. The authors concluded that $\delta^{34}S$ measurements should be combined with $\delta^{13}C$ or $\delta^{15}N$ measurements for accurate interpretation of marine protein consumption in individuals living along the coast.

Privat et al. (2007) used $\delta^{34}S$ values to determine freshwater fish consumption. This study focused on archaeological material (including 10 humans) from the inland Late Bronze Age/Early Iron Age site of Chicha in the south-western Eurasian forest-steppe. There was a broad range of $\delta^{34}S$ values, from 4.2 to 29.5‰, with terrestrial fauna ranging

from 4.2 to 12.3‰ (besides ovicaprid samples, which were determined to have been raised elsewhere) and aquatic animals from 14.8 to 21.8‰ (excluding samples with low N:S). Human $\delta^{34}S$ ranged from 9.5‰ to 21.5‰, with an average of 16.3‰, indicating that fish was a dietary staple, although with such a wide range of values it is difficult to clearly determine the diet. This study also analyzed samples from the Eneolithic site of Bil'shivtse in the western Ukraine, but the $\delta^{34}S$ values overlapped between the freshwater and terrestrial ecosystems. Other studies (Craig et al. 2010; Hu et al. 2009; Nehlich et al. 2010) have also used sulphur isotopes along with carbon and nitrogen isotopes to differentiate between terrestrial and freshwater inputs into diets. Hu et al. (2009) analyzed a Palaeolithic (40 ka BP) human as well as several samples of local archaeological terrestrial and freshwater animals at the inland site of Zhoukoudian, China. The $\delta^{34}S$ of terrestrial animal sulphur was 7.6 ± 0.4‰, while the freshwater value was 5.5‰. The human had $\delta^{34}S$ of 4.1‰, indicating a diet based on freshwater resources, and correlating with the observed 1‰ decrease between diet and consumer collagen (Barnes and Jennings 2007; Richards et al. 2001).

Nehlich et al. (2010) analyzed $\delta^{34}S$ of 19 humans and a variety of animals from five Mesolithic/Neolithic sites in the Danube Gorges, and $\delta^{34}S$ differed between freshwater and terrestrial ecosystems by 8.7‰, allowing an easy distinction between the two environments. Two river water $\delta^{34}S$ values have been published, although not for the portion of the river flowing through the study area, with values of 8.3‰ and 16.8‰. Terrestrial animal $\delta^{34}S$ ranged from 2.7 to 5.3‰. This range is far narrower than that of several other studies (Fornander et al. 2008; Linderholm et al. 2008; Privat et al. 2007). The authors found that humans with low $\delta^{34}S$ also had low $\delta^{15}N$, indicating diets in which the protein component came largely from terrestrial animals, while individuals with high

$\delta^{34}S$ also had high $\delta^{15}N$ due to consumption of freshwater fish. Individuals with intermediate $\delta^{34}S$ ate mixed diets.

Craig et al. (2010) applied sulphur isotope analysis to an assemblage of Late Upper Palaeolithic (18,000 to 13,000 cal BP) human and animal remains in Italy. Eight of the nine humans had very consistent terrestrial animal-rich diets, as reflected in both sulphur and nitrogen isotopes (mean $\delta^{34}S = 12.4\pm1.5‰$), while one individual had an elevated $\delta^{15}N$ value indicating a diet that included marine or freshwater fish. Human $\delta^{34}S$ ranged from 10.4 to 13.7‰, while five animal specimens ranged from 12.2 to 15.0‰.

Even in regions with homogenous geology, sulphur isotope ratios can be of value in identifying immigrant individuals. Vika (2009) analyzed the remains of 12 Bronze Age individuals found in a mass grave in Thebes, Greece, along with several samples of local archaeofauna. Animal $\delta^{34}S$ ranged from 9.9‰ to 16.7‰, and humans ranged from 8.2‰ to 15.1‰, although the 8.2‰ value is an outlier. Excluding this individual, the human $\delta^{34}S$ values range between 12.8‰ and 15.1‰, with an average that is enriched by 1‰ compared with the animals. The female with a value of 8.2‰ is interpreted as an 'outsider.'

Linderholm et al. (2008) analyzed 19 (14 for $\delta^{34}S$) Viking Age individuals from a cemetery in Birka on the west coast of Sweden. Mean $\delta^{34}S$ of humans was $5.2\pm2.5‰$. Animals from Birka had a mean value of $-1.8\pm1.6‰$, while terrestrial animal values from a northern Swedish site had a mean $\delta^{34}S$ value of $5.6\pm9.5‰$, and a site from central Sweden had a mean of $11.1\pm0.6‰$. Variation in $\delta^{34}S$ is attributed to differing geographical origins of the individuals buried, as this was a site on a major trade route. Fornander et al. (2008) analyzed six Middle Neolithic human and 22 faunal samples from coastal Korsnäs, Sweden, where bedrock is dominantly granites and gneisses. Terrestrial fauna had $\delta^{34}S$ values between 6.1 and 13.1‰, while marine animals ranged from 10.2 to

19.8‰. Five human samples ranged from 12.1 to 13.1‰, while the sixth had a value of 16.7‰. Stable isotope evidence was in agreement with archaeological research as to the importance of seal in the diet.

In an analysis of archaeological marine and terrestrial fauna from northern Europe Craig et al. (2006) found notable differences in $\delta^{34}S$ and $\delta^{13}C$ values for six grey seals recovered from the same shell midden. The $\delta^{34}S$ values of these animals ranged from 10.7‰ to 17.4‰, and paired with $\delta^{13}C$ measurements indicate that three of the seals originated from the Baltic, while the other three are likely to have originated from the North Sea. The range of $\delta^{34}S$ in these marine mammals is surprising, especially the values which are far below the approximately 20‰ expected for marine creatures.

Sulphur isotope ratios have also been analyzed in other archaeological human tissues (for instance, hair: Fernández et al. 1999; Macko et al. 1999; and fingernails: Buchardt et al. 2007) to determine the origins of specific individuals based on diet.

In summary, Richards et al. (2001) analyzed samples from nine European sites, while the other studies looked at several samples from a few sites. No currently published studies have analyzed samples throughout a broad geographic region. Most studies analyzed both faunal and human bone collagen, and obtained a large range of values, with humans nearly always having a more restricted range of values. Within each site, values for "resident" humans (those likely sharing the same food sources) are usually remarkably close (Craig et al. 2010; Fornander et al. 2008; Nehlich et al. 2010; Richards et al. 2001). The $\delta^{34}S$ values in the Privat et al. (2007), Nehlich et al. (2010) and Hu et al. (2010) studies separated terrestrial from freshwater resources, allowing different components of human diets to be extrapolated. The fact that freshwater fish have the highest $\delta^{34}S$ values in two studies, yet the lowest in another, illustrates the great variation between freshwater environments throughout the world. The Craig et al. (2006) study also indicates that

marine $\delta^{34}S$ values may not be so consistently elevated throughout the world, and $\delta^{34}S$ in the same species of marine mammal may fluctuate greatly. The Vika (2009) and Linderhom et al. (2008) studies prove the utility of sulphur isotope analysis when applied to cemeteries or mass burials, even with only a limited understanding of regional $\delta^{34}S$ values. The samples from coastal areas in Scandinavia all have lower $\delta^{34}S$ values than coastal sites elsewhere, although those from the Baltic coastline are likely influenced by the low salinity of the Baltic due to mixing of freshwater run-off and open ocean.

Values for archaeological terrestrial fauna throughout Europe and Eurasia range from 2.7‰ to 17.6‰. Ovicaprids have the highest terrestrial animal values in the Vika (2009) and Privat et al. (2007) studies. Richards et al. (2001) also reported a value of 17.7‰ for one *Ovis aries* sample, which is the only ovicaprid found near the coast. *Canis familiaris* exhibit a wide range of $\delta^{34}S$ values in several studies (Craig et al. 2006; Fornander et al. 2008; Linderhom et al. 2008; Privat et al. 2007).

The "Sea Spray Effect" and Coastal Environments

"Sea spray" is the term applied to all marine aerosols formed from the action of breaking waves that are carried away from the sea by wind (de Leeuw 1999). Salt haze is a visible manifestation of this phenomenon, with the same sulphur isotope composition as seawater ($\delta^{34}S$ of +20‰) (Clayton 1972). There appears to be little or no fractionation when sea spray sulphate is incorporated into the atmosphere and rain (McArdle et al. 1998), although rainwater sulphate generally has lower $\delta^{34}S$ than seawater sulphate, primarily due to mixing in the atmosphere (see Krouse 1980 for a brief discussion). Marine organisms, consumers, plants, and animals from coastal areas have $\delta^{34}S$ values similar to ocean water, around +17 to +21‰ for oceanic primary producers and animals feeding in coastal areas (Kusakabe et al. 1976; Peterson & Fry 1987; Richards et al. 2001;

Wadleigh et al. 1994). Individuals living along the coast can therefore have enriched $\delta^{34}S$ values without consuming a substantial amount of marine protein (Richards et al. 2001; Robinson 1987). There is currently no consensus as to how far from the coast this applies, but it seems to be seasonally dependant and varies according to geographic location (Gong et al. 2002; McArdle et al. 1998; Nriagu & Coker 1978; Ohizumi et al. 1997). Obtaining studies that analyze a traverse from coast to inland in a "pristine" area is difficult, as atmospheric mixing between several sources is nearly always an issue. Modern anthropogenic contributions also render current aerosol data incompatible with analysis of archaeological material in more industrialized parts of the world.

Most $\delta^{34}S$ values measured in the atmosphere are a result of mixing from several sources such as marine aerosol, marine biogenic, anthropogenic, and terrigenous (volcanic and biogenic). Marine sulphate is carried inland by wind or brought down with precipitation and incorporated into soils. The other major marine sulphur contribution is biogenic emissions including dimethyl sulphide (DMS), produced by phytoplankton and rapidly oxidized to SO_2 (Calhoun et al. 1991; McArdle et al. 1998), with a mean $\delta^{34}S$ value of $+15.6\pm3.1$‰ measured over the South Pacific Ocean (Calhoun et al. 1991). Similar values have been obtained elsewhere, and sulphate derived from phytoplankton should have $\delta^{34}S$ values around 13 to 22‰ (McArdle et al. 1998). Biogenic sulphur production (both marine and terrestrial) is dependant on temperature, so varies seasonally (Ohizumi et al. 1997).

Wadleigh & Blake (1999) found that $\delta^{34}S$ values of epiphytic lichens in Newfoundland indicate point source pollution from local industrial factories (values around +4‰), and marine sulphate (values around +16‰) immediately along the coast. Further inland, values from 9 to 11‰ are thought to likely represent a "mixing" of marine

sulphur with anthropogenic sources. There was no evidence for long range transport of anthropogenic sulphate from North America (Wadleigh & Blake 1999).

Marine aerosols mixing with a non-marine component might explain why $\delta^{34}S$ values of coastal plants and animals are rarely as high as sea water. *Sphagnum* (peat moss) from two "pristine" (sparsely populated with no industrial history) coastal sites were sampled in Scotland and Ireland, and $\delta^{34}S$ values were both around 15‰, which indicates a mix of sea water sulphate (20‰) and a non-marine component (calculated to 10.7 and 12.3‰) (Novák et al. 2001). Similar results have been found for atmospheric sulphur in North America and Japan (Nakai & Jensen 1967). Long-term sampling at a remote coastal site in north-western South Africa (Brandt-se-Baai) determined that up to 8% of elemental sulphur concentrations measured are potentially attributed to anthropogenic combustion sources over 1400 km away, while 92% were attributable to natural sources (sea spray and oceanic DMS) (Formenti et al. 1999). This site was established in 1992 to record atmospheric conditions before a strip mine 4km away began operations, and to monitor dust generation once mining commenced. Samples for this case study were collected in 1996 and analyzed by proton-induced X-ray emission (PIXE).

"High" and "low" $\delta^{34}S$ values have been used to distinguish between coastal and inland samples in archaeology. It is assumed that coastal isotope values close to marine sulphate indicate influence of sea spray, while lower values from inland environments are too far from the coast to be affected by marine aerosols. Macko et al. (1999) analyzed samples of human hair and results differentiated between coastal and inland locations in South America and Egypt. The Egyptian Coptic mummy samples were removed from Egypt long ago, and unfortunately neither provenance nor distance from the sea is provided, only that they were "inland"; all had $\delta^{34}S$ lower than 10‰. The $\delta^{34}S$ values of Chinchorro mummies from two coastal sites in Chile (Morro and Maderas Enco) and one

inland (Azapa Valley, roughly 13 km from the coast) were also measured. The coastal Chilean mummies had $\delta^{34}S$ around 15‰ (with a low of 13.6‰ and a high of 16.5‰), while the inland site yielded three samples with $\delta^{34}S$ below 10‰ and one with $\delta^{34}S$ of 14.2‰. This individual also had marine $\delta^{13}C$ and $\delta^{15}N$, so is interpreted as a coastal immigrant, indicating the two regions had some interaction. The Azapa Valley site is located in the Atacama Desert, one of the driest in world, and the paucity of precipitation inhibits the transfer of marine aerosols to the soil.

The results from the Macko et al. (1999) study correlate well with those of Richards et al. (2001). In the latter study, $\delta^{34}S$ values at all four inland sites (distance from the sea not provided) range from 1.1‰ to 13.7‰, while $\delta^{34}S$ of samples recovered from five coastal sites (<20km from the sea) range from 15.0‰ to 22.2‰. All samples found along the coast had high $\delta^{34}S$.

Both Vika (2009) and Craig et al. (2010) analyzed animals and humans from the northern Mediterranean, from sites around 25km from the coast and situated on ancient marine limestone and dolomite. In Vika's study, herbivore $\delta^{34}S$ averaged 12.7‰ (range from 9.9‰ to 16.7‰, n=11), while the mean for humans was 13.3$\pm$1.7‰ (range from 12.8‰ to 15.1‰, n=11). Craig et al. (2010) reported values of 12.2‰ to 15.0‰ for animals (n=5) and 10.4‰ to 13.7‰ for human samples (n=8), within the range of those analyzed by Vika. The majority of $\delta^{34}S$ values from these two sites are lower than "marine" values observed by Richards et al. (2001) and Macko et al. (1999), and may indicate mixing of marine sulphate with biogenic terrestrial sulphur, or a contribution from the ancient marine bedrock. Values below 10‰ in archaeological material measured so far seem to indicate a terrestrial origin.

There seems to be no universally applicable definition for ranges of $\delta^{34}S$ values. Generally, anthropogenic and biogenic sources tend to have values around +4‰.

Volcanic and terrestrial biogenic sulphur have values similar to anthropogenic (Lein 1991; McArdle & Liss 1995). Continental sulphur seems to have a mean $\delta^{34}S$ value of around 3.3 to 4‰ (McArdle et al. 1998). Marine biogenic sulphur (primarily oxidized DMS) has values around 16‰ (Calhoun et al. 1991).

Marine sediments in tidal flats, lagoons, shallow bays, and estuaries may be significantly affected by dissimilatory sulphate reduction, leading to $\delta^{34}S$ values ranging from -10 to -20‰ (Nakai & Jensen 1967). Pore water sulphates have a wide range of values, and can be far more enriched or depleted than the water column depending on source and oxidation (Fry et al. 1982). These sediments may host a variety of benthonic plants and animals (grazers and filter feeders) that are found at various positions within the food web. Consequently, it is possible that animals and plants confined to lagoon and estuary-dominated coastal zones may have values that reflect bacterial transfer reactions to a greater extent than marine sea spray (Lamontagne et al. 2007).

Sulphur isotope analysis is particularly useful in estuarine and salt marsh environments due to the large difference between $\delta^{34}S$ values of marine sulphate and $\delta^{34}S$ depleted sulphide (possibly a 30-70‰ difference: Peterson & Fry 1987). Most terrestrial organic matter input has intermediate values, around 0 to 6‰ (Peterson & Fry 1987). Many marine primary producers, such as algae and seaweed (in addition to plankton) have $\delta^{34}S$ values around that of sea water (20.1 to 21.7‰: Lamontagne et al. 2007). Rooted halophytic plants can draw sulphides from anoxic sediments in estuaries and marshes which oxidize to sulphate within the plant (Carlson & Forrest 1982). At higher salinities more sulphate reduction occurs (Lamontagne et al. 2007), and sulphide in sediments has been observed to be on average 50% lighter than sulphate in pore waters (Peterson et al. 1986). In an estuarine study conducted in Australia (Lamontagne et al. 2007) $\delta^{34}S$ values of pelagic fish (2.5 to 13.0‰) appeared more similar to benthic components than anything

from the pelagic zone, and analysis of stomach contents confirmed that the majority of food came from the sea floor. Consumer values between those of plankton and C_4 marsh grasses have also been measured in Georgia (Peterson & Howarth 1987).

There are four major sulphur reserves available to halophytes through root uptake: seawater sulphate, bacterially produced sulphides (isotopically very light: Fry et al. 1982), porewater sulphate (wide range of values, from +9 to +20‰ and higher: Kaplan et al. 1963) in the sediment, and rainwater sulphate (+2 to +16‰: Chukrov et al. 1980; Jensen & Nakai 1961). Marsh grasses typically have low $\delta^{34}S$ values as their primary source of nutrients are the sulphides in the sediment (Peterson et al. 1985).

