Journal of Archaeological Method and Theory, Vol. 13, No. 3, September 2006 (© 2006)
DOI: 10.1007/s10816-006-9009-x

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

R. Alexander Bentley[1,2]

Published online: 29 July 2006

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:

$$^{87}\mathrm{Rb} = {}^{87}\mathrm{Rb}_0 e^{-\lambda t} \tag{1}$$

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.:

$$^{87}\mathrm{Sr} = {}^{87}\mathrm{Sr}_0 + {}^{87}\mathrm{Rb}_0 - {}^{87}\mathrm{Rb}_0 e^{-\lambda t}, \tag{2}$$

where $^{87}\mathrm{Sr}_0$ 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:

$$\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}} = \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_0 + \frac{^{87}\mathrm{Rb}}{^{86}\mathrm{Sr}}(e^{\lambda t} - 1). \tag{3}$$

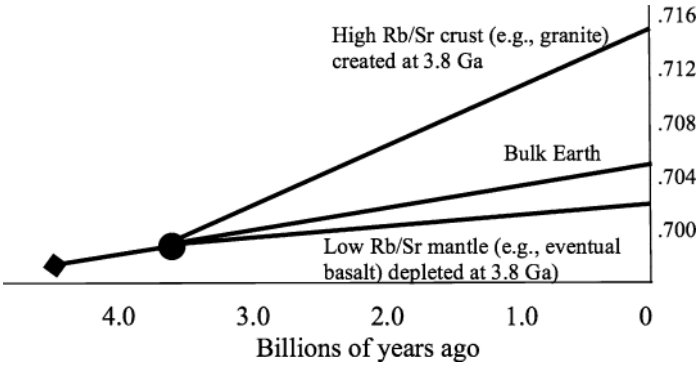

Fig. 1. Sr isotopic evolution of the bulk Earth, high Rb/Sr crust created at 3.8 Ga (giga-annum, or billions of years), hypothetical residual mantle and a mantle being continuously depleted. The $^{87}Sr/^{86}Sr$ of the bulk Earth has evolved along a straight line with slope proportional to the bulk 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

[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:

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

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

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

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

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

The previous section has shown how the $^{87}\mathrm{Sr}$ 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 $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ varies substantially among current geological terrains. Rocks that are very old (>100 mya) with high original Rb/Sr have $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios generally above 0.710, and rocks formed recently (<1–10 mya) with low Rb/Sr ratios have low $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios generally less than 0.704. The Earth's mantle has a relatively uniform and low $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ 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, $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios range from about 0.7035 to 0.707 (Dickin, 1995, pp. 164–169; White, n.d.). Phanerozoic marine limestone and dolomite have intermediate $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of about 0.707–0.709, reflecting the composition of the ocean during their deposition. Overall the

[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

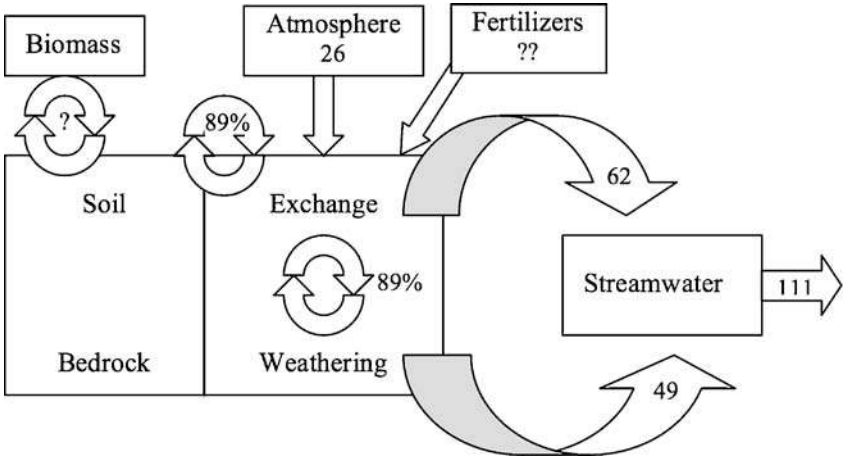

Fig. 2. Modern hydrochemical budget for Sr for a local area, in this case the Strengbach river catchment of the Vosges mountains. Each system is treated as a reservoir, with inputs and outputs, listed in g/ha per year (numbers). The percentages represent the atmospheric contribution to the exchangable 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):

