Strontium Isotopes from the Earth to the Archaeological Skeleton: A Review

R. Alexander Bentley[1,2]

Strontium isotope analysis of archaeological skeletons has provided useful and exciting results in archaeology in the last 20 years, particularly by characterizing past human migration and mobility. This review covers the biogeochemical background, including the origin of strontium isotope compositions in rocks, weathering and hydrologic cycles that transport strontium, and biopurification of strontium from to soils, to plants, to animals and finally into the human skeleton, which is subject to diagenesis after burial. Spatial heterogeneity and mixing relations must often be accounted for, rather than simply "matching" a measured strontium isotope value to a presumed single-valued geologic source. The successes, limitations and future potential of the strontium isotope technique are illustrated through case studies from geochemistry, biogeochemistry, ecology and archaeology.

KEY WORDS: ^{87}Sr-/^{86}Sr-; teeth; tooth; bone; prehistoric migration.

INTRODUCTION

Of all the isotopes that are currently analysed in archaeological skeletal tissues, strontium isotopes are one of the most effective for characterising prehistoric human and animal mobility. Before archaeologists discovered the method, ecologists measured Sr isotopes to map the geographical movement of certain species and environmental materials (e.g., Åberg, 1995; Blum *et al.*, 2000; Chamberlain *et al.*, 1997; Gosz *et al.*, 1983; Koch *et al.*, 1992). Ericson (1985) then introduced the method to archaeologists, suggesting that one could measure strontium isotopes in the teeth and bones of archaeological human skeletons. As with all new archaeometric techniques, subsequent pioneering studies showed the

[1]Department of Anthropology, Durham University, Durham.
[2]To whom correspondence should be addressed at Department of Anthropology, Durham University, 43 Old Elvet, Durham DH1 3HN; e-mail: r.a.bentley@durham.ac.uk.

realistic limitations of the technique, but they were also encouragingly successful in characterising prehistoric human migration in studies at Grasshopper Pueblo in Arizona (Ezzo *et al*., 1997) and of hominins from the Cape region of South Africa (Cox and Sealy, 1997; Sealy *et al*., 1991, 1995; Sillen and Sealy, 1995; Sillen *et al*., 1998), Viking-era Iceland (Price and Gestsdóttir, 2006), Tiwanaku in Peru (Knudson *et al*., 2004), Mayan Teotihuacan (Price *et al*., 2000), Anglo Saxon England (Montgomery *et al*., 2005) and Prehistoric Europe (e.g., Bentley *et al*., 2002; Budd *et al*., 2004; Grupe *et al*., 1997; Müller *et al*., 2003; Price *et al*., 2001). Many other applications are discussed in this paper, all of which suggest a great many more to come, which is why this is a timely point to review the method. It goes without saying that it is usually more effective to measure isotopes besides strontium in the same samples, such as oxygen, carbon or sulphur, and this paper discusses strontium isotopes exclusively only to focus the topic.

Strontium isotopes serve as geochemical signatures that can be used to "source" a prehistoric skeleton to a geologic area, depending on how mobile the individual was during life. The idea is that strontium isotopic signatures are conveyed from eroding geologic materials through soils and the food chain into the human skeleton, where strontium substitutes for calcium in the minerals of skeletal tissue. There are additional, non-geologic sources of strontium in the biosphere, and the key to the method is to match the isotopic signatures from an individual to the *biologically-available* signature at a suspected location of origin. This review paper discuss the challenge of how to connect the strontium isotope ratio measured from archaeological skeletons (usually the tooth enamel), to the prehistoric biochemical environment in which the people lived. This is more involved than simply equating the strontium isotope signature in local bedrock to the signature in the skeleton of a prehistoric person. The strontium isotope ratio ($^{87}Sr/^{86}Sr$) is simply a number, best reported to five decimal digits, that reflects the average of all strontium that has been contributed to the sample. In the case of a prehistoric skeleton, each strontium atom has 'journeyed' through many different stages–perhaps from a partial melt of magma, into an igneous rock mineral, into a stream, into a soil, into a plant stem, decomposed back into the soil, into a plant leaf, into an herbivore, and into the meal of a prehistoric person. Within that person's skeletal tissue, it joins strontium atoms that have followed other routes, some from a different source, such as a different rock mineral, the ocean, or even atmospheric precipitation. After centuries or millennia underground in a human burial, the strontium is finally released again from the skeletal mineral in the modern laboratory and counted by mass spectrometry.

This paper is devoted to describing the variety of pathways, sources, and mixing relationships that characterise the transfer of strontium from rocks to the analysed skeletal sample. It begins by describing how strontium isotopes are used for geochronology and how strontium isotope ratios differ in major rock types, and then how strontium isotope ratios are reflected in weathered materials and

stream waters, plants, animals and people, and finally how strontium isotopes are incorporated into archaeological skeletons.

Strontium Isotopes in Rocks

How strontium isotopes are geographically distributed in the biosphere is largely determined by how ^{87}Sr has evolved in geologic systems. Strontium is an alkaline earth element with a valence of $+2$. Since its ionic radius (1.32 Å) is only slightly larger than that of calcium (1.18 Å), Sr^{2+} substitutes for Ca^{2+} in minerals including plagioclase feldspar, calcite, dolomite, aragonite, gypsum and, most importantly regarding archaeological skeletons, apatite. Strontium has four naturally occurring isotopes. Three of these are non-radiogenic, including ^{84}Sr ($\sim$0.56%), ^{86}Sr ($\sim$9.87%) and ^{88}Sr ($\sim$82.53%). The fourth isotope, ^{87}Sr (7.04%), is radiogenic, as it is formed over time by the β-decay of ^{87}Rb, with a half-life of about 4.88×10^{10} years. Rubidium is an alkalai metal with a similar ionic radius (1.52 Å) to that of potassium, such that Rb^{1+} often substitutes for K^{1+} in minerals such as potassium feldspar, muscovite, biotite, and illite.

The Rb-Sr decay system has been widely used in geochronology and remains one of the most useful geochemical tracers, as ^{87}Sr/^{86}Sr is a function of the relative abundances of rubidium and strontium and the age of the rocks. Specifically, the ^{87}Sr/^{86}Sr ratio in a rock mineral depends on: (1) the ^{87}Sr/^{86}Sr at time the rock crystallized, $t = 0$, (2) the ^{87}Rb/^{86}Sr ratio, which is directly proportional to the Rb/Sr ratio in most cases, and (3) the time t elapsed since formation. As a variant of the general decay equation for radioactive decay, $N = N_o e^{-\lambda t}$ (N is the current amount, λ the decay constant, N_o the initial amount, and t is time), the amount of ^{87}Rb remaining is given by:

$$^{87}Rb = {}^{87}Rb_0 e^{-\lambda t} \tag{1}$$

where the decay constant λ for ^{87}Rb is 1.42×10^{11} yr^{-1}. As this decay produces the daughter isotope, ^{87}Sr, ^{87}Rb decreases by the same amount that ^{87}Sr increases, i.e.:

$$^{87}Sr = {}^{87}Sr_0 + {}^{87}Rb_0 - {}^{87}Rb_0 e^{-\lambda t}, \tag{2}$$

where ^{87}Sr$_0$ is the original amount of ^{87}Sr, at $t = 0$. To compare the ^{87}Sr abundances in different samples, ^{87}Sr abundances are normalized to the non-radiogenic ^{86}Sr, which cancels out variations in total Sr, allowing comparison of ^{87}Sr differences resulting from the decay of ^{87}Rb. If we divide all amounts in Eq. (2) by ^{86}Sr and substitute in Eq. (1), after some algebra this yields:

$$\frac{^{87}Sr}{^{86}Sr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_0 + \frac{^{87}Rb}{^{86}Sr}(e^{\lambda t} - 1). \tag{3}$$
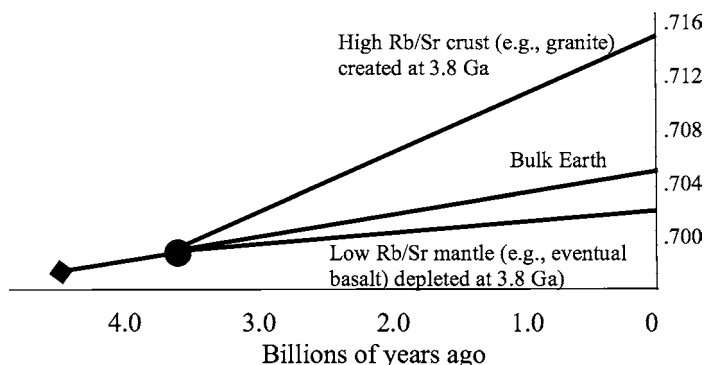
Fig. 1. Sr isotopic evolution of the bulk Earth, high Rb/Sr crust created at 3.8 Ga (giga-annum, or billions of years), hypothetical residual mantle and a mantle being continuously depleted. The $^{87}Sr/^{86}Sr$ of the bulk Earth has evolved along a straight line with slope proportional to the bulk Earth $^{87}Rb/^{86}Sr$ (about 0.085). After White (n.d., Fig. 8.7).

Because $t << 1/\lambda$, a Taylor Series approximation[3] is used to make the simplification $(e^{\lambda t} - 1) \approx \lambda t$, yielding:

$$\frac{^{87}Sr}{^{86}Sr} \cong \left(\frac{^{87}Sr}{^{86}Sr}\right)_0 + \frac{^{87}Rb}{^{86}Sr}\lambda t. \tag{4}$$

Equation (4) has the form of a straight line: $^{87}Sr/^{86}Sr = a + bt$, on a plot of $^{87}Sr/^{86}Sr$ vs. t with slope $b = \lambda\,^{87}Rb/^{86}Sr$ and intercept $a = (^{87}Sr/^{86}Sr)_0$. The Sr isotopic evolution of the Earth and its major silicate reservoirs (the continental crust and mantle) is illustrated in the *isotope evolution diagram* of Fig. 1, showing $^{87}Sr/^{86}Sr$ vs. time. Hence a closed reservoir will evolve along a line whose slope is proportional to the parent-daughter ratio $^{87}Rb/^{86}Sr$, as shown by Eq. (4).

The Rb-Sr decay system produces an array of values from the different minerals of a rock. Given measurements of $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ in a sample, two unknowns remain in Eq. (4): t and the initial ratio $(^{87}Sr/^{86}Sr)_0$. Neither can be calculated from a single sample. However, if $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ can be measured on a second mineral for which t and $(^{87}Sr/^{86}Sr)_0$ are the same, we have two equations and two unknowns, and the difference between Eq. (4) for each

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[3]The Taylor series is a method of approximating a function by the sum of its derivatives. The function e^x has the Taylor series expansion

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

If x is small, then the terms on the right are negligible, and we have

$$e^x \approx 1 + x, \text{ or } (e^x - 1) \approx x.$$

mineral yields:

$$\Delta \frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \Delta \frac{^{87}\text{Rb}}{^{86}\text{Sr}} \lambda t. \tag{5}$$

This shows that a line results if $^{87}\text{Sr}/^{86}\text{Sr}$ is plotted against the quantity $\lambda^{87}\text{Rb}/^{86}\text{Sr}$. This line is known as an *isochron*, and has slope t and intercept $(^{87}\text{Sr}/^{86}\text{Sr})_0$. As can be seen from Eq. (5), the older the system is, the steeper the isochron will be because the differences in $^{87}\text{Sr}/^{86}\text{Sr}$ are built-up over time by differences in $^{87}\text{Rb}/^{86}\text{Sr}$. The slope of the isochron depends only on t, which can be solved for as:

$$t = \frac{1}{\lambda} \left(\frac{\Delta(^{87}\text{Sr}/^{86}\text{Sr})}{\Delta(^{87}\text{Rb}/^{86}\text{Sr})} \right). \tag{6}$$

If two minerals with different Rb/Sr ratios formed within a rock at the same time with the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, then the rock with the higher Rb/Sr ratio will have a higher measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. In other words, a single rock, which partitioned into different minerals when it crystallized, yields a linear array of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, as described by its isochron.

Geological Variation in $^{87}\text{Sr}/^{86}\text{Sr}$

The previous section has shown how the ^{87}Sr content of a rock is a function of how much Rb has been in the rock and for how long. Table I shows typical concentrations of Rb, Sr, K and Ca in natural minerals. Rb is a highly soluble, highly incompatible[4] element, and Sr is also relatively soluble and not quite as incompatible, which is to say that Sr has a smaller ionic radius than Rb, and is more compatible in silica-rich igneous systems, partitioning preferentially into plagioclase. Because of these geochemical differences, Rb/Sr in rocks can vary by several orders of magnitude (Table I), and as a result $^{87}\text{Sr}/^{86}\text{Sr}$ varies substantially among current geological terrains. Rocks that are very old ($>$100 mya) with high original Rb/Sr have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios generally above 0.710, and rocks formed recently ($<$1–10 mya) with low Rb/Sr ratios have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios generally less than 0.704. The Earth's mantle has a relatively uniform and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, about 0.702–0.704 in basalts erupted along mid oceanic ridges, or oceanic islands such as the Hawaiian chain (White *et al.*, 1976; White and Hofmann, 1982). In oceanic island arcs (e.g. Aleutian Islands, Japan, Vanuatu), formed by subduction-related magmatism of mantle/crust mixtures, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from about 0.7035 to 0.707 (Dickin, 1995, pp. 164–169; White, n.d.). Phanerozoic marine limestone and dolomite have intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of about 0.707–0.709, reflecting the composition of the ocean during their deposition. Overall the

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[4]Incompatible elements – such as K, Rb, Cs, Sr, and Ba – tend to be concentrated in the melt phase when melting or crystallization occurs, which over the history of the Earth has enriched the salicious crust in incompatible elements, which are correspondingly depleted in basaltic and ultramafic rocks.

Table I. Typical (i.e., Order of Magnitude) Values/Ranges of Sr and Ca Concentrations, in ppm, in Some Natural Materials, as well as Rb/Sr Ratios for Geologic Materials

Material	Sr	Ca	Rb/Sr
Geologic			
Sandstone	20	40,000	3
Low-Ca granite	100	5,000	2
Deep-sea clay	180	30,000	0.6
Syenite	200	20,000	0.6
Shale	300	20,000	0.5
High-Ca granite	440	25,000	0.3
Ultramafic rock	1	25,000	0.2
Basalt	500	75,000	0.07
Deep-sea carbonate	2000	300,000	0.005
Carbonate	600	300,000	0.005
Soils			
Soil minerals[b,d]	10–1000	24,000	
Labile soil minerals	0.2–20	1,000	
Soil moisture[d]	0.001–0.07	1–4	
Water			
Seawater	8	400	
Rivers	0.006–0.8	15	
Rain	0.001–0.4	1–100	
Snow	0.00001–0.001	0.01–0.1	
Biological			
Edible plants[c]	1–100	3,000–6,000	
Mammal (incl. human) bone[c,d]	100–1000+	∼370,000	
Mammal (incl. human) enamel[e]	50–500+	∼370,000	

Note. This is a rough guide, as specific values can be highly variable. Approximated after Capo *et al*. (1998), with additions from [a]Aubert *et al*. (2002), [b]Bashkin (2002), [c]Burton *et al*. (1999), [d]Elias *et al*. (1982), and [e]Kohn *et al*. (1999).

$^{87}Sr/^{86}Sr$ ratios in rocks of the continental crust vary between 0.702 and 0.750, including older granites, with $^{87}Sr/^{86}Sr$ ratios typically above 0.710 and as high as 0.740, to younger basalts, with lower $^{87}Sr/^{86}Sr$ ratios around 0.703–0.704. These variations are large relative to the instrumental error of modern mass spectrometry measurements (typically ± 0.00001 or better).[5]

The Rb-Sr system allows for a crude transformation from a geological map of bedrock types and ages into a coarse mapping of the expected $^{87}Sr/^{86}Sr$ variations. North America is a good example, because its geologic history covers most of

[5]The instruments of strontium isotope analysis, including the Thermal Ionisation Mass Spectrometer (TIMS) and the more recently developed Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS or just ICP-MS), are outside the subject of this review, as are the clean lab procedures such as purification of strontium through columns of cation exchange resin, loading of TIMS filaments, etc. These procedures as applied to archaeological skeletal materials are described in detail by many of the case studies (e.g., Balasse *et al*., 2002; Bentley *et al*., 2003; Budd *et al*., 2000; Hoppe *et al*., 2003; Montgomery *et al*., 2003b; Müller *et al*., 2003; Trickett *et al*., 2003). The technology is always improving, which more recent publications will inform upon, and excellent summaries of the analytical methodology are provided by Dickin (1995, Chapter 2) and the online textbook of White (n.d.).

the 4.5 billion-year history of the Earth, from the Late Pleistocene volcano at Mount Washington to the 3.96 Ga Acasta Gneiss in Canada (Bowring *et al*., 1989), resulting in a highly varied Sr isotope composition. In an early effort to determine continental evolution rate, Hurley *et al*. (1962) compiled a map of the Rb-Sr ages of rocks in North America. More recently, Beard and Johnson (2000, Fig. 1) demonstrated how Eq. (3) could be used to create a map of Sr isotope compositions of basement rocks of the United States, given the necessary input parameters provided by a digital geologic map, the corresponding geologic ages, average crustal Rb and Sr contents (Hofmann, 1988), and an assumed initial $(^{87}Sr/^{86}Sr)_0$ of 0.705.

Minerals within a single rock can have enormous variability in their $^{87}Sr/^{86}Sr$ ratios. For example, a rock such as granite can have two feldspars with radically differing $^{87}Sr/^{86}Sr$. Plagioclase feldspar in such a granite contains most of the calcium, and also strontium by association, and has very low rubidium; as a result it has a low $^{87}Sr/^{86}Sr$ close to 0.70. Conversely, potassium feldspars, which are the most abundant minerals in granite, have high levels of rubidium and low levels of strontium, with $^{87}Sr/^{86}Sr > 1.0$.

Strontium Isotopes in Environmental Systems

Because different minerals, even from the same rock, differ greatly in both their $^{87}Sr/^{86}Sr$ ratios and their Sr concentrations, the weathering of them will contribute unequally to the biologically-available Sr. In fact, Sr isotopes in an environmental reservoir are best expressed as a *mixing system* of inputs and outputs, including inputs from the atmosphere and bedrock weathering, outputs through stream- and groundwater and intermediate reservoirs that include the biosphere and soil (Fig. 2).

Strontium in rocks is released by weathering, cycled through soils, vegetation and animals, and eventually enters the oceans primarily by river transport of sediments. Over the time scale of these processes, the $^{87}Sr/^{86}Sr$ of each component does not significantly change through the decay of ^{87}Rb into ^{87}Sr, as this occurs with a half-life of 49 billion years. In addition, kinetic and equilibrium fractionations of $^{87}Sr/^{86}Sr$ are negligible at the low temperatures of biology because (unlike lighter elements such as H, C, N and O) the large atomic mass of Sr means that Sr isotopes pass from bedrock to soil into biologically-available solutions without measurably fractionating, i.e. retaining the same ratio of ^{87}Sr to ^{86}Sr (e.g., Graustein, 1989; Graustein and Armstrong, 1983; Hurst and Davis, 1981; Kawasaki *et al*., 2002). Furthermore, any possible fractionation in $^{87}Sr/^{86}Sr$ would be corrected for upon mass spectrometry anyway, by a routine normalization to the constant $^{88}Sr/^{86}Sr$ ratio of 8.37521 (Beard and Johnson, 2000).

Because minerals with different Sr concentrations and $^{87}Sr/^{86}Sr$ ratios weather at different rates, a geological map of $^{87}Sr/^{86}Sr$ variations in bedrocks is
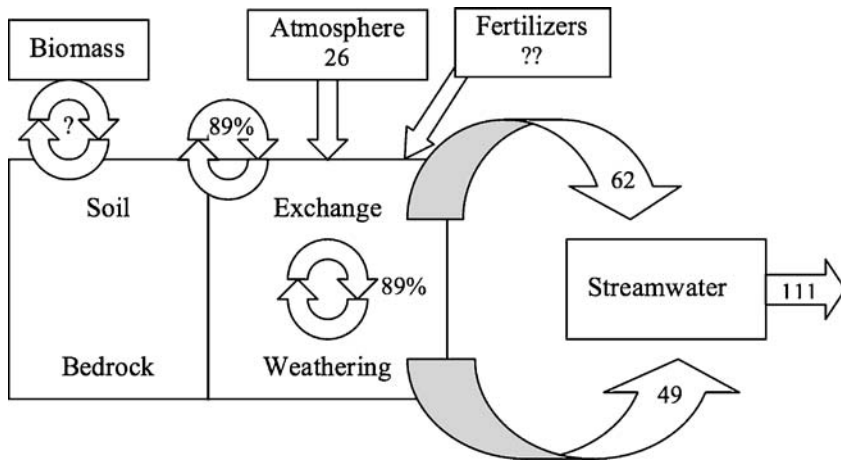
Fig. 2. Modern hydrochemical budget for Sr for a local area, in this case the Strengbach river catchment of the Vosges mountains. Each system is treated as a reservoir, with inputs and outputs, listed in g/ha per year (numbers). The percentages represent the atmospheric contribution to the exchangable Sr in the upper soil horizon, and the weathering input to the deep saprolite (chemically weathered rock). Adapted from Probst *et al.* (2000, Fig. 6), with "fertilizers" added.

not always sufficient to predict the ^{87}Sr/^{86}Sr entering the environmental Sr cycle. For example, many rocks with high ^{87}Sr/^{86}Sr also have low Sr levels (e.g., sandstone, Table I), so that their weathering makes a reduced impact on the ^{87}Sr/^{86}Sr in soils. The simplest model assumes mixing between two end-members, perhaps a low Sr, high ^{87}Sr/^{86}Sr granitic sandstone and a high-Sr, lower ^{87}Sr/^{86}Sr carbonate, for example. Beard and Johnson (2000, Fig. 2, Appendix 1), showed how measured soil and rock samples will fall along a mixing line, which forms a concave-up curve (Fig. 3a), because one end-member contributes more Sr than the other. Many researchers often prefer to plot the ^{87}Sr/^{86}Sr ratios against 1/Sr instead of Sr (e.g., Montgomery and Evans, 2006), so that the data plot as a straight line from one end-member to the other (Fig. 3b).

Mixing equations are used in conjunction with strontium isotope measurements to determine the relative contribution of individual inputs to the reservoir of interest. The following equation is used to predict the ^{87}Sr/^{86}Sr ratio in one reservoir, (^{87}Sr/^{86}Sr)$_{mix}$, from a mixture of n components (Capo *et al.*, 1998, pp. 210–211):

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{mix} = \frac{J_1(^{87}\text{Sr}/^{86}\text{Sr})_1 + J_2(^{87}\text{Sr}/^{86}\text{Sr})_2 + \cdots + J_n(^{87}\text{Sr}/^{86}\text{Sr})_n}{J_1 + J_2 + \cdots + J_n}, \quad (7)$$

where J_i represents the input amount of Sr from component i. For a two component system, the contribution of Sr from component number 1 to a mixture can be
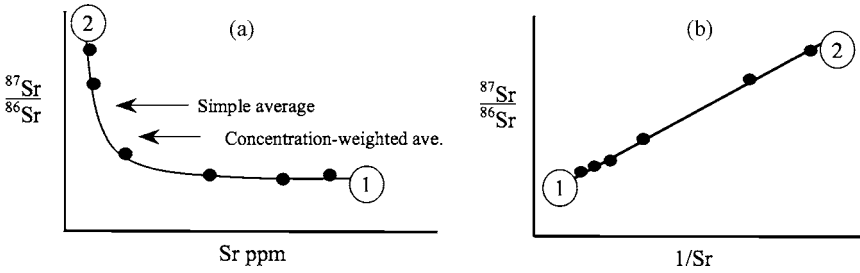
Fig. 3. (a) simplified version of a mixing model with two hypothetical end-members (circled numbers), showing how soil and rock samples (filled circles, hypothetical data) will fall along a curved, concave-up mixing line such that the biologically available Sr is closer to the concentration-weighted average (rather than simple average) of the $^{87}Sr/^{86}Sr$ ratios of the end-members. After Beard and Johnson (2000, Fig. 2). (b) The data plotted against 1/Sr instead of Sr.

calculated from the isotopic ratios of the mixture and the two components:

$$\frac{J_1}{J_1 + J_2} = \frac{(^{87}Sr/^{86}Sr)_{mix} - (^{87}Sr/^{86}Sr)_2}{(^{87}Sr/^{86}Sr)_1 - (^{87}Sr/^{86}Sr)_2} \tag{8}$$

As described below, mixing equations such as Eqs. (7) and (8) are generally applicable, as J_n can represent the Sr concentrations of whole-rock end-members, or Sr fluxes in rivers, or Sr content of the foods in an animal's diet.

Rivers

The concentration of Sr in river water around the world averages 0.06 ppm and varies from about 0.006 to 0.8 ppm (Capo *et al.*, 1998). Rivers carry most of the weathering products from the continents to the oceans (other material is carried by winds and glaciers), mostly as suspended load, but a small yet significant fraction of the Sr in rivers is in dissolved form. Sediments carried by rivers are only representative of rocks undergoing erosion, and elevated regions erode faster and therefore generate more sediment than low plains. Since tectonically active areas are typically elevated relative to stable areas, sediments are biased toward younger crust, and will have lower Sr isotope ratios (White n.d., Chapter 13).