In areas where marine sulphate is the dominant source of sulphur (such as New Zealand: Kusakabe et al. 1976) it is possible to follow $\delta^{34}S$ values from the coast to inland, and even across islands (Kusakabe et al. 1976; Wadleigh & Blake 1999). Measuring the distance that marine aerosols penetrate inland is complicated in most other regions, and depends on wind strength and direction, precipitation, and mixing of sulphur sources.

CHAPTER 4: METHODOLOGY

Sample Selection

A total of 37 archaeological human samples and 33 archaeological animal samples were selected for analysis (Table 1). Seven samples of recent (historic to present day: Table 3) animal bone were also included to assess possible industrial contamination and act as a reference to the archaeological materials. The archaeological samples date to around 4500-2000 BP, so are assumed to be the bones of hunter-gatherers or potential dietary sources of these people. To test the validity of sulphur isotopes in distinguishing geologic terrain, a variety of samples were included from the Western Cape Province, along both the southern and western coasts to the Fold Belt Mountains inland. These regions are environmentally distinct (geology, climate, flora, fauna), and subsequently, the animals and humans in the area should show regional $\delta^{34}S$ signals (see Chapter 3). Proximity to the ocean is also an important factor. The human samples include individuals who consumed mostly terrestrial foods and others consuming marine foods based on previous $\delta^{13}C$ and $\delta^{15}N$ measurements. Nearly all bone material was already a part of the University of Cape Town's (UCT) collection and was housed in the Archaeology Department. Four additional archaeological samples were selected from the Iziko Museum of Cape Town to provide faunal data for a region in which only human samples were represented. Stable carbon and nitrogen isotope values have already been published for the majority of these samples, as well as ^{14}C dates on most of the humans. A few samples, primarily those from Hoffman's/Robberg Cave, are presented for the first time. Most of the human samples were not excavated by archaeologists, but either discovered by accident or before the days of meticulous documentation, providing little information concerning burial context. Most of the animal bone used in this study came from

excavations conducted by UCT, and ages were taken from the dates of the excavation units from which they derive. Preservation is typically excellent due to the burial context in shell middens and dry rock shelters. Only bone collagen (acid-insoluble bone protein) was used for this study.

All samples have a University of Cape Town Archaeometry Laboratory number (UCT), a Max Planck Institute for Evolutionary Anthropology number (S-EVA), and for the human samples, a museum accession number (i.e. SAM-AP or UCT-MED) given by the various physical anthropology departments at museums in South Africa. To facilitate comparison with other studies of these same skeletons, the museum accession number will be used when referring to human samples and the UCT lab number will be used for the animal specimens. A list of all relevant identification numbers for each sample is provided (Table 1).

Small chunks of bone (less than 0.5g) were cut from all specimens. These were cleaned in the Archaeometry Laboratory at UCT with a Dremel cutting tool and sandpaper to remove the outer layer of debris and contaminants. Only freshly exposed bone was used for analysis. Discolored and obviously degraded (e.g. chalky or crumbling) bone was avoided during sampling. Burned bone was also avoided, as pre-depositional burning has been found to accelerate collagen loss and may alter carbon and nitrogen isotope ratios (DeNiro 1985). When two representatives of the same animal species were analyzed from the same site, only diagnostic long bones were sampled to ensure individuals were not sampled twice.

An effort was made to include several recent (modern and historic) samples from the Western Cape region, as studies done elsewhere in the world indicate industrial pollution may render modern sulphur isotope results unusable (Faure 1977; Peterson & Fry 1987; Richards et al. 2001). This problem is thought to be much less of an issue for

Table 1: Sample Identification

MPI S-EVA #	UCT #	Museum Accession #	Animal[1,2]	Latin Name	Skeletal Element	Location	Age or 14C Date
9845	3250		Red Hartebeest	*Alcelaphus uselaphus*	Jaw	Elands Bay Cave	300-1600 BP
9846	3251		Red Hartebeest	*Alcelaphus buselaphus*		Elands Bay Cave	8000 BP
9847	5014		African Buffalo	*Syncerus caffer*		Nelson Bay Cave	1930±60 BP
9848	5003		African Buffalo	*Syncerus caffer*		Nelson Bay Cave	5860±70 to 5890 ±70 BP
9849	5017		African Buffalo	*Syncerus caffer*		Nelson Bay Cave	4520±60 BP
9850	3937		Angulate Tortoise	*Chersina angulata*	Carapace	Kasteelberg B	700-1300 BP
9851	3939		Angulate Tortoise	*Chersina angulata*	Carapace	Kasteelberg B	700-1300 BP
9852	3938		Angulate Tortoise	*Chersina angulata*	Carapace	Kasteelberg B	700-1300 BP
9853	13164		Helmeted Turtle	*Pelomedusa subrufa*	Carapace	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9854	13157		Large Seal		Scapula	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9855	13158		Cape Fur Seal	*Arctocephalus pusillus*	Scapula	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9856	13159		Steenbok	*Raphicerus campestris*	Mandible	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9857	13160		Rock Hyrax	*Procavia capensis*	Maxilla	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9858	13161		Dassie Fish	*Diplodus sargus capensis*	Premaxilla	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9859	13162		Galjoen	*Dichistius capensis*	Supraoccipital	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9860	13163		B Musselcracker	*Cymatoceps nasutus or C. cristiceps*	Premaxilla	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9861	13165		Whale		Rib?	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9862	13166		Cape Cormorant	*Phalacrocorax capensis*	Femur	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9863	13167		Gannet	*Morus capensis*	Humerus	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9864	13168		Gannet	*Morus capensis*	Humerus	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9865	13169		Sooty Shearwater	*Puffinus griseus*	Synsacrum	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9866	13170		Shy Albatross	*Thalassarche cauta*	R. Ulna Shaft	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9867	13171		Shy Albatross	*Thalassarche cauta*	R. Ulna Shaft	Hoffmans/Robberg Cave	ca. 4000-3000 BP
9868	880		Dune Mole Rat	*Bathyergus suillus*	Maxilla	Leipoldville	Recent
9869	4434		Red Hartebeest	*Alcelaphus uselaphus*		VV1- Voelvlei 1	420-2000 BP
9870	1670		Bushpig	*Potamochoerus porcus*	Maxilla	Knysna Forest	Recent

MPI S-EVA #	UCT #	Museum Accession #	Animal[1,2]	Latin Name	Skeletal Element	Location	Age or 14C Date
9871	5278		Ostrich	*Struthio camelus*	Femur	DeHoop	Recent
9872	2080		Grysbok	*Raphicerus melanotis*	Femur	Byneskranskop	Recent
9873	723		Rock Hyrax	*Procavia capensis*	Mandible	Aspoort	Recent
9874	719		Porcupine	*Hystrix africa-eaustralis*	Cranium	Doornbos	Recent
9875[3]	13172		Cow	*Bos taurus*	Radius	Oudepost	ca. 300 BP
9876	13173		Kingklip	*Genypterus capensis*	Vertebra	Hout Bay	Modern
9877	13174		Tortoise		Carapace	Elands Bay	8000 BP
9878	5605	A 1186	Human		Rib	Whitchers Cave	2880±60 BP
9879	5611	A 1184 VI	Human		R. Femur	Whitchers Cave	5120±70 BP
9880	5612	A 1184 VII	Human		R. Femur	Whitchers Cave	2750±60 BP
9881	5223	NMB 1273	Human		L. Rib	Matjes River	3050±60 BP
9882	5429	UCT-MED 214	Human		Tibia	Oakhurst	4900±60 BP
9883	5234	NMB 1704	Human		L. Femur	Plettenberg Bay	760±50 BP
9884	5609	A 1055	Human		Rib	Keurbooms River	1080±40 BP
9885[4]	5602	NMB not acc SS 2	Human		L. Rib	Matjes River	5370±70 BP
9886	5213	SAM-AP 1879	Human		Rib	Robberg, Knysna	3440±60 BP
9887	5218	UCT-MED 107	Human		R. Femur	Near Knysna	2290±50 BP
9888	5195	SAM-AP 4824 (B)	Human		R. Tibia	Tucker's Cave	2210±50 BP
9889	10851	NMB 1707	Human		Cranium	Plettenberg Bay	1394±24 BP
9890	12905	Noetsie 2	Human		Rib	Noetsie Burial #2	3190±40 BP
9891	12904	Noetsie 1	Human		Rib	Noetsie Burial #1	3800±40 BP
9892	1691	SAM-AP 4637	Human			Gordons Bay	3541±26 BP
9893	1683	SAM-AP 5041	Human			Melkbosch	2010±50 BP
9894	1684	SAM-AP 5040	Human			Bokbaai	3570±60 BP
9895	1053	UCT-MED 331	Human			Wyegang	2100±70 BP
9896	4443	UCT-MED 158	Human			Llandudno	3190±60 BP
9897	1730	SAM-AP 5091	Human			Yzerfontein	2830±50 BP
9898	1682	SAM-AP 5082	Human			Hout Bay	2150±60 BP
9899	1686	SAM-AP 6075	Human		Rib	Saldanha	1330±40 BP
9900	1679	SAM-AP 5095	Human			Saldanha	2660±70 BP
9901	4446	UCT-MED 220	Human		Rib	Bloubergstrand	2100±21 BP
9902	1051	UCT-MED 112	Human			Darling coast	4445±50 BP
9903	1898	SAM-AP 6149	Human			Melkbosch	1440±70 BP

MPI S-EVA #	UCT #	Museum Accession #	Animal[1,2]	Latin Name	Skeletal Element	Location	Age or 14C Date
9904	1211	SAM-AP 6052	Human		Juvenile Rib	Byneskranskop 3	2780±50 BP
9905	5666		Human		Juvenile L. Rib	Eland Cave	2145±50 BP
9906	5668	SAM-AP 6315	Human		Juvenile Rib	Watervals Rivier	1985±50 BP
9907	457/1314	SAM-AP 1449	Human		Rib	Clanwilliam	2230±100 BP
9908	1209	SAM-AP 6050	Human		Rib	Byneskranskop 3	1480±50 BP
9909	4442	UCT-MED 120	Human		Rib	Karbonkelberg	1960±50 BP
9910	3137		Human			Elands Bay	2670±80 BP
9911	1092	UCT-MED 373	Human			Elands Bay Cave	3835±50 BP
9912	5613	A 1184 VIII	Human		R. Femur	Whitchers Cave	4920±60 BP
14037[5]	13177		Bovid Size 2		Metapodial	Aspoort	Late Holocene
14038[5]	13178		Sm. Bovid		Second phalanx	Aspoort	Late Holocene
14039[5]	13179		Med. Bovid		Humerus	Aspoort	Late Holocene
14040[6]		KRF 2 D III LBA 2	Med. Bovid		Carapace	Klipfonteinrand	
14041[6]		KRF 2 OHBD 1	Tortoise		Carapace	Klipfonteinrand	
14042[6]		KRF 2 D OHBD 2	Tortoise		Radius	Klipfonteinrand	
14043[6]		KRF 2 EIVMBS 1	Med. Bovid		Metapodial	Klipfonteinrand	
14044[7]	13180		Bovid		Ulna	Hout Bay	Pre-colonial, post 2000
14045[7]	13181		Sm. Bovid		Metapodial	Hout Bay	Pre-colonial, post 2000
14046[7]	13182		Lg. Bovid		Rib	Hout Bay	Pre-colonial, post 2000
14047[7]	13183		Sm. Bovid		Rib	Hout Bay	Pre-colonial, post 2000

The Museum Accession Number is the number of the skeleton in the institution where it is housed. UCT-MED: Dept. of Human Biology, UCT; NMB: National Museum, Bloemfontein; SAM-AP: Iziko-S African Museum, Cape Town

Notes:

1. Human skeletons have been dated individually by radiocarbon analysis of bone collagen, while the ages of faunal specimens are taken from the dates of the excavation units from which they derive.
2. Faunal specimens from Hoffman's/Robberg Cave (H/RC) were recovered in 2008 from disturbed deposits in square R23
3. Sample S-EVA 9875 was found at a Dutch East India Company outpost
4. Sample S-EVA 9885/NMB ss2 not accessioned, referred to in text as UCT 5602
5. Samples S-EVA 14037, 14038, and 14039 came from excavations reported by Smith & Ripp, SAAB 1978
6. Samples S-EVA 14040, 14041, 14042, 14043 are housed in the Iziko-S African Museum, Cape Town
7. Samples S-EVA 14044, 14045, 14046, and 14047 came from 1995 excavations by ACO at Fisherman's World

the Western Cape of South Africa, as the level of industrial activity is far less than Europe and North America, and many of the samples come from sheltered cave sites. Seven recent samples (dating from the last 25 years) were selected from throughout the region to determine whether modern contaminants are an issue.

The edible tissue of one modern limpet (*Patella oculus*) and Mediterranean mussel (*Mytilus galloprovincialis*, n=7) were also sampled. These shellfish were collected from Kalk Bay in early winter. Although the Mediterranean mussel is an invasive species that would not have been available in this area in the past, shellfish was an important inclusion to this study as it was a staple dietary item for prehistoric coastal inhabitants. Isotope results unfortunately were not available by the time of submission of this thesis.

Collagen Extraction and Stable Carbon and Nitrogen Isotope Analysis at UCT

$\delta^{13}C$ and $\delta^{15}N$ of most specimens had previously been measured in the Stable Isotope Laboratory in the Archaeology Department at the University of Cape Town. Specimens analyzed for the first time as part of this thesis were prepared according to the standard collagen extraction protocol used in this lab (Sealy & van der Merwe 1986; Sealy 1997). After surface cleaning, as previously described, small chunks of bone were weighed, then placed in approximately 1-2% HCl (~1.4ml concentrated HCl diluted with about 130 ml distilled water) at room temperature. This process removes carbonates, phosphates, and fulvic acids. The acid was changed every other day, and decalcification took seven to ten days. Decalcification was complete when the samples were translucent and flexible. The samples were rinsed multiple times in distilled water, then treated for 8-24 hours with 0.1M NaOH to remove base-soluble contaminants such as humic acids and lipids. The time the samples were left in the base depended upon the preservation and contamination of the samples. After removal, the samples were soaked in distilled water

for another week (with occasional changes of water) until the pH returned to 7, then freeze-dried. Samples were left loosely covered overnight before being re-weighed and collagen yields calculated. According to Schwarcz & Schoeninger (1991), if the dry weight of the collagen is greater than 25% of the original bone weight it is not fully demineralized.

Samples of three archaeological fish bones from Hoffman's/Robberg Cave (UCT 13161, 13162, and 13163) dissolved completely during the first attempt at collagen extraction. They were soaked in dilute HCl for 14 days, then in NaOH for 24 hours, as all three samples were very dark and remained somewhat hard throughout the course of the treatment. By the time they came out of the NaOH, all samples were very small and delicate. After two days in distilled water, nothing remained of them. All three were re-sampled and treated with more dilute (<1ml) HCl for 5-6 days, with only one acid change. They were then soaked in 0.1 M NaOH for 8 hours. Upon removal from the base, all samples appeared to be more intact than the first attempt. Even with the gentle extraction procedure the collagen yields were low (4.0%, 8.2%, and 3.5%, respectively). As other samples from Hoffman's/Robberg Cave gave much larger collagen yields, the small, thin size of the fish samples and the compositional differences between fish bone and mammal and bird bone may have led to more rapid degradation.

Upon removal from the freeze-drier, four samples of archaeological bird collagen (UCT 13167, UCT 13168, UCT 13170, and UCT 13171) appeared shriveled and yellow and were quite hard. Although they seemed fully decalcified, they were placed in dilute HCl (<1 ml) for five additional days followed by five days in distilled water, and freeze-drying. The color and texture remained unusual, but the samples were included in analysis.

Stable carbon and nitrogen isotope ratios were measured at the Archaeometry Lab in the Department of Archaeology, University of Cape Town. Approximately 0.65mg of collagen was weighed into tin capsules, and then combusted to N_2 and CO_2 in an automated carbon and nitrogen analyzer (Carlo Erba) coupled to a continuous-flow isotope ratio mass spectrometer (Finnigan-MAT 252). Laboratory standards of chocolate, valine, and seal bone were included in each run. These are regularly measured against international standards IAEA N1 and N2, and NBS 21. Instrument precision errors (σ) on repeated measurements of homogenous material were less than $\pm$0.06‰ for $\delta^{15}N$ and $\pm$0.1‰ for $\delta^{13}C$. Results are reported with $\delta^{15}N$ relative to atmospheric nitrogen (AIR) and $\delta^{13}C$ relative to Vienna Pee Dee Belemnite (VPDB).

Collagen Extraction at MPI-EVA

In the Stable Isotope Laboratory of the Max Planck Institute for Evolutionary Anthropology, ultra-filtration is standard procedure for preparing collagen from bone samples for isotopic analysis. It is particularly effective at removing contaminants, which is crucial for sulphur isotope studies due to the limited amount of sulphur in bone collagen and the high possibility of contamination. Extraction protocol follows a modified Longin method (as explained in Richards & Hedges 1999).

Bone samples prepared and analyzed at MPI-EVA were between 500-1000mg in weight, an amount that should produce the 10mg of collagen required for analysis if the bone is well preserved. As most specimens used for this study were very well preserved, enough collagen was obtained to measure sulphur isotopes in duplicate for all but nine of the samples and carbon and nitrogen isotopes in duplicate for all but 24 samples.