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

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

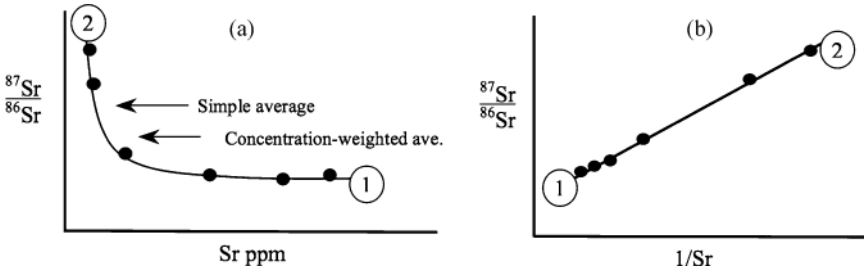

Fig. 3. (a) simplified version of a mixing model with two hypothetical end-members (circled numbers), showing how soil and rock samples (filled circles, hypothetical data) will fall along a curved, concave-up mixing line such that the biologically available Sr is closer to the concentration-weighted 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

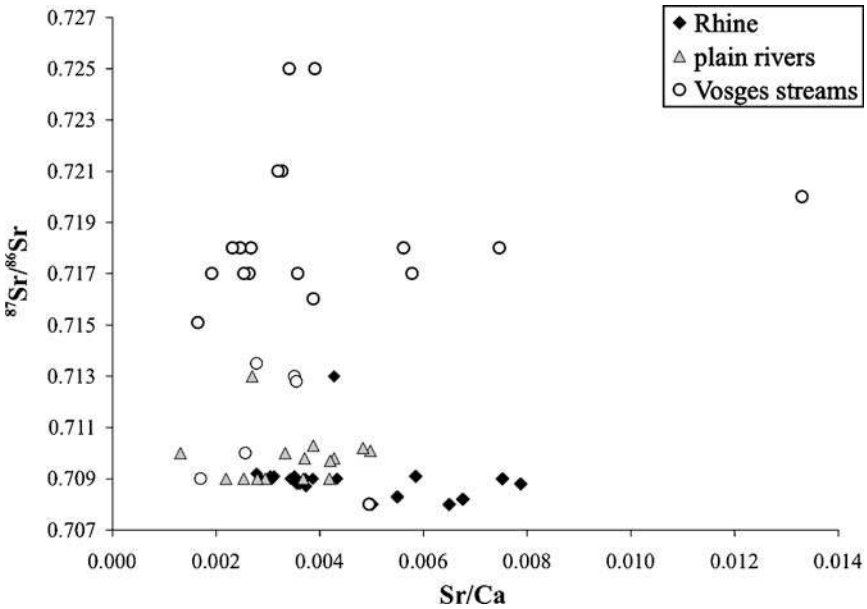

Fig. 4. $^{87}Sr/^{86}Sr$ vs. Sr/Ca in water samples from the Upper Rhine Valley. The Vosges drainages have a strontium isotope composition distinct from the lower Rhine Valley. The samples represent the dissolved load of these rivers. After Tricca *et al.* (1999, Fig. 2).

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 ($\sim$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,

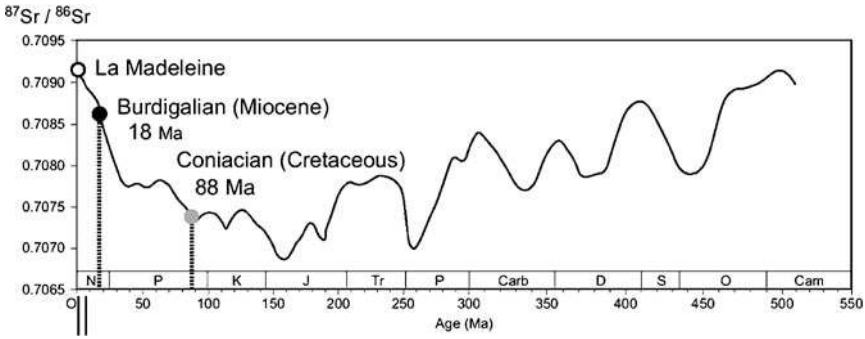

Fig. 5. $^{87}Sr/^{86}Sr$ in seawater through Phanerozoic time determined from the analysis of phosphate and carbonate fossils. Based on data from McArthur *et al*. (2001), this figure is adapted from Vanhaeren *et al*. (2004, Fig. 4), showing their candidate sources for archaeological shell artefacts 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 northern 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-