As mentioned above, the erosion products that enter the river may not necessarily have isotopic compositions of the rocks as a whole. Compared with calculating the average of regional rock components, weighted by erodeable concentrations (Beard and Johnson, 2000), river composition is often a more convenient representation of the $^{87}Sr/^{86}Sr$ in the nutrient pool available to solids and plants. Also, geochemists have already measured the isotopic composition of dissolved or suspended loads in many rivers (e.g., Goldstein and Jacobsen, 1987; Négrel and Deschamps, 1996; Palmer and Edmond, 1989; Tricca *et al.*, 1999), with $^{87}Sr/^{86}Sr$ that appears to be consistent over a range of flow rates (Bain *et al.*, 1998).

At high elevations, where weathering rates are high, $^{87}Sr/^{86}Sr$ in stream waters and bedrock are often more closely correlated, as in the Vosges mountains of France, for example. In a granitic, high-$^{87}Sr/^{86}Sr$ area of the Vosges, Aubert *et al.* (2002) found that during periods of low stream flow, waters had lower Sr concentrations and lower $^{87}Sr/^{86}Sr$ ratios than during high flow periods. Up to a point (discharge < 9 l/s), there was a positive linear relationship between $^{87}Sr/^{86}Sr$ and discharge, and with very high flow rates the $^{87}Sr/^{86}Sr$ in the water nearly reached that of the bedrock (Aubert *et al.*, 2002). Similarly, in the Tyrol region of Alpine Austria, Hoogewerff *et al.* (2001) found that stream water samples closely reflected the geologically-expected $^{87}Sr/^{86}Sr$ ratios, whether in stream samples in areas of marine limestone (0.707–0.708, reflecting $^{87}Sr/^{86}Sr$ in Jurassic/Cretaceous seawater), or in the central crystalline Alps (0.720–0.725, old gneisses with high Rb/Sr). In this particular case, local streamwater $^{87}Sr/^{86}Sr$ ratios were predictive of those in local humans. Although skulls of people who lived in historic times had slightly higher $^{87}Sr/^{86}Sr$ ratios (0.7088–0.7098) than expected for their homes in a limestone region of Alpine Austria, Hoogewerff *et al.* (2001) reasoned that the slight difference was due either to diagenesis of the limestones and/or preferential leaching from the soils. In a nearby area predominated by gneiss, Hoogewerff *et al.* (2001) found that the historic skull $^{87}Sr/^{86}Sr$ ratios (0.7120–0.7320) were close to the ratios in local water samples.

At lower elevations, the link between local bedrock and river content is blurred, because rivers tend to carry a mix of upstream rocks and solids as well as precipitation. By the same token, because rivers are also depositing that same material on their floodplains, the $^{87}Sr/^{86}Sr$ ratio in a river sample can often provide an excellent basis for predicting the $^{87}Sr/^{86}Sr$ available to plants and animals at different localities. There can be some difference in $^{87}Sr/^{86}Sr$ between river water and ground water. In southern Germany, the dissolved load of the Rhine river has a $^{87}Sr/^{86}Sr$ ratio of about 0.7085, while groundwater samples from the same valley average 0.7087 (Tricca *et al.*, 1999). In central America, Hodell *et al.* (2004) found that water samples from the lowlands of the northern Yucatan Peninsula had a greater range of $^{87}Sr/^{86}Sr$ than in the southern lowlands, because the deeper water table in the southern lowlands allowed the $^{87}Sr/^{86}Sr$ of surface waters to more closely reflect the exposed limestone.

One particularly convenient study area for strontium isotope analysis of archaeological skeletons is the Upper Rhine Valley, which is part of a large graben some 40 km wide, extending almost 300 km from Basel, Switzerland, to Mainz, Germany. In this area, the strontium isotopic content of groundwater and river water has been extensively studied. Within the graben are Jurassic deep-sea deposited rocks (siltstones, evaporites and carbonates) from which we expect intermediate $^{87}Sr/^{86}Sr$ ratios (0.708–0.709). Stream water values reflect this, as Tricca *et al.* (1999) measured $^{87}Sr/^{86}Sr$ ratios of 0.70847 ± 0.00009 in the dissolved load of the Rhine river (Fig. 4). Although ratios from the suspended load are as high as
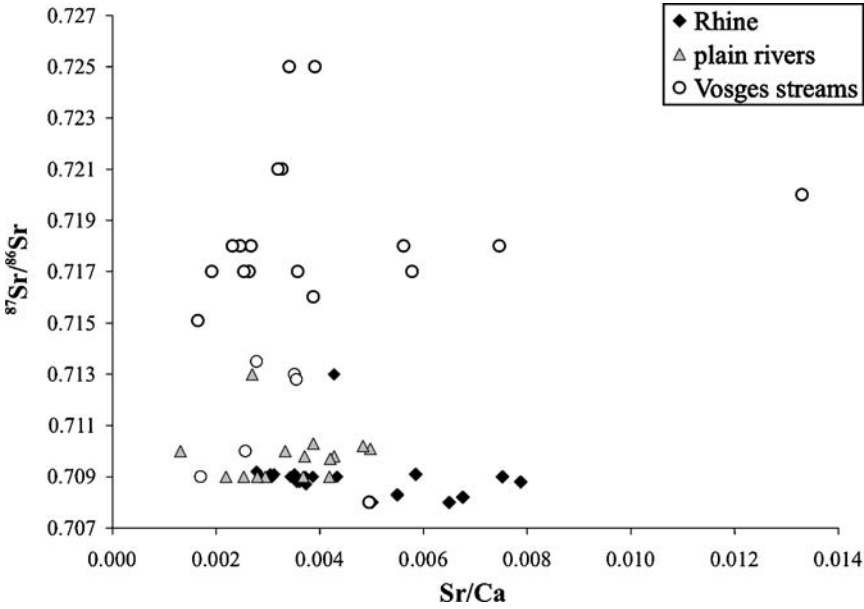
Fig. 4. $^{87}Sr/^{86}Sr$ vs. Sr/Ca in water samples from the Upper Rhine Valley. The Vosges drainages have a strontium isotope composition distinct from the lower Rhine Valley. The samples represent the dissolved load of these rivers. After Tricca *et al.* (1999, Fig. 2).

0.7117, when these solids were leached in 1 N HCl, $^{87}Sr/^{86}Sr$ in the leachates was 0.7084 or lower (Tricca *et al.*, 1999). The Rhine contains Sr from sources of pollution (Buhl *et al.*, 1991), but upstream toward the Alps the $^{87}Sr/^{86}Sr$ ratios in the unpolluted Upper Rhine are between 0.7083 and 0.7085, which is consistent with calcareous sediments of the Alps (Tricca *et al.*, 1999, p. 143).

On either side of this valley are the Vosges (France) and Black Forest (Germany) mountains, both part of the same horst formation of Palaeozoic granites, granodiorites and metamorphic rocks about 300–400 million years old, with high $^{87}Sr/^{86}Sr$ ratios (>0.715) typical of these old, high Rb/Sr rocks. The stream water values bear this out, as $^{87}Sr/^{86}Sr$ ratios in different Vosges range from about 0.717 to 0.725 (Tricca *et al.*, 1999; Aubert *et al.*, 2002). Between the alluvial plain of the Rhine and the Vosges are foothills with transitional $^{87}Sr/^{86}Sr$ ratios close to 0.710, which represent a mixture between highly radiogenic water discharging from the Vosges and groundwater in the upper Rhine valley (Tricca *et al.*, 1999). In this area, the nearer the sampling to the mountains, the higher the $^{87}Sr/^{86}Sr$ ratios. In fact, the two plain-river ratios above 0.713 (Fig. 4) are just downstream from a merging tributary flowing directly out of the Vosges mountains (Tricca *et al.*, 1999, p. 144).

In any case, preliminary to any bio-archaeological sampling, the stream water data already confirm a convenient strontium isotopic difference between crystalline uplands (>0.715) and marine-sedimentary lowlands (0.708–0.710), making the Upper Rhine Valley an ideal region to study human mobility through Sr isotopes (Bentley and Knipper, 2005a).

A more complex terrain, studied by Hodell *et al*. (2004), lies in the highlands of southern Guatemala, where a chain of young (Tertiary and Quaternary) volcanoes has created thick sequences of pumice and ash that are overlain by thin, rich soils. As Hodell *et al*. (2004) expected from young basaltic deposits, they found that plants, water and rocks from this region all had $^{87}Sr/^{86}Sr$ ratios ranging from 0.703 to 0.704. Because these volcanic highlands have eroded to form the Quaternary alluvium on the adjacent coastal plain, this coastal area also yielded $^{87}Sr/^{86}Sr$ ratios of about 0.704. The metamorphic region of Guatemala contains a whole range of rock types and ages, including outcrops of serpentinite, granite, diorite, phyllite, schists, marble and migmatite. Consequently, this province shows substantial differences in $^{87}Sr/^{86}Sr$ ratios between areas in close proximity. The $^{87}Sr/^{86}Sr$ ratio in Lake Izabal (~ 0.708), for example, is consistent with its river input from the weathering of limestones, which erode more quickly than crystalline rocks. Ratios from the Motagua River Valley of about 0.706 reflect a mixing value from the hydrothermal alteration of ocean basalt (0.704) with seawater (0.707–0.709) during subduction. In river samples from the Maya Mountains of Belize, which are underlain by 125–320 Ma sedimentary and volcanic rocks, Hodell *et al*. (2004) measured the highest $^{87}Sr/^{86}Sr$ ratios in their study region (0.712–0.715), as they had expected from these old, high Rb formations.

Oceans

As erosion and weathering constantly delivers material from the continents to the oceans as sediment, seawater has a $^{87}Sr/^{86}Sr$ ratio representative of the average of weathered continental crust from around the world. Due to the long residence time of Sr in seawater (millions of years), compared to the turnover time of the oceans (millennia), $^{87}Sr/^{86}Sr$ is homogeneous throughout the world's oceans at any given time. The variation of $^{87}Sr/^{86}Sr$ in seawater through the Phanerozoic has been determined from the analysis of carbonate and phosphate fossils. Currently, the seawater $^{87}Sr/^{86}Sr$ ratio is 0.7092, but it has varied over geologic time between about 0.707–0.709, as shown in Fig. 5.

Whereas the strontium isotopic composition of deep-sea sedimentary rocks reflects the geologic sources of their component sediments (Dasch, 1969), shells and carbonates precipitated from the seawater itself reflect the seawater $^{87}Sr/^{86}Sr$ ratio at the time of their formation. This can sometimes be exploited to determine the source of archaeological shell artifacts. By comparing $^{87}Sr/^{86}Sr$ in Neolithic ornaments made of *Spondylus* shells to the marine strontium isotope curve,
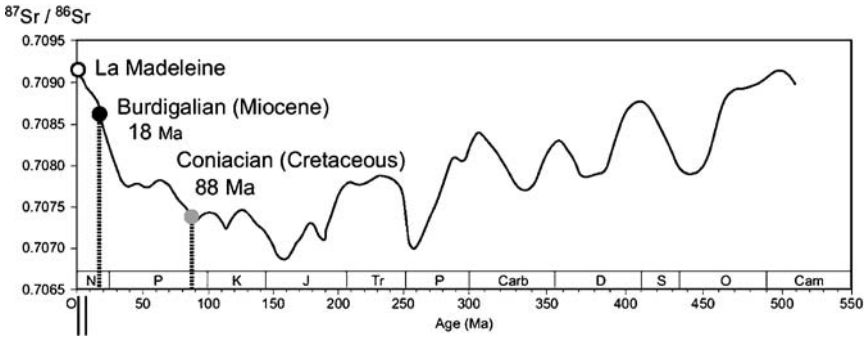
Fig. 5. ^{87}Sr/^{86}Sr in seawater through Phanerozoic time determined from the analysis of phosphate and carbonate fossils. Based on data from McArthur *et al.* (2001), this figure is adapted from Vanhaeren *et al.* (2004, Fig. 4), showing their candidate sources for archaeological shell artefacts from southwest France.

Shackleton and Elderfield (1990) were able to identify the *Spondylus* ornaments that were from fossil deposits (^{87}Sr/^{86}Sr < 0.7092) versus beach shell (^{87}Sr/^{86}Sr = 0.7092 during the Neolithic). Similarly, Vanhaeren *et al.* (2004) measured ^{87}Sr/^{86}Sr in Upper Palaeolithic shell beads from the La Madeleine child burial (about 10,000 BP) in the south-west of France to identify the origin of the beads. The possible origins of this *Dentalium* shell used to make the beads was presumed to be either fossils from Miocene outcrops inland near modern Bordeaux, or the marine shells from the early Holocene shoreline about 40 km further west. The ^{87}Sr/^{86}Sr ratios measured in the beads were all very close to 0.7092, whereas the expected ratios from Miocene fossils was about 0.7085 (Fig. 5). The determination of the distant, coastal origin of the beads have helped Vanhaeren *et al.* (2004) to characterize the exchange networks of prehistoric hunter-gatherers.

In preparations for tests on humans from the ancient Maya area of the Yucatan Peninsula, Hodell *et al.* (2004) analyzed ^{87}Sr/^{86}Sr from over two hundred samples of water, rock, soil, and plants from Mexico, Guatemala, and Honduras. Over the entire area, ^{87}Sr/^{86}Sr ratios ranged from 0.704 to 0.720. Much of the Yucatán Peninsula consists of a carbonate platform with outcropping marine limestone. Because the platform has been uplifted and tilted, the exposed limestone strata get progressively older from the north, with Pliocene–Pleistocene deposits along the north coast of the lowlands, which grade into Miocene limestones in north-ern Yucatán, Eocene limestones in north-central Yucatán, and finally Paleocene and Cretaceous limestones in northern Guatemala and Belize. Consequently, one can predict the ^{87}Sr/^{86}Sr in these areas by matching the limestone ages with the ^{87}Sr/^{86}Sr seawater curve in Fig. 5. For the last 100 Ma, ^{87}Sr/^{86}Sr in seawater has increased, and as they expected, Hodell *et al.* (2004) found a correspond-
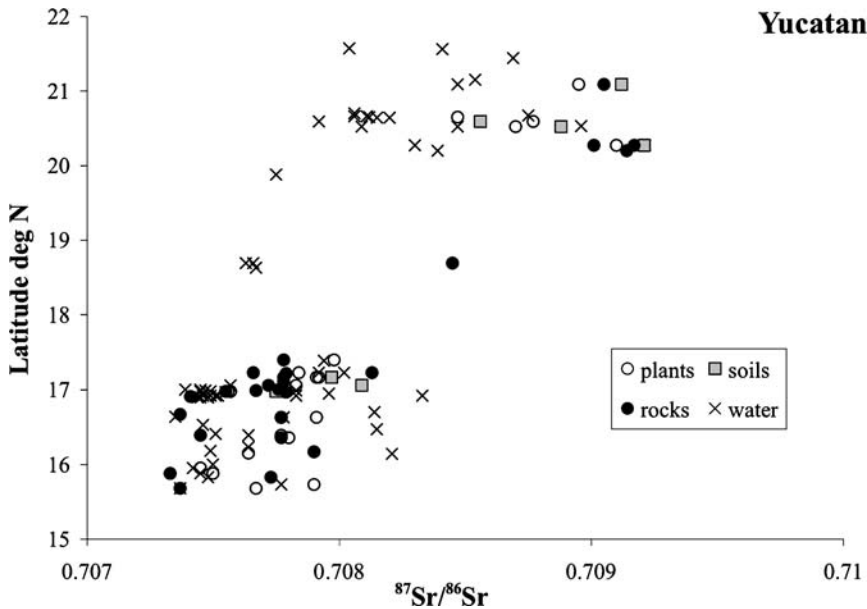
Fig. 6. $^{87}Sr/^{86}Sr$ of bedrock, soils, and plants from the Maya Lowlands versus degrees north latitude, as measured by Hodell *et al.* (2004).

ing increase in $^{87}Sr/^{86}Sr$ from about 0.707 in the south to 0.709 in the north (Fig. 6).

Strontium Isotopes in Soils and Plants

In biogeochemical studies, analyses and models of Sr cycling in soils are made because Sr can be used as a proxy for calcium (Åberg *et al.*, 1990). The typical concentration of plant-available Sr in soil ranges from 0.2 to 20 ppm (Åberg *et al.*, 1990; Capo *et al.*, 1998; Elias *et al.*, 1982; Miller *et al.*, 1993). The major contributors to Sr in soil are mineral weathering, ground and stream waters, atmospheric deposition, and, in modern contexts, fertilizers (Åberg *et al.*, 1989; Borg and Banner, 1996; Graustein, 1989; Graustein and Armstrong, 1983; Kennedy and Derry, 1995; Poszwa *et al.*, 2000). With significant exceptions (discussed below), mineral weathering usually predominates, such that knowledge of the local bedrock geology can be used as a first-order estimate of the $^{87}Sr/^{86}Sr$ range in a particular area (Beard and Johnson, 2000; Capo *et al.*, 1998). On the Yucatan Peninsula, Hodell *et al.* (2004) found only small random differences between bedrock $^{87}Sr/^{86}Sr$ ratios and ratios in soil, plants and water, with variation on the order of 0.00016 in the karst lowlands, and 0.00069 in the highland volcanic province.

Given the different Sr concentrations, ^{87}Sr/^{86}Sr ratios, and weathering potentials of different minerals, it follows that local soils can exhibit a range of ^{87}Sr/^{86}Sr ratios, depending on the differential weathering of minerals and the mixing of various sources of sediment inputs to the soil. Strontium can also be significantly (sometimes > 50%) *removed* by weathering of soils, preferentially from volcanic and carbonate components relative to continental silicate components (e.g., Borg and Banner 1996; Chadwick *et al.*, 1999). In the balance of these inputs and outputs, some areas are relatively homogeneous. Alluvial soils, for instance, contain a mixture of sediments from sources weathered upstream. A geologically diverse area, however, can show substantial local variability in whole soil ^{87}Sr/^{86}Sr ratios. In South Africa, Sillen *et al*. (1998) found ^{87}Sr/^{86}Sr ratios ranging almost from 0.7 to 0.9 in soils over different geological substrates within a 15 km radius around the Swartkrans early hominid site (Fig. 7). Soils were even quite variable on a single substrate, with whole soil samples on dolomite varying from about 0.768 to 0.821 (Fig. 7). This large variability in ^{87}Sr/^{86}Sr was probably due to variation in individual mineral content of the samples. Hypothetically, we can consider the Swartkrans soil as a mixture of the local dolomite, with ^{87}Sr/^{86}Sr of 0.7086, and soil derived from local Archaean granite, with a ^{87}Sr/^{86}Sr ratio of 0.900 (Sillen *et al.*, 1998, pp. 2465, 2467). If we assume for simplicity that the two end-members weathered as whole rocks, Eq. (8) tells us that the mixture would have to include
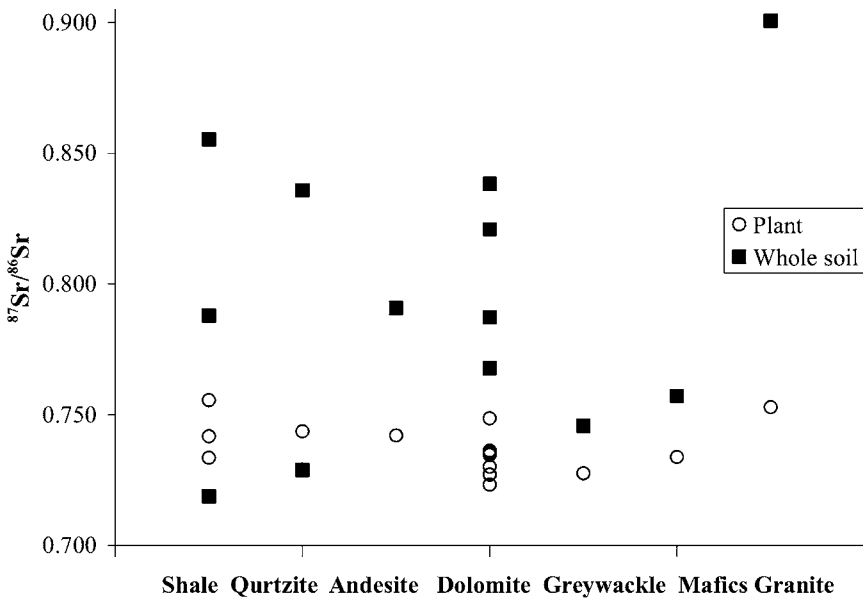

Fig. 7. ^{87}Sr/^{86}Sr measured by Sillen *et al*. (1998) for plants and whole soils in the vicinity of Swartkrans, South Africa. After Sillen *et al*. (1998, Fig. 2, Table II).

41% of its Sr from Archaean granite material to account for the lowest ^{87}Sr/^{86}Sr ratio (0.787) measured by Sillen *et al*. (1998) in the dolomite area, and 58% for the highest ratio (0.821). The point is that a difference of 17% in the relative contributions of these end-members is not much, especially for colluvial soils from the rocky Swartkrans hillside that Sillen *et al*. (1998) collected in 200 mg samples. The mixing-in of the high-^{87}Sr/^{86}Sr granite fraction would also explain why the whole soils all have higher ^{87}Sr/^{86}Sr than the plants growing on them (Fig. 7).

Considering the variation in the soil samples, what is striking is the relative consistency in the ^{87}Sr/^{86}Sr ratios in plants for each geologic terrain (Fig. 7). In measuring plants along multiple transects of several hundred meters, Sillen *et al*. (1998) found that plants growing alongside a stream reflected the ^{87}Sr/^{86}Sr ratios of the stream waters derived from the local dolomite, while plants in the drier areas away from the stream more closely reflected available soil strontium. Similarly, in a study of tropical rainforest trees in French Guyana, Poszwa *et al*. (2002) found that the range of ^{87}Sr/^{86}Sr in leaves (0.714–0.716) was narrow compared to that of bulk soils (0.720–0.770). In other words, the plant-available ^{87}Sr/^{86}Sr reflects a more consistent average of the local biologically-available strontium than whole soils. Benson *et al*. (2003) for example, were able to source archaeological maize from Pueblo Bonito, New Mexico, to locations 80–90 km away around the San Juan Basin (a major rift zone), where the variation in ^{87}Sr/^{86}Sr at each site, reduced through the averaging of plants, was less than the variation between sites. As discussed below, this averaging effect increases in herbivore bones and further up the food chain (Burton *et al*., 1999).

In drier areas, wind-transported dust (loess) can contribute substantially to the Sr in soils, and it can be locally derived, or travel great distances, even 6,000 km across the Pacific from Asia to Hawai'i (Chadwick *et al*., 1999). It can thus be difficult to predict whether a certain patch of loess should have a local or an exotic Sr isotope signal. Much of central Europe, for example, is covered in loess, and the measured ^{87}Sr/^{86}Sr in loess samples from northern Europe range from 0.713 to 0.716 in Brittany and Normandy and as high as 0.730 in Belgium (Gallet *et al*., 1998, Table III). Returning to the discussion of the Upper Rhine Valley, a pertinent question is whether lowland loess, rather than crystalline mountains, could be responsible for the higher ^{87}Sr/^{86}Sr in the plains rivers. Using a two end-member mixing model to estimate the relative contributions (i.e., J_1 and J_2 in Eq. (8)) we see that even if the ^{87}Sr/^{86}Sr of local loess were as high as 0.715 and dissolved into the average plain river (0.710), the loess would have to account for 60% $(= (0.713 - 0.710)/(0.715 - 0.710))$ of the dissolved Sr load to bring the ^{87}Sr/^{86}Sr to the level of these two plain rivers (0.713).

Atmospheric Sources

The ^{87}Sr/^{86}Sr ratio in soils is generally a function of soil depth, because as depth increases, bedrock weathering becomes more important relative to

atmospheric sources (Probst *et al*., 2000). Analyzing coniferous trees, Poszwa *et al*. (2004) found that $^{87}Sr/^{86}Sr$ of bioavailable Sr generally increased in soils in relation to depth, due to minerals being weathered. Different species such as spruce and pine from the same area can have different $^{87}Sr/^{86}Sr$ ratios. Spruce trees, for example, re-cycle Sr from the litterfall up to 12 times more than pine trees do (Poszwa *et al*., 2004). These differences are probably not because the Sr cycling process is species-specific *per se*, but more likely they are controlled by the differences in the soil parent material where the trees have their roots (Dijkstra *et al*., 2003). In a tropical rainforest (in French Guyana), Poszwa *et al*. (2002) found that tree $^{87}Sr/^{86}Sr$ ratios were similar for all species studied, and close to litter and near-surface roots Sr-$^{87}Sr/^{86}Sr$ ratios, but that there was a gradient of $^{87}Sr/^{86}Sr$ in the tree roots with depth, indicating that the litter and upper soil layers retained the Sr deposited by rain. Kennedy *et al*. (2002) similarly found that atmospheric sources dominated the nutrient pool for trees of a temporate forest in southern Chile. This indicates that Sr and Ca cycling can become decoupled from bedrock in tropical environments (Kennedy *et al*., 2002).