Once at the MPI-EVA the bone samples were given an S-EVA number and crushed to fit into a 13ml test tube. The bone weight was recorded before the test tube was

filled with approximately 10ml of 1.0M HCl at room temperature. This concentration of acid was chosen due to time constraints and the thickness and preservation of the samples. The samples were left at room temperature for 48 hours, covered loosely with tin foil. Starting the process at room temperature helped to decalcify the samples relatively rapidly. After two days the acid was removed with a pipette and replaced with a refrigerated 0.5M HCl solution. Cold acid was used to reduce the rate of the reaction. The samples were again covered with tin foil to prevent contamination and most samples were left at room temperature. The smaller samples, or ones nearing complete decalcification, were put into the refrigerator at 4°C. Every two days the acid was replaced (using cold 0.5M HCl) until all samples were fully decalcified. This process took between 6 and 20 days, depending on the size and quality of the bone fragments. Decalcification was determined by the flexibility and translucence of the sample and lack of effervescence.

Once demineralized, the samples were rinsed three times with deionized water to neutralize the pH. The test tubes were filled to the top (approximately 13ml) with deionized water (to prevent oxidation), three drops of 0.5M HCl were added to each tube to achieve a pH of 3, and the tubes were sealed. The samples were then covered with tin foil and placed in a Rotilabo Block Heater H250 at a temperature of 70°C. At around 58°C Type 1 collagen begins to break down, so 70°C ensures that the collagen dissolves completely. The samples were left to gelatinize in the heater block for 48 hours, and were then ready for ultra-filtration.

The samples were first filtered through Ezee filters (5-8 microns, Elkay Laboratories Ltd.) to remove any insoluble residues. To remove manufacture contaminants, such as carbon, the Amicon Ultra-4 Millipore 30 kDa filter centrifuge tubes were cleaned by filing with 0.5M NaOH and then centrifuged (Thermo Scientific Megafuge 1.0) for 15 minutes. The NaOH was discarded, and the tubes then filled with

deionized water and centrifuged twice, for 15 minutes each time. The 'cleaned' tubes were then filled with the gelatinized collagen and centrifuged at 2500 rpm for varying amounts of time, depending on the quality (well preserved material takes longer). After each rotation cycle the <30 kDa fractions were removed and saved temporarily to ensure enough sample for a duplicate run if any of the samples failed to yield enough of the long collagen chains; then the tubes were topped up with more gelatinized collagen. Eventually only the >30 kDa chains remained, along with the remaining insoluble residue. Care was taken to pipette out only the gelatinized collagen, which was placed in a clean test tube.

The tubes containing the >30 kDa fractions were covered with parafilm and left at -28°C overnight to ensure they were frozen solid, then freeze dried for 48 hours. Upon removal from the freeze drier the samples were immediately weighed and transferred to a 1.5 ml micro-tube and collagen yields were calculated.

Two samples (UCT 9869 and 9877) failed to produce enough collagen for a single run. One sample (UCT 13162) yielded only 4 mg of collagen. As it is a fish, only 6 mg are needed. Seven other samples (UCT 5017, 3937, 3938, 13160, 13166, 13172, and 5195) were a few milligrams short of enough collagen for a duplicate run. To allow these seven samples to be run in duplicate and UCT 13192 to be run once, the 10-30 kDa fractions were ultra-filtered following the same procedure, but using Amicon Ultra-4 Millipore 10 kDa filters. This material was added to the 30 kDa fraction for the duplicate runs (and single run for UCT 13162).

Preparation for IRMS Analysis

Samples for sulphur isotope analysis were weighed out, in duplicate, into 5 x 12mm tin capsules and topped with 1mg V_2O_5 to catalyze combustion and maintain consistency (Morrison et al. 2000; Nehlich & Richards 2009). Optimal sample weights

were 10mg of collagen for mammals, birds, and reptiles, and 6mg of collagen for fish. Combustion takes place in a Heka Euro Vector elemental analyzer at 1010˚C and the resulting gas is reduced over ~800˚C copper to minimize the quantity of SO_3 (Giesemann et al. 1994; Kester et al. 2001; Ueda & Krouse 1986; Nehlich & Richards 2009). The resultant gases are then transported under a helium flux of ~95ml/min to a Poropak 0.8m GC column (at 84˚C) and separated (Yun et al. 2005), prior to channeling with a ConFlo III into the Thermo-Finnigan Delta V Plus mass spectrometer (Nehlich & Richards 2009). The CO_2 and N_2 gasses are diluted with helium gas and consequently only SO and SO_2 gasses are analyzed at masses 48, 50, 64, and 66 (Nehlich & Richards 2009). Once acquired, the $\delta^{34}S$ values are measured against a sulphur gas standard and corrected for oxygen isotope mass variations (Coleman 2004; Fry et al 2002).

A set of international inorganic (NBS127, S1, S2, S3, and SO-5) and organic (NIST bovine liver 1577b and IVA protein casein) standards were analyzed daily. The average standard deviation (σ) for thirteen repeats was 0.13‰. All results are reported in units per mil (‰) and are expressed relative to VCDT.

For carbon and nitrogen isotope analysis, 0.5mg of collagen was weighed out in duplicate for each sample and placed in a 6 x 4mm tin capsule. Samples were combusted in a Flash EA 2112 coupled to a Delta XP (Thermo-Finnigan). Once again, each sample was analyzed in a separate run than its duplicate. The standard deviation of the Methionine standard (average of seven daily measurements) was better than 0.12‰ for $\delta^{13}C$ and 0.06‰ for $\delta^{15}N$; and for the NBS Liver 1577b standard, 0.05‰ for $\delta^{13}C$ and 0.04‰ for $\delta^{15}N$ on all but one day. This particular run of 20 samples resulted in a standard deviation of 0.52‰ for $\delta^{13}C$, with values for $\delta^{15}N$ within the previously stated range. Results are expressed relative to VPDB for $\delta^{13}C$ and AIR for $\delta^{15}N$.

CHAPTER 5: RESULTS

Collagen Quality Assessment

The collagen yields, C, N, and S elemental ratios, and stable isotope values for all samples prepared and analyzed at the MPI-EVA are presented in Table 2. Collagen yields range from 0.8% to 8.8% by weight. Fresh modern bone contains about 22% collagen by weight (van Klinken 1999), but ultra-filtration reduces collagen yield, so that a value of 5% by weight typically indicates well preserved material (Jørkov et. al 2007). Nearly all collagen extracts had atomic C:N ratios between 2.9 and 3.6. Only four samples had higher C:N ratios: UCT 4434, a red hartebeest; UCT 13173, a modern kingklip; UCT 13174, a tortoise (dating to 8000 BP); and UCT 5666, a human rib. Samples UCT 4434 and UCT 13174 had collagen yields below 1%, and were excluded from the study as they contained insufficient material for sulphur isotope analysis. UCT 13173 also had a relatively low collagen yield (1.9%) and very high sulphur content (1.12%, when the expected value should be between 0.40 - 0.85% per Nehlich & Richards 2009). The sample had C:S and N:S of 113 and 28, respectively, below the range expected for intact modern fish collagen. This sample has also been excluded from the study. Human sample UCT 5666 yielded 5.1% collagen which contained 52.1% carbon, clearly signaling contamination with extraneous carbon. As a result, its C:N ratio was high (4.84), although the sulphur content (0.23%) was within the normal range, as were C:S and N:S at 614 and 127, respectively. The collagen extract prepared at MPI-EVA was dark brown in color. Collagen extracted at UCT, according to the methods described in Chapter 4 including treatment with sodium hydroxide, was whitish in color and had C:N of 3.69. This specimen was excavated from a very organic-rich archaeological context

Table 2: Stable Carbon, Nitrogen, and Sulphur Isotope Data

UCT #	Museum Accession #	Animal	Location	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	$\delta^{34}S$ ‰	Amount %S	C:N atomic	C:S atomic	N:S atomic	Collagen Yield %
3250		Red Hartebeest	Elands Bay Cave	-17.4	11.2	16.2	0.27	3.25	469	144	5.2
3251		Red Hartebeest	Elands Bay Cave	-20.1	8.5	16.7	0.20	3.26	620	190	4.2
5014		African Buffalo	Nelson Bay Cave	-12.8	5.3	18.9	0.23	3.23	514	159	4.0
5003		African Buffalo	Nelson Bay Cave	-11.9	4.6	18.7	0.19	3.20	691	216	3.1
5017*		African Buffalo	Nelson Bay Cave	-12.8	4.5	17.9	0.18	3.25	652	200	3.5
3937*		Angulate Tortoise	Kasteelberg B	-21.4	8.9	16.9	0.18	3.24	854	264	2.3
3939		Angulate Tortoise	Kasteelberg B	-18.9	6.2	17.2	0.17	3.22	651	202	4.7
3938*		Angulate Tortoise	Kasteelberg B	-21.9	8.7	17.7	0.18	3.27	661	202	2.5
13164		Helmeted Turtle	Hoffmans/Robberg Cave	-23.3	3.1	17.1	0.25	3.21	491	153	4.8
13157		Large Seal	Hoffmans/Robberg Cave	-11.0	15.2	15.5	0.24	3.11	517	166	3.9
13158		Cape Fur Seal	Hoffmans/Robberg Cave	-14.4	13.6	16.4	0.24	3.15	538	171	5.1
13159		Steenbok	Hoffmans/Robberg Cave	-19.6	6.1	20.2	0.45	3.26	262	80	4.3
13160*		Rock Hyrax	Hoffmans/Robberg Cave	-20.4	6.6	17.4	0.24	3.21	503	157	2.2
13161		Dassie fish	Hoffmans/Robberg Cave	-11.5	13.8	17.6	0.61	3.22	185	57	0.8
13162*		Galjoen	Hoffmans/Robberg Cave	-11.9	12.5	16.7	0.51	3.31	237	71	0.8
13163		B Musselcracker	Hoffmans/Robberg Cave	-12.5	15.6	15.7	0.52	3.22	226	70	0.9
13165		Whale	Hoffmans/Robberg Cave	-20.7	6.4	15.2	0.23	3.22	529	164	4.2
13166*		Cape Cormorant	Hoffmans/Robberg Cave	-12.3	16.2	17.2	0.29	3.27	420	129	4.9
13167		Gannet	Hoffmans/Robberg Cave	-11.8	15.8	16.7	0.30	3.29	416	126	4.1
13168		Gannet	Hoffmans/Robberg Cave	-11.4	15.9	16.9	0.31	3.23	399	124	5.2
13169		Sooty Shearwater	Hoffmans/Robberg Cave	-13.9	16.9	17.5	0.30	3.29	414	126	5.9
13170		Shy Albatross	Hoffmans/Robberg Cave	-16.7	15.0	16.2	0.31	3.18	393	123	6.4
13171		Shy Albatross	Hoffmans/Robberg Cave	-16.9	15.4	15.7	0.27	3.19	431	135	4.9
880		Dune Mole Rat	Leipoldville	-20.3	14.3	14.7	0.32	3.30	367	111	4.1
[4434]		Red Hartebeest	VV1- Voelvlei 1	-13.3	7.3			3.73			0.2
1670		Bushpig	Knysna Forest	-20.5	8.1	16.3	0.23	3.24	528	163	6.2
5278		Ostrich	DeHoop	-23.0	5.5	13.9	0.32	3.28	371	113	7.3
2080		Grysbok	Byneskranskop	-22.4	5.0	16.2	0.33	3.33	363	109	4.6
723		Rock Hyrax	Aspoort	-19.2	16.6	11.3	0.26	3.25	476	147	7.8
719		Porcupine	Doornbos	-19.5	12.7	12.9	0.23	3.18	560	176	8.8

UCT #	Museum Accession #	Animal	Location	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	$\delta^{34}S$ ‰	Amount %S	C:N atomic	C:S atomic	N:S atomic	Collagen Yield %
13172*		Cow	Oudepost	-19.4	8.2	18.0	0.33	3.27	356	109	3.9
[13173]		Kingklip	Hout Bay	-14.5	15.3	14.4	1.12	4.03	113	28	1.9
[13174]		Tortoise	Elands Bay	-22.6	10.7			3.96			0.1
5605	A 1186	Human	Whitchers Cave	-16.4	8.2	17.0	0.18	3.22	661	206	3.7
5611	A 1184 VI	Human	Whitchers Cave	-15.4	10.3	16.3	0.19	3.23	625	194	4.3
5612	A 1184 VII	Human	Whitchers Cave	-15.0	9.6	16.1	0.21	3.15	505	161	4.2
5223	NMB 1273	Human	Matjes River	-15.2	12.3	18.0	0.42	3.20	288	90	4.8
5429	UCT-MED 214	Human	Oakhurst	-15.2	9.5	17.2	0.25	3.27	485	148	1.9
5234	NMB 1704	Human	Plettenberg Bay	-11.5	9.7	16.9	0.23	3.22	479	149	5.4
5609	A 1055	Human	Keurbooms River	-14.4	12.1	13.2	0.22	3.19	526	165	8.1
5602	NMB not acc SS 2	Human	Matjes River	-13.6	14.4	15.4	0.18	3.32	662	200	4.1
5213	SAM-AP 1879	Human	Robberg, Knysna	-11.4	17.8	17.2	0.31	3.24	398	123	5.4
5218	UCT-MED 107	Human	Near Knysna	-11.5	17.5	14.8	0.22	3.21	526	164	5.3
5195*	SAM-AP 4824 (B)	Human	Tucker's Cave	-14.6	14.5	14.8	0.23	3.24	530	164	3.2
10851	NMB 1707	Human	Plettenberg Bay	-14.9	10.8	14.5	0.24	3.17	510	161	5.4
12905	Noetsie 2	Human	Noetsie Burial #2	-14.4	12.1	13.7	0.20	3.23	589	182	5.1
12904	Noetsie 1	Human	Noetsie Burial #1	-12.7	16.1	13.8	0.19	3.19	639	200	3.6
1691	SAM-AP 4637	Human	Gordons Bay	-17.2	10.8	16.0	0.19	3.26	627	192	5.8
1683	SAM-AP 5041	Human	Melkbosch	-18.1	10.2	17.1	0.24	3.25	494	152	3.0
1684	SAM-AP 5040	Human	Bokbaai	-17.8	11.6	16.5	0.18	3.22	632	196	5.3
1053	UCT-MED 331	Human	Wyegang	-18.5	13.1	16.4	0.22	3.25	558	172	3.5
4443	UCT-MED 158	Human	Llandudno	-11.5	14.2	13.3	0.20	3.28	674	206	5.5
1730	SAM-AP 5091	Human	Yzerfontein	-14.4	13.0	14.5	0.20	3.25	647	199	7.3
1682	SAM-AP 5082	Human	Hout Bay	-11.5	15.7	13.3	0.22	3.18	508	160	6.6
1686	SAM-AP 6075	Human	Saldanha			14.8	0.22				5.5
1679	SAM-AP 5095	Human	Saldanha	-12.8	15.7	14.3	0.22	3.24	566	175	3.7
4446	UCT-MED 220	Human	Bloubergstrand	-11.8	16.4	13.2	0.21	3.20	574	179	6.7
1051	UCT-MED 112	Human	Darling coast	-12.0	17.9	12.9	0.20	3.25	592	182	4.8
1898	SAM-AP 6149	Human	Melkbosch	-14.5	13.5	16.4	0.23	3.24	524	162	6.2
1211	SAM-AP 6052	Human	Byneskranskop 3	-15.7	12.1	17.3	0.21	3.26	573	176	7.3
5666		Human	Eland Cave	-20.8	13.8	16.3	0.23	4.84	614	127	5.1
5668	SAM-AP 6315	Human	Watervals Rivier	-18.7	15.5	16.9	0.23	3.23	513	159	6.6

UCT #	Museum Accession #	Animal	Location	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	$\delta^{34}S$ ‰	Amount %S	C:N atomic	C:S atomic	N:S atomic	Collagen Yield %
457/1314	SAM-AP 1449	Human	Clanwilliam	-17.6	14.7	16.8	0.34	3.27	352	108	5.1
1209	SAM-AP 6050	Human	Byneskranskop 3	-14.2	12.5	15.7	0.23	3.24	549	169	7.4
4442	UCT-MED 120	Human	Karbonkelberg			14.0	0.20				5.1
3137		Human	Elands Bay	-11.8	13.9	14.0	0.23	3.23	528	163	5.7
1092	UCT-MED 373	Human	Elands Bay Cave	-13.5	16.1	13.1	0.21	3.23	585	181	5.8
5613	A 1184 VIII	Human	Whitchers Cave			15.5	0.18				3.8
13177		Bovid Size 2	Aspoort	-17.1	13.2	12.8	0.21	3.22	608	189	2.0
13178		Sm. Bovid	Aspoort	-18.6	7.5	15.3	0.19	3.26	612	188	2.0
13179		Med. Bovid	Aspoort	-18.4	10.2	13.3	0.25	3.23	491	152	1.7
	KRF 2 D III LBA 2	Med. Bovid	Klipfonteinrand	-18.6	12.7	17.3	0.25	3.39	439	129	1.0
	KRF 2 OHBD 1	Tortoise	Klipfonteinrand								0.4
	KRF 2 D OHBD 2	Tortoise	Klipfonteinrand								0.0
	KRF 2 EIVMBS 1	Med. Bovid	Klipfonteinrand	-20.0	11.4	16.4	0.20	3.22	601	186	1.9
13180		Bovid	Hout Bay	-12.1	7.4	12.3	0.18	3.22	675	209	2.8
13181		Sm. Bovid	Hout Bay	-17.9	9.3			3.25			1.2
13182		Lg. Bovid	Hout Bay	-11.2	7.6	8.5	0.21	3.20	580	181	5.4
13183		Sm. Bovid	Hout Bay	-16.9	8.7			3.39			1.5

*Asterisk indicates samples that required the addition of the 10 kDa fraction
[…] brackets indicate samples that have been excluded from the study

(Sealy et al. 2000) and was clearly contaminated with humics which were largely removed by the UCT treatment, but not by the MPI-EVA protocol which did not include treatment with sodium hydroxide (similar results were observed in Jørkov et. al 2007 with other material). The $\delta^{13}C$ value of the collagen extracted at MPI-EVA is therefore likely to be less reliable than that prepared at UCT, but since there is no indication of sulphur contamination, the $\delta^{34}S$ value should be reliable. The three archaeological fish specimens (UCT 13161, 13162, and 13163) from which it was difficult to extract collagen at UCT (see Chapter 4) produced collagen yields at MPI-EVA of below 1%. Although little collagen was available, these samples were analyzed (two in duplicate). C:N, C:S, and N:S ratios were acceptable and the $\delta^{34}S$, $\delta^{13}C$, and $\delta^{15}N$ values were therefore included in this study.