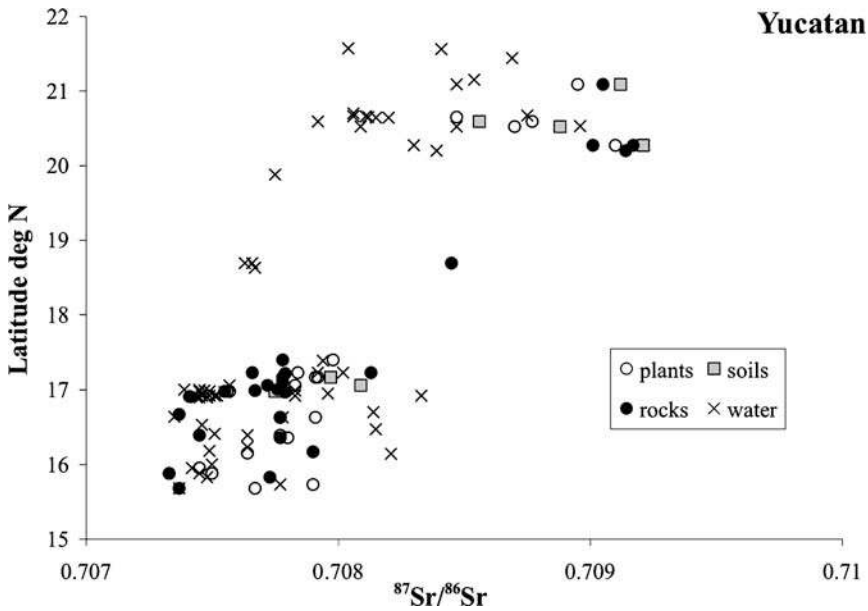

Fig. 6. $^{87}Sr/^{86}Sr$ of bedrock, soils, and plants from the Maya Lowlands versus degrees north latitude, as measured by Hodell *et al*. (2004).

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

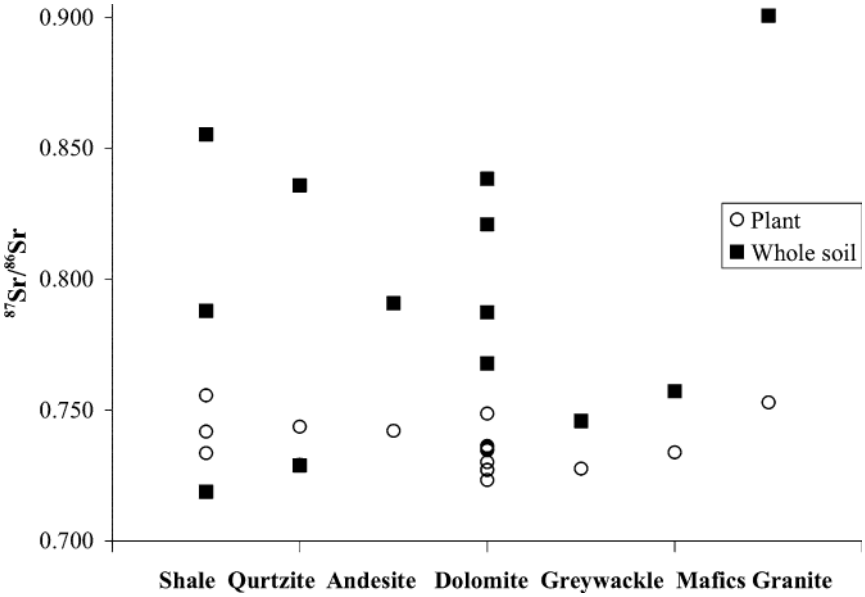

Fig. 7. $^{87}Sr/^{86}Sr$ measured by Sillen *et al*. (1998) for plants and whole soils in the vicinity of Swartkrans, South Africa. After Sillen *et al*. (1998, Fig. 2, Table II).