Atmospheric Sr is also part of the plant cycle in mountainous areas. In the Sangre de Cristo Mountains of New Mexico, 50–75% of the strontium in local vegetation derived from atmospheric deposition (Graustein and Armstrong, 1983; Miller *et al*., 1993). In a small spruce forested area of the Vosges mountains of eastern France, with up to 150 cm/year precipitation, Probst *et al*. (1992, 2000) found that about 50% of the dissolved Sr in the streamwaters is derived from the atmosphere, including open field precipitation ($^{87}Sr/^{86}Sr \sim 0.710$) and throughfall ($^{87}Sr/^{86}Sr \sim 0.712$). Throughfall contains terrestrial dust with slightly more radiogenic Sr, which is 5–10 times more concentrated than Sr in open field precipitation (Probst *et al*., 2000). The Sr contribution from atmospheric sources thus reflects a weighted average (Eq. (8)). For example, rainwater in the Massif Centrale has $^{87}Sr/^{86}Sr$ ratios varying from 0.7090 to 0.7106 (Négrel *et al*., 2001), with its constituents (dust, seawater, pollution etc.) being weather-dependent, but the mean $^{87}Sr/^{86}Sr$ weighted by percentage rainfall (0.7094) is lower than the simple average of the high and low because the low-$^{87}Sr/^{86}Sr$ constituents contribute proportionately more Sr.

Nonetheless, rock weathering is still the major contributor of Sr at high elevations. Even with modern polluted precipitation ($^{87}Sr/^{86}Sr < 0.710$) supplying half the Sr available to modern plants in Vosges – much of which is modern pollution (Sanusi *et al*., 1995)—Probst *et al*. (2000) showed that Sr available to modern plants in the soil solutions there nonetheless have a substantially radiogenic Sr content ($^{87}Sr/^{86}Sr \sim 0.724$) due to weathering of the bedrock end-member (0.735–0.740). In upland Scotland, where the nearby seawater dominates the $^{87}Sr/^{86}Sr$ ratio in rain, the ratios in stream waters are nonetheless constant and characteristic of Sr released from weathered minerals and soil (Bacon and Bain, 1995).

Sea-Spray

In coastal areas, the strontium isotopes can be dominated by sea-spray or rainwater deriving from evaporated seawater. On the basaltic Hawaiian Islands, a substantial fraction of the strontium in plants and soils comes from marine sources (through rain or sea-spray) reaching over 50% marine strontium in soils at the coast (Chadwick *et al.*, 1999; Whipkey *et al.*, 2000). The atmospheric contribution is the greatest on the older islands of the Hawaiian chain, where the volcanic basalts are the most highly weathered and hence the most depleted of available Sr (Chadwick *et al.*, 1999; Kennedy *et al.*, 1998; Vitousek *et al.*, 1999). However, even in younger, less-depleted Hawaiian volcanic rocks, 30% of the plant-available Sr is derived from the atmosphere (Vitousek *et al.*, 1999). Figure 8 shows how Whipkey *et al.* (2000) found the plant-available reservoir in a soil profile 50 m from the Hawaiian coast to be affected by seawater strontium. At this site, the ^{87}Sr/^{86}Sr of the local Hawaiian basalt is about 0.7035, yet the buffelgrass growing at the surface has a ^{87}Sr/^{86}Sr of about 0.709, very close to the seawater ratio of 0.7092, indicating that <10% of its Sr is from the basalt. Even at 300 cm depth, seawater still accounts for 50% of the plant-available Sr, as the ^{87}Sr/^{86}Sr is above 0.706 (Whipkey *et al.*,

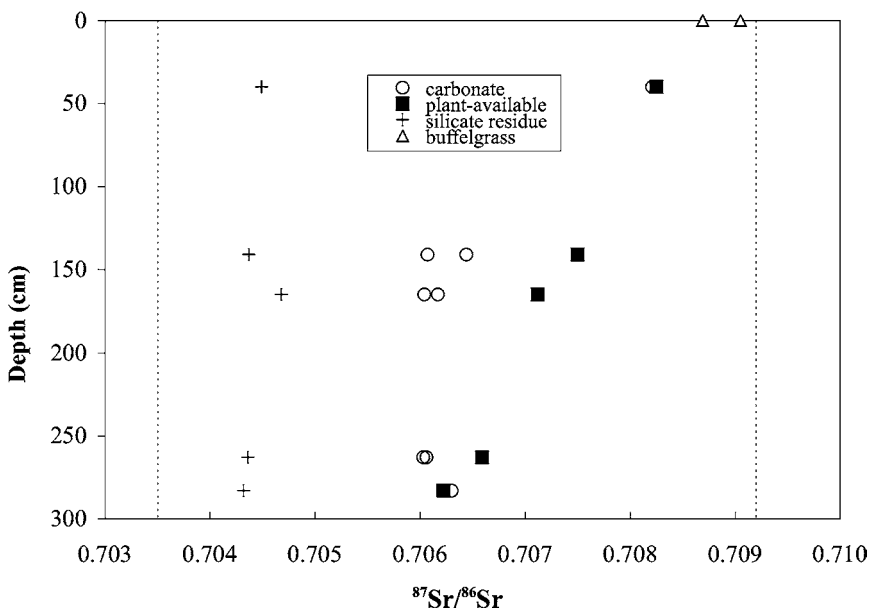**Fig. 8.** ^{87}Sr/^{86}Sr measured by Whipkey *et al.* (2000) in samples of buffelgrass, soil carbonate, plant-available reservoir, soil carbonate and silicate residue from a soil profile at South Point, Hawai'i. Dashed lines show seawater (0.7092) and local basalt (0.7035) ratios for comparison. After Whipkey *et al.* (2000, Fig. 1).

2000). We see this effect at other coastal sites, such as a shrimp farm in the coastal town of La Empalizada, Guatemala, where basaltic $^{87}Sr/^{86}Sr$ ratios are expected to be about 0.704, yet where Hodell *et al.* (2004) found $^{87}Sr/^{86}Sr$ ratios of 0.7081 and 0.7089 from a plant and a water sample, which clearly reflects seawater sources of strontium. Similarly, in studies on the Outer Hebrides, Montgomery (2002; Montgomery *et al.*, 2003a; Montgomery and Evans, 2006) has found that, despite the island being underlain by radiogenic granites and gneisses ($^{87}Sr/^{86}Sr \sim 0.715$), seawater strontium dominates the biosphere, with Bronze age human, herbivore, and other biospheric ratios falling below 0.7105.

Sr from Modern Fertilizers

In modern contexts, agricultural fertilizers can be a significant contribution of Sr to the local groundwater and soil solution. On the coastal plain in Maryland, for example, Early Tertiary marine carbonates have a relatively non-radiogenic $^{87}Sr/^{86}Sr$ of about 0.708, and fertilizers with relatively radiogenic ratios (~ 0.715) have raised the $^{87}Sr/^{86}Sr$ ratios of oxic groundwaters to 0.713–0.715 (Böhlke and Horan, 2000). The effect is primarily dependent on the age of the groundwater: deeper and older (35 or more years since recharge) suboxic groundwaters have $^{87}Sr/^{86}Sr$ between 0.708 and 0.710, more consistent with the marine sedimentary basement in Maryland (Böhlke and Horan, 2000, Fig. 4). In France, Négrel and Deschamps (1996) used the $^{87}Sr/^{86}Sr$ ratios of anthropogenic and natural sources to determine the geochemical budget of a small watershed in the Massif Centrale. Their findings indicate that 10% of the Sr comes from rainwater input, 40% to 80% from fertilizers and 15% to 50% from rock weathering. Agricultural fertilizers are also a major pollutant of the Rhine river and its tributaries (Négrel and Deschamps, 1996), but since their $^{87}Sr/^{86}Sr$ ratios (0.707–0.7085) are not much different from the expected geologic values in the Upper Rhine Valley, the effect is practically undetectable.

Despite all these extra sources of Sr, the local geology still has a large effect on the $^{87}Sr/^{86}Sr$ in most environments, especially in pre-modern times, when road dust and industry pollution were much less significant contributors to locally produced foods (Åberg *et al.*, 1998). In areas that are not extremely weathered or under very high annual levels of precipitation, bedrock weathering is the primary determinant of plant and soil $^{87}Sr/^{86}Sr$ ratios (Bern *et al.*, 2005). For Mauna Loa, Hawai'i, Vitousek *et al.* (1999, Fig. 2) report that the $^{87}Sr/^{86}Sr$ ratio in plant leaves growing at sites with moderate rainfall (200 cm/year or less) range between 0.7040 and 0.7045, which is much closer to the weathering sources (0.7035) than to rainwater (0.7092). Studies by Stewart *et al.* (2001) amid the different microclimates of the Kohala Peninsula, Hawai'i, suggest that the supply of Sr by weathering increases steadily with rainfall in areas of lower mean annual rainfall (<140 cm), which then decreases dramatically as the soils become depleted in weatherable parent

material. On semiarid sites inland on Hawai'i, the labile cation budget is dominated by basalt weathering (Capo *et al*., 1998), and even in high-rainfall areas, most of the soil silicate strontium in high-rainfall sites is still derived from the original parent material, with only 5–50% of rainwater strontium exchanging with the reservoir of plant-available Sr (Stewart *et al*., 2001). Although Whipkey *et al*. (2000) found that 50% of the Sr in their soil profile at South Point, Hawai'i originated from sea spray, the other 50% of Sr was supplied by tephra weathering, despite the site being just 50 m from the Pacific Ocean.

'Biopurification' of Sr in Animals and Humans

Most archaeologists are familiar with the measurement of Sr/Ca ratios in skeletal tissues (Sr levels are typically low in non-skeletal tissues) to infer paleodiets (e.g., Sillen and Kavanagh, 1982; Schoeninger, 1979), as research several decades ago, on environmental ^{90}Sr, led it to be known that the Sr/Ca ratio decreases up the food chain. This process, called *biopurification* (Elias *et al*., 1982), occurs because only 10–40% of Sr ingested by mammals is physiologically absorbed, as compared to the 40–80% of dietary Ca that is absorbed (e.g., Burton *et al*., 1999, 2003; Comar *et al*., 1957; Lengemann, 1963; McClellan, 1964). The reduction in Sr/Ca is thus about a factor of five per trophic level, that is, the Sr/Ca in plants is about 20% of that in than in their soils, Sr/Ca in herbivore bones is about 20% of the average of the plants they eat, and Sr/Ca in carnivore bones is 20% of that in the herbivores they eat. For a diet of multiple components *i,* this is simply expressed as (Burton and Wright, 1995):

$$\left(\frac{Sr}{Ca}\right)_{diet} = \frac{\sum\limits_{i} Sr_{diet}}{\sum\limits_{i} Ca_{diet}}, \quad \text{and} \tag{9}$$

$$\left(\frac{Sr}{Ca}\right)_{bone} \approx 0.2 \left(\frac{Sr}{Ca}\right)_{diet} \tag{10}$$

In addition, biopurification also reduces the *variance* in the Sr/Ca by several orders of magnitude moving up the trophic levels, despite larger variations in the actual concentrations of Sr and Ca (Elias *et al*., 1982). After thousands of individual analyses of soils, waters, plants, animal bones and human bones, Burton *et al*. (1999, 2003; also Price *et al*., 2002, Table III) found ranges of ± 0.09940 for Sr/Ca in soils, ± 0.00957 for plants, ± 0.00090 for herbivore bones, and ± 0.00036 for carnivore bones. In terms of the coefficient of variation (s.d./value), this equates to a reduction in Sr/Ca variability from 145% in soils to 20% in carnivores. Among human bones, the overall standard deviation for log(Sr/Ca) was found to

be only 0.13 log units,[6] equating to $\pm 5\%$ coefficient of variation (Burton *et al.*, 2003).

The reduction of variance due to biopurification applies not only to Sr/Ca, but also to $^{87}Sr/^{86}Sr$. The $^{87}Sr/^{86}Sr$ variation in animal skeletons is dramatically reduced from that of the plants and soils, as herbivores eat a mix of plant materials from their local area, and the $^{87}Sr/^{86}Sr$ in their diet is averaged over the time of the formation of the skeletal tissue. Evidence of this includes studies of $^{87}Sr/^{86}Sr$ in soil, plants, caterpillars, snails, and birds (Blum *et al.*, 2000; Chamberlain *et al.*, 1997), in migrating salmon (Koch *et al.*, 1992), and in elephants (Hall-Martin *et al.*, 1993; Koch *et al.*, 1995; van der Merwe *et al.*, 1990; Vogel *et al.*, 1990), all of which show a low standard deviation in $^{87}Sr/^{86}Sr$ ratios among animal groups. In tabulating multiple studies of this sort from all over the world and ages ranging from 7000 years ago to present (Table II), Price *et al.* (2002) found that the coefficient of variation in $^{87}Sr/^{86}Sr$ for local animal bones, tusks or horns was always less than 0.6% in studies of modern animal bones. Among the studies shown in Table II, the largest coefficient of variations come from animals that range widely over geologically-diverse terrains, including rhinos, elephants, birds and salmon. Domestic cattle can also have a relatively large $^{87}Sr/^{86}Sr$ range if they were led elsewhere for pasturing, but prehistoric domestic pigs, often kept and fed locally, can have low variance in $^{87}Sr/^{86}Sr$ (Bentley, 2004, Bentley *et al.*, 2004, Bentley and Knipper, 2005a). Small mammals, including mice, guinea pigs, rabbits, and squirrels, have the lowest within-site variation in $^{87}Sr/^{86}Sr$, with standard deviations in Table II no larger than 0.0003 (excepting the few modern rats sampled by Hoppe *et al.*, 1999).

Defining the Local $^{87}Sr/^{86}Sr$ Range

It is desirable to characterise the 'local' strontium isotope signature for a particular archaeological site. In averaging the biologically-available $^{87}Sr/^{86}Sr$ ratio of their local feeding territories, small animal values may serve as predictors for the local $^{87}Sr/^{86}Sr$ in mammals. In their study of mammoth migration, Hoppe *et al.* (1999) analyzed $^{87}Sr/^{86}Sr$ in rodent teeth (as well as pants and surface water) to help map the biologically-available $^{87}Sr/^{86}Sr$ across Florida and Georgia. Concerning humans, Table II shows that the ranges (1 σ) in the $^{87}Sr/^{86}Sr$ ratios for small mammals (bones and/or enamel) are very close to the range of human bone values for several independent studies. At Grasshopper Pueblo in Arizona, the $^{87}Sr/^{86}Sr$ ratios in whole rocks (sandstones, limestones) and soil range from 0.70893 to 0.71627 around the area (Ezzo *et al.*, 1997; Price *et al.*, 2002). In contrast, variability in small animal bone from Grasshopper was less by several orders

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[6]Sr/Ca exhibits logarithmic, not normal, distributions so that quantitative comparisons require the use of log(Sr/Ca) such that factor of five reduction in Sr/Ca equates to a shift in log(Sr/Ca) of 0.7 (Burton *et al.*, 2003).

Table II. Mean, Sample Size (n), and Standard Deviation (s.d.) of $^{87}Sr/^{86}Sr$ Levels in Natural Populations

Species	Material	n	Mean $^{87}Sr/^{86}Sr$	s.d. $^{87}Sr/^{86}Sr$	Location	Reference
Pig	enamel	6	0.70922	0.00003	Khok Phanom Di, Thailand	Bentley (2004)
Rabbit	bone	5	0.70922	0.00004	Aztalan, WI, USA	Price et al. (2002)
Rabbit	bone	8	0.70463	0.00005	Teotihuacan, Mexico	Price et al. (2000)
Human child	enamel	17	0.70932	0.00006	Khok Phanom Di, Thailand	Bentley (2004)
Goat/sheep	enamel	6	0.70791	0.00007	Çatalhöyük, Turkey	Meiggs et al. (2005)
Elephant	bone	6	0.71153	0.00008	Addo Park, S. Africa	Vogel et al. (1990)
Salmon	bone	5	0.70919	0.00010	Hatchery, OR, USA	Koch et al. (1992)
Squirrel	bone & enamel	5	0.70925	0.00012	Cahokia, IL, USA	Price et al. (2002, Table II)
Pig	enamel	10	0.70946	0.00017	Vaihingen, Germany	Bentley et al. (2004)
Guinea pig	bone	3	0.70625	0.00018	Moquegua, Peru	Knudson et al. (2004)
Bird	egg contents	6	0.71281	0.00018	Downer Forest, VT, USA	Blum et al. (2001)
Deer	bone	12	0.71029	0.00022	Vermont, WI, USA	Price et al. (2002, Table II)
Caterpillar	body	8	0.71317	0.00029	Downer Forest, VT, USA	Blum et al. (2001)
Mouse	bone & enamel	10	0.71000	0.00031	Grasshopper, AZ	Ezzo et al. (1997)
Goat/sheep	enamel	8	0.70961	0.00035	Vaihingen, Germany	Bentley et al. (2004)
Deer	bone	6	0.71295	0.00041	Oneida, WI, USA	Price et al. (2002, Table II)
Human child	enamel	17	0.70932	0.00051	Vaihingen, Germany	Bentley et al. (2003)
Cattle	enamel	14	0.70934	0.00056	Vaihingen, Germany	Bentley et al. (2004)
Bird	egg contents	8	0.71900	0.00057	Hubbard Brook, NH, USA	Blum et al. (2001)
Bird	eggshell	17	0.71285	0.00059	Downer Forest, VT, USA	Blum et al. (2001)
Bird	eggshell	16	0.71912	0.00068	Hubbard Brook, NH, USA	Blum et al. (2001)
Elephant	bone	21	0.70518	0.00079	Amboseli Park, Kenya	Koch et al. (1995)

Note. Listed in by standard deviation in increasing order. Adapted from Price et al. (2002, Table II), with recent studies added.

Table II. Continued

Species	Material	n	Mean ^{87}Sr/^{86}Sr	s.d. ^{87}Sr/^{86}Sr	Location	Reference
Salmon	bone	5	0.71982	0.00090	Hatchery, ME, USA	Koch et al. (1992)
Rhino	horn	12	0.71693	0.00096	Umfolozi, S. Africa	Hall-Martin et al. (1993)
Rhino	horn	16	0.71161	0.00112	Mkuze, S. Africa	Hall-Martin et al. (1993)
Elephant	bone	6	0.72380	0.00130	Namibian Desert, S. Africa	Vogel et al. (1990)
Bird	bone	4	0.71211	0.00129	Downer Forest, VT, USA	Blum et al. (2001)
Snail	shell	6	0.71923	0.00134	Hubbard Brook, NH, USA	Blum et al. (2000)
Caterpillar	body	9	0.71908	0.00140	Hubbard Brook, NH, USA	Blum et al. (2001)
Rat	enamel	3	0.70870	0.00150	Northeastern Florida, USA	Hoppe et al. (1999)
Rat	enamel	3	0.71170	0.00160	Southern Geogia, USA	Hoppe et al. (1999)
Bird	bone	4	0.71696	0.00205	Hubbard Brook, NH, USA	Blum et al. (2001)
Rhino	horn	8	0.71511	0.00208	Hluhluwe, S. Africa	Hall-Martin et al. (1993)
Rhino	horn	7	0.71340	0.00212	Addo Park, S. Africa	Hall-Martin et al. (1993)
Rhino	horn	8	0.71837	0.00306	Etosha Park, S. Africa	Hall-Martin et al. (1993)
Rhino	horn	7	0.70675	0.00389	Pilanesberg, S. Africa	Hall-Martin et al. (1993)

of magnitude, averaging 0.71000 ± 0.00031 in local mice, which was close to the average (0.71018 ± 0.00050) in the prehistoric human enamel samples (Table III). Beard and Johnson (2000), who also advocated analyzing local groundwater to determine the concentration-weighted Sr isotope composition, demonstrated how the biologically available Sr, as reflected in the bones of mice from Grasshopper Pueblo in Arizona, yielded a tight cluster of $^{87}Sr/^{86}Sr$ ratios that was quite close to the concentration-weighted average of the regional end-members (see Fig. 3a; also Beard and Johnson, 2000, Fig. 2).

The danger with sampling modern animals is that they may consume imported foods, or local foods with exotic Sr introduced through fertilizer or airborne sources of strontium. A better way to characterise the prehistoric, biologically-available local strontium isotope signature is to measure the *archaeological* teeth of an animal species that lived locally (Bentley *et al*., 2004; Price *et al*., 2002). This strategy minimizes the problems of environmental variability (as the animal acquires an averaged signature from the area), modern anthropogenic strontium, and diagenesis (to which tooth enamel is resistant). Since different species occupy different regions with varying home ranges, the choice of local animal is best made specifically for the particular site, using both archaeological evidence and, if possible, measuring $^{87}Sr/^{86}Sr$ in enamel samples from different species. Depending on the prehistoric period and location of each site, other possible 'local' species include domestic dogs or other pets. Once a suitable local species is identified, prehistoric enamel samples from different locations can then be used to map $^{87}Sr/^{86}Sr$ in the prehistoric region.

Because their amino acid requirements (Hare *et al*., 1991; Howland *et al*., 2003; van der Merwe *et al*., 2003) and diets are similar to that of humans, domestic pigs may often be a good species to use to define the local $^{87}Sr/^{86}Sr$ range for humans. In domestic pigs, the tooth enamel mineralises starting before birth until the 2nd–3rd month for M1, between the 1st and 8th month for M2, P3 and P4, and between the 3rd and 13th month for M3 (Hillson, 1986, p. 207, Fig. 3.9). Since Neolithic times, pigs have lived locally around farming settlements (Greenfield, 1988), most likely eating human by-products such as rotting vegetables, crop wastes, table scraps and human and animal excrement (Gregg, 1988, pp. 118–122). At the Neolithic village of Vaihingen (ca. 5450–5000 BC), $^{87}Sr/^{86}Sr$ ratios in enamel samples from domestic animals (Fig. 9) revealed that the standard deviation for pigs (± 0.00017) was less than half that of caprines (± 0.00035) or cattle (± 0.00056), and even less than the variance from the human bones (Fig. 9). If the pigs were not fed some restricted diet, this implies that the pigs' diet came from a smaller (or more homogeneous) area than the humans. On the basis of the Vaihingen study (Bentley *et al*., 2004), Bentley and Knipper (2005a) used archaeological pig enamel from sites around southern Germany to map the prehistoric strontium isotope ratios, which confirmed an upland-lowland difference in strontium isotopes, as well as identifying a subtle ($\sim 2\%$) upland-lowland difference in carbon isotopes.

Table III. Mean ^{87}Sr/^{86}Sr for Archaeological Animal Bone and Human Enamel. Adapted from Price *et al.* (2002, Table II), with Recent Data Added

| Location	Species	Animal mean ^{87}Sr/^{86}Sr (s.d.)	Human enamel mean ^{87}Sr/^{86}Sr (s.d.)	Reference
Grasshopper, Arizona	Mouse	0.71000 (31)	0.71018 (50)	Ezzo *et al.* (1997)
Teotihuacan, Mexico	Rabbit	0.70463 (5)	0.70501 (80)	Price *et al.* (2000)
Aztalan, Wisconsin	Rabbit	0.70922 (4)	0.71021 (40)	Price *et al.* (2002, Table II)
Vaihingen, Germany	Pig	0.70946 (17)	0.70942 (50)	Bentley *et al.* (2004)
Chen Chen, Peru	Guinea pig	0.07625 (18)	0.070696 (25)[a]	Knudson *et al.* (2004)
Khok Phanom Di, Thailand	Pig	0.70922 (3)	0.70938 (15)	Bentley (2004)

[a]2 outliers excepted.
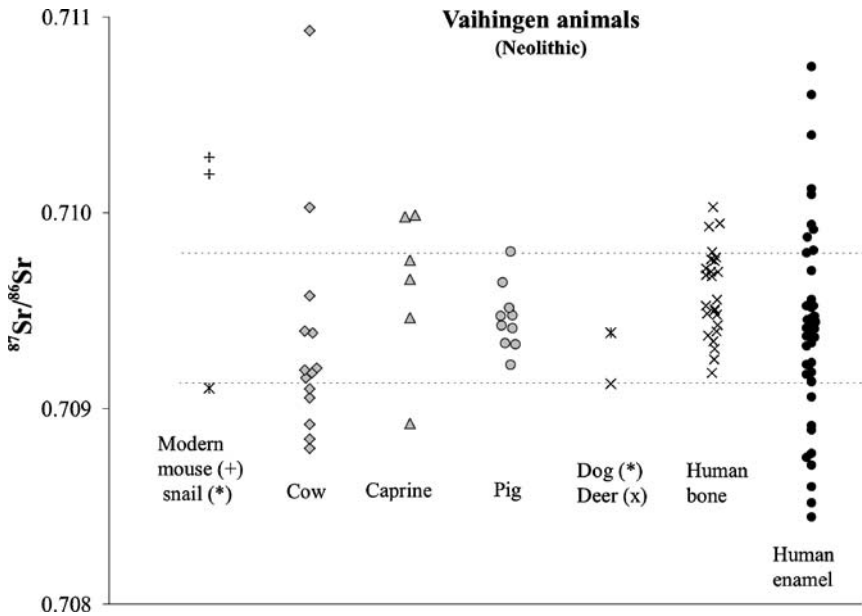
Fig. 9. ^{87}Sr/^{86}Sr in Neolithic human and animal tooth enamel from Vaihingen, along with values from human bones, a few modern mice and snail shells. After Bentley *et al.* (2004, Fig. 5).