Sulphur contents for all samples included in the study ranged from 0.17% to 0.45% in bird, reptile, and mammalian collagen, and 0.51% to 0.61% in fish collagen. The mean for humans is 0.22±0.03% (n=34), 0.24±0.05% for the mammals and birds (n=33) and 0.55±0.06% for fish (n=3). These values compare well with those reported by Nehlich and Richards (2009): 0.28±0.07% for modern mammals and birds and 0.63±0.08% for modern fish. Only two samples: NMB 1273 (a human) and UCT 13159 (an archaeological steenbok) are outliers with significantly higher sulphur contents (0.42 and 0.45%S, respectively). Nehlich and Richards also included outliers with higher sulphur contents in their data set, and these values are within the range they report.

Based on amino acid composition, modern mammalian and bird bone collagen has C:S of 600±300, but most archaeological samples have lower ratios (Nehlich & Richards 2009). Atomic C:S in mammal, reptile, and bird bones measured in this study range from 262 to 854, with only two samples (UCT 13159 and NMB 1273, which also have high sulphur wt%) having slightly lower ratios. Nehlich & Richards (2009) suggest that atomic

N:S should be in the range of 200±100. N:S in these samples ranges from 80 to 264, with the two previously mentioned samples having the lowest values. Looking at humans alone, C:S ranged from 352 to 674, with a mean of 556, and N:S from 108 to 206, with a mean of 170.

As reported by Nehlich & Richards (2009), atomic C:S ratios for fish bone collagen are expected to be 175±50, with N:S of 60±20. Despite the low collagen yields, the three archaeological fish (UCT 13161, UCT 13162, and UCT 13163) all have atomic ratios that fall within the expected ranges (185, 237, and 226 for C:S; and 51, 71, and 70 for N:S).

Table 3 displays the percent sulphur, C:N, C:S, and N:S ratios for the seven modern animals. Six yielded enough material for analysis in duplicate of all three isotopes, and these have $\delta^{34}S$ values similar to those of the archaeological specimens, and atomic ratios within the expected ranges. The percentages of sulphur in the collagen samples also lie within the 95% confidence interval for archaeological specimens as defined by Nehlich & Richards (2009). In all respects the "recent" bones appear very similar to the samples 2000-4000 years old, with no sign of industrial contamination. This is as expected, given the low level of modern industrial activity in the region, and thus analysis of contemporary animals can be used in developing a sulphur isotope map of the region, to supplement measurements on archaeological specimens.

Table 3: Recent Material

UCT #	Species	Location	S Amount [%]	C:N	C:S	N:S
880	Dune Mole Rat	Leipoldville	0.32	3.30	367	111
1670	Bushpig	Knysna Forest	0.23	3.24	528	163
5278	Ostrich	DeHoop	0.32	3.28	371	113
2080	Grysbok	Byneskranskop	0.33	3.33	363	109
723	Rock Hyrax	Aspoort	0.26	3.25	476	147
719	Porcupine	Karoo	0.23	3.18	560	176
13173	Kingklip	Hout Bay	1.12	4.03	113	28

Eight samples (marked with an asterisk in Table 2) required the addition of the 10 kDa fraction, seven for a duplicate ('B') run, and one sample (UCT 13162) for a single ('A') run. In every case, the 10 kDa ultra-filtered residues had a lower sulphur weight percent than the 30 kDa fraction, but the differences were inconsistent and never greater than 0.07% (UCT 3937); and slightly higher C:S and N:S ratios. The percentages of carbon and nitrogen were also lower in the 10 kDa fractions. When all "A" and "B" runs were averaged, the seven samples met all preservation criteria.

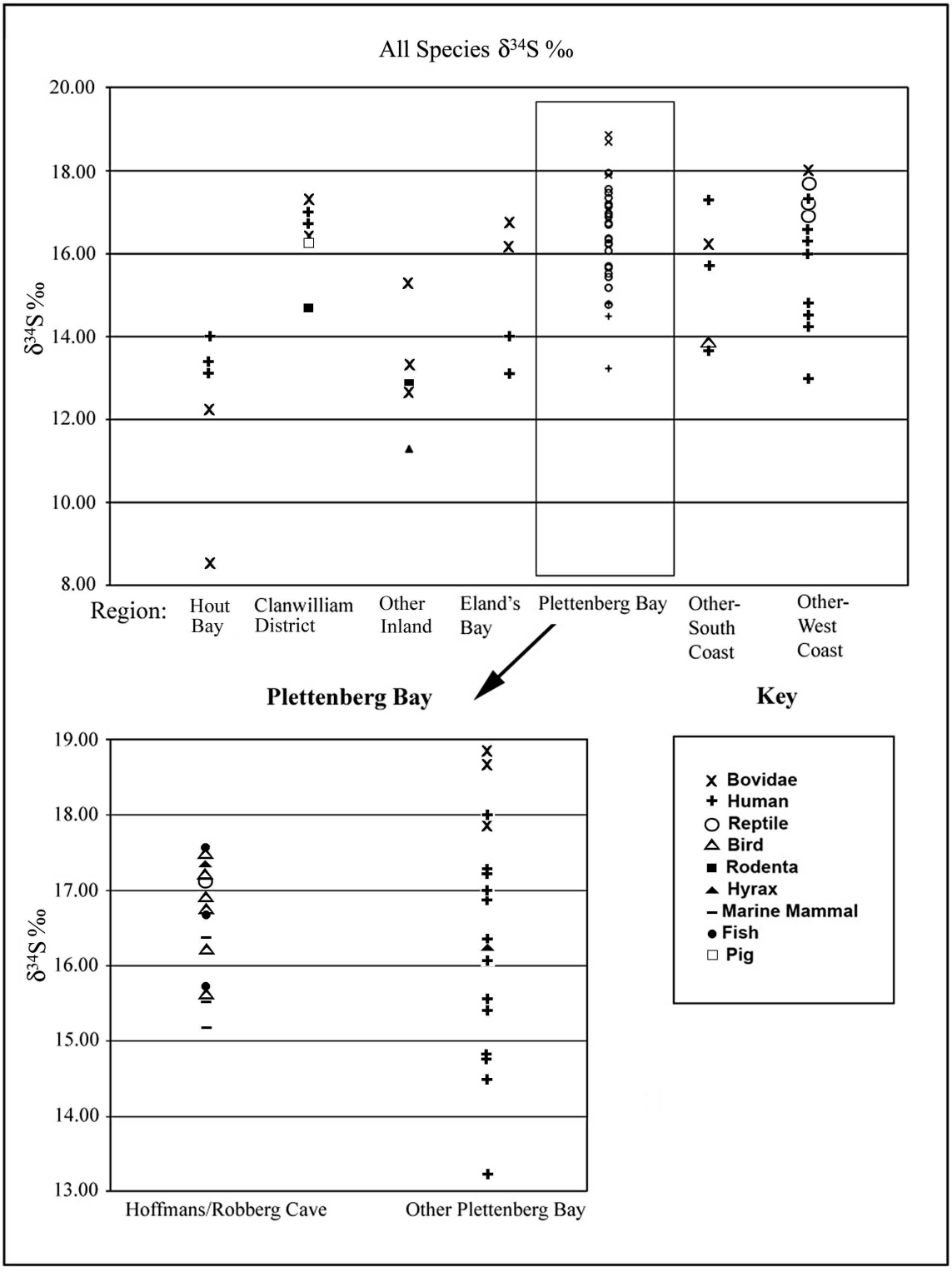
Sulphur Stable Isotope Values of Animal Samples

The $\delta^{34}S$ values range from 8.5‰ to 20.2‰ for all species in the study (Table 2), although the highest value (20.2‰ for the archaeological steenbok UCT 13159) should be regarded with caution, since this sample had a high sulphur content of 0.45%. Figure 5 displays the values in each geographic region.

The $\delta^{34}S$ values of the faunal samples (excluding UCT 13159) range from 8.5‰ to 18.9‰. The six lowest values derive from inland samples and the samples from Hout Bay. The higher values include animals from both south and west coasts. Interestingly, Bovidae specimens yielded the highest and lowest $\delta^{34}S$ values seen in this study, although values for multiple bovids from the same site tend to cluster.

The 18 animal samples from the south coast sites of Hoffman's/Robberg Cave and Nelson Bay Cave (located on the Robberg Peninsula in Plettenberg Bay) are the largest group of faunal samples from one area. Their $\delta^{34}S$ values range from 15.2‰ to 18.9‰ (20.2‰ if UCT 13159 is included), all within the range seen for coastal dwellers in previous studies (Macko et al. 1999; Richards et al. 2001). Some of the lowest $\delta^{34}S$ values of the area come from marine animals: 15.2‰ and 15.5‰ for the whale and a seal, respectively. The other Cape Fur Seal has a slightly higher value of 16.4‰. The three

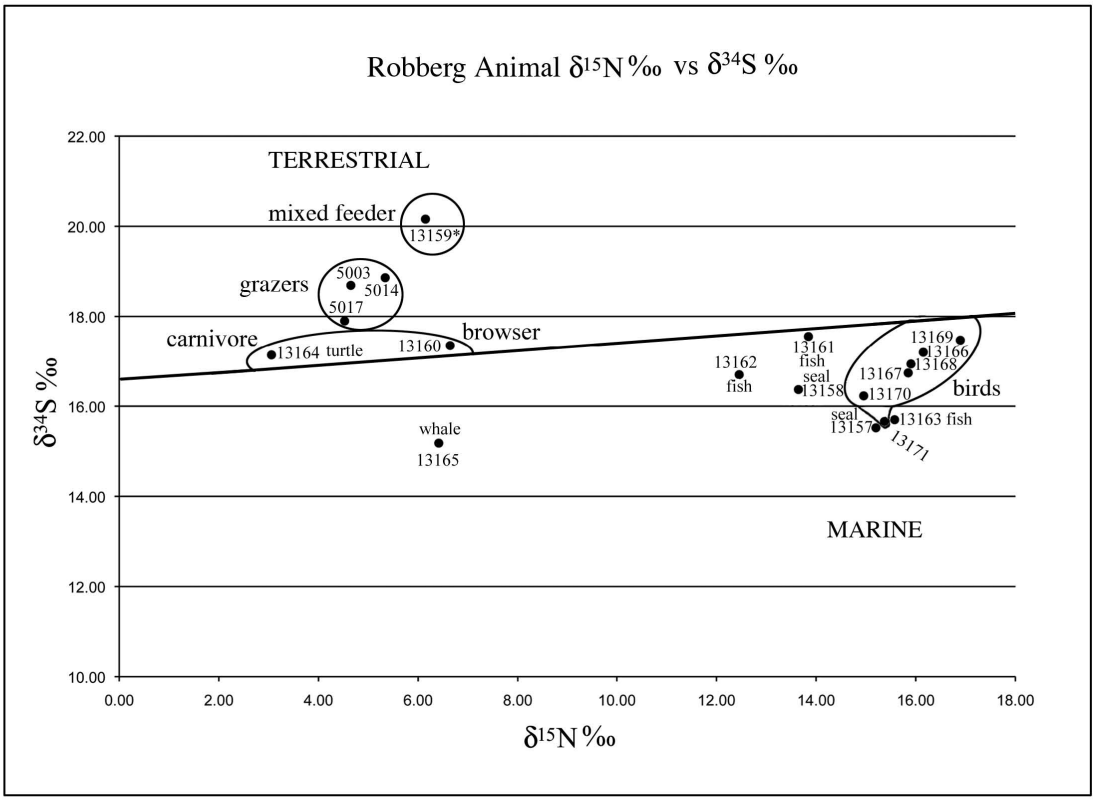
Figure 5: $\delta^{34}S$ ‰ Values of All Samples by Geographic Region



fish samples have $\delta^{34}S$ values of 15.7‰, 16.7‰ and 17.6‰, all within the range of oceanic fish (14‰ to 19‰) reported by Nehlich & Richards (2009). Six pelagic birds were included in this study: two gannets with very similar $\delta^{34}S$ values (16.7 and 16.9‰), two Shy Albatross (15.7 and 16.2‰), a Cape Cormorant (17.2‰), and a Sooty Shearwater (17.5‰). The three African Buffalo have the most elevated $\delta^{34}S$ (17.9‰, 18.7‰ and 18.9‰). When plotted with $\delta^{15}N$ values (Figure 6) the marine animals (including birds that fed on marine fish) are separated from terrestrial by both $\delta^{15}N$ and $\delta^{34}S$ (although only $\delta^{34}S$ groups the whale with the other marine specimens). Although unidentifiable from the bone fragment, the whale sample most likely came from a Southern Right Whale, a plankton feeder with a C_3-based diet. The $\delta^{13}C$ value of this sample, -20.7‰, is similar to others from archaeological sites (Sealy & van der Merwe 1986), although the $\delta^{15}N$ value (6.4‰) is very low (Sealy et al. 1987). The $\delta^{34}S$ value is consistent with phytoplankton being the source of food, as values can be 13‰ or lower (Lamontagne et al. 2007; McArdle et al. 1998). The six land animals have a restricted range of $\delta^{34}S$ values, from 17.1 to 18.9‰ (or 20.2‰). The twelve marine animals (including birds) have a range from 15.2 to 17.6‰, indicating that although there is some overlap, $\delta^{34}S$ values do distinguish between marine and terrestrial animals. In this instance, $\delta^{34}S$ values also separate browsers (hyrax) from grazers (the three buffalo) and the mixed feeder (steenbok). The turtle, a carnivore, is separated from the herbivores by $\delta^{15}N$. The bushpig (UCT 1670), from nearby Knysna, has a $\delta^{34}S$ value of 16.3‰, similar to other terrestrial animals in the area.

The other two animals from the south coast are UCT 5278, an ostrich, and UCT 2080, a grysbok. Both these samples were from the western end of the southern coast, near Cape Agulhas. The grysbok has a $\delta^{34}S$ value of 16.2‰, while the ostrich has a value of 13.9‰. De Hoop, the nature reserve where the ostrich lived, extends several kilometers

Figure 6: $\delta^{34}S$ and $\delta^{15}N$ Values for Eighteen Animal Samples from Robberg Penninsula



* Note: Sample 13159 has a sulphur weight percent that is above normal range.

inland from the coast, but would still be expected to be influenced by sea spray. It is unclear whether there is localized variation in sulphur isotope ratios here, or whether this is a single anomalous specimen.

Animal samples from the west coast derive from Leipoldville, Elands Bay, Kasteelberg, Oudepost, and Hout Bay. A wide range of $\delta^{34}S$ values is seen in these samples, from 8.5 to 18.0‰. The 17th century cow from Oudepost (UCT 13172) has the highest value of 18.0‰, followed by the three Angulate Tortoises from Kasteelberg (16.9‰, 17.7‰, and 17.2‰ for UCT 3937, UCT 3938, and UCT 3939, respectively). Two red hartebeest from Elands Bay, around 62km to the north, have similar $\delta^{34}S$ (16.2‰ and 16.7‰ for UCT 3250 and UCT 3251). The site of Kasteelberg is located on a granite outcrop, while Elands Bay is surrounded by marine-derived sands, but these geological discrepancies do not appear to make a difference in the $\delta^{34}S$ values. The recent dune mole rat (UCT 880) from Leipoldville has a somewhat lower $\delta^{34}S$ value of 14.7‰, although the site is within 15km of the sea.

The two bovids from Hout Bay (UCT 13180 and UCT 13182) provide some of the most unexpected results. Their $\delta^{34}S$ values (12.3 and 8.5‰) are lower than all but one inland sample (UCT 723). The $\delta^{13}C$ values of these bovid samples, at -12.1 and -11.2‰, are indicative of C_4 vegetation ($\delta^{15}N$ 7.4 and 7.6‰), suggesting that the Hout Bay valley once had a significant grassy component. The skeletal elements were too incomplete to be identified to species, but the large grazers likely to have been in the area are hartebeest and buffalo. Any 'sea spray effect' should certainly apply here, so these $\delta^{34}S$ values must be attributed to some other influence.