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*.,

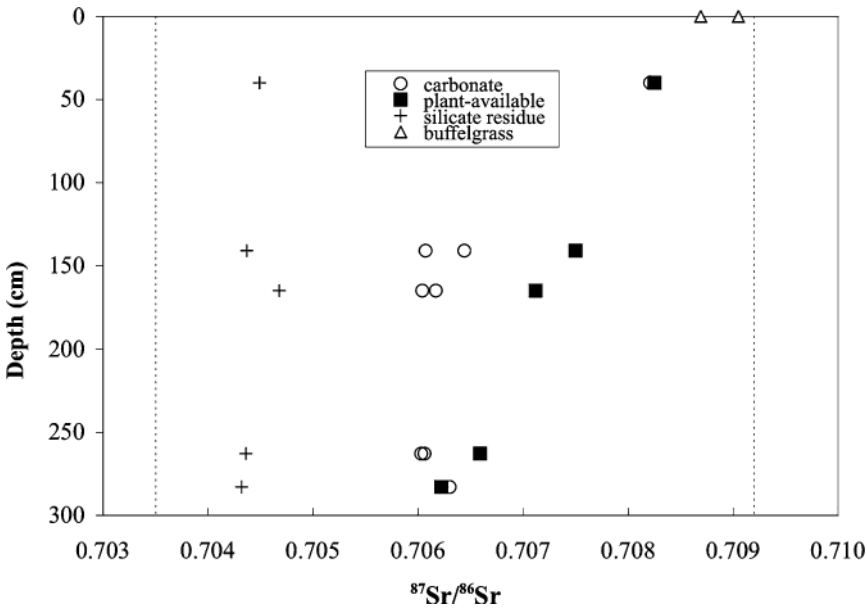

Fig. 8. $^{87}Sr/^{86}Sr$ measured by Whipkey *et al*. (2000) in samples of buffelgrass, soil carbonate, plant-available reservoir, soil carbonate and silicate residue from a soil profile at South Point, Hawai'i. Dashed lines show seawater (0.7092) and local basalt (0.7035) ratios for comparison. After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

$$\left(\frac{\mathrm{Sr}}{\mathrm{Ca}}\right)_{\mathrm{diet}} = \frac{\sum_i \mathrm{Sr}_{\mathrm{diet}}}{\sum_i \mathrm{Ca}_{\mathrm{diet}}}, \quad \text{and} \tag{9}$$

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

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 ($1\ \sigma$) 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

[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.

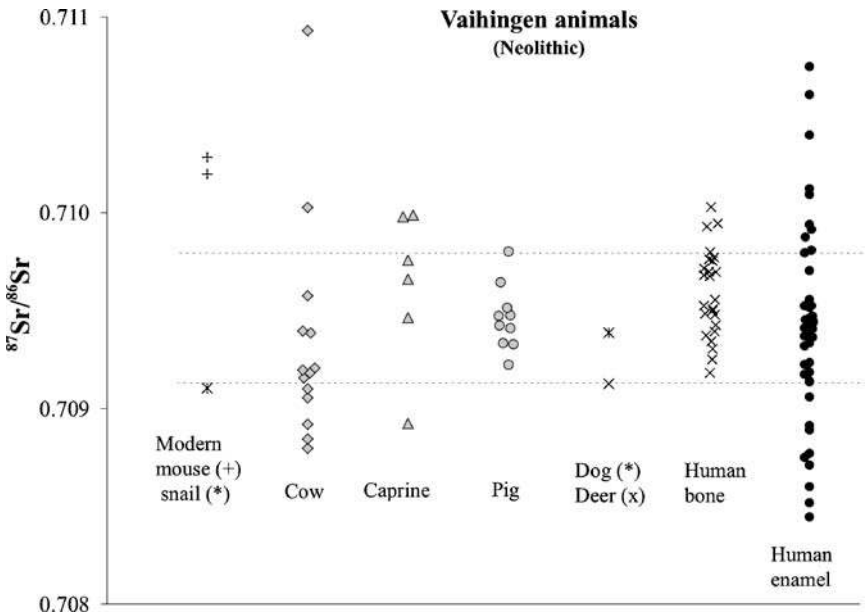

Fig. 9. $^{87}Sr/^{86}Sr$ in Neolithic human and animal tooth enamel from Vaihingen, along with values from human bones, a few modern mice and snail shells. After Bentley *et al*. (2004, Fig. 5).