Strontium Isotopes in the Skeleton

The discussion to this point shows the complexity of movements of Sr isotopes before they even reach the human skeleton, but also the averaging effect of biopurification moving up the food chain. Unfortunately, it is not currently practicable to measure calcium isotopes themselves, as variations in ^{40}Ca abundances (produced by long-lived ^{40}K decay) are not large enough to be detected above the other Ca isotope variations resulting from natural mass-dependent fractionations[7] (Beard and Johnson, 2000). Elements chemically similar to Ca, such as Sr, Ba and Pb, occasionally substitute for Ca in the calcium phosphates and apatites of skeletal tissues (Ezzo, 1994a). There are still various opinions about which elements may enter those sites *in vivo*. Kohn *et al.* (1999, Table I) list Na, Mg, Zn, Sr, Ba and U as elements which substitute into the Ca site of enamel phosphate, and are therefore useful for studies of diet (or chronology in the case of U). However, Ezzo (1994a, 1994b) has pointed out only cations in the $+2$ valence state can substitute for Ca in living bones and teeth, with differences in atomic size controlling the

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[7] However, the stable mass-dependent (non-radiogenic) Ca isotopes (e.g., ^{42}Ca/^{44}Ca) show great promise as a tool to determine trophic level in the food chain, and may be particularly effective in the future when combined with radiogenic isotopes of Sr (C. Johnson, pers. communication; see DePaolo, 2004).

amount of substitution. Iron, which has a $+2$ state and shows fascinating variation in isotopic fractionation within the human body (Walczyk and von Blanckenburg, 2002), is unfortunately present at parts per trillion levels in living teeth, which is too low to register above the parts per million levels of post-burial contamination (Kang *et al.*, 2004; Kohn *et al.*, 1999). Of the $+2$ elements, the most useful so far have been barium, lead, and particularly strontium, which has an ionic radius only slightly larger than that of Ca.

The application of strontium isotope analysis toward archaeology came with the realization (Ericson, 1985) that one might identify migrant individuals who moved between geologic regions by comparing $^{87}Sr/^{86}Sr$ in adult tooth enamel, composed between four and twelve years of age, and in the bones, which remodel throughout life and therefore representative of adulthood. In theory, if the teeth and bones of a skeleton have different signatures, then the person spent his/her last years in a different geochemical province than during his/her youth (Ericson, 1989; Sealy *et al.*, 1991).

In cases involving modern skeletons, or archaeological skeletons that have been extraordinarily well preserved, bone and tooth $^{87}Sr/^{86}Sr$ ratios can be successfully compared. In sampling modern elephant bones in Amboseli Park, Kenya, Koch *et al.* (1995) found a negative correlation between carbon and strontium isotope ratios (Fig. 10) that they interpreted as due to mixing between two regions between which the elephants migrated – C_3-rich bushlands on Precambrian soils (low $\delta\ ^{13}C$, high $^{87}Sr/^{86}Sr$) and C_4-rich grassland on volcanic soils (higher $\delta\ ^{13}C$, low $^{87}Sr/^{86}Sr$). Comparing these results to the $\delta\ ^{13}C$ patterns from the teeth, Koch
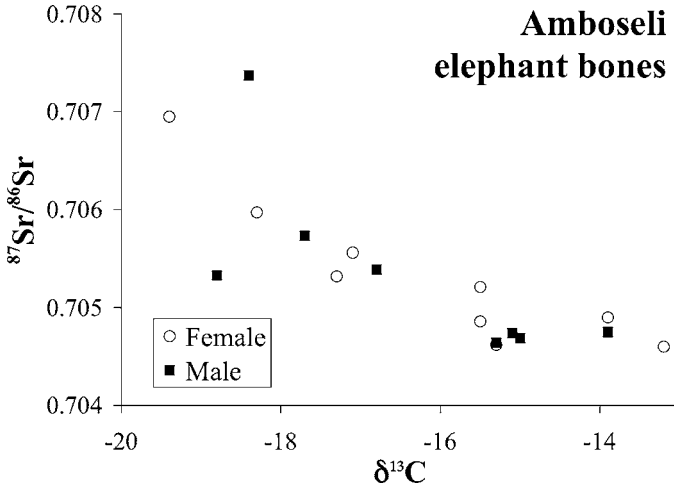

Fig. 10. Carbon and strontium isotopes in elephant bones from Amboseli Park, Kenya. Note the concave-up mixing line, similar in form to Fig. 3a. After Koch *et al.* (1995, Fig. 3 and Table I).

et al. (1995) were able to conclude that in the early 1970's, elephants migrated regularly between the grassland and the bushland, whereas those who died in the 1980's migrated less and spent most of their time grazing in the grasslands.

Even better temporal resolution could be possible via measurements of bone, which undergoes continual replacement of its inorganic phase (Price *et al*., 2002), such that different individual bones potentially contain information on the age of a migrant person when he/she moved, as the rate of turnover in different bones differs according to the ratio of active osteoclasts (which precipitate hydroxyapatite) and osteoblasts (which dissolve hydroxyapatite). Dense cortical bone remodels over a period of decades, while trabecular bone remodels with turnover times as short as a few years for the ribs and the iliac crest (Hill, 1998; Jowsey, 1961; Mulhern and Van Gerven, 1997; Price *et al*., 2002, Fig. 7; Teitelbaum, 2000).

If we assume that a migrant individual moved only once from one place to another during his or her lifetime, it is possible to model how the $^{87}Sr/^{86}Sr$ ratio in the different bones approach the local ratio at different rates. How close the bone value is to the local signature is a function of both the turnover rate of the bone, and the time that the migrant individual was in residence. Schweissing and Grupe (2003) demonstrate how $^{87}Sr/^{86}Sr$ changes in a skeletal tissue that was formed over a time span in which the individual migrated from Place A to Place B. Figure 11 shows their model for how the $^{87}Sr/^{86}Sr$ in the tissue, which is a running average, would evolve over time of mineralization. In Place A, the ratio of the tissue is *a*, until the migration to Place B (point d in Fig. 11), when the Sr isotope ratio is *b*. As the tissue remodels, more Sr with isotopic ratio b is incorporated into it, and the $^{87}Sr/^{86}Sr$ gradually approaches that of the new habitat. A quantitative model of this is provided by Beard and Johnson (2000, Appendix 2), for the evolution of
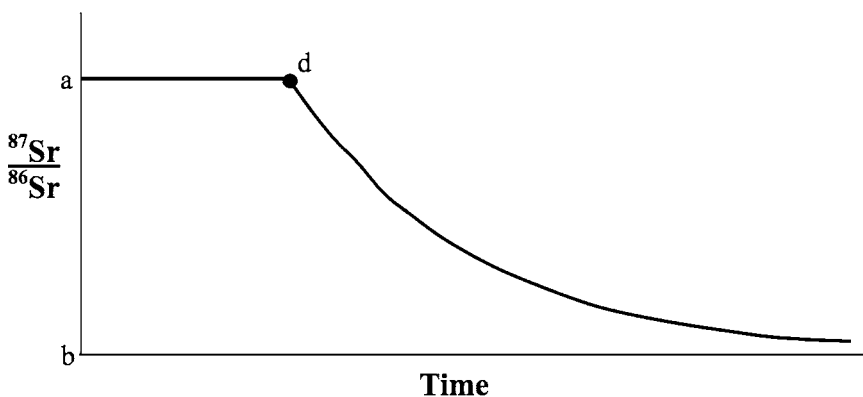

Fig. 11. Model by Schweissing and Grupe (2003, Fig. 2) for the gradual change in Sr isotope signature in skeletal tissue that formed before and after migration (at point d) between areas of different $^{87}Sr/^{86}Sr$ ratios (a and b).

$R_{\text{bone}}(t)$, the ^{87}Sr/^{86}Sr ratio through time:

$$R_{\text{bone}}(t) = R_B - (R_B - R_A)e^{-t/\tau}, \tag{11}$$

where R_A and R_B refer to the ^{87}Sr/^{86}Sr ratios at Place A and Place B respectively, τ is the residence time of Sr in bone, and t is the time since migration from A to B. If a person's tooth enamel formed in Place A, the childhood environment, and that person subsequently migrated to Place B, the place of burial, then ^{87}Sr/^{86}Sr in the enamel is R_A, and R_B is the ^{87}Sr/^{86}Sr at the place of burial. The ^{87}Sr/^{86}Sr measured in the bone is $R_{\text{bone}}(t)$, and given the Sr turnover time τ of the particular bone, the time t since this single migration event is given by (Beard and Johnson, 2000):

$$t = -\tau \ln \left(\frac{R_B - R_{\text{bone}}}{R_B - R_{\text{tooth}}} \right). \tag{12}$$

One study providing reliable ^{87}Sr/^{86}Sr from archaeological human bones involved the famous "Iceman," a Bronze Age man who died approximately 3200 B.C. in the Alps near the modern border of Italy and Austria. The body, encased in glacier ice for the subsequent millennia, was so spectacularly well-preserved that the people who found it in September 1991 thought a recreational hiker had lost his way in the snow. With less than 0.01 ppm Sr measured in the surrounding glacier (Hoogewerff et al., 2001), the Sr in the Iceman's bones was also very well-preserved, as normal human bone has between 50 and 500 ppm. Hoogewerff et al. (2001) measured a ^{87}Sr/^{86}Sr ratio of 0.71797 from the fumur of the Iceman and 0.71863 from his rib. These ratios did not match nearby marine limestones (0.707–0.708). Instead, the ratios matched the crystalline (mostly gneiss) Vinschgau and Ötztal areas of the Alps, where ^{87}Sr/^{86}Sr in stream waters ranges from 0.720 to 0.725 and the range among bones of local people from historic times is 0.712–0.717 (excepting one outlier). Because bones have different turnover rates for Sr, Hoogewerff et al. (2001) reasoned that their small but significant ^{87}Sr/^{86}Sr difference between rib and femur indicated that that the Iceman had traveled between crystalline areas. In a subsequent study of the Iceman, Müller et al. (2003, Fig. 2C) measured ^{87}Sr/^{86}Sr ratios of about 0.7178 in cortical bone from his femur ($\sim$20–30 years of age), about 0.7185 in trabecular bone from the femur (34–40 years), and 0.7194 in the intestinal contents of his last days (when he was 40–50 years old). Although Müller et al. (2003) concluded that the Iceman spent his lifetime to the south of the discovery site - in contrast with Hoogewerff et al. (2001) - both studies clearly indicate the Iceman's mobility as an adult through analyses of multiple samples.

Isotopic Contamination and Buried Bone

Unfortunately for the technique as originally conceived, archaeological bone is often contaminated during burial (Fig. 12), as the groundwater strontium that
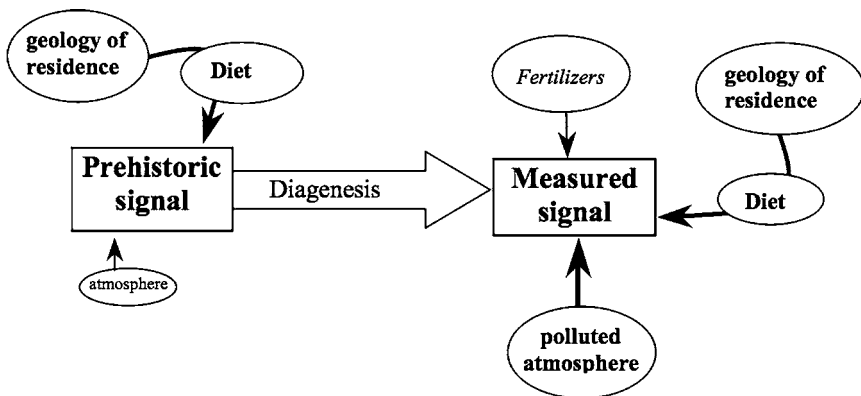
Fig. 12. Schematic diagram showing the "noise" potentially obscuring the prehistoric geologic isotope signature from what is measured in archaeological skeletons and in modern fauna.

penetrates the bone after burial can overwhelm or even replace the *in vivo* strontium in its mineral portion (e.g., Collins and Riley, 2000; Hedges, 2002; Hoppe *et al.*, 2003; Lee-Thorp, 2002; Nelson *et al.*, 1986; Nielsen-Marsh and Hedges, 2000a; Price, 1989; Price *et al.*, 1992; Tuross *et al.*, 1989). Diagenetic Sr can be incorporated in fossils in several ways. The most pervasive is pore-filling by secondary minerals and/or absorption in microcracks or onto the surfaces of original hydroxyapatite crystals (Nelson *et al.*, 1986), as the rate of degradation is often dependent on the porosity of the bone (Robinson *et al.*, 2003).

Post-burial contamination is the reason why it may not be reliable to define the local $^{87}Sr/^{86}Sr$ range based on the average $^{87}Sr/^{86}Sr$ of samples of human bones from the site, plus or minus two standard deviations (e.g., Grupe *et al.*, 1997, 1999; Price *et al.*, 1994, 2001). Although the average in archaeological human bones may be a useful baseline, given that their contamination comes from local ground water solutions, the contamination will also reduce the standard deviation of $^{87}Sr/^{86}Sr$ values, which therefore narrows the local range as defined by them (Horn and Müller-Sohnius, 1999).

It has been argued that diagenetic strontium can often be removed from skeletal samples by proper sample cleaning such as with weak acid (e.g. Nielsen-Marsh and Hedges, 2000a; Price *et al.*, 1992, 1994; Sealy *et al.*, 1991; Sillen and Sealy, 1995). The idea is that leaching the bone sample in 5% acetic will dissolve away the diagentic strontium present in carbonate in the pore spaces, while retaining the original dietary Sr more strongly bound in the Ca site of the bone hydroxyapatite (Koch *et al.*, 1992; Price *et al.*, 1994; Sillen, 1986). Sillen (1986) suggested that because diagenetic Sr is concentrated in secondary mineral phases that are more soluble than biogenic hydroxyapatite, the biogenic Sr could be isolated through a series of sequential leaches in 0.1 N buffered acetic

acid (pH = 4.5) solutions. Sillen (1986) suggested that these sequential leachates would remove material in order of solubility - diagenetic carbonate first, followed biogenic hydroxyapatite, with diagenetic apatites (fluorapatite and chlorapatite) remaining in the residual powder after leaching.

The weak acid leaching technique has had mixed success. It appears to have successfully isolated primary Sr content and isotope composition in buried prehistoric human bones from the arid Southwestern United States (Ezzo *et al*., 1997; Price *et al*., 1994). Price *et al*. (1994), following Sillen (1989), monitored the Ca/P ratio in 5% acetic acid leachates of archaeological bones, finding that as the bones are repeatedly soaked in 1 ml aliquots, the Ca/P ratio in the first solutions have a high Ca/P ratio, reflecting the relative of abundance Ca in highly soluble diagentic minerals such as calcite, but in subsequent washes Ca/P asymptotically approaches 2.1:1, reflecting the stoichiometry of biogenic hydroxyapatite: [$Ca_9(PO_4)_{4.5}(CO_3)_{1.5}(OH)$] (Driessens and Verbeeck, 1990). Price *et al*. (1994) argued that once the Ca/P ratio was near its biogenic value of 2.1, what remained within the bone sample was largely the biogentic calcium and strontium. Similarly, Hoppe *et al*. (2003) found that leaches in 0.1 N acetic acid (buffered to pH 4.5) reduced the amount of diagenetic Sr (35% to 95% before pretreatment) in bone samples from Holocene seals of West Greenland and California as well a Miocene whale from Maryland. Figure 13 shows their results from the California fur seal. Hoppe *et al*. (2003) used a simple mixing model (equivalent to Eq. (8)) to estimate the diagenetic Sr content of each sample, by substituting the original marine $^{87}Sr/^{86}Sr$ ratio (0.7092 for the Holocene or 0.7086 for the Miocene, see Fig. 5) as one end-member, and $^{87}Sr/^{86}Sr$ measured in the burial matrix as the other end-member. In the bone sample from a Greenland harbour seal, Hoppe *et al*. (2003) found that the first leachates contained primarily diagenetic Sr, because their $^{87}Sr/^{86}Sr$ ratios (0.75365) were close to that in local terrestrial animals (0.75376, Nelson *et al*., 1986).

While there is no doubt that leaching in weak acid removes at least some diagentic strontium from contaminated bone, if diagenesis has taken more insidious forms than just filling of pore spaces, including re-crystallization of hydroxyapatite or direct exchange with Sr or Ca in the original hydroxyapatite crystals, then weak acid treatment cannot isolate the biogenic Sr, which may even have been completely replaced during burial (Budd *et al*., 2000; Horn *et al*., 1994; Nelson *et al*., 1986; Radosevich, 1989; Sillen, 1986; Tuross *et al*., 1989). Nelson *et al*. (1986) made a simple test by measuring $^{87}Sr/^{86}Sr$ in the bones of Holocene marine mammals, with an expected biogenic ratio of that in seawater, 0.7092, and concluded that diagenetic Sr from the burial sediments (with a different $^{87}Sr/^{86}Sr$) had completely replaced the biogenic Sr in the bones. Diagenesis is accelerated by microbial deterioration that can happen rapidly after death (Collins *et al*., 2002), and Beard and Johnson (2000) found that the leaching technique was not able to recover the primary Sr content and isotopic composition from human bones that
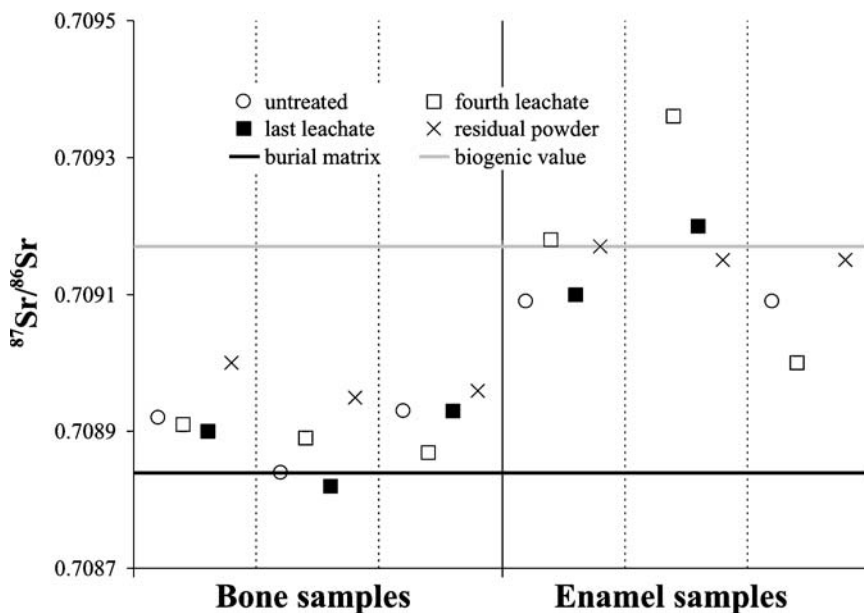
Fig. 13. The ^{87}Sr/^{86}Sr ratios measured by Hoppe *et al.* (2003) from sequential acid leaching of bone and enamel samples from a Holocene California fur seal. The samples were treated with sequential leaches of unbuffered 0.1 N acetic acid. Also shown are the original biogenic ^{87}Sr/^{86}Sr ratio and the ^{87}Sr/^{86}Sr ratio in the surrounding matrix, the presumed diagenetic end-member. After Hoppe *et al.* (2003, Fig. 1).

had been buried for only 20 years in the hot humid climate of Vietnam. Comparing tooth enamel and bone values of individuals, Beard and Johnson (2000, Fig. 5) found Sr levels in the bones to be several times higher, and ^{87}Sr/^{86}Sr significantly more variable, than in tooth enamel. Similarly, Hoppe *et al.* (2003) determined that at least 80% of the diagenetic Sr remained in their marine mammal bone samples after pre-treatment, and although infrared analyses showed that weak acid selectively removed a highly carbonated apatite phase from their Miocene whale bone, the residue also contained fluorapatite, a diagentic apatite. Diagenetic Sr had been incorporated through direct exchange with ground water, thus making it impossible to isolate a biogenic pool by selective leaching (Hoppe *et al.*, 2003).

Acid leaching may even re-crystallize some of the dissolved secondary carbonate Sr back into the bone. This is quite likely for acids stronger than 1.0 N (Hoppe *et al.*, 2003; Nielsen-Marsh and Hedges, 1997; Sillen and Sealy, 1995), but even weak (0.1 N) acetic acid may begin to remove biogenic Sr from bone before it has removed all the diagentic Sr, such that the most biogenic Sr appears in the last leachate rather than in the residual bone powder (Hoppe *et al.*, 2003).

Like bone, tooth dentine is also highly susceptible to contamination, because it contains pores as large as 1 μm, much larger than its phosphate crystals, which are smaller than 0.1 μm (Kohn *et al.*, 1999). For a sample of prehistoric and medieval human teeth from the U.K., Budd *et al.* (2000) found that 15–100% of the Sr in dentine was diagenetic, accumulated from the burial environment. Fortunately, the story for human tooth *enamel* is quite different. Because tooth enamel is denser, harder and more inert than bone or dentine, it is more resistant to post-burial isotopic contamination than bone or dentine (Budd *et al.*, 2000; Driessens and Verbeeck, 1990; Hillson, 1997; Kohn *et al.*, 1999; Kolodny *et al.*, 1996; Pate and Brown, 1985; Price *et al.*, 1985; Sharp *et al.*, 2000). The main reason for this is that the phosphate crystals in enamel are relatively large (>1 μm), and the structure is compact, with little pore space (Kohn *et al.*, 1999). Tooth enamel is about 96% Ca phosphate by weight, with the composition $Ca_{4.5}[(PO_4)_{2.7}(HPO_4)_{0.2}(CO_3)_{0.3}](OH_{0.5})$, and human tooth enamel generally has lower Sr concentrations as compared to bone (Ezzo *et al.*, 1997; Price *et al.*, 1994).

Repeated studies prove that fossil tooth enamel contains much less diagenetic Sr than bone or dentine (e.g., Chiaradia *et al.*, 2003; Hoppe *et al.*, 2003; Horn *et al.*, 1994; Koch *et al.*, 1997; Lee-Thorp and Sponheimer, 2003; Sharp *et al.*, 2000; Trickett *et al.*, 2003). Finding significant differences between enamel and dentine but only minor differences between dentine and soil, Budd *et al.* (2000) concluded that enamel is less susceptible to diagenesis than dentine or bone. Similarly, Chiaradia *et al.* (2003) studied 12 human burials spanning the Neolithic to the Bronze age from the Sion area of Switzerland, and Fig. 14 shows that the $^{87}Sr/^{86}Sr$ ratios in dentine samples are nearly constant around 0.70860 and very close to those of the soil, whereas the $^{87}Sr/^{86}Sr$ in the enamel is more varied and consistently different from the soil. In hippo enamel almost 4 million years old (Kohn *et al.*, 1999) or even in fossil dinosaur teeth more than 100 million years old (Bocherens *et al.*, 1994), tooth enamel has been shown to be resistant to Sr contamination. Measuring the fossil and modern animal tooth enamel by electron microprobe at a μm scale, Kohn *et al.* (1999) found that concentrations of secondary minerals were only 0.3% in enamel, but about 5% in dentine. Similarly, Chiaradia *et al.* (2003) used point microprobe analyses to measure Sr concentrations across the cross-section of an incisor from a Bronze age human individual, and found systematically higher Sr concentrations in the dentine (Sr $= 950 \pm 180$ ppm) than in the enamel (Sr $= 270 \pm 31$ ppm) (Fig. 15). Since Sr concentrations in dentine and enamel are similar during life (Budd *et al.*, 2000), it is likely that the higher Sr contents of the dentine are due to post mortem Sr addition (Fig. 16).

What relatively small amount of diagenetic Sr that does exist in fossil tooth enamel appears to reside in secondary minerals in pore spaces that may be removed by weak acid. Hoppe *et al.* (2003) found that, although up to 80% of diagenetic Sr remained in fossil bone after pre-treatment, weak acid removed over 95% of
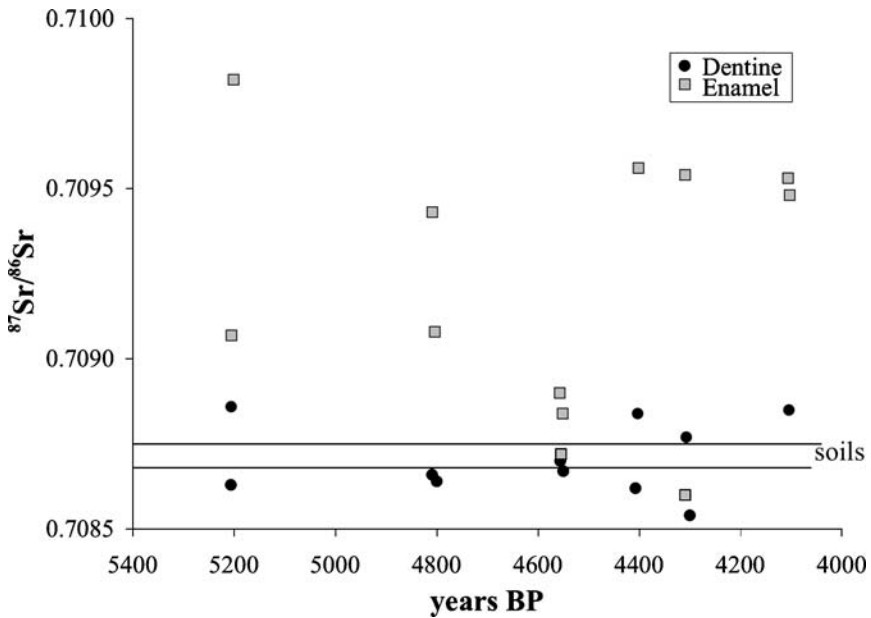
Fig. 14. ^{87}Sr/^{86}Sr vs. age diagram of archaeological teeth from Switzerland, analyzed by Chiaradia *et al.* (2003). Also shown is the range of ^{87}Sr/^{86}Sr for local soils, toward which the dentine values have gravitated by isotopic exchange. After Chiaradia *et al.* (2003, Fig. 10).

diagenetic Sr from fossil tooth enamel samples, whose ^{87}Sr/^{86}Sr ratios converged towards the expected biogenic ratios after pre-treatment (Fig. 13). All but one of the Holocene seal enamel samples analyzed by Hoppe *et al.* (2003) displayed the greatest percentage of biogenic Sr in residual powders, rather than in late

Fig. 15. Sr concentration profile through a crown section of a Bronze age tooth from Sion Sous-Scex, Switzerland. After Chiaradia *et al.* (2003, Fig. 9).