As described in Chapter 3, terrestrial animals from non-coastal localities typically have $\delta^{34}S$ values below 14.0‰ (Craig et al. 2010; Hu et al. 2010; Macko 1999; Nehlich et al. 2010; Privat et al. 2007; Richards et al. 2001). The inland samples in this study are

from sites located between 70 and 140km from the coast and had $\delta^{34}S$ values ranging from 11.3 to 17.3‰. Two bovids from Klipfonteinrand in the Fold Belt Mountains, about 95 km from the coast, had the highest $\delta^{34}S$ values for this region (17.3 and 16.4‰ for KRF 2 D III LBA 2 and KRF 2 EIVMBS 1). Four humans from sites nearby also have unexpectedly high $\delta^{34}S$, as discussed in the following section. Just inland of the mountains, the porcupine from Doornbos (UCT 719) has a much lower $\delta^{34}S$ value of 12.9‰, similar to terrestrial sulphur isotope values reported in the literature. The final sampling locality, Aspoort, is roughly 140km from the coast and some distance inland of the mountains. Three animals from Aspoort (a rock hyrax and two bovids) have $\delta^{34}S$ values of 11.3‰, 12.8‰, and 13.3‰ (for UCT 723, UCT 13177 and UCT 13179, respectively), while one small bovid (UCT 13178) had a somewhat higher $\delta^{34}S$ value of 15.3‰. The last animal was found in an archaeological cave site, so it is possible that part of the animal was carried to the site, as the $\delta^{15}N$ value (7.5‰) is also much lower than the other two bovids. It appears that, at least in this region, high $\delta^{34}S$ values extend some distance inland. Possible reasons for this phenomenon will be explored in the next chapter.

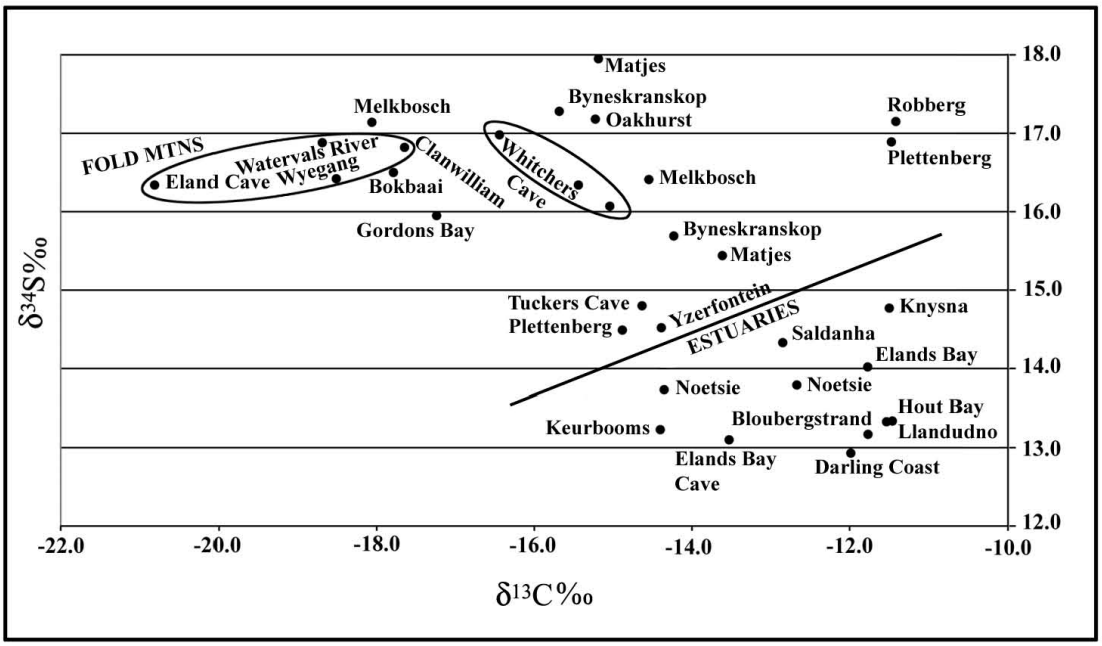
The three Angulate Tortoise samples from the west coast have similar $\delta^{34}S$ values to the Helmeted Turtle (16.9‰, 17.2‰, 17.7‰, and 17.1‰) from the south coast, although the percent sulphur for all three Kasteelberg tortoises is 0.17% to 0.18%, yet 0.25% for the turtle. The tortoises are browsers from dry warm regions, while the turtle is a carnivorous freshwater species. This turtle is the only freshwater animal analyzed in this study, and its $\delta^{34}S$ value does not separate it from the marine animals.

Sulphur Isotope Values of Human Samples

The 34 intact human skeletal samples analyzed in this study have $\delta^{34}S$ ranging from 12.9‰ to 18.0‰. The most positive value (18.0‰) is for NMB 1273 from Matjes River, the sample with unusually high sulphur weight percent (0.42%), and C:S and N:S of 288 and 90 respectively. Both these values fall slightly below the ranges expected for well preserved material. Excluding this individual, $\delta^{34}S$ values for humans ranged from 12.9‰ to 17.3‰. The lowest $\delta^{34}S$ values come from the west coast and the highest values from south coast sites, but there is a great deal of variation. At most sites, the human samples have a more restricted range in $\delta^{34}S$ values than the animal samples. Figure 7 displays a $\delta^{13}C/\delta^{34}S$ scatterplot of all human samples by location.

All fifteen southern coast skeletons come from a stretch of coastline about 80km long, and the range of $\delta^{34}S$ values is 13.2‰ to 17.2‰. Of these, seven come from the Robberg Peninsula and Plettenberg Bay area (NMB 1273, NMB 552, SAM-AP 1879, NMB 1704, NMB 1707, SAM-AP 4824(B), and A1055), and their $\delta^{34}S$ values range from 14.5‰ to 17.2‰. SAM-AP 1879 from the Robberg Peninsula has one of the higher $\delta^{34}S$ values at 17.2‰. Two samples were found in Plettenberg Bay town (NMB 1704 and NMB 1707) and have $\delta^{34}S$ of 16.9‰ and 14.5‰. The lowest $\delta^{34}S$ value for a human from the vicinity of Plettenberg Bay is 13.2‰ for A1055, buried along the Keurbooms River and dating to 1080±40 BP. By this time, the earlier emphasis on high marine protein diets had been replaced by more mixed marine/terrestrial diets, both at Robberg/Plettenberg Bay and elsewhere around the southern and western Cape coasts (Jerardino et al. 2008; Parkington et al. 1988; Sealy 2006; Sealy & van der Merwe 1988). This individual ($\delta^{13}C$ -14.4‰ and $\delta^{15}N$ 12.1‰) conforms to this pattern, with a diet in which terrestrial plant foods and/or low trophic level marine food like shellfish may have played a larger part. The relatively low $\delta^{15}N$ paired with this $\delta^{34}S$ value indicates minimal fish consumption.

Figure 7: Site Distribution of $\delta^{34}S$ vs. $\delta^{13}C$ for Human Samples

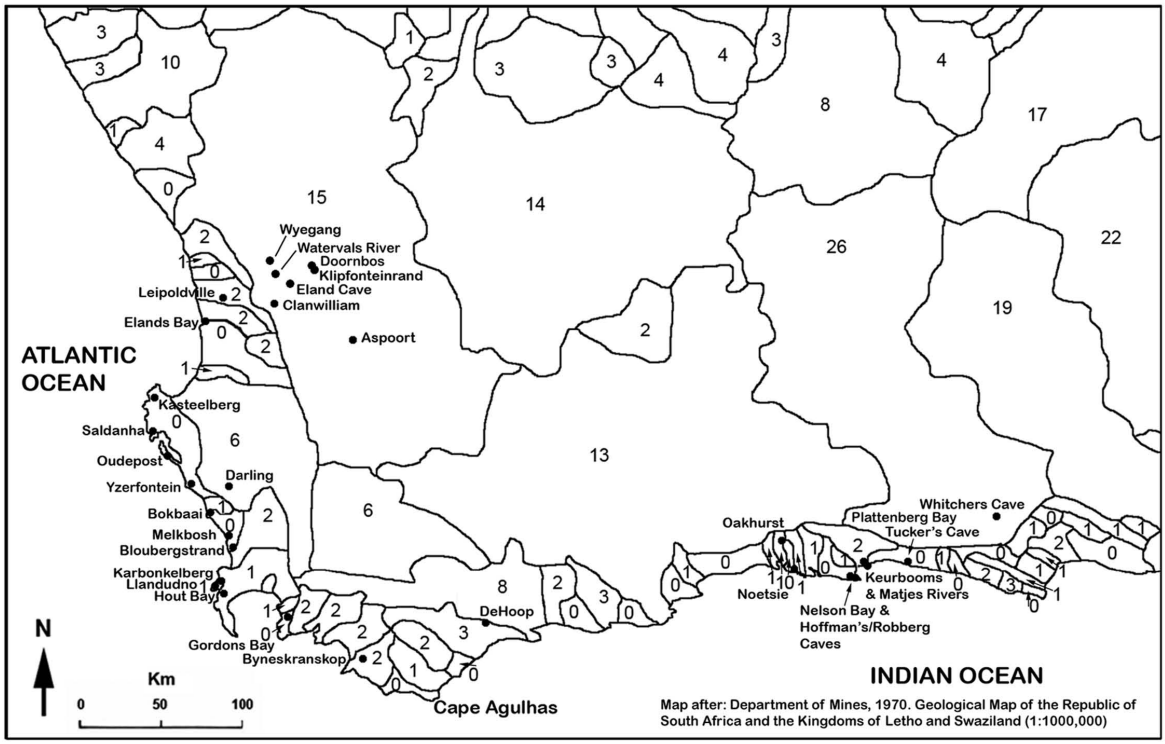


The mountain catchment area of the Keurbooms River may have also influenced $\delta^{34}S$ values of the area immediately around the river. The Keurbooms River valley contains exposed Enon Formation sediments (Shone 2006).

A few kilometers east of the Keurbooms River is the site of Matjes River, which yielded two of the skeletons analyzed in this study. NMB 1273 has been described previously, with a $\delta^{34}S$ of 18.0‰. NMB 552 has a rather lower $\delta^{34}S$ value of 15.4‰. Slightly further east in a more forested area is Tucker's Cave, from where SAM-AP 4824(B) was recovered. The $\delta^{34}S$ value (14.8‰) is relatively low and $\delta^{13}C$ and $\delta^{15}N$ values (-14.6‰ and 14.5‰) indicate a marine/mixed diet.

The human found at Knysna (UCT-MED 107) has a $\delta^{34}S$ value of 14.8‰, suggesting that the $\delta^{34}S$ values in this area are linked to local geology or ecology rather than proximity to the sea. The two human samples from the site of Noetsie (3190±40 and 3800±40 BP), in-between Knysna and Plettenberg Bay, have similar $\delta^{34}S$ values (13.7‰ and 13.8‰ for UCT 12905 and UCT 12904, respectively), although the site is located directly on the coast, and $\delta^{13}C$ and $\delta^{15}N$ values indicate diets with significant marine components, especially for 12904 ($\delta^{13}C$= -14.4 and -12.7‰; $\delta^{15}N$= 12.1 and 16.1‰). Few small watersheds supply a large amount of freshwater to the area of Knysna and Noetsie (see Figure 8) and several lakes are present around Knysna, which could help explain the consistently lower $\delta^{34}S$ values. These two locations also contain exposed Bredasdorp Group (on-shore coastal Cenozoic) deposits, which are dominantly terrigenous and occur stratigraphically above the Enon Formation (Roberts et al. 2006). Large lagoons were also dominant features of both these landscapes. The only animal sampled from this area is a modern bushpig (UCT 1670) from the forest around Knysna, which has a $\delta^{34}S$ value of 16.3‰. Interestingly, sample UCT-MED 214 has a $\delta^{34}S$ value of 17.2‰ although it was found at Oakhurst, 14km inland from the sea and slightly west of Knysna. The low $\delta^{15}N$

Figure 8: Archaeological Site Distribution with Drainage Basin Outlines and Stream Order



Note: The size of the drainage basins and their corresponding stream order are relatively small in both the Atlantic and Indian Ocean coastal sites in comparison to similar hydrologic properties associated with inland archaeological sites. Consequently, hydrogeochemical properties of the coastal drainage basins are influenced by environmental conditions in their immediate neighborhood.

value (9.5‰) indicates that consumption of marine foods is not a likely explanation for the higher $\delta^{34}S$ value.

Four skeletons from Whitcher's Cave also have higher $\delta^{34}S$ values (17.0, 16.3, 16.1, and 15.5‰ for A1186, A1184 VI, A1184 VII, and A1184 VIII, respectively). This site is in the southern portion of the Fold Belt Mountains, 14km from the coast, and the $\delta^{15}N$ values for three of these individuals (8.2, 10.3, 9.6‰; no MPI data is available for A1184 VIII, but a value of 10.5‰ was previous measured at UCT) indicate an almost exclusively terrestrial diet (Sealy & Pfeiffer 2000). Unfortunately these skeletons were recovered in the 1920s, and no fauna is available from this site for analysis.

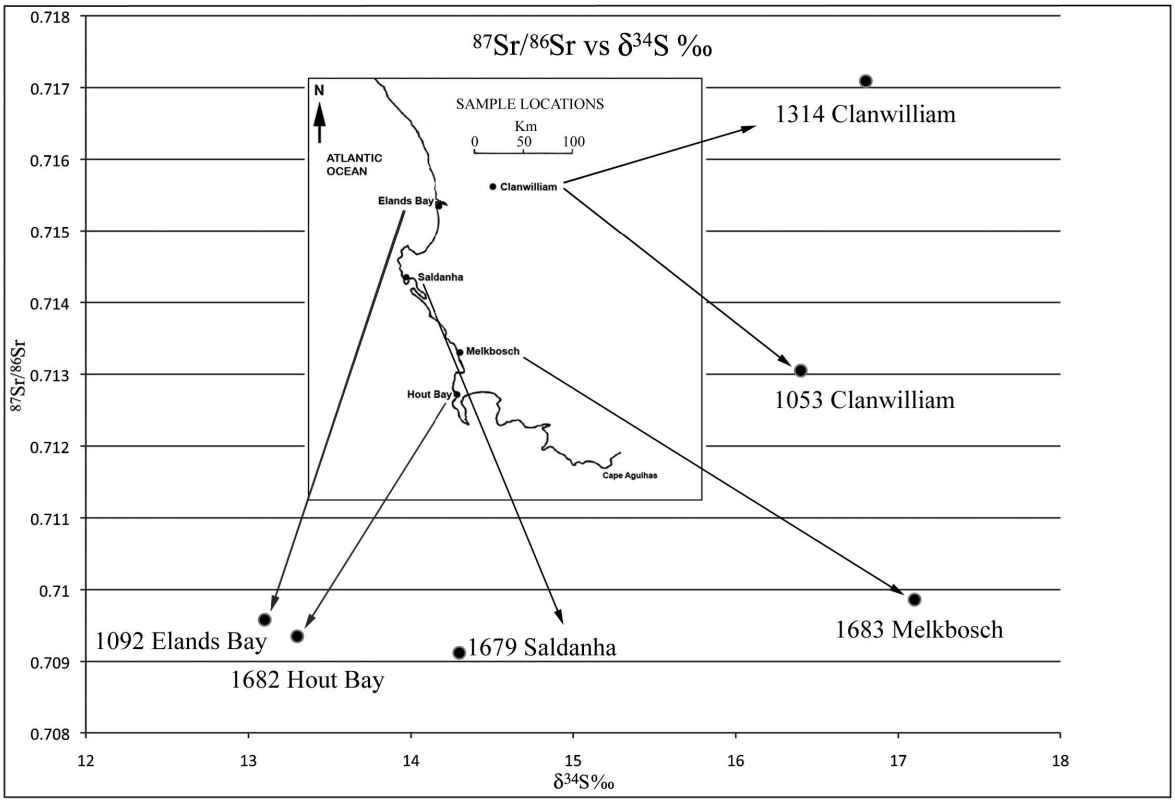
Two human samples from Byneskranskop (SAM-AP 6050 and SAM-AP 6052, dating to 2780±50 and 1480±50 BP, respectively) have $\delta^{34}S$ values of 15.7‰ and 17.3‰, similar to the modern grysbok from the same locality (16.2‰, UCT 2080). This site is only a few kilometers from the coast so the values could be influenced by the "sea spray effect."