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

[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 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

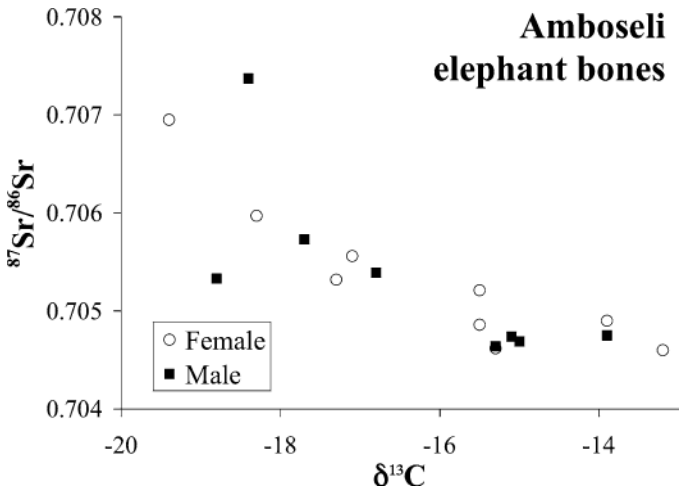

Fig. 10. Carbon and strontium isotopes in elephant bones from Amboseli Park, Kenya. Note the concave-up mixing line, similar in form to Fig. 3a. After Koch *et al*. (1995, Fig. 3 and Table I).

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

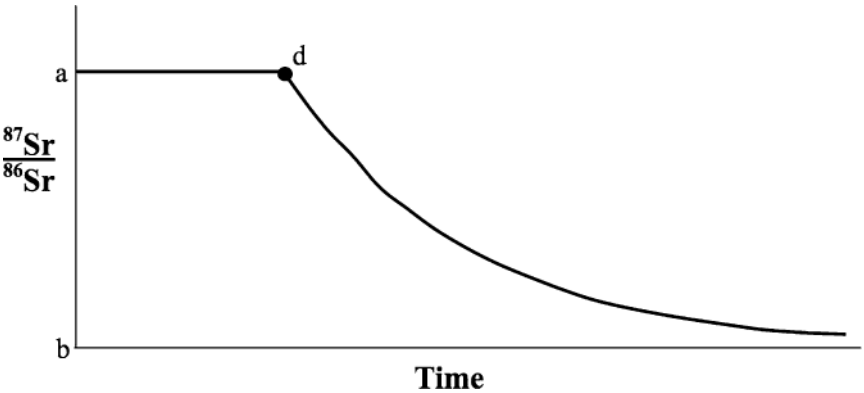

Fig. 11. Model by Schweissing and Grupe (2003, Fig. 2) for the gradual change in Sr isotope signature in skeletal tissue that formed before and after migration (at point d) between areas of different $^{87}Sr/^{86}Sr$ ratios (a and b).

$R_{\text{bone}}(t)$, the $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ in the enamel is R_A, and R_B is the $^{87}\text{Sr}/^{86}\text{Sr}$ at the place of burial. The $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of about 0.7178 in cortical bone from his femur (~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

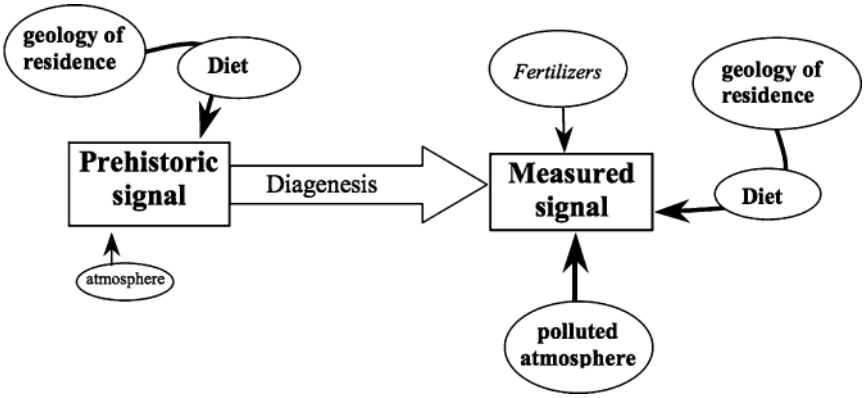

Fig. 12. Schematic diagram showing the "noise" potentially obscuring the prehistoric geologic isotope signature from what is measured in archaeological skeletons and in modern fauna.