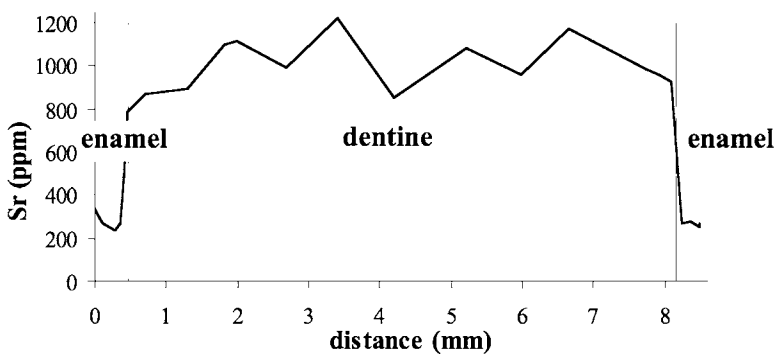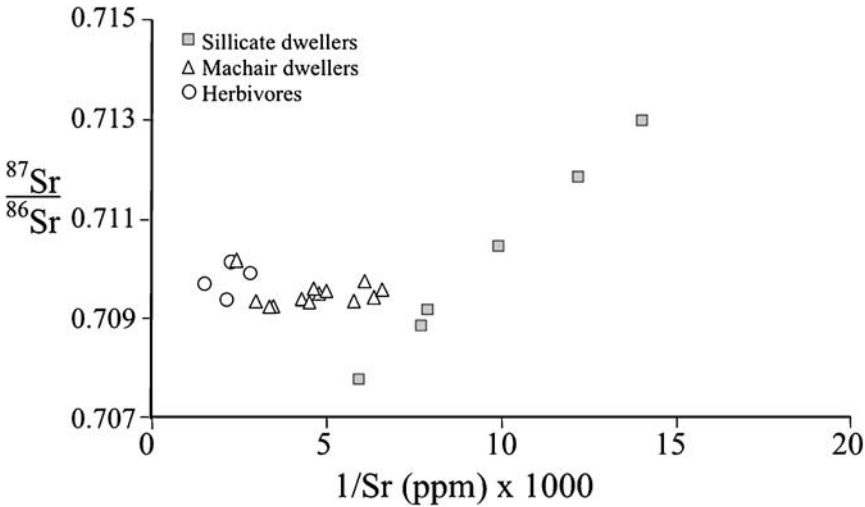**Fig. 16.** Measurements by Montgomery *et al.* (n.d.) on human enamel from the Outer Hebrides, Scotland. For the silicate data array, $r^2 > 0.98$. After Montgomery and Evans (2006; Fig. 7).

stage leachates, suggesting they did not contain significant amounts of diagenetic fluorapatite.

Interpreting $^{87}Sr/^{86}Sr$ in Human Tooth Enamel

Because archaeological bone is often too contaminated to be of much use for Sr isotopic studies, most current studies focus exclusively on tooth enamel, which forms during childhood and undergoes relatively little change after it is mineralized (Hillson, 1997). In some studies, a non-local $^{87}Sr/^{86}Sr$ ratio in enamel simply and clearly identifies an immigrant to the community, for example at Tiwanaku in Peru (Knudson *et al.*, 2004), cave mummies in Bolivia (Knudson *et al.*, 2005), Vikings in Iceland (Price and Gestsdóttir, 2006) and, quite remarkably, African slaves in colonial Mexico (Price *et al.*, 2006). An example of a fairly clear-cut case comes from the Maya city of Copan, where a vaulted tomb chamber was found to contain the bones of a single individual placed on a stone bier and adorned by several large and spectacular jade objects. This robust male, a little over 5′6 tall of about 55 years of age when he died, is suspected to be K'inich Yax K'uk' Mo', the founder of the Classic Copan dynasty in 426 AD. Obtaining multiple samples, Buikstra *et al.* (2003) measured the $^{87}Sr/^{86}Sr$ ratios between 0.70736 and 0.70788 from the tooth enamel of K'inich Yax K'uk' Mo'. As part of their characterization of the Yucatan region mentioned above, Hodell *et al.* (2004) found a narrow range of $^{87}Sr/^{86}Sr$ ratios 0.7062–0.7068 in plant and water samples from Copan. The researchers could then identify K'inich Yax K'uk' Mo' as an "outlier" at

Copan, demonstrating that he did not spend his childhood in the Valley of Mexico (Buikstra *et al.*, 2003; Hodell *et al.*, 2004).

Technically speaking, however, a single $^{87}Sr/^{86}Sr$ ratio from enamel does not automatically distinguish a migrant from Place A to Place B from a person who travelled widely throughout childhood, since a non-local $^{87}Sr/^{86}Sr$ ratio only implies that that person once ate foods which, averaged over the formation of the enamel (cf. Fig. 11), came from non-local sources. This returns us to the concept of mixing lines from the beginning of this review. Montgomery *et al.* (n.d.) have given explicit consideration of how plotting $^{87}Sr/^{86}Sr$ versus 1/Sr, as in Fig. 3b, can reveal distinct arrays of data points indicative of distinct human groups, even though those groups might overlap considerably in their $^{87}Sr/^{86}Sr$ ratios alone (Figure 16).

If there is the means (such as Optimal Foraging Analysis) to model a 'menu' of what certain people ate and where those foods came from, mixing equations can be used to calculate what the overall enamel-averaged $^{87}Sr/^{86}Sr$ ratio should be. This happens to be particularly convenient for Neolithic southwestern Germany where, by using optimal foraging analysis, Gregg (1988, p. 178) had already published an estimate of the optimal diet (in terms of calories). Gregg's estimate for Neolithic farmers included about 3% wild plants and 11% wild game, which is actually quite close to the percentages of wild animal bones actually found at Early-LBK sites in Baden-Württemberg (Arbogast, 2000). To estimate a maximum $^{87}Sr/^{86}Sr$ ratio for farmers, Bentley *et al.* (2003) considered a hypothetical Neolithic farmer who ate 85% local domestic foods with $^{87}Sr/^{86}Sr$ of 0.70958, a typical value for the lowlands of southwestern Germany, and the remaining 14% wild foods with $^{87}Sr/^{86}Sr$ of 0.71670, characteristic of the granitic uplands of the Vosges and Black Forest mountains. The expected $^{87}Sr/^{86}Sr$ could then be modelled by adding up all the dietary contributions, which can be plugged in as the J_i parameters into Eq. (8), as shown in Table IV.

There are two ways one might calculate J_i in this case. The first is to treat Sr as the input on its own, as implied by Eq. (8). The alternative, and probably better, way is to weight each component by the calcium concentration, under the assumption that strontium makes its way into human skeletal tissue only by "hitch-hiking" with calcium. Applying Eq. (8) to the data in Table IV, we arrive at an expected $^{87}Sr/^{86}Sr$ of 0.70975 by basing the J_i on % of diet and Sr ppm alone, and adding the Ca-weightings yields the same value in this particular case (but it can make a difference in other cases). The values of J_i show the relative importance of the different dietary components on the overall $^{87}Sr/^{86}Sr$, and Table IV shows that the lowland cereals (high in Sr and Ca) at these dietary proportions are overwhelmingly dominant in this model, followed by upland plants, and the rest, including meat, are negligible. The advantage of such a model is that we can now vary the different dietary components and see what the effect would be. There are many possibilities. For instance, we can increase the amount of upland meat at the expense of lowland cereals, leaving everything else the same. As Fig. 17

Table IV. Example of a Model of Parameters J_i Needed to Predict Overall ^{87}Sr/^{86}Sr via Eq. (8)

i	Food	Hypothetical ^{87}Sr/^{86}Sr	% of diet†	Ca (ppm)	Sr (ppm)	Sr/Ca	$J_i = \% \times$ Sr ($\times 10^9$)	Ca-wt $J_i = \% \times$ Ca $\times$ Sr ($\times 10^9$)
1	upland meat	0.71670	11	100	0.1	0.001	11	0.0011
2	upland berries, acorns	0.71670	3	3000	6	0.002	180	0.54
3	lowland meat	0.70958	15	100	0.1	0.001	15	0.0015
4	lowland cereals	0.70958	63	3000	12	0.004	7560	22.7
5	lowland cow's milk	0.70958	8	500	0.2	0.0004	16	0.008
	Total		100					

Note. This uses a "menu" derived by a detailed optimal foraging analysis (Gregg, 1988), to model hypothetical Neolithic farmers living in low- ^{87}Sr/^{86}Sr lowlands but also obtaining some of their diet from high-^{87}Sr/^{86}Sr crystalline uplands. All Ca and Sr concentrations are approximate for example only, as real-world values vary considerably. Detailed data on Sr and Ca can be found in studies by Mitchell (1957), Jury *et al.* (1960), Elias *et al.* (1982), Gilbert *et al.* (1994), Burton and Wright (1995) and Burton *et al.* (1999), among others.
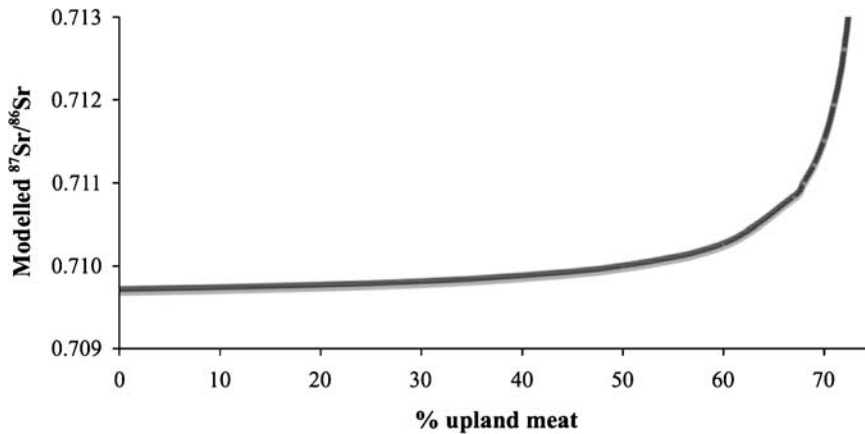
Fig. 17. Modelled effect of varying the proportion of upland meat (^{87}Sr/^{86}Sr = 0.7167), at the expense of lowland cereals (^{87}Sr/^{86}Sr = 0.7096). The model uses Eq. (8) and calculates J_i using Ca-weighted values, as per Table IV.

shows, in this model meat must account for over half the diet before noticeably affecting ^{87}Sr/^{86}Sr, due to its low Sr and Ca content compared to cereals. Applied to Neolithic Germany, this provides some basis for identifying livestock herders who used the uplands, provided the dietary assumptions are reasonable (Bentley and Knipper, 2005b).

Recently, there has been some interest in the possibility of microsampling human enamel at the resolution of its growth layers, called *striae of Retzius* (Fig. 18), or even more finely, at the level of prism cross striations, which are about 2–5 μm apart and reflect the circadian rhythm of enamel matrix secretion (Hillson, 1997, p. 153). ^{87}Sr/^{86}Sr in groups of these could theoretically be sampled by laser ablation or microdrilling of tooth enamel (e.g., Dolphin *et al*., 2003; Kang *et al*., 2004), but there is uncertainty as to whether the *mineralization* of these layers occurs in the same sequential fashion such that a time sequence of ^{87}Sr/^{86}Sr would be preserved at this resolution. As Montgomery and Evans (2006; also Fincham *et al*., 1999) discuss with respect to Sr isotope analysis, the biomineralization of tooth enamel is essentially the transformation of an organic gel into mineral over a series of five distinct phases. The first phase (secretion and formation) involves formation of thin crystallites, which comprise only 10% of the final enamel weight, but it is not until the last phase (maturation) that the hydroxyapatite crystals grow laterally through an abrupt increase in mineral ions (Fig. 18). Hence it is possible that, although the prism cross striations of enamel may reflect growth on a daily scale, the actual mineralization of enamel appears to take place in multiple directions over the months-years of the maturation phase, over which the ^{87}Sr/^{86}Sr in the enamel may be averaged. For this reason Montgomery and
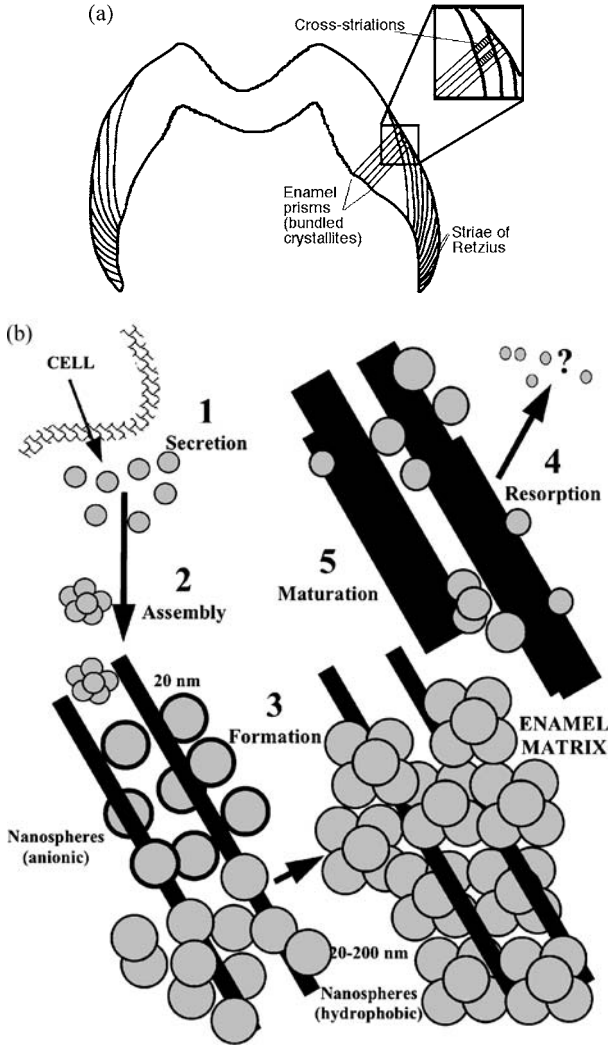
Fig. 18. (a): Schematic molar cross-section showing enamel microstructure. After Smith *et al.* (2003, Fig. 1). **(b):** Schematic diagram by Fincham *et al.* (1999) for enamel biomineralization, under which (1) amelogenins are synthesized and secreted by the ameloblast cell, (2) single amelogenins are assembled into 'nanospheres' of about 20 nm diameter, (3) nanospheres are electrostatically aligned with the enamel crystallites, spacing them at 20-nm, followed by further assembly of nanospheres, which stabilizes the continued growth of the enamel crystallites by ion accretion, (4) nanospheres are broken down into smaller fragments and resorbed by ameloblasts, and (5) with nanospheres removed, crystallites thicken and eventually fuse to generate the mature enamel. After Fincham *et al.* (1999, Fig. 8).

Fig. 19. Permanent crown formation of in human tooth enamel. Ages vary from this guide; more detailed descriptions are available from other sources (e.g., Fincham *et al*., 1999; Hillson, 1997; Reid and Dean, 2006). After Hillson (1986, Fig. 2.4).

Evans (2006) recommend measuring $^{87}Sr/^{86}Sr$ in bulk enamel samples rather than attempting to measure $^{87}Sr/^{86}Sr$ on a microscopic scale. However, until a conc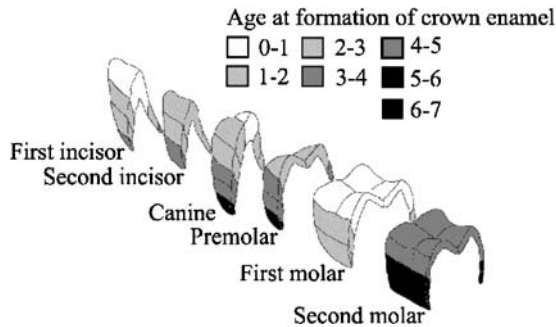lusive microsapmling study is done, it seems premature to give up hope for discovering meaningful $^{87}Sr/^{86}Sr$ differences within a single human tooth.

In any case, there certainly is much potential to measure multiple $^{87}Sr/^{86}Sr$ ratios over the course of childhood by analysing *different* molars from the same individual, which grow at sequential ages of childhood (Fig. 19). In their Iceman study, Müller *et al*. (2003, Table S2a) measured ratios from 0.72106 to 0.72146 in the canine enamel, formed mostly between 2 and 4 years of age, and 0.71999–0.72061 in the 1st and 2nd premolar enamel ($3^{1/2}$–$5^{1/2}$ years), suggesting either that the Iceman was mobile during childhood (potentially related to pasturing of livestock?) or else that small differences in diet provenience during the respective times of enamel formation carried significant $^{87}Sr/^{86}Sr$ differences due to the complexity of the Alpine geology.

For certain animals other than humans, it is more straightforward to sample Sr isotopes along the direction of enamel growth, as long as they are sampled sequentially in the way that the tooth grows for the particular species (Balasse, 2003). This has been a practice with carbon and oxygen isotopes for some time. Koch *et al*. (1995) micro-sampled across the growth laminations of the dentine in elephant teeth in order to obtain a record of $\delta^{13}C$ at roughly 3-month intervals during an elephant's lifetime. By sampling the enamel in 3 mm bands up from the cervical margin of the molar, Fricke and O'Neil (1996) found a cyclical pattern in $\delta^{18}O$ down the length of the third molar of a modern sheep, and also a fossil bison (500 BP), which reflected seasonal changes. In pioneering studies of sequential Sr isotope sampling from large mammal teeth, Hoppe *et al*. (1999) tracked mammoth migration and Balasse *et al*. (2002) presented a temporal $^{87}Sr/^{86}Sr$ record for approximately the first two years of a cow's life. Following

this example, Bentley and Knipper (2005b) measured $^{87}Sr/^{86}Sr$ in excavated LBK cattle enamel at regular intervals along the growth axis of the tooth (Fig. 20), which confirmed that transhumance was practiced at Neolithic Vaihingen in Germany.

Variance Among Populations

Finally, given all the challenges to determining where a single individual childhood from strontium isotopes, there is much more than can be said when measuring $^{87}Sr/^{86}Sr$ in a *population*. There may be clusters of enamel $^{87}Sr/^{86}Sr$ ratios that may then correlate with other characteristics of the burial or skeleton, such as sex, artefacts, burial direction/position or pathology (Bentley, 2001; Bentley *et al*., 2004). In particular, the variance in the $^{87}Sr/^{86}Sr$ ratios may be higher for one group than another, particularly males versus females (e.g., Bentley *et al*., 2002, 2005). Without strictly defining local ranges for their study sites, Bentley *et al*. (2002) were still able to characterise early Neolithic women as significantly more mobile than the men, which may be reflecting a patrilocal pattern of marital residence (the woman moves upon marriage), which is independently indicated by geographic patterns in modern and ancient European genes (e.g., Haak *et al*., 2005; Seilestad *et al*., 1998). In Thailand, a contrasting pattern has been observed at two sites related to early agriculture, Ban Chiang and Khok Phanom Di, where it is actually the female signatures that become local over time, in an abrupt fashion (Fig. 21), whereas the male pattern of variance continues unchanged at each site. At Khok Phanom Di, a coastal site, the male $^{87}Sr/^{86}Sr$ ratios are near the seawater value throughout the site's occupation (Bentley, 2004). At Ban Chiang, an inland site, the $^{87}Sr/^{86}Sr$ ratios show a wide variance throughout (Bentley *et al*., 2005). This is consistent with hunting-gathering at Ban Chiang by males because, as Montgomery and Evans (2006) point out, if the bulk of the strontium is incorporated into enamel (via the mineralization model in Fig. 18) over a few months, then "differences between individuals may result simply from seasonal differences rather than a change of residence. . ." If so, this implies for the Ban Chiang males that similar hunter-gatherer practices may have yielded a wide range of signatures. More generally, it means that group variances in $^{87}Sr/^{86}Sr$ may often be more interpretable than group means or individual $^{87}Sr/^{86}Sr$ ratios.

CONCLUSION

Concluding this article might best be done by summarising the topics discussed with suggested further reading. Basic texts on strontium isotope geochemistry include Faure (1986), Dickin (1995), and White (n.d.). Åberg (1995) and others (Åberg *et al*., 1989, 1990) did early work on strontium fluxes in the environment, a topic reviewed in detail by Capo *et al*. (1998) that continues to be explored particularly in relation to non-geologic strontium sources (Åberg *et al*.,
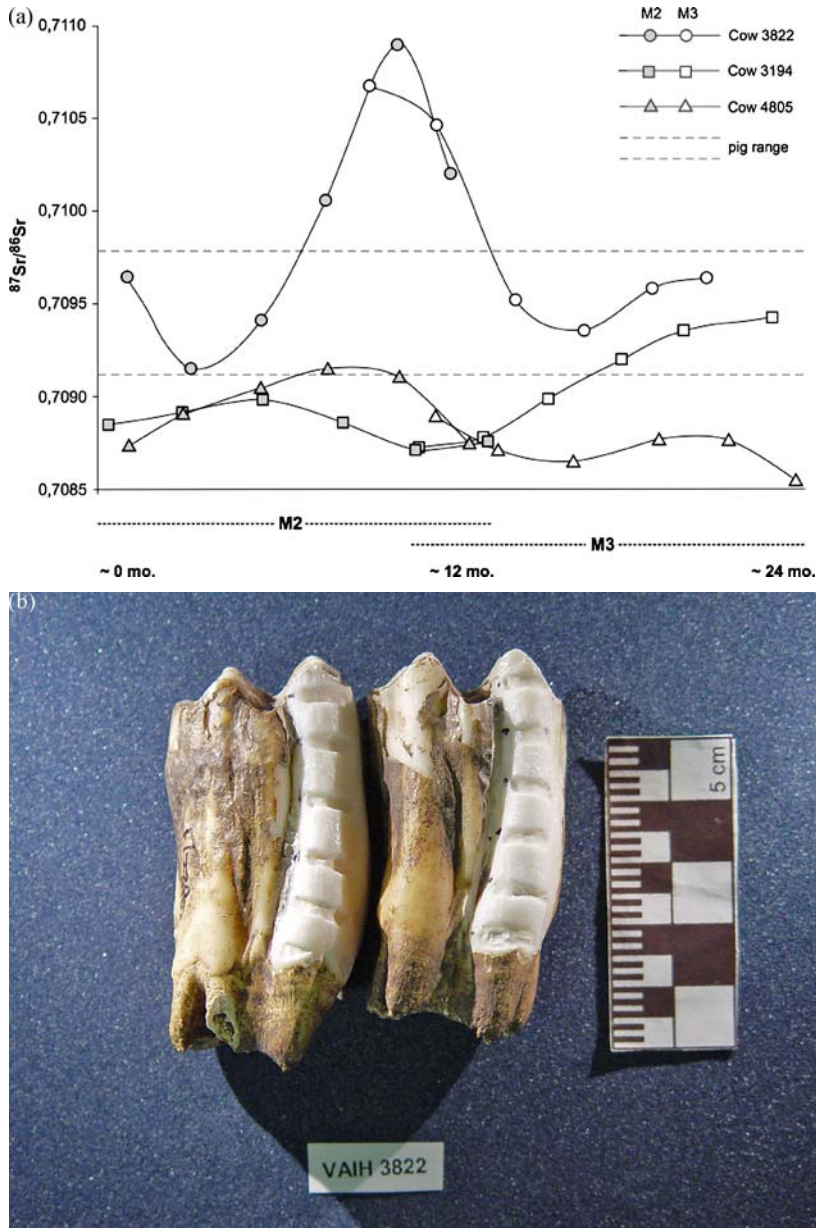
Fig. 20. Sequential sampling of $^{87}Sr/^{86}Sr$ in teeth from three different cows at Vaihingen, Neolithic Germany. Cattle teeth grow at different times after birth, with the second molar (M2) growing from about birth to about ten months, and the third molar (M3) growing from about age 10 months to about 2 years old. After Bentley and Knipper (2005b).
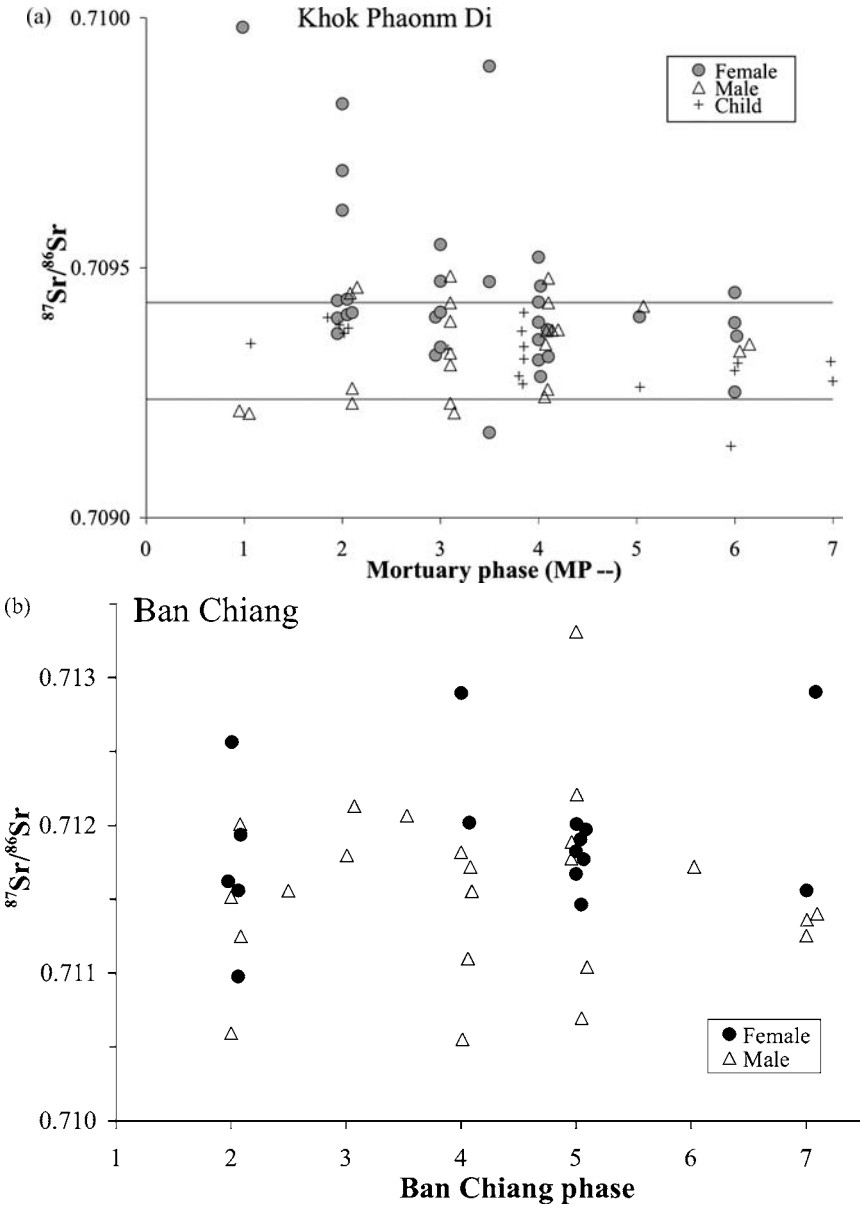
Fig. 21. $^{87}Sr/^{86}Sr$ in human enamel from Ban Chiang (Bentley, *et al.*, 2005) and Khok Phanom Di (Bentley, 2004), by chronological phase. Grey dashes: approximate local ranges, which at Khok Phanom Di is consistent with seafood and/or costal resources (and males as fishermen).