Two distinct patterns are apparent among the humans in the southwestern corner of the west coast, a span of 85km "as the crow flies," from Bokbaai to Gordons Bay. Humans SAM-AP 5041, SAM-AP 5040, and SAM-AP 4637 (from Melkbosch, Bokbaai, and Gordons Bay, respectively) have terrestrial $\delta^{13}C$ (-18.1, -17.8, and –17.2‰, respectively) and $\delta^{15}N$ values (10.2, 11.58, 10.8‰), yet higher $\delta^{34}S$ values (17.1, 16.5, and 16.0‰). The human samples found near Hout Bay show an opposite pattern. The human from Hout Bay (SAM-AP 5082) has a surprising lower $\delta^{34}S$ value (13.3‰), despite strongly marine $\delta^{13}C$ and $\delta^{15}N$ values (-11.5 and 15.7‰). The two other samples from the immediate area (UCT-MED 158 and UCT-MED 120) have similar $\delta^{34}S$ values (13.3 and

14.0‰, respectively), and UCT-MED 158 has "marine" $\delta^{13}C$ and $\delta^{15}N$ values (-11.5‰ and 14.2‰; no MPI $\delta^{13}C$ and $\delta^{15}N$ information is available for UCT-MED 120, but previous UCT measurements are -13.5 and 14.2‰). A human found in Bloubergstrand (UCT 220; 35 km from Hout Bay) has near identical values ($\delta^{34}S$= 13.2‰, $\delta^{13}C$= -11.8‰ and $\delta^{15}N$= 16.4‰). The two bovids discussed above (UCT 13180 and UCT 13182) from Hout Bay also have low $\delta^{34}S$ values (12.3‰ and 8.5‰) for this study. Similar $\delta^{34}S$ values seem to be common in human skeletons elsewhere on the western coast as well. This pattern is particularly unexpected as strontium (Sr) isotope results indicate that recent marine sands are the dominant geological feature along the coastal plain (Figure 9) (Sealy et al. 1991), and sulphur isotopes were expected to show the same signal. The human sample UCT-MED 112, found near Yzerfontein, has a $\delta^{34}S$ value of 12.9‰, although $\delta^{13}C$ and $\delta^{15}N$ values for this sample (-12.0‰ and 17.9‰) indicate a diet heavy in marine protein. The human from Yzerfontein (SAM-AP 5091) has a slightly higher $\delta^{34}S$ value of 14.5‰, and its $\delta^{13}C$ and $\delta^{15}N$ values indicate a more mixed diet (-14.4‰ and 13.0‰, respectively).

The two humans from Saldanha (SAM-AP 6075 and SAM-AP 5095) have $\delta^{34}S$ values of 14.8‰ and 14.3‰. MPI carbon and nitrogen isotope data are only available for SAM-AP 5095, and indicate a marine-food based diet (-12.8‰ and 15.7‰). Previous UCT $\delta^{13}C$ and $\delta^{15}N$ results for SAM-AP 6075 are -15.0 and 17.1‰. The two human samples from Elands Bay have $\delta^{34}S$ values of 13.1‰ and 14.0‰ (UCT-MED 373 and UCT 3137, respectively) and marine-diet $\delta^{13}C$ and $\delta^{15}N$ ($\delta^{13}C$= -13.5 and -11.8; $\delta^{15}N$= 16.1 and 13.9).

Figure 9: $^{87}Sr/^{86}Sr$ vs. $\delta^{34}S$ of Six Human Samples Plotted with Geographic Location



Note: $^{87}Sr/^{86}Sr$ data taken from Sealy et al. 1991

In contrast, the four humans (UCT 5666, UCT-MED 331, SAM-AP 1449, and SAM-AP 6315) found in the Fold Belt Mountain sites of Eland Cave, Wyegang, Clanwilliam, and Watervals Rivier all have higher $\delta^{34}S$ values (16.8, 16.9, 16.3, and 16.4‰, respectively), despite terrestrial $\delta^{13}C$ values. They were all found in different sites, yet the $\delta^{34}S$ values are remarkably similar. These values are also similar to the two bovids from nearby Klipfonteinrand (KRF 2 D III LBA 2 and KRF 2 EIVMBS 1, with $\delta^{34}S$ values of 17.3 and 16.4‰). These $\delta^{34}S$ values are difficult to explain here. Could this area be under the influence of the "sea spray effect"? Both bovids from Elands Bay (UCT 3250 and UCT 3251), roughly 105km to the west and on the coast, have marine $\delta^{34}S$ values. Yet the non-contemporary humans from the same area have lower $\delta^{34}S$ values (14.0‰ and 13.1‰ for UCT 3137 and UCT-MED 373). Relatively high $\delta^{15}N$ values in the inland human samples (13.8, 13.1, 14.7, 15.5‰) could indicate freshwater fish consumption, although $\delta^{15}N$ values are notoriously difficult to interpret in this region due to aridity (Sealy et al. 1987). The most likely explanation for the consistently elevated $\delta^{34}S$ values in the Fold Belt Mountains is a combination of geology (ancient marine sedimentary rock formations) and marine aerosols. Rainfall is limited in this region, and weathering is slow. Vegetation is also somewhat sparse, so decaying organics do not contribute substantially to soil formation. This results in a relatively homogenous environment throughout all the sites and until around Klipfonteinrand, when a change in facies occurs from the Table Mountain Group sandstones to the marine Malmesbury shale (Parkington and Poggenpoel 1971; Thamm and Johnson 2006).

Comparison of UCT and MPI-EVA Data

Table 4 presents the $\delta^{13}C$ and $\delta^{15}N$ values for 59 collagen samples extracted and analyzed at both the Max Planck Institute (MPI) and the University of Cape Town. Most

Table 4: Comparison of UCT and MPI $\delta^{13}C$ and $\delta^{15}N$ Measurements

	Museum	UCT Collagen		MPI Collagen			Difference	
UCT Cat.	Accession #	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$(‰)	$\delta^{13}C$	$\delta^{15}N$
3250		-17.5		-17.4	11.2	16.2	0.13	
3251		-20.0		-20.1	8.5	16.7	0.09	
5014		-10.9	5.3	-12.8	5.3	18.9	1.85	0.02
5003		-12.5	3.9	-11.9	4.6	18.7	0.68	0.79
5017		-12.5	3.9	-12.8	4.5	17.9	0.35	0.66
3937		-21.5		-21.4	8.9	16.9	0.12	
3939		-19.4		-18.9	6.2	17.2	0.52	
3938		-21.8		-21.9	8.7	17.7	0.07	
13164		-22.7	3.3	-23.3	3.1	17.1	0.67	0.19
13157		-11.5	14.7	-11.0	15.2	15.5	0.49	0.54
13158		-12.7	15.3	-14.4	13.6	16.4	1.67	1.66
13159		-19.2	5.4	-19.6	6.1	20.2	0.39	0.75
13160		-20.3	6.3	-20.4	6.6	17.4	0.06	0.30
13161		-10.5	13.7	-11.5	13.8	17.6	0.98	0.14
13162		-10.4	12.4	-11.9	12.5	16.7	1.52	0.02
13163		-12.1	15.6	-12.5	15.6	15.7	0.38	0.03
13165		-20.8	5.7	-20.7	6.4	15.2	0.12	0.73
13166		-12.3	15.7	-12.3	16.2	17.2	0.03	0.48
13167		-11.7	17.7	-11.8	15.8	16.7	0.07	1.83
13168		-11.7	15.6	-11.4	15.9	16.9	0.31	0.30
13169		-13.9	16.5	-13.9	16.9	17.5	0.02	0.44
13170		-12.3	16.4	-16.7	15.0	16.2	4.40	1.39
13171		-17.2	15.4	-16.9	15.4	15.7	0.33	0.01
880		-20.3	14.4	-20.3	14.3	14.7	0.01	0.14
4434				-13.3	7.3			

	Museum	UCT Collagen		MPI Collagen			Difference	
UCT Cat.	**Accession #**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{34}S$(‰)**	**$\delta^{13}C$**	**$\delta^{15}N$**
1670		-20.3	7.9	-20.5	8.1	16.3	0.19	0.22
5278				-23.0	5.5	13.9		
2080		-21.6	4.7	-22.4	5.0	16.2	0.77	0.30
723		-21.4	14.3	-19.2	16.6	11.3	2.22	2.31
719		-20.6		-19.5	12.7	12.9	1.10	
13172				-19.4	8.2	18.0		
13173				-14.5	15.3	14.4		
13174				-22.6	10.7			
5605	A 1186	-17.0	8.3	-16.4	8.2	17.0	0.56	0.06
5611	A 1184 VI	-14.9	9.6	-15.4	10.3	16.3	0.54	0.71
5612	A 1184 VII	-15.6	8.4	-15.0	9.6	16.1	0.56	1.23
5223	NMB 1273	-15.4	11.6	-15.2	12.3	18.0	0.21	0.68
5429	UCT 214	-14.4	10.2	-15.2	9.5	17.2	0.83	0.68
5234	NMB 1704	-12.2	9.3	-11.5	9.7	16.9	0.73	0.41
5609	A 1055	-13.2	12.4	-14.4	12.1	13.2	1.20	0.34
5602	NMB not acc SS 2	-13.5	13.0	-13.6	14.4	15.4	0.11	1.40
5213	SAM-AP 1879	-11.1	17.5	-11.4	17.8	17.2	0.31	0.35
5218	UCT 107	-13.3	17.9	-11.5	17.5	14.8	1.80	0.35
5195	SAM-AP 4824 (B)	-14.6	14.4	-14.6	14.5	14.8	0.03	0.09
10851	NMB 1707	-14.9	10.6	-14.9	10.7	14.5	0.02	0.17
12905		-14.5	11.9	-14.4	12.1	13.7	0.15	0.16
12904		-12.9	15.7	-12.7	16.1	13.8	0.23	0.38
1691	SAM-AP 4637	-17.2	10.5	-17.2	10.8	16.0	0.04	0.26
1683	SAM-AP 5041	-17.9	10.2	-18.1	10.2	17.1	0.16	0.05
1684	SAM-AP 5040	-17.7	11.3	-17.8	11.6	16.5	0.09	0.26
1053	UCT 331	-18.4	10.5	-18.5	13.1	16.4	0.12	2.55
4443	UCT 158	-12.1	14.5	-11.5	14.2	13.3	0.59	0.33
1730	SAM-AP 5091	-14.9	12.8	-14.4	13.0	14.5	0.50	0.24

	Museum	UCT Collagen		MPI Collagen			Difference	
UCT Cat.	**Accession #**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**$\delta^{34}S$(‰)**	**$\delta^{13}C$**	**$\delta^{15}N$**
1682	SAM-AP 5082	-11.6	15.9	-11.5	15.7	13.3	0.07	0.23
1686	SAM-AP 6075	-15.0	17.1			14.8		
1679	SAM-AP 5095	-13.2	15.7	-12.8	15.7	14.3	0.35	0.01
4446	UCT 220	-11.5	16.5	-11.8	16.4	13.2	0.24	0.15
1051	UCT 112	-11.2	16.9	-12.0	17.9	12.9	0.76	0.98
1898	SAM-AP 6149	-14.4	13.3	-14.5	13.5	16.4	0.11	0.19
1211	SAM-AP 6052	-15.4	11.9	-15.7	12.1	17.3	0.24	0.22
5666		-18.9	13.2	-20.8	13.8	16.3	1.96	0.63
5668	SAM-AP 6315	-18.7	14.0	-18.7	15.5	16.9	0.01	1.52
457/1314	SAM-AP 1449	-17.3	14.4	-17.6	14.7	16.8	0.35	0.29
1209	SAM-AP 6050	-13.9	12.2	-14.2	12.5	15.7	0.31	0.31
4442	UCT 120	-13.5	14.2			14.0		
3137		-11.8	13.9	-11.8	13.9	14.0	0.01	0.06
1092	UCT 373			-13.5	16.1	13.1		
5613	A 1184 VIII	-14.9	10.5			15.5		
13177				-17.1	13.2	12.8		
13178				-18.6	7.5	15.3		
13179				-18.4	10.2	13.3		
	KRF 2 D III LBA 2			-18.6	12.7	17.3		
	KRF 2 OHBD 1							
	KRF 2 D OHBD 2							
	KRF 2 EIVMBS 1			-20.0	11.4	16.4		
13180				-12.1	7.4	12.3		
13181				-17.9	9.3			
13182				-11.2	7.6	8.5		

of the collagen extractions and analyses done at UCT were carried out for earlier studies, and the results have been reported elsewhere (Sealy & van der Merwe 1985, 1986; Sealy 1997; Sealy 2006; Sealy & Pfeiffer 2000; Sealy et al. 2000). The comparison is of interest because of the considerably more rigorous extraction protocol at MPI (decalcification followed by gelatinization and ultra-filtration, using purified reagents) compared with only decalcification at UCT). The MPI $\delta^{15}N$ values were slightly higher than the UCT equivalents (mean difference 0.54±0.58, range 0.0 to 2.6‰), while MPI $\delta^{13}C$ values were on average slightly less positive than the UCT values (mean difference -0.55±0.74, range 0.0 to 4.5‰). Considering that the standard deviation of repeated measurements of homogenous material on the mass spectrometer is typically ~0.2‰, these differences are not large.

Nine samples (listed in Table 5) showed a difference of more than 1.0‰ in $\delta^{13}C$, while seven showed a difference of this magnitude for $\delta^{15}N$. One (UCT 5666) has already been discussed. The $\delta^{13}C$ value obtained at MPI was 1.9‰ more negative than that measured at UCT, reflecting humic contamination. This is a problem for samples recovered from organic-rich depositional contexts, which require treatment with NaOH to remove extraneous carbon-containing compounds.

Table 5: Problematic Samples

Catalog Number	Material	Abnormal Collagen Extraction		Difference between analyses		Comments
		UCT	MPI-EVA	$\delta^{13}C$	$\delta^{15}N$	
UCT 5014	Bovine			1.85		
UCT 13158	Seal			1.67	1.66	
UCT 13161	Fish	X		0.98		Humic Substances
UCT 13162	Fish	X		1.52		Humic Substances
UCT 13167	Bird	X			1.83	Unusual Collagen
UCT 13170	Bird	X		4.40	1.39	Unusual Collagen
UCT 723	Hyrax			2.22	2.31	Recent
UCT 719	Porcupine			1.10		Recent
A 1055	Human			1.20		
UCT 5602	Human	X			1.40	
UCT-MED 107	Human			1.80		
UCT-MED 331	Human				2.55	
UCT 5666	Human		X	1.96		Carbon Contamination
SAM-AP 6315	Human				1.52	

Five of the samples listed in Table 5 had problematic collagen extraction at UCT. The sample with the greatest difference in both $\delta^{13}C$ and $\delta^{15}N$ values was UCT 13170, an archaeological shy albatross bone. At UCT, this yielded collagen that appeared shriveled and yellow (see Chapter 4). The sample appeared fully decalcified and the C:N ratio (3.18) indicated that the collagen chains were intact. At MPI, no unusual color or texture was observed, while the C:N ratio was also 3.18. When run at the MPI, this sample had slightly higher percentages of carbon and nitrogen (44.9%C and 16.5%N, compared with 43.5%C and 15.9%N at UCT), and a $\delta^{13}C$ measurement that was 4.4‰ more negative than at UCT. The $\delta^{15}N$ value determined at MPI was 1.4‰ lower than at UCT. The difference in $\delta^{13}C$, in particular, is far in excess of likely analytical error. Sample UCT 13167 (an archaeological gannet) also had the same unusual appearance, yet only the $\delta^{15}N$ values are significantly different (difference of 1.83). Interestingly, the other two samples with the same unusual extracted collagen (samples UCT 13168 and UCT 13171, also birds) had similar $\delta^{13}C$ and $\delta^{15}N$ values at UCT and MPI.

Sample UCT 723, a modern (late 20th century) rock hyrax, had a difference of 2.2‰ in $\delta^{13}C$ and 2.31‰ in $\delta^{15}N$ between UCT and MPI, although all standard quality control criteria were met in the MPI run. The UCT values were determined for a much earlier study (Sealy 1986; Sealy & van der Merwe 1986). This is true also of another modern sample, UCT 719, which showed a difference of 1.1‰ in $\delta^{13}C$ at the two labs. There is also an inter-lab difference of 1.7‰ in both $\delta^{13}C$ and $\delta^{15}N$ for sample UCT 13158, yet both analyses show a high degree of integrity in the extracted collagen. The MPI % carbon and nitrogen values were slightly higher (45.2% and 16.7%, compared with UCT's 42.5% and 15.4%), and the isotope ratios less positive. Collagen extracted from sample NMB 552 yielded similar $\delta^{13}C$ values in both laboratories, but $\delta^{15}N$ values which differ by 1.4‰, with the MPI value being more positive. This human bone sample was quite dark and may have suffered some contamination which was removed by the NaOH in the UCT preparation.

Summary of Results

The animal samples (n=37) provide a compelling view of the behavior of $\delta^{34}S$ for the Western Cape Province, as all but four specimens found along the coast (UCT 5278, UCT 880, UCT 13180, and UCT 13182) have a coastal signal. The 'truly' coastal samples have the largest $\delta^{34}S$ range; from 8.5 to 18.9‰, incorporating the highest and lowest values of this study and indicating that the "sea spray effect" does not apply perfectly to the Western Cape Province. Ten of the total 48 samples have $\delta^{34}S$ values under 14‰, and an additional eight have values under 15‰, with the low values spread out between twelve different sites. All other animals, even those from the same sites as the depleted human samples, have $\delta^{34}S$ values above 15‰. It appears that the 'sea spray effect' and the ancient marine sedimentary rocks which are ubiquitous in the Fold Belt Mountains

provide some control over the overall sulphur stable isotope distribution. Thus, 83% of the animals sampled for this study have $\delta^{34}S$ values indicative of their provenance based on proximity to the sea. The marine animals from Hoffman's/Robberg Cave are separated from the terrestrial animals by $\delta^{34}S$ values (Figure 6), although the lower $\delta^{34}S$ values in marine carnivores are difficult to interpret.