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

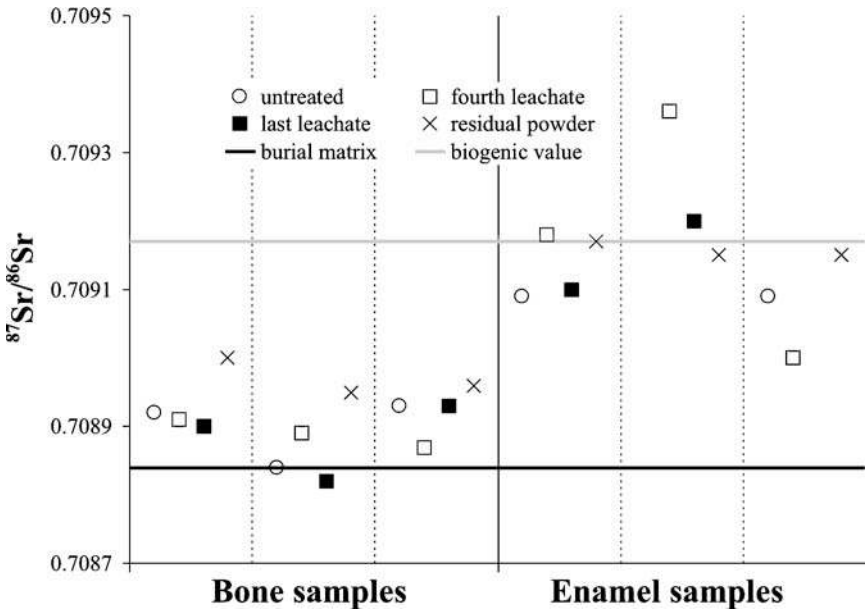

Fig. 13. The $^{87}Sr/^{86}Sr$ ratios measured by Hoppe *et al.* (2003) from sequential acid leaching of bone and enamel samples from a Holocene California fur seal. The samples were treated with sequential leaches of unbuffered 0.1 N acetic acid. Also shown are the original biogenic $^{87}Sr/^{86}Sr$ 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

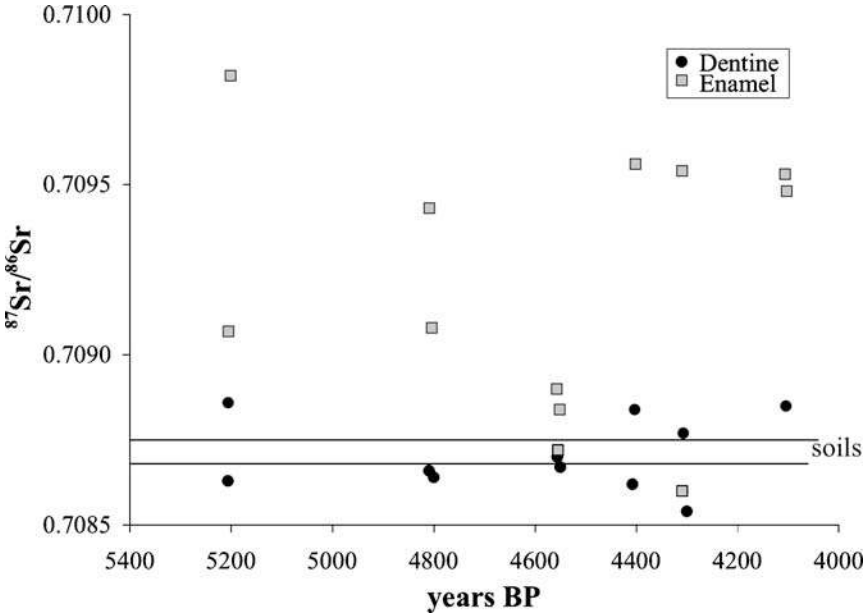

Fig. 14. $^{87}Sr/^{86}Sr$ vs. age diagram of archaeological teeth from Switzerland, analyzed by Chiaradia *et al*. (2003). Also shown is the range of $^{87}Sr/^{86}Sr$ for local soils, toward which the dentine values have gravitated by isotopic exchange. After Chiaradia *et al*. (2003, Fig. 10).