1998; Bern *et al*., 2005; Chadwick *et al*., 1999; Kennedy *et al*., 1998; Vitousek *et al*. 1999; Whipkey *et al*., 2000). The subject of biopurification of strontium and barium with trophic level was discussed in detail by Elias *et al*., (1982), explored in ecology (Blum *et al*., 2000, 2001; Capo *et al*., 1998; Chamberlain *et al*., 1997), and brought to the attention of archaeologists largely by Burton and others (Burton and Wright, 1995; Burton *et al*., 1999, 2003). The question of how to 'map' the biologically available strontium isotope signature was discussed by Price *et al*. (1994), Ezzo *et al*. (1997) and Beard and Johnson (2000) concerning modern mice at Grasshopper Pueblo, and in archaeological faunal tooth enamel by Bentley *et al*. (2004) and Bentley and Knipper (2005a). Sillen *et al*. (1998) provided perhaps the most cautionary tale about mapping $^{87}Sr/^{86}Sr$ among a complex of varied sources on a local scale, whereas Hodell *et al*. (2004) were among the first to produce a coherent $^{87}Sr/^{86}Sr$ map in soil and water samples over a large region. Following Ericson's (1985) seminal introduction to measuring strontium isotopes in human skeletons, pioneering studies focused on sites in South Africa (e.g., Sealy *et al*., 1991, 1995), Arizona (Ezzo *et al*., 1997; Ezzo and Price, 2002; Price *et al*., 1994) and Germany (e.g., Horn *et al*., 1994; Grupe *et al*., 1997, 1999; Price *et al*., 1998). As is the natural progression in science, the technique then subject to greater scrutiny, with important advances made on the understanding of the diagenesis, extending from the longer history of investigating these issues with carbon and nitrogen isotopes (Collins *et al*., 2002; Hedges, 2002; Hoppe *et al*., 2003; Horn *et al*., 1994; Kohn *et al*., 1999; Sharp *et al*., 2000; Wang and Cerling, 1994). Research has greatly elucidated the relative preservation of strontium isotopes in the microstructures of teeth, particularly the relative robustness of tooth enamel to post-burial Sr isotopic contamination (e.g., Balasse *et al*., 2002; Budd *et al*., 2000; Chiaradia *et al*., 2003; Montgomery *et al*., 2003b; Sharp *et al*., 2000; Trickett *et al*., 2003). Finally, mixing models, an underlying topic of this review, have been presented in sophisticated detail by Phillips and Koch (2002) regarding carbon and nitrogen isotopes, which could easily be applied to mixing models for strontium isotopes (cf. Beard and Johnson, 2000; Capo *et al*., 1998; Montgomery *et al*., n.d.; Montgomery and Evans, 2006; Schweissing and Grupe, 2003).

This review has focused on strontium isotopes only for the sake of isolating the topic, and of course the best way to increase to power of the isotopic data is to measure other isotopes and trace elements in the same samples (Kelly *et al*., 2005; Price, 1989), especially lead isotopes (e.g., Ghazi, 1994; Montgomery *et al*., 2000, 2003b), oxygen and carbon isotopes (e.g., Balasse *et al*., 2002; Bentley *et al*., 2005; Budd *et al*., 2004; Hoppe, 2004; Kohn, 1996) and strontium and barium trace element concentrations (e.g., Beard and Johnson, 2000; Burton and Price, 1990; Burton *et al*., 1999, 2003; Ezzo *et al*., 1997; Gilbert *et al*., 1994; Montgomery *et al*., n.d.; Schoeninger, 1979; Sealy and Sillen, 1988; Sillen, 1986, 1992; Sillen *et al*., 1995). If material from the body is available, most often collagen from the bones but also possibly hair, fingernails or even flesh, then a whole new set of

carbon, nitrogen, sulphur and other isotope analysis becomes available, of which the literature is too vast to cite here except for a few general introductions and new applications (e.g., DeNiro and Epstein, 1978; Gilbert *et al.*, 2004; Heaton, 1999; Hedges *et al.*, 2006; Koch *et al.*, 1994; Müller *et al.*, 2003; Richards *et al.*, 2001; Schoeninger *et al.*, 1983; Schoeninger, 1985; Schoeninger and Moore, 1992; Tieszen, 1991; Tieszen *et al.*, 1983; van der Merwe, 1982; Vogel and Van Der Merwe, 1977; White, 1993). Finally, it goes with out saying that, as in any science, strontium isotope data are most effective as part of multiple independent lines of evidence (Ezzo and Price, 2002), especially the contexts of the burials and other archaeological evidence that bring the isotope data to life.

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ON ISOTOPES AND OLD BONES*

J. A. LEE-THORP

*Division of Archaeological, Geographical and Environmental Sciences, University of Bradford,
Bradford, West Yorkshire BD7 1DP, UK*

*This review charts the developments and progress made in the application of stable light
isotope tools to palaeodietary adaptations from the 1970s onwards. It begins with an outline
of the main principles governing the distribution of stable light isotopes in foodwebs and
the quality control issues specific to the calcified tissues used in these analyses, and then
proceeds to describe the historical landmark studies that have marked major progress, either
in their archaeological applications or in enhancing our understanding of the tools. They
include the adoption of maize agriculture, marine-focused diets amongst coastal hunter–
gatherers, trophic level amongst Glacial-period modern humans and Neanderthals, and the
use of savannah resources by early hominins in Africa. Particular attention is given to the
progress made in addressing the challenges that have arisen out of these studies, including
issues related to the routing of dietary nutrients. I conclude with some firm, and some more
speculative, pointers about where the field may be heading in the next decade or so.*

INTRODUCTION

The application of stable light isotope ratio analysis to past human diets has by now reached
a certain level of maturity. It is over 30 years since the first pioneering publications appeared
reporting the application of stable carbon isotopes to the uptake of maize amongst prehistoric
woodland Americans (Vogel and van der Merwe 1977; van der Merwe and Vogel 1978). These
first elegant applications built on a series of discoveries related to carbon isotope pathways in
plant photosynthesis (e.g., Smith and Epstein 1971), the observations and experience garnered
by radiocarbon chemists (e.g., Berger *et al*. 1964; Tamers and Pearson 1965; Bender 1968;
Longin 1971; Hassan and Ortner 1977), and then controlled diet experiments (DeNiro and
Epstein 1978) and observations from free-ranging animals (Vogel 1978) that provided the
essential information about transfer of dietary isotope composition to animals' tissues.

The distinct advantage of a stable isotope natural abundance approach for dietary studies is
that it reflects the foods *actually* eaten by an individual, or a group of individuals, rather than
a palimpsest of waste of uncertain duration that typically preserves only a tiny fraction of the
original material and overlooks those organic remains with low survival rates, such as plant
foods. In the North American case, the results were decidedly unexpected, and prompted a
re-examination of the earlier archaeological evidence for the formation of complex societies,
and the adoption and spread of maize agriculture. They also prompted a longstanding debate
about *how much* maize was reflected in the collagen isotope values, and the broader debate
around this issue still permeates isotope dietary studies.

The main challenges are about what the isotopic composition of various human tissues really means in terms of quantifiable dietary components—whether there is over- or under-representation, how we deal with issues of equifinality and variability, and whether the measured isotopic values have remained intact over the passage of time. We need to understand how *post mortem* processes may impact on the primary dietary information. These problems were posed early on and, in spite of clear advances, a significant number of the challenges are still current today.

As part of *Archaeometry's* 50th anniversary year, we were asked to chart the course of our field over the past half century or so, paying particular attention to the contributions that have appeared in this journal. Because the fundamental developments of stable light isotope ecology have taken place within many disciplines, the pioneering studies are scattered across an extremely wide literature, from geochemistry (the original 'home' discipline), to plant and animal sciences, archaeology and general science. This journal has published pioneering studies on the application of stable light isotope ratio analysis to Classical marbles in the Mediterranean (e.g., Herz 1992), but contributions in isotope applications to palaeodiets have tended rather to be directed at the issues of preservation of calcified tissues. In particular, a special 2002 issue of *Archaeometry* was devoted to the Fourth Bone Diagenesis meeting. For the purposes of this review, I have concentrated on the most fruitful major dietary applications, and on charting the subsequent progress in addressing the major issues that have arisen out of these studies. As alluded above, they include the issues of interpretation of quantity (*how much*), routing of dietary nutrients (*how representative*), and diagenesis in different tissues (*how reliable* are the analyses of bone and enamel, organic and inorganic components).

Because of the breadth of the field, I confine the review to a few exemplary studies, including the adoption of maize agriculture, marine-focused diets amongst coastal hunter–gatherers, trophic level amongst Glacial-period modern humans and Neanderthals, and the use of savannah resources by early hominins in Africa. Finally, I provide some pointers to the directions in which the field is heading, including high-resolution life history applications. As a start, it is useful to consider the main principles of stable light isotopes in foodwebs, and issues of preservation and quality control, before we consider specific applications to human diets.

<center>STABLE ISOTOPES AS DIETARY TRACERS</center>

Target tissues

This review focuses on calcified tissues, since bones and teeth are by far the most common vertebrate tissues surviving into the archaeological record, although keratinous tissues such as hair and nails occasionally survive in more recent, special circumstances. The patterned isotope distributions described below are archived and analysed in bones and teeth, which are composite tissues made up of complex organic molecules and minerals. Collagen is the main protein in bone and dentine that provides the source for organic carbon ($^{13}C/^{12}C$),[1] nitrogen ($^{15}N/^{14}N$) and, to a lesser extent, oxygen ($^{18}O/^{16}O$), sulphur ($^{34}S/^{32}S$) and, most recently, hydrogen (D/H). It is composed of multiple helical peptide fibrils stippled with a fine, poorly crystalline

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[1] By convention, stable isotope ratios are expressed in the δ notation, in parts per thousand (per mille or °/₀₀) relative to an international standard, as $\delta^x Z = (R_s/R_{ref} - 1) \times 1000$, where R is the isotope ratio ($^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, D/H or $^{34}S/^{32}S$). For carbon isotopes, the standard is the marine limestone PDB; oxygen and hydrogen isotopes may be expressed relative to PDB or to Standard Mean Ocean Water (SMOW), depending on the material being analysed; for nitrogen isotopes it is Ambient Inhalable Reservoir (AIR); and for sulphur isotopes it is the Canyon Diablo Triolite meteorite (CDT). Negative values denote that the sample has lower abundances of the heavier isotope than does the standard.

'cement' of mineral. Bone mineral and enamel are highly substituted biological calcium phosphate apatites, differing subtly in their chemistry and properties, from which $^{18}O/^{16}O$ can be determined from phosphate, and $^{13}C/^{12}C$ and $^{18}O/^{16}O$ from substituted carbonate. The timespan captured in these tissues differs. Since bone is a living tissue that turns over regularly within the life of an individual, isotope values reflect long-term averages that depend on the age of the individual. A recent study based on radiocarbon showed that turnover slows dramatically after full maturity is achieved (Hedges *et al.* 2007). In contrast, tooth enamel and dentine are incremental tissues that form during a limited, mostly juvenile, period of an individual's life, with the exception perhaps of the third molar. Consequently, isotope values reflect conditions at that time, although there is a little secondary dentine formation, and the nature of amelogenesis and primary and maturation mineralization in enamel means that time intervals are not discrete (see below).

Natural abundances of stable isotopes in foodwebs

The stable isotopes of an element differ slightly in their nuclear mass as a result of differences in the number of neutrons, leading to small but significant differences in their thermodynamic and kinetic properties (Sharp 2007). Molecules containing the higher-mass, rarer isotope tend to accumulate in the thermodynamically most stable component of a system—for instance, in the liquid rather than gaseous phase—or are slower to react in mass-sensitive kinetic reactions. In equilibrium, and incomplete or multidirectional physical and biochemical processes, the result is fractionation or partitioning. The principles governing physico-chemical fractionation are relatively well understood theoretically and empirically, and thus they provide a means of tracking the pathways of the 'life' elements through a complex series of chemical transformations.

The largest source of carbon isotope variability occurs in primary producers on land and in the oceans. In land plants, the two dominant photosynthetic pathways, C_3 and C_4 (after the number of carbon atoms fixed in the first product), differ in their net discrimination against ^{13}C during fixation of CO_2 (Smith and Epstein 1971; O'Leary 1981; Farquhar *et al.* 1989). In C_3 photosynthesis, strong discrimination against ^{13}C during CO_2 fixation by ribulose biphosphate carboxylase/oxygenase (RUBISCO) results in more negative $\delta^{13}C$ values in virtually all trees, woody shrubs, herbs and temperate or shade-loving grasses. Because plants following the C_4 pathway (tropical grasses and many sedges) concentrate CO_2 in bundle-sheath cells prior to release into the RUBISCO cycle, and as all of it is converted, fractionation is not expressed. C_4 photosynthesis is believed to be a relatively recent adaptation for lower pCO_2 and high solar radiation in the growing season (Ehleringer *et al.* 1997), so distribution of C_4 plants is confined to environments with such conditions. In C_3 plants $\delta^{13}C$ varies widely, from about -24 to $-36‰$ (global mean $-26.5‰$) depending on light intensity, temperature, humidity, moisture and recycling of CO_2 (O'Leary 1981; Farquhar *et al.* 1989; van der Merwe and Medina 1991). C_4 plant $\delta^{13}C$ (global mean $-12.5‰$) is less variable. Economically important C_3 cereals include wheat, barley, oats and rice, as well as all root staples such as potato, manioc and yam, while important C_4 plants include maize, sorghum, millet and cane sugar. In general, marine primary producers (e.g., phytoplankton, algae, diatoms and radiolaria) are enriched in ^{13}C compared to those in terrestrial C_3 ecosystems, because the source of carbon is mainly dissolved bicarbonate, which has relatively high $\delta^{13}C$ compared to atmospheric CO_2. The mean $\delta^{13}C$ is about $-20‰$ (Smith and Epstein 1971), but values vary.

Plant $\delta^{13}C$ values are reflected in the tissues of consumers. In the first controlled feeding experiment, DeNiro and Epstein (1978) showed that $\delta^{13}C$ of the whole animal is very similar to that of its diet (where it is possible to measure the whole organism), but there is partitioning

among tissues according to their chemistry and biosynthetic pathways. Thus isotopic differences, often expressed as Δ (difference) or ε (enrichment factor), vary between diet and particular tissues. The difference between diet and collagen $\delta^{13}C$ is generally about +5‰, as first observed by van der Merwe and Vogel (1978), based on their values for humans in a mono-isotopic C_3 biome. This offset is supported by many later studies of free-ranging herbivores (e.g., Sullivan and Krueger 1981; Lee-Thorp *et al*. 1989). Two well-controlled dietary experiments showed that the relationship is largely between dietary protein and collagen, because dietary amino acids are preferentially utilized for collagen tissue construction (Ambrose and Norr 1993; Tieszen and Fagre 1993) (see discussion below). A small trophic-level effect of about +1 to 2‰ is observed in subsequent steps, among omnivores and carnivores, and including humans.

Bone or enamel carbonate is formed in equilibrium with blood bicarbonate and its $\delta^{13}C$ is closely related; these values in turn are controlled by catabolic and respiratory processes (Krueger and Sullivan 1984; Passey *et al*. 2005b). The offset between dietary and bone carbonate $\delta^{13}C$ averages about +12‰ (Krueger and Sullivan 1984; Lee-Thorp *et al*. 1989); however, this varies according to body mass and dietary physiology. The controlled feeding studies for mice (DeNiro and Epstein 1978) and rats (Ambrose and Norr 1993) found Δ of <10‰; observations of many free-ranging herbivores suggest ~12‰, and analyses of horses gave 14‰ (Cerling and Harris 1999). More recently, results from controlled feeding studies of several small to large species suggested that offsets varied from +11 to +13.5‰ (Passey *et al*. 2005b). A likely cause of a large $\Delta_{diet-carb}$ is expiration of varying amounts of ^{13}C-depleted methane (Hedges and van Klinken 2000).

For nitrogen isotopes, variability in ecosystems reflects the balance between biological nitrogen fixation, complex recycling within the biosphere, and re-release of N_2 (Robinson 2001). Atmospheric N_2 is globally uniform in isotope composition, with a low $\delta^{15}N$ composition (0‰ by definition). On land, soils and plants are slightly higher in ^{15}N compared to atmospheric N_2 (Delwiche and Steyn 1970); soil and plant $\delta^{15}N$ is typically about +1–4‰ subject to variability caused by environmental aridity, leaching (with high precipitation), anoxia and salinity (Shearer *et al*. 1978; Heaton 1987; Handley and Raven 1992). A general 'rule of thumb' is that soil $\delta^{15}N$ is weakly inversely related to rainfall (Handley *et al*. 1999), but in practice the relationship that holds, although still variably, where mean annual rainfall is <400 mm (Heaton 1987). In the oceans, the most abundant form of nitrogen available to primary producers is recycled nitrate, with an average $\delta^{15}N$ value of about +5–6‰ in the productive upwelling centres along ocean margins (Liu and Kaplan 1989).

Nitrogen isotopes vary with trophic level, and a stepwise trophic shift of +2–6‰ in $\delta^{15}N$ from plants to herbivores, and from herbivores to carnivores, has been widely documented in marine and terrestrial foodwebs (DeNiro and Epstein 1981; Minigawa and Wada 1984; Schoeninger and DeNiro 1984; Sealy *et al*. 1987). In long marine foodchains, the effect is a stepwise enrichment in ^{15}N, resulting in distinct high $\delta^{15}N$ values in most marine foods and consumers (Minigawa and Wada 1984), compared to terrestrial foods (Schoeninger and DeNiro 1984). Freshwater ecosystems behave similarly to marine systems, so that freshwater foods also have high $\delta^{15}N$, although their $\delta^{13}C$ does not follow the same pattern as the marine system (Dufour *et al*. 1999). The trophic shift is probably the result of loss of ^{15}N-depleted excretion products (urea in the case of most animals; Ambrose 1991). However, as summarized by Hedges and Reynard (2007), there is considerable diet to tissue variability amongst species with different physiologies—we do not know what it is for humans, it may not be linear, and the effects of high- or low-protein diets are not well understood. Logically, if the process of urea loss/body ^{15}N-enrichment continues, values in animal tissues should become progressively

higher with age. This is not observed, however, and it may be the case that isotope effects leading to trophic enrichment in ^{15}N are more marked in certain phases of maturation.

Biochemical processes induce minimal sulphur isotope fractionation in plants (Trust and Fry 1992) and in higher foodweb levels according to a single controlled feeding study (Richards *et al*. 2003b), so their distribution is largely governed by variations in underlying geology on land (ranging in δ^{34}S from −22 to +22‰), and the contrast with the uniform composition of the oceans (δ^{34}S = +20‰). Krouse pioneered the application of sulphur isotopes to studies of location and human diets (e.g., Krouse *et al*. 1987), but earlier applications were limited by the large amounts of bone collagen required until improvements in continuous flow methods for sulphur isotopes emerged. Given the uniform oceanic composition, marine diets are detectable, but because of a strong sea-spray effect, marine-like δ^{34}S also reflects coastal or even island residence. Therefore δ^{34}S must be applied in combination with δ^{13}C and δ^{15}N (Richards *et al*. 2003b).

It is well known that the global distribution of hydrogen and oxygen isotopes is largely bound up with their behaviour in water (Dansgaard 1964). In animal tissues, however, analysis and interpretation of the two isotopes is separated because of the nature of the tissue archives. Studies of δ^{18}O in vertebrate bone and enamel mineral have a long history, with attention directed towards exploring δ^{18}O in apatite phosphate or carbonate as a palaeoclimate indicator (Longinelli 1984; Luz *et al*. 1984; Luz and Kolodny 1985). Dietary ecology is implicated, since water and oxygen in food contribute to body water δ^{18}O, to a degree influenced by an animal's drinking habits and thermophysiology (Luz and Kolodny 1985; Bocherens *et al*. 1996; Kohn 1996; Sponheimer and Lee-Thorp 2001). Because hydrogen isotopes exchange rapidly and readily, studies have focused on non-exchangeable, tightly bound hydrogen in organic molecules. This work is in its infancy, in part related to the analytical difficulties. One recent study demonstrated that in addition to providing indications of ambient climate conditions, trophic-level effects are observed (Reynard and Hedges 2008). The implications of these variations for human diets have not yet been explored.

PRESERVATION AND QUALITY CONTROL

If we are to use stable isotopes as tracers in fossil or subfossil bones and teeth, we must be confident that the original isotope values have not been altered substantially *post mortem* and *post-burial*. All ancient calcified tissues are subject, inevitably, to some measure of alteration and, in fact, almost all bones and teeth disappear completely, relatively quickly, unless a narrow range of optimal conditions are met. The pathways of diagenesis in bone, dentine and enamel, and in the organic and inorganic components of these tissues, vary markedly because of their chemical and structural differences, while the main external influences remain those of moisture and pH, microbial attack, temperature and time (Hare 1980; Collins *et al*. 2002; Hedges 2002; Lee-Thorp 2002; Berna *et al*. 2004). Clearly, a close relationship exists between bone preservation (or the converse) and site formation processes (Weiner and Bar-Yosef 1990; Bell *et al*. 1996; Berna *et al*. 2004; Jans *et al*. 2004). In spite of the different pathways, the survival or destruction of the organic and inorganic components often appears to operate in concert, particularly for bone, which is a porous structure providing ready access to microbes and water, and where collagen and bioapatite provide some mutual protection (Hedges 2002).

Collagen

The stability and degradation of the major protein in bone and dentine, collagen, has been extensively studied because of its importance not only in isotopic but also radiocarbon and

racemization studies. On geological time-scales, collagen is short-lived compared to fossilized bioapatite, but it is a very robust biomolecule, and it has been repeatedly shown that measurable amounts of collagen can survive under optimal conditions for well over 100 000 years (Jones *et al.* 2001). Collagen denatures when hydrogen bonds are broken and thereafter fibrils dissolve away relatively quickly, explaining collagen's sensitivity to moisture, temperature and pH conditions. Collins *et al.* (2002) provided a synthesis of current understanding of the degradation of collagen and other biomolecules in the same special issue of *Archaeometry*. Non-collagenous proteins—in particular, osteocalcin—also survive in ancient bone but, disappointingly, their survival rate has proved to be poorer than that of collagen (Smith *et al.* 2005).