There appears to be significant regional variation in $\delta^{34}S$ values of coastal terrestrial animals. The largest data set and the highest $\delta^{34}S$ values (ranging from 15.2‰ to 18.9‰) come from the Robberg Peninsula samples, with one human and a variety of animals making up the sample set. This is the only coastal area with consistently high $\delta^{34}S$ values for all species. The elevated values could be due to the constant supply of high trophic level marine protein provided by seal colonies and the proximity to the ocean.

All five samples from the Hout Bay area have low $\delta^{34}S$ values. On the southern coast, both Whitcher's Cave and Oakhurst, roughly 14km inland, have yielded human skeletons with terrestrial carbon and nitrogen isotope values, in combination with high $\delta^{34}S$. On the west coast, the same applies to animals and humans from the Fold Belt Mountains. Moving inland of the Fold Belt $\delta^{34}S$ values decrease, and most samples from Aspoort and Doornbos have $\delta^{34}S$ values under 14‰.

Possible explanations for the patterns described above are discussed in the next chapter, which also assesses how these results compare to those obtained elsewhere in the world.

CHAPTER 6: DISCUSSION AND CONCLUSIONS

Previous publications limited $\delta^{34}S$ analysis to several individuals from a few separate sites, while this thesis analyzed samples from 34 sites within a large region. The complexity of the regional environment was surprising, particularly the degree to which variability in local geomorphology and hydrology influence sulphur isotope values. Variation was seen between individual areas, and $\delta^{34}S$ values of multiple samples from a single location are strikingly similar (Elands Bay Cave, Kasteelberg, Saldanha, Hout Bay, Noetsie, Whitcher's Cave, and the five Cape Fold Mountain sites: Clanwilliam, Watervals Rivier, Wyegang, Eland Cave, and Klipfonteinrand).

In the previous chapter, $\delta^{34}S$ values were reported ranging from 15.2 to 17.6‰ for marine animals in this study. Few $\delta^{34}S$ values are published for archaeological marine fauna, but the results seen here fit within the range measured by Fornander et al. (2008) (10.2 to 19.8‰) and Craig et al. (2006) (10.7 to 17.4‰) for northern European marine animals. In this study, $\delta^{34}S$ of coastal terrestrial animals ranged from 8.5 to 20.2‰. This wide range shows that the "sea spray effect" appears to vary in importance even in areas immediately adjacent to the ocean.

The entire Western Cape Province study area is "flooded" in marine sulphate, as evidenced by a higher range of $\delta^{34}S$ values than seen in several other studies (Craig et al. 2010; Hu et al. 2010; Nehlich et al. 2010; Privat et al. 2007; Richards et al. 2001). There is regional variation in $\delta^{34}S$ of coastal terrestrial animals and humans, indicating isotopically distinct habitats within the broad, mostly ancient marine-derived bedrock (and recent marine sands) of the region. The geology of the region is relatively uniform, and differences in the geologic substrates of individual sites do not seem to be the main determinant of $\delta^{34}S$ values.

Whereas sea spray or geology may have been the dominant factors influencing $\delta^{34}S$ values in coastal consumers in previous studies, the situation in the Western Cape Province is more complicated, as evidenced by sites such as Melkbosch and Bloubergstrand. These two sites are within 6km of each other, and share similar Cape Granite Suite/Malmesbury basement rocks. Both are situated along the shoreline, with a slight marshy habitat. Yet $\delta^{34}S$ values vary significantly (13.2‰ for the human from Bloubergstrand: UCT 220; 17.1‰ and 16.4‰ for the humans from Melkbosch: SAM-AP 6149 and SAM-AP 5041). The three individuals were found in the same area, yet sought food from different ecosystems. Tortoises from Kasteelberg also had high $\delta^{34}S$ values, while humans and bovids from Hout Bay had low values, despite similar granitic geologic substrates.

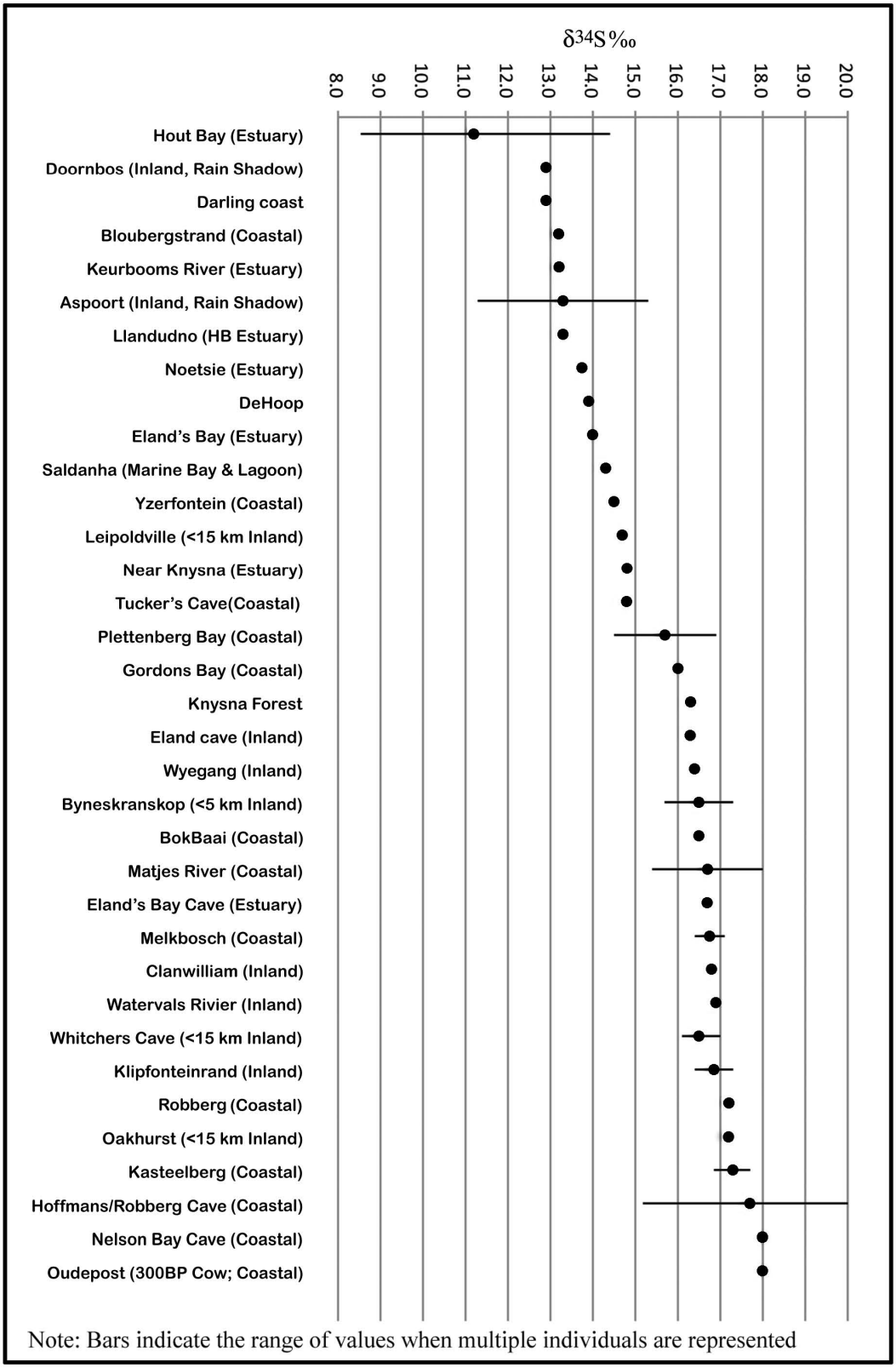
Of the nine animals sampled from the west coast, only the two bovids from Hout Bay had $\delta^{34}S$ below 14‰. Of the fourteen humans sampled on the west coast, ten had $\delta^{34}S$ values below 14‰. In these samples with low values, $\delta^{13}C$ and $\delta^{15}N$ indicate diet was mostly marine-based, which implies these humans lived along the coast and were not migrant individuals. The coastal sites with low $\delta^{34}S$ values in humans all have a significant feature in common: the presence of a large lagoon, estuary, or marsh.

Throughout the study area, higher $\delta^{34}S$ values presumably indicate more marine sulphate, while lower values imply a heavy bacterially-generated sulphide input. The "sea spray effect" is certainly an influence, as evidenced by samples from the Robberg Peninsula, the most marine-influence-dominant environment sampled. In this site, all species have high $\delta^{34}S$ values, likely due to sea spray as this is a rocky shoreline with constant wave action and wind. Values in animals and humans sampled around coastal Hout Bay are much lower than expected for individuals living adjacent to the ocean, and

appear more influenced by estuarine/marshland sulphide resources than by marine sulphate.

Inland sites on the ocean side of the Fold Belt Mountains are likely influenced by marine aerosols, either as wind-blown sulphate or sulphate precipitated by rain and absorbed into the soil. This $\delta^{34}S$ value of approximately 20‰ is modified within plants which also take up a fair amount of bacterially reworked sulphate from the soil (lower $\delta^{34}S$ value). This mixed value is consumed by animals and humans. The rock types in the study area should have rather moderate to high $\delta^{34}S$ values, as most of the basement rocks are ancient marine derived and not sulphide-enriched igneous rocks (the Cape granite is very low in iron sulphide concentrations, except for very small mineralized plutons such as at Saldanha and Darling: Scheepers & Schoch 2006). Black reducing shale is present in several areas, but the bedrock of all environments sampled is predominantly oxidizing ancient marine and near-shore derived. In areas with a fast moving freshwater resource (such as Whitcher's Cave and the Fold Belt Mountain sites) $\delta^{34}S$ values are quite high as the bacterial contents of these environments are relatively low. In areas where freshwater was mainly supplied by sluggish lagoonal systems, such as the Hout Bay estuary/marsh, Knysna lakes, estuary at Noetsie, and the Keurbooms River estuary, $\delta^{34}S$ values in all species sampled are low. Although soils with moderately well developed A horizons (more organic components) in heavily forested environments generally have more bacterial action along the root package, sulphate reduction does not appear to reduce values significantly, as samples from the Knysna forest, Whitcher's Cave, and Oakhurst all have high $\delta^{34}S$ values. Samples from forested Hout Bay and Noetsie have low $\delta^{34}S$ values, but these are likely due to the stagnant and ponded surface water supplies. When all potential sulphur contributions are considered for each site, definite patterns emerge based on the presence and availability of sulphate and sulphide sources. Figure 10

Figure 10: Location, Ecosystem & $\delta^{34}S$ Values for Animals and Humans



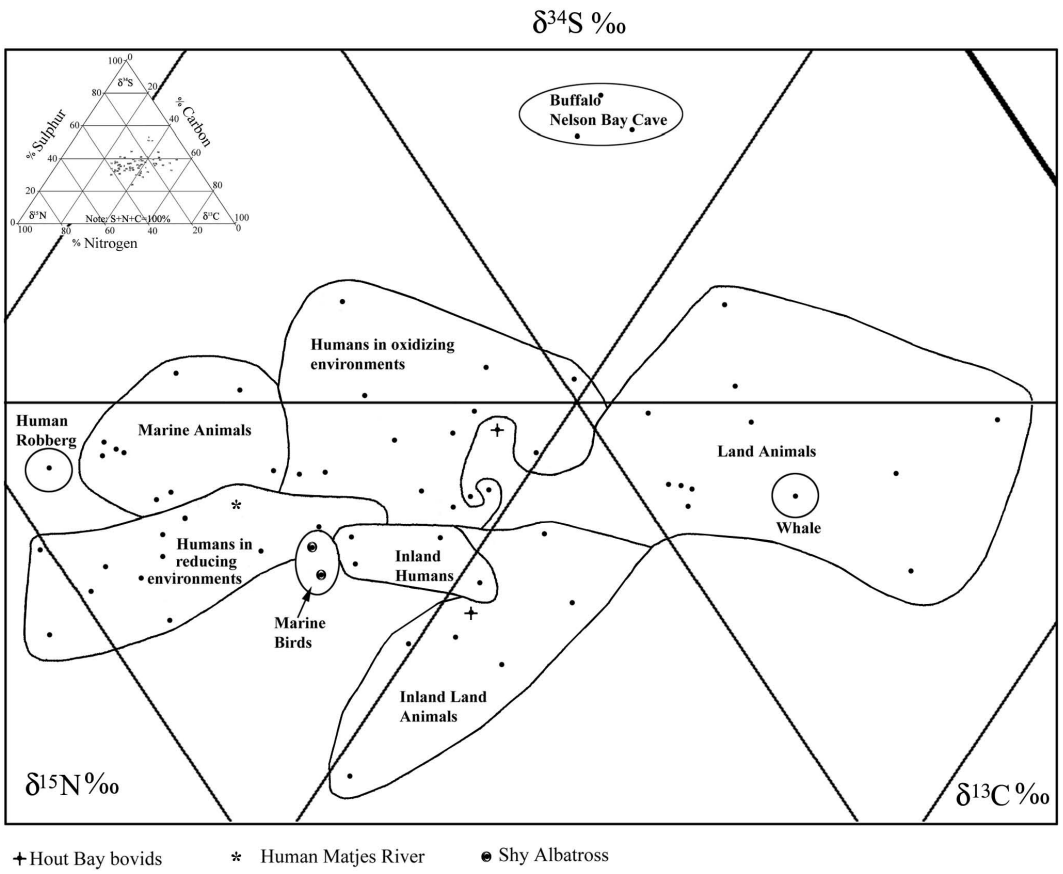
Note: Bars indicate the range of values when multiple individuals are represented

displays $\delta^{34}S$ value ranges for all sites, along with notation indicating whether sites were coastal, inland, or include a significant estuary. Figure 11 is a triangular plot with the variables of all samples displayed in relative proportion to each other.

The "Sea Spray Effect"

The majority of terrestrial animal bones from coastal sites in this study have high $\delta^{34}S$ values. Previous researchers have reported a similar pattern and attributed it to marine aerosols and precipitation (Macko et al. 1999; Richards et al. 2001). The pre-colonial inhabitants of the Western Cape were hunter-gatherers (the most recent skeletons may be the remains of pastoralists), and likely somewhat mobile, although to what extent has not been conclusively determined. If sea spray is the dominant influence for $\delta^{34}S$ values, it is difficult to determine why it would apply in most, but not all areas. Also perplexing is why the "sea spray effect" does not apply to humans as completely as it does to animals, particularly along the west coast. Human samples (SAM-AP 1449, SAM-AP 6315, UCT-MED 331, and UCT 5666) from the four Fold Belt Mountain sites have high $\delta^{34}S$ values and terrestrial $\delta^{13}C$ and $\delta^{15}N$ values, whereas many humans from the west coast have low $\delta^{34}S$ values and marine $\delta^{13}C$ and $\delta^{15}N$ values (SAM-AP 5080, UCT-MED 158, UCT-MED 120, UCT 220, UCT-MED 112, SAM-AP 5091, SAM-AP 6075, SAM-AP 5095, UCT-MED 373, and UCT 3137). This pattern is the reverse of what was expected. It would appear that the Fold Belt Mountains are not far enough inland or orographically high enough to avoid marine influence. Four of the five samples found inland of the mountains have unmistakably "terrestrial" values (all under 13.3‰), so apparently once the mountains are crossed the "sea spray effect" is no longer a factor. Perhaps a combination of geology and precipitation high in marine sulphate contributed to these values. The "low" values seen in animals from Doornbos and Aspoort are higher

Figure 11: Animal and Human $\delta^{13}C$, $\delta^{15}N$ and $\delta^{34}S$ Triangular Plot



Note: This ternary scatter graph plot displays the relative proportions of three positive variables on the three axes. Actual concentrations are not displayed, nor are negative values. All negative $\delta^{13}C$ values have been converted to positive values.

than others observed elsewhere (Hu et al. 2009; Linderholm et al. 2008; Nehlich et al. 2010; Privat et al. 2007; Richards et al. 2001), indicating a high $\delta^{34}S$ sulphate contribution from the environment, presumably the ancient marine bedrock and a small input of marine precipitation. In the areas with higher rainfall, more marine aerosols are brought down with precipitation which could elevate the $\delta^{34}S$ value. There is no easy explanation for the low $\delta^{34}S$ values along the western coast, which should geographically be influenced by marine aerosols. For this region proximity to the coast, and sea spray, are not the only determinants of $\delta^{34}S$ values, although they appear to be major factors when there are no other significant sulphur inputs.

Estuarine Environments

Within the Western Cape marine sulphate "flooded" environment, $\delta^{34}S$ values of individual habitats are controlled by the amount of bacterial sulphate reduction, which in turn is influenced by the local geomorphic character of the surface hydrology and levels of organic production. Quiescent to semi-quiescent freshwater environments such as lakes, lagoons, estuaries, marshes and sluggish rivers allow for organic accumulations, which are responsible for elevated bacterial concentrations and result in lower $\delta^{34}S$ values of primary producers. With large scale sampling, $\delta^{34}S$ measurements paired with $\delta^{13}C$ and $\delta^{15}N$ may be able to further clarify which aspects of individual coastal environments palaeo-populations were exploiting for dietary resources.