It seems that even when a large proportion of the original collagen molecules have disappeared, the isotopic composition remains intact. Uniform purification procedures are now used, all of which are modifications of the original Longin (1971) method. Chunks or powdered bone/dentine samples are demineralized in dilute HCl, nowadays at low temperature (5°C; see Richards and Hedges 1999a; Jones *et al.* 2001), followed by a gelatinization step, then filtration and freeze-drying, before small amounts are combusted and the CO_2 and N_2 introduced into a mass spectrometer. Standard deviations of replicate measurements are generally about ±0.1‰ for carbon and ±0.2‰ for nitrogen. Highly degraded collagen or humic contamination can produce altered stable isotope ratios but, again, standard protocols provide a straightforward, satisfactory quality control for collagen. Calculation of molar C:N ratios, and collagen yield and weight per cent C and N (Ambrose 1990), are routinely practised by the stable isotope community. The C:N measure in particular has proved to be extremely robust. The isotopic integrity of collagen, even in cases where little survives (~2%) was puzzling until it was shown that protein sequence and stable isotope information remain intact until a critical threshold of denaturation of fibrils and (high) loss is reached (Koon 2007).

Bioapatites

Although the minerals in bone and enamel are both biological apatites, they differ in ways that reflect their function, and also strongly influence diagenetic pathways. Bone apatite is highly substituted (including about 6% of CO_3^{2-}) with very low crystallinity,[2] so that it is a reactive material (Driessens *et al.* 1978; LeGeros 1991). Enamel apatite, on the other hand, has fewer substitutions (~3% CO_3^{2-}), higher crystallinity and density (LeGeros 1991) and higher-order prismatic structures (Boyde 1967). The organic matrix of mature enamel consists of very small amounts (<1%) of phosphoproteins and amelogenins, whereas the proportion of collagen remains high (~20–30%) in bone and dentine. The trend for bioapatites *post mortem* (where conditions are conducive to survival) is towards greater stability following processes of recrystallization and crystal growth (or Ostwald ripening). In bone, crystallinity indicators such as X-ray diffraction and Fourier transform infra-red show rapid increases after death, even in the absence of environmental promoters (Trueman *et al.* 2004), but changes in enamel are minimal even after very long periods (Lee-Thorp and van der Merwe 1987; Ayliffe *et al.* 1994). Recrystallization can introduce foreign ions into the crystal structures, but it is not inevitable that the original isotope composition is altered, as rearrangements and incorporation can be internal, drawn from surrounding fluid. In the case of enzymatically catalysed microbial attack (Blake *et al.* 1997; Sharp *et al.* 2000) combined with recrystallization, however, significant

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[2] The term *crystallinity* denotes both size and perfection of crystals; in other words, poor crystallinity implies both internal distortion and small crystal size.

alteration of $\delta^{18}O$ was observed in bone phosphate, in spite of the belief that the strength of the P–O bond rendered it immune to diagenesis (Luz and Kolodny 1985). Enamel is not immune; Schoeninger *et al.* (2003) has shown that recrystallization to fluoroapatite can affect the isotopic composition of fossils from the tufa-rich Lake Turkana region. Over longer time-scales, ionic or isotopic exchange/diffusion processes may continue in both tissues, and precipitation of foreign minerals in cracks and pores includes pyrites, silicates and simple carbonates (Hassan and Ortner 1977).

The net result of these properties and observations is that bone apatite is vulnerable to the kinds of diagenesis that may frequently influence isotope composition, while enamel remains relatively immune. Most workers have responded by switching to enamel as sample material. Nevertheless, tooth enamel and bone are not equivalent in terms of the window reflected in an individual's life, as bone provides a broader perspective than that reflected in enamel. It has been argued that subfossil bone apatite can yield valuable information in many cases (Lee-Thorp and Sponheimer 2003), so we should not discard these opportunities too quickly.

There is less agreement on protocols for detecting meaningful alteration of apatite, for eliminating contaminants and for establishing quality controls than is the case for collagen. This is because of uncertainty about the pathways and effects of diagenesis on isotopic composition and how best to gauge them, and because pretreatment protocols designed to eliminate contaminants can also introduce artefacts. It has been observed that many of the standard indicators of diagenesis do not correlate with one another (Hedges 2002) and, furthermore, they may indicate little about isotope alteration (Trueman *et al.* 2008). For instance, expected $\delta^{18}O$ distinctions between human groups in Mexican sites held, even though crystallinity was clearly altered (Stuart-Williams *et al.* 1996).

Unlike collagen, testing for reliability of apatite isotopic composition requires tests that rely on intrinsic natural isotopic variability. One approach is to establish a comparative $\delta^{13}C$ scale from animals that are known C_3 and C_4 feeders to mark the endpoints, against which unknowns can be compared (as first set out in Lee-Thorp and van der Merwe 1987). This works well, but there are limitations—it only applies in regions with distinct C_3 and C_4 floras, and there can be difficulties in assigning appropriate diets for long-extinct animals. Nevertheless, where it has been applied, the results have shown a remarkable robusticity in enamel $\delta^{13}C$ (e.g., Cerling *et al.* 1997). In making such present/past comparisons, we need to take into account that $\delta^{13}C$ of atmospheric CO_2, on which plants depend, has changed from about −6.5‰ in the pre-industrial era to −8‰ today as a result of fossil fuel burning (Friedli *et al.* 1986). At the same time, however, the fossil effect has not yet had a measurable effect on marine $\delta^{13}C$ values, and this difference could complicate studies of marine versus non-marine human diets.

Assessment of the reliability of $\delta^{18}O$ values is more intractable, because of the inherent variability of the system. One approach is to rely on the predictable variability within a faunal assemblage (Bocherens *et al.* 1996; Sponheimer and Lee-Thorp 2001); for instance, hippopotamus $\delta^{18}O$ is consistently lower than that of other animals in African faunal assemblages (Bocherens *et al.* 1996). A more universal test is to establish that predicted intra-annual $\delta^{18}O$ holds for high-resolution analyses of tooth crowns, following the approach established by Balasse (2003). Another is the comparison of $\delta^{18}O$ from the carbonate and phosphate ions, since the isotopic offset is known (Bryant *et al.* 1996; Iacumin *et al.* 1996), although there is some internal and inter-species variability (Martin *et al.* 2008).

Most standard purification procedures first eliminate the organic component of the powdered sample by means of weak NaOCl or H_2O_2, followed by etching in a weak, often buffered, acetic acid solution. The rationale is that the acid first attacks the more reactive phases comprising

the simple carbonate contaminants and more soluble apatite, whether biogenic or diagenetic. The dilute acetic acid protocol originally developed by Harold Krueger has remained in use with modifications (Sullivan and Krueger 1981; Lee-Thorp and van der Merwe 1987; Krueger 1991; Koch *et al*. 1997). Both steps in the protocol can induce chemical and isotopic artefacts, so the duration of the reactions must be limited, especially where the material is reactive. For instance, drilling produces very small particles that are significantly more reactive, and prolonged immersion can induce recrystallization. Our laboratory currently uses these protocols for very limited periods (30 and 5–10 min, respectively) in order to avoid dissolution and recrystallization. It should be pointed out that these weak acid protocols have limitations where material has been converted to highly stable fluoroapatite; in these cases the altered material—which may occur in patches—must be avoided.

MAIZE AGRICULTURE

The first application of $\delta^{13}C$ in human bone collagen from sites in North America was carefully chosen to represent the relatively simple case of importation of an isotopically distinct C_4 crop, maize, into a mono-isotopic C_3 environment (Vogel and van der Merwe 1977; van der Merwe and Vogel 1978). These authors found that the bone collagen of individuals in Northeastern American sites showed no isotope shift consistent with consumption of C_4 maize until about AD 1000, and thereafter bone collagen $\delta^{13}C$ increased sharply, reaching levels that suggested very high maize consumption, over 60%, by AD 1500 (Fig. 1). Subsequently, others have augmented these studies in similar or related areas where maize was an introduced crop, and produced similar results (e.g., Buikstra and Milner 1991).

It was the apparent *absence* of maize prior to AD 1000 that was most surprising, because there were strong indications that subsistence and social patterns were changing in the Early Woodland groups prior to this time. Was it possible that collagen $\delta^{13}C$ was under-estimating maize consumption prior to AD 1000? And were the proportions of C_4 carbon in collagen (50–60%) represented in the Late Woodland populations, as shown in several studies, consistent with the osteological evidence for the development of severe dietary deficiencies in some populations (Larson 1995)?
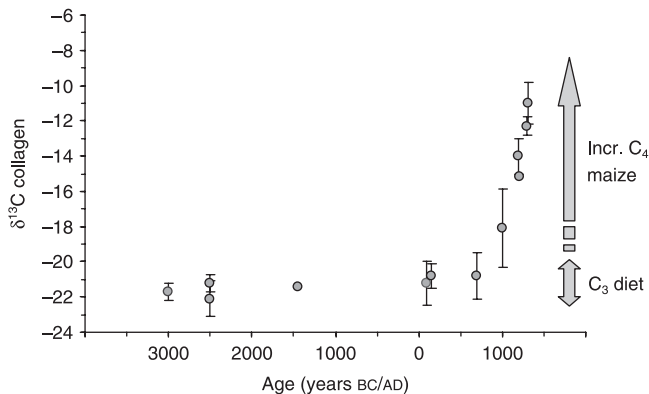

Figure 1 *Shifts in bone collagen $\delta^{13}C$ values of skeletons from Archaic and Early and Late Woodland sites in Northeastern America over* c. *5000 years. Age is given in calibrated years* BC/AD, *and the $\delta^{13}C$ data are shown as means and standard deviations. The data are from Vogel and van der Merwe (1977) and van der Merwe and Vogel (1978).*
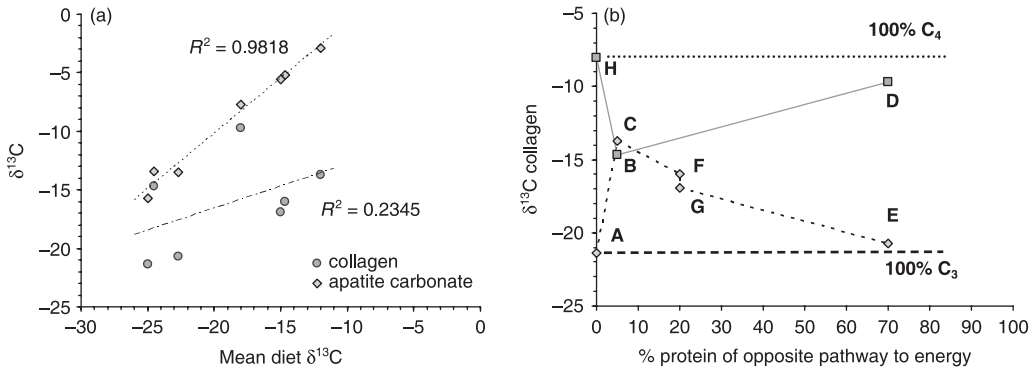
Figure 2 *The results of the Ambrose and Norr (1993) controlled feeding study. (a) A plot of $\delta^{13}C$ in bone collagen and apatite carbonate expressed against mean dietary $\delta^{13}C$ shows significant deviations for the collagen/diet expression. (b) Bone collagen $\delta^{13}C$ plotted against the percentage of protein of opposite pathway to energy components (lipids and carbohydrates). Each point represents a particular diet: A has 20% C_3 protein and C_3 energy, B 5% C_4 protein and C_4 energy, C 5% C_3 protein and C_4 energy, D 70% C_4 protein and C_3 energy, E 70% C_3 protein and C_4 energy, F and G both have 20% C_3 protein and C_4 energy, and H' is a hypothetical 100% C_4 diet. The results show that the protein pathway has a disproportionate effect on bone collagen $\delta^{13}C$.*

The results sparked a long-running debate about whether or not dietary proteins are preferentially routed to collagen, because if they are, foods high in starch and/or lipids (such as maize), could be greatly under-represented in collagen $\delta^{13}C$. Alternatively, all dietary macronutrients might contribute to construction of collagen, known informally as the 'scrambled egg' model (van der Merwe 1982). Since it is known that several essential amino acids present in collagen cannot be manufactured *in vivo* in mammals, the odds seemed weighted towards the former model. But hard evidence was lacking. Krueger and Sullivan (1984) put together a model based on first principles and their observations for differences between collagen and bone apatite carbonate $\delta^{13}C$ from animals at different trophic levels, and humans, which suggested that collagen $\delta^{13}C$ preferentially reflected the dietary protein, while bone carbonate $\delta^{13}C$ reflected rather the energy components. Data from a larger number of free-ranging herbivores, omnivores and carnivores were consistent with this idea (Lee-Thorp *et al.* 1989). Only after two carefully designed controlled feeding studies were carried out, however, did it become very clear that dietary protein was indeed preferentially routed to collagen, and also that bone apatite carbonate almost perfectly reflected the entire diet (Fig. 2 (a); see also Ambrose and Norr 1993; Tiezsen and Fagre 1993). The rat study used extreme differences in the isotope composition of proteins and energy (starch and lipid) sources to demonstrate that even small amounts of protein of opposite C_3 or C_4 pathway to the rest of the diet forced large shifts in collagen $\delta^{13}C$ (Fig. 2 (b); see also Ambrose and Norr 1993). The apatite results demonstrate that bone carbonate is strongly influenced by catabolism of *all* dietary macronutrients in both studies. Two later compound specific studies of the same material showed that (i) $\delta^{13}C$ of cholesterol, which is closely related to carbon oxidation pathways, is directly related to the bone carbonate $\delta^{13}C$ pattern (Jim *et al.* 2004) and (ii) modelling of the $\delta^{13}C$ results for individual amino acids suggests that, minimally, over 50% of dietary proteins are routed directly to collagen (Jim *et al.* 2006). In high-protein diets, more non-essential amino acids will be directly routed to collagen with no fractionation, while in low-protein diets, conditionally and non-essential amino acids would need to be synthesised *de novo* from non-protein sources and would thus be more dissimilar to dietary protein $\delta^{13}C$ composition (Jim *et al.* 2006).
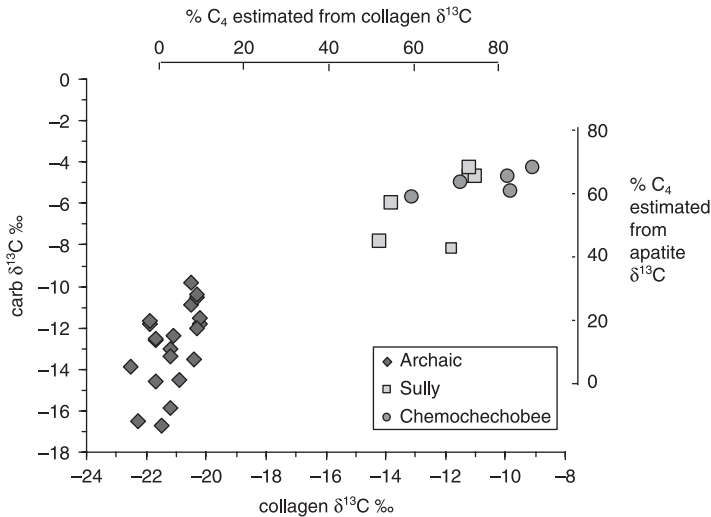
Figure 3   *A bivariate plot of δ¹³C from bone carbonate and bone collagen for skeletons from Archaic (early, non-maize) sites, and from the sites of Sully and Chemochechebee (both later sites with maize). The bone carbonate δ¹³C values used here are the results obtained using 0.1 M acetic acid pretreatment. A scale showing the percentage of C_4 carbon in the diet, as estimated from both fractions, is shown on the opposite axis. Data are from Koch* et al. *(1997).*

While rats are not humans and the experimental diets forced large differences, clearly these data have important implications for human dietary studies. In the maize case, the strong implication is that small amounts of maize in the diet will not be detectable by $\delta^{13}C$ analysis of collagen. In the course of a study on possible diagenesis and the effects of sample pretreatment on bone apatite, Koch *et al.* (1997) obtained a suite of $\delta^{13}C$ data on the collagen and bone carbonate from skeletons in Archaic and later sites. The results for the Archaic material suggest that up to 20% of C_4 carbon estimated from the apatite data remains 'invisible' in collagen (Fig. 3). Large inputs of C_4 maize carbon in the more recent sites were reflected in both collagen and apatite, but small differences nevertheless suggest that the two components are reflecting slightly different dietary macronutrient sources (Fig. 3).

Ambrose *et al.* (2003) were able to reveal status-related differences amongst individuals from Cahokia in access to dietary protein (Ambrose *et al.* 2003), using combined collagen and apatite isotope analysis. Status-related differences were apparent from grave goods, stature and pathologies amongst two groups, suggesting that the low-status group subsisted on very nutrient poor, possibly very high maize, diets. However, collagen $\delta^{13}C$ showed little difference between the two and the $\delta^{15}N$, while higher in the high-status individuals, was not very illuminating (Fig. 4). Bone carbonate analysis showed clearly a much larger proportion of C_4 in the low-status individuals' diets compared to that of the high-status individuals (Fig. 4).

Given the invisibility of low levels of maize in bone collagen, and in spite of the greater dangers of alteration of the bone carbonate, more recently several researchers have adopted the principle of analysing both tissue components to study dietary differences and address questions such as intensification (e.g., Harrison and Katzenberg 2003). Application of bone carbonate $\delta^{13}C$ data has revealed dietary components that have no protein whatsoever—in one case, cane sugar in the diets of Marianas Islanders (Ambrose *et al.* 1997). Clearly, this dual approach is
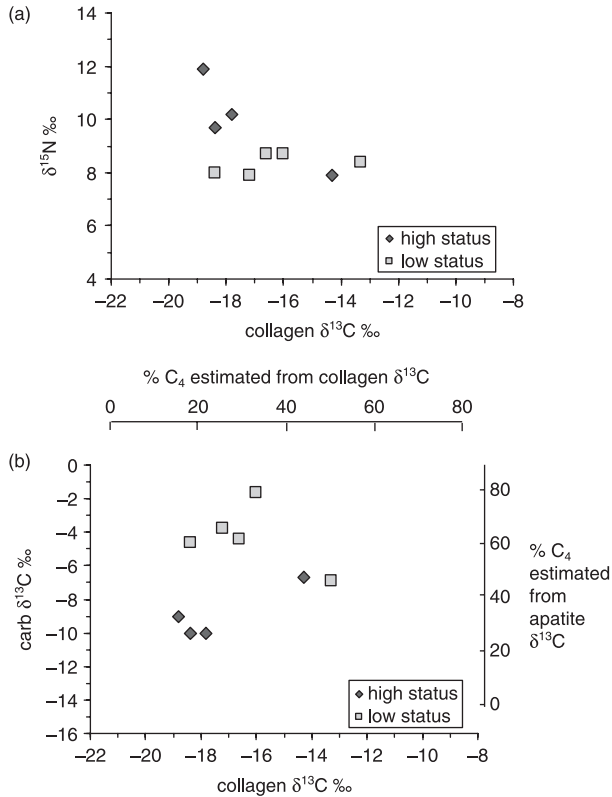
(a)

(b)

Figure 4 *Standard bivariate plots of (a) $\delta^{15}N$ and $\delta^{13}C$ from bone collagen for high- and low-status individuals from Cahokia Mound 72 and (b) $\delta^{13}C$ for bone carbonate plotted against collagen $\delta^{13}C$ for the same individuals. The data are from Ambrose* et al. *(2003).*

useful for scenarios where low-protein plants might form an important dietary component, because they would tend to be invisible in both the conventional archaeological record, and in the more standard collagen isotope approach.

MARINE-RICH DIETS

Radiocarbon chemists first observed that bone collagen $\delta^{13}C$ values from coastal people were high. The first significant publications to exploit these observations documented diachronic shifts from high-$\delta^{13}C$, marine-rich diets in the Danish Mesolithic to low-$\delta^{13}C$, terrestrial diets in the Neolithic (Tauber 1981; see also Fig. 5), and the exploitation of salmon and other marine resources in the American Northwest Pacific (Chisholm *et al.* 1982). These developments were followed shortly afterwards by the demonstration of $\delta^{15}N$ distinctions between marine and terrestrial foods (Schoeninger and DeNiro 1984), including a survey of historic and archaeological human groups following different subsistence patterns, which incorporated Tauber's Mesolithic samples (Schoeninger *et al.* 1983). The isotope distinctions between marine and terrestrial C_3 diets have since been applied around the world: just two study areas are discussed here.
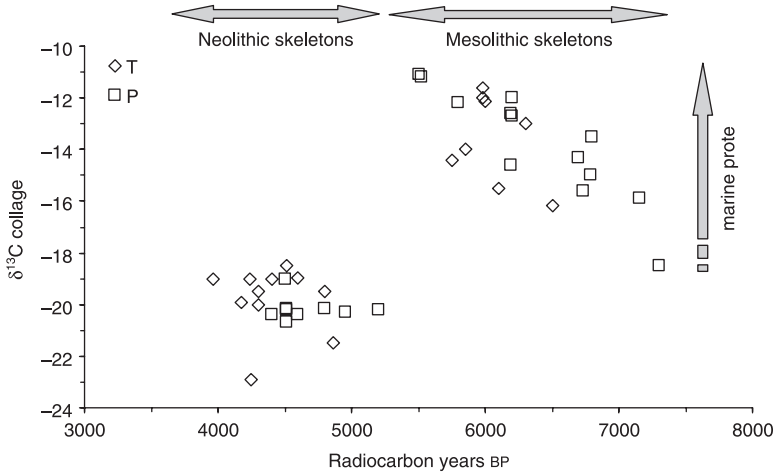
Figure 5 *A plot of radiocarbon ages (in radiocarbon years* BP*) and associated human collagen* $\delta^{13}C$ *values from Mesolithic and Neolithic contexts in Denmark, using data combined from Figures 1 and 2 in Richards* et al. *(2003a), using data from work by Persson (marked P, as squares) and Tauber (marked T, as diamonds) in the diagram. In the case of the Tauber data, the radiocarbon ages were converted from calibrated ages* BC *to uncalibrated radiocarbon years* BP *for comparability (Richards* et al. *2003a).*

Sealy applied these stable isotope differences to identify group distinctions and to test models of hunter–gatherer seasonal mobility during the Holocene in the southwestern Cape, South Africa (Sealy and van der Merwe 1985, 1986, 1988). One of the distinctive features of this study was that the interpretations of human diets were based on an extremely thorough isotopic survey of the regional terrestrial and marine foodwebs, rather than on global averages. Carbon isotope analysis of collagen showed clearly that skeletons buried at the coast were uniformly higher in ^{13}C than those buried inland of the coast (Fig. 6). Many collagen δ^{13}C values were so high (−11 to −12‰) that they resembled values of marine mammals, suggesting that human diet was often completely dominated by marine foods. The exact interpretation of these data has been disputed, as well as a question about how significant were the isotopic and dietary differences between the coastal and inland skeletons (Parkington 1991).

When nitrogen isotopes were included further important points emerged. First, many δ^{15}N values for small local game animals were anomalously high, probably due to the effects of low mean annual rainfall (<400 mm a^{-1}; see Sealy *et al.* 1987), and, second, components of the marine foodweb of known importance as food items, such as shellfish, were quite low in δ^{15}N. These results showed that the terrestrial/marine cutoff point of +10‰ proposed by Schoeninger and DeNiro (1984) does not always hold in all environments. In an expansion of the study to the southern Cape coast, where there are modest components of C$_4$ in the ecosystem and moister conditions, the combination of δ^{13}C and δ^{15}N proved more useful, showing again that inter-group dietary distinctions were maintained (Sealy 1997).

In Europe, the original Tauber data have been augmented, and the geographical area expanded to other parts of Scandinavia, to Britain, and southwards to Brittany and Portugal. The pattern of a sharp shift in human bone collagen δ^{13}C from the Mesolithic to the Neolithic has remained intact, and is also reflected in a shift to lower δ^{15}N values (Richards and Hedges 1999a,b; Schulting and Richards 2001; Richards *et al.* 2003a). While some doubts were raised about the spread of radiocarbon dates (Milner *et al.* 2004), almost all newer data with calibrated
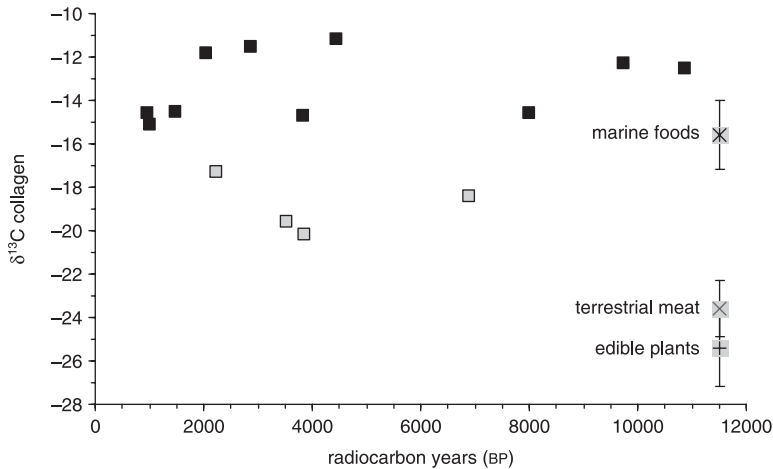
Figure 6   *Bone collagen δ¹³C values obtained from skeletons buried at the coast (solid squares) and in inland locations (grey squares) of the southwestern Cape, South Africa, plotted against age in radiocarbon years. Means and standard deviations are shown on the right-hand edge of the diagram for the following classes of foods: marine foods, terrestrial meat and terrestrial plants, all from the same region. The data are from Sealy and van der Merwe (1985).*

dates fits the same pattern. Redating of three burials from Dragsholm, which were in close proximity to each other and had originally given close ages although assigned as Mesolithic (two females) and Neolithic (one male), effectively provided greater separation in time (Price *et al.* 2007). It is clear that a sharp, culturally related economic shift occurs, from a hunter–gatherer subsistence mode that included a good deal of marine fish and shellfish in the Mesolithic, to a terrestrial diet, focused rather on cereals and domestic animals, as Richards and co-workers have argued (Richards *et al.* 2003a; Richards and Schulting 2006). The observation about the high marine content of coastal Mesolithic diets is not in dispute; rather, it is the magnitude and apparent completeness of the shift that occurs with the Neolithic. Archaeologists have argued that modest amounts of fish bone and shell at Neolithic sites show a pattern in which fish continue to be exploited, and have argued that alternative explanations should be sought (Milner *et al.* 2004; Fischer *et al.* 2008). So the argument in this case is not so much about whether there was over-representation of marine foods in the Mesolithic (although this should be subject to scrutiny) but, rather, whether there is some way in which marine fish is under-represented in Neolithic bone collagen.

Both the European Mesolithic/Neolithic and the South African coastal hunter–gatherer studies have raised important questions and debates that partly concern the intrinsic meaning of the isotope data, and partly concern the 'fit' with other contextual archaeological evidence (and its interpretations). Are the very large amounts of marine foods represented in the southwestern Cape coast bone collagen δ¹³C values reasonable, or is marine food greatly over-represented? It is now understood that collagen δ¹³C preferentially reflects the protein component of the diet, and that the relationship shifts with the amount of protein (Fig. 2; see also Ambrose and Norr 1993; Tieszen and Fagre 1993), strongly suggesting that the latter is the case, especially if the terrestrial component of the diet was low in protein. In the southwestern Cape, the Fynbos biome is poor in large game, and stable terrestrial sources available to foragers were seasonally abundant starchy corms and other plant foods (Sealy and van der Merwe 1986). A limited study on the bone apatite carbonate of some of the human skeletons suggested that some ¹³C-depleted

components of the diet were not well-represented in collagen $\delta^{13}C$. The effect of this difference (high collagen $\delta^{13}C$/low apatite $\delta^{13}C$) is a small difference between the tissues, or small $\Delta_{collagen-apatite}$ (Lee-Thorp *et al.* 1989). These insights, however, do not change the finding that coastal and inland foragers differ in bone collagen isotope composition.

Is there some way in which the European Neolithic bone collagen $\delta^{13}C$ can be reconciled with inferences from the contextual evidence? The issue of shellfish consumption can be relatively easily explained; shellfish residues are over-represented in the archaeological record because they generate a very large amount of debris for caloric return, whereas, because of their low trophic position, they have relatively low $\delta^{13}C$ and $\delta^{15}N$ flesh values compared to fish and marine mammals. Another issue is that the fishbone residues found in modest amounts at Neolithic sites are apparently not reflected in human bone collagen isotope values. However, if one considers that some of these residues are from freshwater or anadromous species such as eel, they may represent foods low in ^{13}C (Dufour *et al.* 1999), rather than high as is the case for marine fish. It has been suggested that a combination of modest inputs of marine and freshwater fish, in combination, would effectively cancel each other (Fischer *et al.* 2008). One problem with this neat solution is that freshwater fish are also high in $\delta^{15}N$, which is not consistent with the Neolithic human bone collagen values. Given the consistency of the Mesolithic to Neolithic pattern, and the tight clustering of Neolithic human bone collagen $\delta^{13}C$ and $\delta^{15}N$, it seems clear that even if modest amounts of shellfish and fish, marine or freshwater, were consumed, the dietary shift observed in the skeletal collagen isotope values marks a sharp and distinct economic and cultural change. Interestingly, at least in the British Isles, marine foods only re-appear as regular items in human diets during medieval times (Müldner and Richards 2005).

<div align="center">DIETS IN DEEP TIME</div>

A good deal of effort has gone into extending isotope analyses to more remote time periods in order to address dietary questions during earlier periods of human evolutionary history. As can be seen in the foregoing sections, most of the existing isotope research has concentrated on bone collagen $\delta^{13}C$ and $\delta^{15}N$. In order to push further back in time, researchers have had to either extend collagen-based methods or develop methods based on the mineral phase. They have done both. Recent progress in extracting good-quality collagen from older material has shown that it can survive under the right conditions for up to 200 000 years (Ambrose 1998; Richards and Hedges 1999a; Jones *et al.* 2001). This has made it possible to analyse the bone collagen of Late Pleistocene hominins in Europe, where temperatures have been low for most of this time. Applications deeper in time have required the development and testing of apatite-based methods, which quickly settled on tooth enamel as a far more reliable material that retained biogenic isotope compositions (Lee-Thorp and van der Merwe 1987; Ayliffe *et al.* 1994; Wang and Cerling 1994; Lee-Thorp 2002). These developments, coupled with improvements in mass spectrometry that greatly reduced sample size requirements and increased throughput, opened the way to apply isotope methods to very old fossil teeth of australopiths and early *Homo*. One advantage is that enamel apatite $\delta^{13}C$ reflects the composition of the entire diet.

Late Pleistocene Neanderthal diets

Stable isotope studies of Neanderthal diets began with analysis of a single 40 000-year-old Neanderthal individual and associated fauna from Marillac, France (Bocherens *et al.* 1991).

Although the authors in this first study relied for quality control on amino acid profiles that might be considered inadequate today, and not much can be deduced from one individual, later analyses at this site (Fizet *et al*. 1995) showed that the original data were robust. The first Marillac study, and analyses of older faunal material from Vindija, Croatia and other sites (Ambrose 1998) paved the way for subsequent analyses of Neanderthal specimens at Marillac (Fizet *et al*. 1995), Scladina, Awirs and Betche-al-Roche Caves in Belgium (Bocherens *et al*. 1997, 2001) and Vindija (Richards *et al*. 2000).

In the mono-isotopic C$_3$ European environment, bone collagen δ^{13}C reveals little about Neanderthal diet, except that there is no evidence of a preference for dense, forested environments (Bocherens *et al*. 1997; Richards *et al*. 2000). The focus has been entirely on δ^{15}N composition, which has been used to address the question of trophic level and meat consumption. Given the frequency of injuries, evidence for close contact hunting, and the frequency of stress episodes (in the form of enamel hypoplasias) amongst Neanderthals (Trinkhaus 1995), their hunting (or scavenging) success has been the subject of a great deal of debate. One hypothesis was that Neanderthals had lower hunting success and trophic levels compared to Upper Palaeolithic modern humans (Ambrose 1998).

All isotopic data in the literature show that Neanderthals have high δ^{15}N compared to contemporaneous (or near-contemporary) herbivores such as horse (*Equus caballus*), reindeer (*Rangifer tarandus*) and bison (*Bison priscus*), and similar to carnivorous wolves (*Canis lupus*), hyenas (*Crocuta spelaea*) and lions (*Panthera spelaea*) (Bocherens *et al*. 1991, 2001, 2005; Fizet *et al*. 1995; Richards *et al*. 2000). When the data from all western and central European sites are combined, Neanderthal δ^{15}N is significantly higher than that of herbivores and also slightly higher than that of carnivores (Fig. 7). The mean difference between average herbivore and Neanderthal δ^{15}N is about +5‰ and sometimes higher. Richards *et al*. (2000, 2001) and

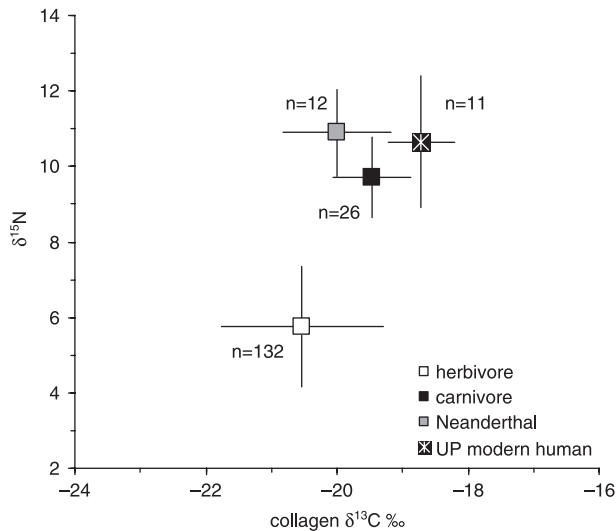Figure 7 *A bivariate plot of the means and standard deviations for δ^{15}N and δ^{13}C for herbivores, carnivores, Neanderthals and Upper Palaeolithic modern humans from Glacial-period European sites. The data for the sites of Marillac, La Berbie, Scladina, Vindija and Carniac have been combined from Bocherens* et al. *(1991, 1997, 2001), Fizet* et al. *(1995) and Richards* et al. *(2000, 2001), while the UP modern human data are drawn from several sites, using data from Richards* et al. *(2001), Pettit* et al. *(2003) and Schulting* et al. *(2005).*

Bocherens *et al*. (2005) have argued that Neanderthals were high-level carnivores, with little of their dietary protein coming from plant foods, and, further, that they relied on herbivores with relatively high δ^{15}N, such as mammoths (*Mammuthus primigenius*), or even the consumption of omnivorous bears (*Ursus* spp.) (Richards *et al*. 2000; Bocherens *et al*. 2001). Bocherens *et al*. (2005) applied a mixing and resource partitioning model developed in modern ecosystem studies to calculate a statistical probability that a major component of Neanderthal diet was mammoth. There are significant constraints, however, to the application of such a statistical model in ancient ecosystems where there are large numbers of unknowns, which were not met in this case.

Although direct stable isotope data comparisons between Neanderthals and Upper Palaeolithic *Homo sapiens* (UP humans) from similar periods and places are not possible, one can compare average values. Richards *et al*. (2001) argued that since δ^{15}N for a suite of near-contemporary ~30 000-year-old Upper Palaeolithic modern humans was even higher than that for the Neanderthal data existing at the time, in addition to a dependence on animal foods they might also be incorporating freshwater fish and fowl resources in their diets. If that was the case, it would indicate an early broad-spectrum foraging base. However, the addition of new Neanderthal and Upper Palaeolithic human data shows that any δ^{15}N differences are not statistically significant (Sponheimer and Lee-Thorp 2007). Little attention has been paid to the small difference in δ^{13}C between Neanderthals and UP humans (Fig. 7); it may reflect differences in preferred environments or prey, or simply that climate conditions differed.

The main rationale behind the application of stable isotope analyses to Neanderthal and UP human diets is related to the question of trophic level, but this is also where we have the greatest interpretive problems. Interpretations offered so far for the large enrichment in ^{15}N between the mean for hominins and for associated herbivores are that they preferred to exploit the game that happened to be relatively high in ^{15}N. This interpretation assumes a 'standard' trophic enrichment of +3‰, yet, as pointed out by Hedges and Reynard (2007), we do not know that this is the correct offset for humans. It is also not at all clear that the relationship between dietary and collagen δ^{15}N is linear (Hedges and Reynard 2007), meaning that one cannot readily determine 'shades' or degrees of carnivory, or more properly, high-protein diets. Controlled feeding studies have suggested that the amount and quality of protein in the diet may affect the diet-tissue δ^{15}N spacing (Δ) and that Δ is higher in herbivores fed protein in excess of their requirements (Sponheimer *et al*. 2003). Therefore, thresholds may operate. The isotope data for Glacial-age Neanderthals and UP humans in Europe illustrate the problems for interpreting δ^{15}N data in a palaeo-ecosystem for which we have no modern analogues. In spite of these caveats, however, it would appear that both Neanderthals and UP humans almost certainly consumed large quantities of protein-rich animal foods.

Early hominin diets

Isotopic studies of early hominins are grounded primarily upon the δ^{13}C distinctions between C_3 and C_4 plants, since, in the African savannah environments that they occupied, all carbon dietary sources from trees, bushes, shrubs and herbs are distinct in ^{13}C compared to those from tropical grasses and some sedges. δ^{13}C analysis provides opportunities to test hypotheses about their primary dietary habits. Amongst the South African hominins, where a good deal of the dietary research has taken place, it was widely believed that *Australopithecus africanus* consumed primarily fruits and leaves, and some animal foods, while *Paranthropus robustus* concentrated more on plant foods that tended to be small, hard items and that caused greater occlusal enamel pitting (summarized in Lee-Thorp and Sponheimer 2006).
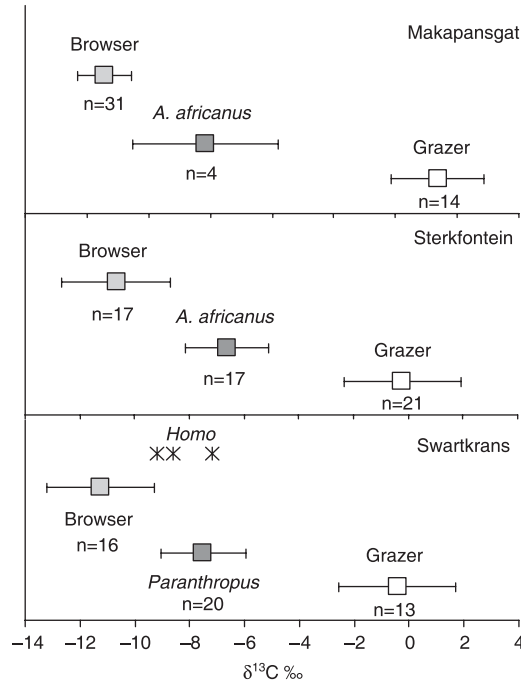
Figure 8 *The distributions of δ^{13}C, shown as means and standard deviations, in the enamel of C$_3$-feeders (typical browsers), C$_4$-feeders (typical grazers) and hominins from the sites of Makapansgat (≥ 3 Ma), Sterkfontein Member 4 (c. 2.4–2.6 Ma) and Swartkrans (c. 1.7 Ma). The figure is redrawn from Lee-Thorp* et al. *(2003).*

The prediction, then, would be that *A. africanus* and *P. robustus* should have δ^{13}C values indistinguishable from those of C$_3$ browsers and frugivores. Analysis of more than 40 hominin specimens from the sites Makapansgat, Sterkfontein, Kromdraai and Swartkrans, spanning a period of about 1.5–3.0 million years, however, demonstrates that the δ^{13}C of both australopiths and the few early *Homo* individuals is very distinct from that of coexisting C$_3$-consumers such as browsers (Fig. 8). Furthermore, *A. africanus* and *P. robustus* mean values are indistinguishable in spite of the passage of time and shifts in environmental conditions (Lee-Thorp *et al.* 2003). If we take the mean δ^{13}C of C$_4$- and C$_3$-consuming herbivores as indicating the C$_4$ and C$_3$ 'endpoints', we can estimate that, on average, both *Australopithecus* and *Paranthropus* obtained over 30% of their carbon from C$_4$ sources, while the estimate for *Homo* is possibly a little lower (although uncertain, given that $n = 3$). All taxa were eating considerable quantities of C$_4$ resources, which must have consisted of grasses, sedges, or animals that ate these plants.

This result was unexpected, since extant apes consume minimal or no C$_4$ resources even when they live in relatively open habitats, and suggests a fundamental niche difference between the australopiths and extant apes. The distinction between the hominins and other fauna cannot be ascribed to diagenesis, as there is no evidence that browser or grazer δ^{13}C is altered, and diagenesis should affect all fauna. The association with C$_4$ resources persists throughout environmental trends that sees shifts from relatively closed Pliocene habitats at the earlier sites (~2.4–3.0 Ma) through to more open environments after *c.* 1.7 Ma (Lee-Thorp *et al.* 2003; see also Fig. 8). Within each site, and where there are sufficient samples, australopith δ^{13}C data are

more variable than most modern and fossil taxa analysed in southern Africa to date, suggesting that they were opportunistic primates with wide habitat tolerances.

Alone, the $\delta^{13}C$ data allow firm conclusions to be drawn only about the proportions of carbon from C_3 and C_4 sources, but not about what the actual resources were. Lee-Thorp *et al.* (2000) argued that savannah grasses are unlikely staple foods for hominins, since they are relatively nutrient poor, small packages, and that consumption of C_4-consuming insects and vertebrates is a more plausible explanation. Closer examination of various possibilities, such as edible, starchy sedges and termites, suggests that none of them, on their own, offers a satisfactory explanation for the significant C_4 contribution. One other possible source of information may be found in enamel $\delta^{18}O$. As discussed above, $\delta^{18}O$ from apatite carbonate or phosphate is influenced by dietary ecology, including trophic behaviour. In two southern African modern ecosystems examined, suids (warthog), some primates and in particular all faunivores (i.e., carnivores and insectivores) have relatively low $\delta^{18}O$ compared to the herbivores (Lee-Thorp and Sponheimer 2005). The reasons are not entirely clear; in the case of suids, it may reflect reliance on underground storage organs, and for faunivores, a high proportion of dietary lipids and proteins or, equally, a heavy reliance on drinking water. Australopith $\delta^{18}O$ data from Makapansgat and Swartkrans overlap with those of carnivores in the same strata (Lee-Thorp *et al.* 2003). Although tantalizing, the interpretation of low $\delta^{18}O$ values for hominins is still obscure, and the topic requires further study.

Despite these uncertainties, the isotope data have shown that australopiths increased their dietary breadth by consuming C_4 resources, whatever those resources were. A fundamental difference between hominins and extant apes, therefore, might be that when confronted with increasingly open areas, apes continued to use the foods that are most abundant in forest environments, whereas early hominins began to exploit the new C_4 resources.

WHERE DO WE GO FROM HERE?

Clearly, the field of isotopic dietary reconstruction has taken enormous strides since the first applications in the mid-1970s. Many promising new developments, such as high-resolution intra-individual sampling and life history applications, were not included in the discussions above, because they are still under development. They are included in my admittedly subjective list of where I believe we should be heading in the future.

Isotope distributions in modern and palaeo-ecosystems

One area that requires more intensive and broader effort is to improve our understanding of the natural distributions of stable isotopes in different kinds of ecosystems, and under various conditions. In trying to understand the past, we apply, sensibly, principles of uniformitarianism, but our information is frequently garnered either at site-based or at global scales, and little at the regional scale. One of the distinctive features of the Sealy and van der Merwe study of Holocene coastal hunter–gatherers was the thorough coverage of the environmental and isotopic context across an entire region, for both the past and the present (Sealy *et al.* 1987; Sealy and van der Merwe 1988). We need more such regional contextual studies. Admittedly, accomplishing such a goal is frequently very difficult, because many regions have been completely altered by millennia of human agricultural activity. Furthermore, at many agricultural-era archaeological sites, the faunal material is often limited to a few domesticated animals, thus reducing our ability to capture elements of the broader ecosystem. However, refugia do remain even in heavily altered regions of the world.

In studying palaeo-ecosystems, we frequently encounter conditions very different to those of today, and we may need to be creative in locating modern ecosystems that are at least roughly comparable. A good example is the last Glacial period in Eurasia. Patterning of $\delta^{13}C$ and $\delta^{15}N$ in many of the fauna analysed in Neanderthal and palaeontological sites in south-western Europe suggests that the carbon and nitrogen cycles were (variably) significantly different under glacial conditions (e.g., Bocherens *et al.* 2005; Stevens *et al.* 2008), but in order to understand these patterns we may need to look elsewhere—for instance, towards the fringes of the tundras of Siberia.

Expanding the isotope toolkit

Most of this review has concentrated on developments related to $\delta^{13}C$ and $\delta^{15}N$ from collagen, and $\delta^{13}C$ from enamel apatite, but brief sections on hydrogen, oxygen and sulphur have shown that there is some rationale for expanding investigations of those isotope systems for palaeodietary purposes. From first principles and the existing studies, it could be argued that $\delta^{34}S$ is less promising as a palaeodietary indicator, because the main delineator is the singular value for marine organisms, while everything else is highly variable.

The pointers to trophic patterning in δD and $\delta^{18}O$, obtained independently in different contexts, offer promising new avenues for investigation. The inter-species variability in $\delta^{18}O$ in phosphate or enamel carbonate emerged unexpectedly in the pursuit of other goals. A handful of opportunistic comparative studies of suites of African fauna suggest that faunivory may be detectable based on distinct low $\delta^{18}O$ values for animals such as hyena and bat-eared foxes (Lee-Thorp and Sponheimer 2005), but there is clearly a good deal of overlap and variability. Furthermore, in order to determine whether the pattern holds more widely, the distribution of $\delta^{18}O$ amongst suites of fauna from cool, temperate environments should be tested. That δD in collagen holds potential for trophic-level information has only recently been reported, and the information obtained so far is based largely on a modest suite of mostly domestic animals (Reynard and Hedges 2008). The demonstration that δD holds trophic-level information, *and* that the patterns survive in archaeological biomolecules, shows great promise. Since the behaviour of hydrogen and oxygen isotopes is almost always linked, further steps could be directed at bringing the two together, based on biomolecules. So far the research has been completely decoupled, because $\delta^{18}O$ was studied in the mineral and δD in the organic phases.

More information from smaller biomolecular units

The discussion of routing of dietary components concluded with the outcome of compound-specific isotope analyses of amino acids and cholesterol from a controlled feeding study (Jim *et al.* 2004, 2006). Those two examples demonstrate that a good deal more detailed information about biochemical pathways can be extracted from compound-specific approaches, rather than (or in addition to) the bulk sampling approaches in broad use so far. Another promising example is the development and application of a $\delta^{13}C_{glycine-phenylalanine}$ index to detect the presence of marine foods in the diet (Corr *et al.* 2005). The advantage of this approach is that it is independent of the presence of C_4 plants in the environment, a major complicating factor in distinguishing marine from terrestrial diets using bulk collagen methods in certain regions. More broadly, compound-specific approaches, carried out in the context of carefully directed controlled feeding studies, remain the most promising avenues for providing the kind of detailed

coupled biochemical and isotopic information required to address those tricky, previously intractable problems of quantification of dietary elements (i.e., how much marine food, how much maize). Further promising avenues would include the means to detect previously undetectable dietary items, such as freshwater fish and even plant foods. That would constitute a very significant step.

Developments in sampling and analysis

Recent developments in mass spectrometry, and particularly in the automated delivery of sample to the mass spectrometer for isotopic analysis, mean that multiple, very small samples can be rapidly analysed. These developments have opened up many opportunities. High-resolution, serial analyses of vertical transects down tooth crowns are not new; Balasse pioneered manual high-resolution serial sampling of domestic and wild fauna in order to determine seasonal patterns and examine domestic animal management (Balasse 2003).

   Laser-ablation sampling systems coupled to stable light isotope mass spectrometers, while not yet widely available, hold a good deal of promise for further reducing sample size requirements while still obtaining maximum intra-tooth information (Sharp and Cerling 1996). Laser ablation damage is minimal, a factor that makes it a much more attractive proposition for museum curators and could thus facilitate access to larger numbers of fossil specimens. There are, of course, many limitations. For instance, the gas released by laser ablation of tooth enamel contains oxygen from several sources, but it is mainly a mixture from the phosphate (~90%) and carbonate (~10%) compartments. Since $\delta^{18}O$ from phosphate and carbonate in the same tooth or bone differs by ~9‰, the gaseous mixture reflects both and is not directly comparable to existing data. An application to hominin teeth demonstrated, for the first time, the extent of intra-annual variability in contributions of C_4 resources to the diets of South African *Paranthropus* specimens (Sponheimer *et al*. 2006). High-resolution transects of tooth crowns, or of the dentine roots for isotope analysis, hold enormous potential for addressing questions about the life histories of individuals in the past. Several studies have investigated the age at which important culturally influenced biological events occur, particularly the duration of breastfeeding and the age of weaning, using mostly manual sampling methods (e.g., Wright and Schwarcz 1998; Fuller *et al*. 2003). Smaller sample size requirements and rapid, automated analysis now provide the means for greater resolution in such approaches, while minimizing damage. These are rosy possibilities, but in enamel there are inherent constraints in the amount of information that may be extracted, due to the intrinsic patterns of tooth crown formation. Maturation occurs for many months after primary enamel is laid down, thus dampening the isotopic 'input' signal (Balasse 2003; Passey *et al*. 2005a). Thus higher sampling and analytical resolution may not necessarily translate into a similar resolution of information.

   Stable light isotope analysis is one of the very few methods capable of identifying events within the lives of individuals, and also for identifying dietary and life history differences between individuals, in addition to the opportunities for broader scale inter-group and even inter-species comparisons. Thus the approach can operate at many scales. So far, the broader scale has been favoured, partly because it allows statistical confirmation of trends and comparisons. With new developments in mass spectrometry enabling finer-scaled sample analysis, minimal damage and high sample throughput, not to mention the developments in analysis of compound specific amino acids and lipids, the forthcoming decade should see the realization of the full potential of stable light isotope approaches.

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