Freshwater run-off is significantly reduced today from what it was in the past, due to prevalence of invasive alien vegetation and irrigation for agriculture. Estuaries and lagoons were likely larger in pre-colonial times than they are today. With increased salinity more sulphate reduction occurs (Lamontagne et al. 2007).

Samples from the region around the Hout Bay valley (including Karbonkelberg and Llandudno) have the lowest $\delta^{34}S$ values. Vegetation has changed drastically, but historic reports indicate that this area was once heavily wooded. The two bovids from Hout Bay (UCT 13180 and UCT 13182) have $\delta^{13}C$ values indicative of significant C_4 vegetation consumption (-12.1 and -11.2‰). Prehistorically the Hout Bay valley likely contained a significant brackish water component which could have supported a variety of grasses. Soils were poor and vegetation limited in the valley uplands, making the valley floor, with a basement of sandstone and granite and freshwater provided by three perennial rivers, the most likely foraging and hunting habitat for animals and humans (Buchanan 1977). Many seagrasses, such as *Ruppia,* (a C_4 plant common in South African estuaries) draw nutrients from the reducing sediments and have lower $\delta^{34}S$ values (Peterson & Howarth 1987; Peterson et al. 1986). The $\delta^{13}C$ values of the two grazing bovids suggest that if a marshland was present in this area, then it was a major resource. A brackish water environment, with a constant supply of organics and bacterial reduction, could explain the low $\delta^{34}S$ value of the human (SAM-AP 5082; $\delta^{34}S$ 13.3‰) despite the extremely "marine" $\delta^{13}C$ and $\delta^{15}N$ values (-11.5 and 15.67‰, respectively). The two other samples from the immediate area (UCT-MED 158 and UCT-MED 120) also have low $\delta^{34}S$ values (13.3 and 14.0‰, respectively) and UCT-MED 158 has "marine" $\delta^{13}C$ and $\delta^{15}N$ values (-11.5‰; 14.2‰; no $\delta^{13}C$ and $\delta^{15}N$ MPI information is available for UCT-MED 120, but values of -13.5 and 14.25‰ have previously been measured at UCT). Wind patterns follow a clear path (as evidenced by sand blow) up one side of the valley, over the Karbonkelberg ridge and ultimately provide sand to the beach near Llandudno on the other side of Karbonkelberg. Massive sand dunes attest to this transport pattern. Presumably most sea spray would also be blown along this path. These constantly re-worked dunes could support little vegetation, so animals and humans likely foraged from the forested opposite

wall of the valley or the marshy valley floor. Most edible vegetation was likely influenced by the reducing lagoonal environment more than by sea spray, resulting in the low $\delta^{34}S$ values of consumers from the area. Another human found in Bloubergstrand (35 km north of Hout Bay) has near identical values ($\delta^{34}S$= 13.2, $\delta^{13}C$= -11.8 and $\delta^{15}N$= 16.4). The similarity in values indicates that the human from Bloubergstrand had access to a similar marsh-derived resource base.

Both human samples from Saldanha (SAM-AP 6075 and SAM-AP 5095) have low $\delta^{34}S$ values, suggesting that most of the sulphur contribution to diet came from an estuarine habitat, whereas the three tortoises (UCT 3937, 3938, and 3939) with high $\delta^{34}S$ values likely foraged in drier areas. The nearby Langebaan Lagoon is purely salt water and 17km long. An influx of ocean water is provided twice a day by the tide, although the shallow waters at the southern tip create a well developed salt marsh. These diverse habitats within one large lagoon would provide a variety of resources for mussels and shrimp, and if the lagoon could be "mapped" based on $\delta^{34}S$ of mussels it might be possible to determine from which part humans were collecting food, along with an understanding of the values of other food sources. The Khoi cow specimen from nearby Oudepost is a much more recent sample (approx. 300 BP), and likely was highly mobile traveling with its herd (Smith 1984). The $\delta^{34}S$ value of this sample likely incorporates several environments, and would not be expected to look like the lagoon.

Archaeological shells identified from the ancient Knysna Lagoon are all species that live in warm estuarine environment and often burrow into muddy sand, suggesting that there was a low-tide mudbank related to the estuary (Marker & Miller 1993). The Keurbooms Estuary also experienced a rise in sea level ending around 3980 BP (Reddering 1988). This estuary is fed by a large river of the same name. Excavations at the open site of Noetsie revealed large accumulations of shellfish and several species of

fish (Orton & Halkett 2007). The midden is located near the entrance of the river to the ocean, and a large ponded reservoir of water continues well into the valley.

The Verlorenvlei, near Elands Bay, is a large coastal freshwater lake with a small estuary connecting the lake to the sea, and is classified as both oligotrophic lake and marshland/reedswamp (Burgers 1991). Significant marshlands grow along the main river into the lake, and dominant vegetation types include macrophytes, mixed sedges, reeds, and water lilies (*Nymphaea capensis*) (ibid.). Fish species include both freshwater (*Galaxias zebratus*- Cape galaxia and *Barbus burgi*) and estuarine (such as *Lithognathus lithognanthus*-white steenbras, *Liza richardsonii*-haarder, and *Mugil cephalus*-mullet) (ibid.). Similar to Langebaan, $\delta^{34}S$ values of primary producers should vary greatly throughout the different habitats provided by the lake, and it may be possible to determine where particular consumers were feeding.

Ribbed mussels (*Geukensia demissa*) were analyzed (Peterson et. al 1985) throughout an ocean-to-inner marsh transect in Cape Cod, USA, with $\delta^{34}S$ values ranging from +0.5 to +19.2‰. $\delta^{34}S$ of the oceanic mussels were similar to plankton while mussels from small creeks and the inner reaches of the marsh had significantly lower values, closer to marsh grass. Bottom dwellers such as clams were found to have low $\delta^{34}S$ (+2.6‰) (Peterson et al. 1985). This remarkable difference in $\delta^{34}S$ of available sulphur within one environment illustrates the need to sample not only one representative of a species, but several collected from a variety of locations prehistoric people may have sourced food from, and all represented shellfish species should be sampled. If mussels can exhibit such a wide range of values in one area depending on sulphate or sulphide sources, and the same observation applies to South Africa, then this could help explain the different $\delta^{34}S$ values in consumers at each site. Most marsh plants are C_4 grasses with low $\delta^{34}S$ values, and would have been selected by grazers. Based on $\delta^{13}C$ values, all animals sampled at

west coast sites other than Hout Bay were C_3 feeders and would not have eaten estuarine plants, and their $\delta^{34}S$ values would rather be influenced by marine sulphate. While $\delta^{15}N$ values (15.7, 14.2, 16.4‰ for SAM-AP 5082, UCT-MED 158, and UCT 220) in the humans from Hout Bay with low $\delta^{34}S$ values do not directly imply shellfish consumption, the $\delta^{34}S$ values could also be related to high trophic level marine consumers feeding in the bay. A seal colony is present on an island near Hout Bay, and animals are frequently seen feeding on schools of fish along the shoreline of the bay. Carnivorous deep water fish have also been observed hunting primarily in estuarine environments (Lamontagne et al. 2007), so perhaps these pelagic fish with potentially low $\delta^{34}S$ values provided easy hunting opportunities for humans in the bay.

Inland Environments

The five "inland" sites in the Clanwilliam district (Eland Cave, Watervals Rivier, Wyegang and Klipfonteinrand; SAM-AP 1449 is designated simply 'Clanwilliam' and presumably came from somewhere close to the town) extend from the seaward side of the Fold Belt Mountains over the top of the range, roughly 70 to 95km from the coast and in an area of limited rainfall. All $\delta^{34}S$ values are remarkably uniform and high. As suggested by Privat et al. (2007), elevated human $\delta^{15}N$ paired with high $\delta^{34}S$ values could indicate a diet with a strong reliance on freshwater fish. Nitrogen isotope data can be compromised due to the aridity of the region (Sealy et al. 1987), but the $\delta^{13}C$ values clearly reflect little seafood input into the human diet. Sulphur isotope ratios must be controlled by geology and climate for this region. The animal from Doornbos, just inland of the mountains and in a rain shadow has a very low $\delta^{34}S$ value, as do most of the bovids from Aspoort, also inland of the Fold Belt Mountains but somewhat farther south, and approximately 110km from the coast. These are both areas of very low rainfall. Fast-

flowing perennial rivers such as the Olifants and the Doorn provide fresh water near all these sites. These rivers are not associated with extensive areas of wetland. River sediments are derived from weathering of local bedrock and reworked, so river $\delta^{34}S$ values should be similar to the local geology. The elevated values of all samples from this area presumably indicate ancient marine rocks and marine aerosol and precipitation contribution, with little input from sulphate reducing bacterial sources.

As discussed in the Literature Review chapter, $\delta^{34}S$ values of consumers are typically around 1‰ lower than their diets (Barnes & Jennings 2007; Richards et al. 2001). Human $\delta^{34}S$ values should therefore be slightly lower than those of the animals they consumed. Table 6 presents mean $\delta^{34}S$ values for the six sites where both humans and animals were sampled. Animal samples from Elands Bay have very similar $\delta^{34}S$ values (16.2‰ and 16.7‰ for UCT 3250 and UCT 3251, respectively), while the two human samples from the same site have values much lower than the animals (13.1‰ and 14.3‰ for UCT-MED 373 and UCT 3137, respectively). The same pattern is seen in the human and bushpig from Knysna, and for the grysbok and one of the humans from Byneskranskop (SAM-AP 6050). The other human (SAM-AP 6052) has a value 1‰ higher than the animal. All three humans from Hout Bay (13.3, 13.3 and 14.0‰) have $\delta^{34}S$ values higher than the two bovids (12.3 and 8.5‰). The human from Robberg was likely consuming a variety of animal protein. Obviously there is not enough information to draw any conclusions, but it is probable based on $\delta^{34}S$ values that the many of the animals sampled at these sites were consumed by the humans. The mean $\delta^{34}S$ value of the nine animals from the west coast is 15.4‰ $\pm$ 3.1. The mean of the fourteen humans from the west coast is 14.5‰ $\pm$ 1.4, almost exactly 1‰ lower than the animals. The same is true for the south coast: the mean of 21 animal samples (UCT 13159 excluded) is 16.6‰$\pm$1.2, while the mean of the 16 human samples (NMB 1273 excluded) is

15.6‰±1.3, exactly 1‰ lower than the animals. For the Fold Belt Mountain inland samples, human and animal samples have very similar $\delta^{34}S$; the mean of two animal samples is 16.9‰±0.6, while the mean of four humans is 16.6‰±0.3. Based on shell midden contents, shellfish were the dominant dietary resources, and none of these were analyzed. Although terrestrial fauna are little represented in the archaeological assemblage, these results show that they could have been a consistent protein source, although shellfish $\delta^{34}S$ values must be acquired. At Elands Bay, Hout Bay, Byneskranskop, Knysna, and the Robberg Peninsula both animals and humans were analyzed. In general, where $\delta^{34}S$ values of animals are high, those of humans are also high. The exception to this pattern is Elands Bay, where two humans have $\delta^{34}S$ values approximately 3‰ lower than the two animals.

Table 6: Sites with both Humans and Animals

	Animal mean ‰	Human mean ‰	Difference ‰
Elands Bay	16.5	13.7	2.8
Knysna	16.3	14.8	1.5
Byneskranskop	16.2	16.5	-0.3
Hout Bay	10.4	13.5	-3.1
Robberg	17.1	17.2	-0.1
Fold Belt Mountains	16.9	16.6	0.3

Suggestions for Future Work

It would be beneficial for future studies to sample terrestrial animals (both grazers and browsers) and the suite of shellfish and crustaceans from the coastal sites that had low $\delta^{34}S$ values in humans, but no animals for comparison (Saldanha, Bloubergstrand, Yzerfontein, Keurbooms River, and Noetsie). Mussel shell should indicate sulphate incorporated into the shell during growth (Peters et al. 2010), so potentially it would be possible to measure $\delta^{34}S$ in archaeological shell to identify the habitat the mussels were

selected from (Carell et al. 1987). Fresh and brackish water fish should also be analyzed; archaeological specimens would be best, but modern species that were also consumed in antiquity could be sufficient.

One major problem with sampling modern plants is that atmospheric values have changed dramatically in parts of the world as anthropogenic sulphur has altered the sulphate composition of the atmosphere. Anthropogenic contributions are commonly detected even in pristine environments, presumably making the $\delta^{34}S$ analysis of modern plants incompatible with archaeological remains. Based on the similarities in $\delta^{34}S$ values of modern and archaeological animals analyzed in the Western Cape, it may be possible to sample a wide range of modern edible plant resources to acquire a $\delta^{34}S$ library of the landscape. To determine if modern plants can be reliably relatable to archaeological, limited archaeological plant residues should also be sampled.

Another interesting avenue for future research is the possibility $\delta^{34}S$ values reflect nutritional deficiencies. A few controlled feeding experiments have indicated such phenomena could be observed in animals (see Literature Review). If this course of research has potential, it would be interesting to analyze $\delta^{34}S$ on the samples that have long been the focus of $\delta^{13}C$ and $\delta^{15}N$ analysis. If the overall reduction in size of Holocene foragers around 3500 BP is due to a decrease in available protein, this could be reflected in $\delta^{34}S$ values. To interpret the results, a wide range of skeletons throughout a long expanse of time is essential for comparison purposes, a need which this skeleton assemblage meets. Although, the populations before and after this period of study in the Western Cape Province may not be the best case study for this theory, as prior to 3500 BP people were likely highly mobile, and after 2000 BP pastoralism was introduced; both could result in different $\delta^{34}S$ values than the semi-sedentary population sampled for this thesis.

Additional controlled feeding experiments are also vital to understanding sulphur metabolism in mammals.

Conclusions

This thesis analyzed sulphur isotopes in a variety of archaeological animal and human samples selected from a wide array of habitats in the Western Cape of South Africa. The aim of this initial research was to create a $\delta^{34}S$ "baseline map" of the region, in the hopes of determining if future analysis is warranted, and if so, to suggest further avenues of exploration.

The Western Cape Province of South Africa is a "sulphate flooded" environment, with few sulphide producing basement rocks. Modern (aerosol input and sea water sulphate) and ancient (weathering ancient marine sediments with high $\delta^{34}S$) sources both contributed to the $\delta^{34}S$ values, with bacterial action as the main modifier. Estuarine and slow-moving water environments greatly influence sulphur values. Thus, modification of the marine "flood" $\delta^{34}S$ values appears to be more influenced by surface hydrology and accompanying bacterial transfer than rock weathering.

"Megamiddens" along the west coast attest to the importance of shellfish in Later Stone Age diets, and if some of this shellfish were procured from brackish water environments it would likely have lower $\delta^{34}S$ values than marine-derived shellfish. Little can be assumed without actual values, but it would appear that humans and animals sampled along the west coast were selecting their food sources from areas of similar geology, but with different aquatic inputs. The Robberg Peninsula is the only unequivocally "marine" site sampled, with no immediate source of freshwater food stock. All terrestrial animal and human samples have high $\delta^{34}S$ values, indicating that the freshwater source was fast moving or did not provide dietary resources, and that most

vegetation was selected from the peninsula or other environment high in marine sulphate. The Hout Bay valley was the most restricted estuarine environment (little food resource that wasn't connected to the estuary and marshlands), and $\delta^{34}S$ values of all species are the lowest of this study, indicating that bacterially reduced sulphate was likely a major factor.

To fully understand the $\delta^{34}S$ values, ecosystem variables should be identified and defined, and sulphur isotope ratios mapped throughout the environment. Further assessment of sulphur isotopes in the Western Cape region would greatly benefit from a transect taken from both the south and west coasts and over the Fold Belt Mountains to observe the extent of the "sea spray effect" and the $\delta^{34}S$ values of similar plant species in areas of different bedrock and rainfall. It would also be informative to analyze rodents from the different sites to collect baseline animal values for each region.

Without further understanding of the ecology and comprehensive $\delta^{34}S$ analysis of possible contributions, this interpretation is merely speculation. The Western Cape of South Africa provides numerous ecological environments for further study. This area is not as affected by anthropogenic pollution as most of the Northern Hemisphere, and it may be possible to use modern samples as analogues to archaeological material.

The aims and objectives of this study were met as $\delta^{34}S$ values, paired with stable carbon and nitrogen analysis, show potential in defining distinct aspects of ecosystems as sources of dietary protein. In the Western Cape Province of South Africa, the degree to which variability in local geomorphology and hydrology influence sulphur isotope values was surprising. Although based on few samples, inhabitants of individual sites seem to group together, with human values more complex than animal.

Interpretation of $\delta^{34}S$ values is complicated and environmental and ecological factors at each individual site must be considered before reflecting on the region as a whole. Without widespread sampling, defining value ranges is difficult, and studies based

on a small number of samples should be regarded with caution as they can be prone to over-interpretation.

While difficulties with interpreting $\delta^{34}S$ exist, they are not insurmountable. As with stable carbon and nitrogen isotope analysis decades ago, an interdisciplinary perspective and application of the methodology to a diverse array of research questions can help identify and understand the potential contribution of sulphur isotopes to palaeodietriary studies. With recent technological advances increasing the availability of equipment, more archaeologists may incorporate $\delta^{34}S$ analysis into their research. As data accumulate and parameters become more clearly defined, difficulties with interpretation will be diminished.

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