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

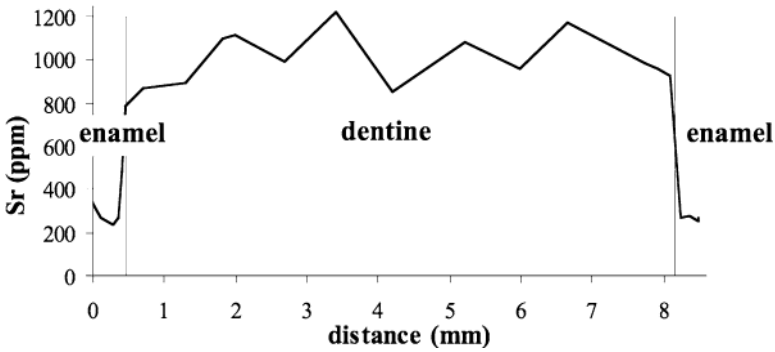

Fig. 15. Sr concentration profile through a crown section of a Bronze age tooth from Sion Sous-Scex, Switzerland. After Chiaradia *et al*. (2003, Fig. 9).

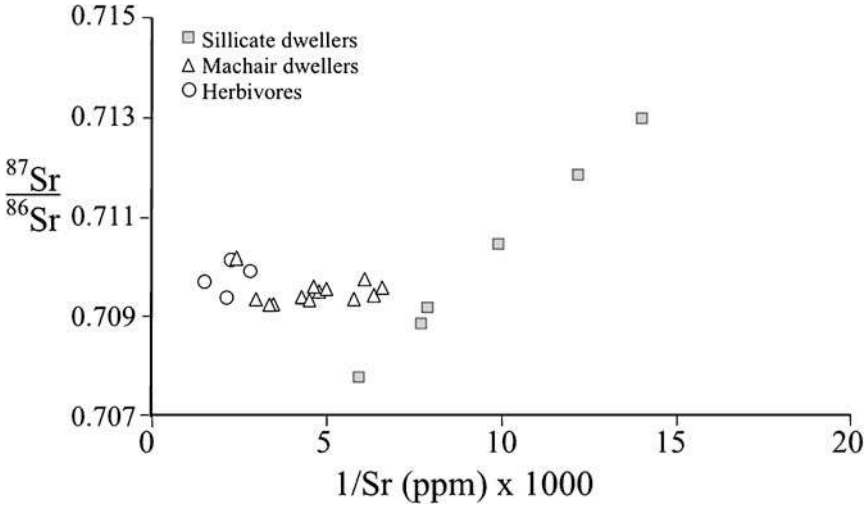

Fig. 16. Measurements by Montgomery *et al.* (n.d.) on human enamel from the Outer Hebrides, Scotland. For the silicate data array, $r^2 > 0.98$. After Montgomery and Evans (2006; Fig. 7).

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.

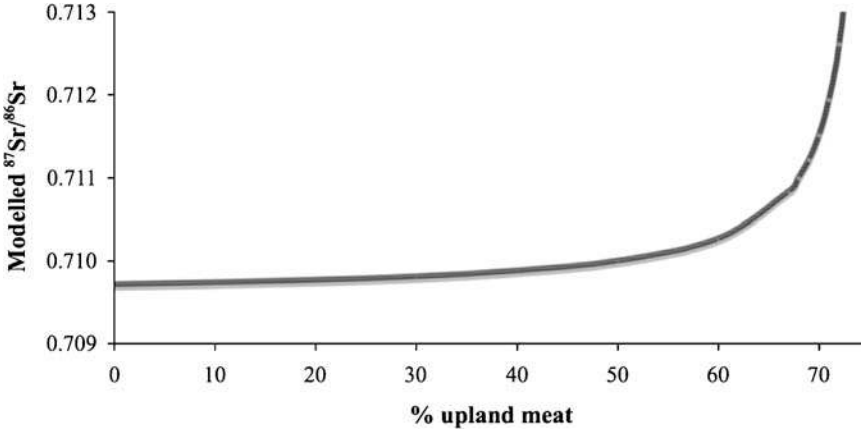

Fig. 17. Modelled effect of varying the proportion of upland meat ($^{87}Sr/^{86}Sr = 0.7167$), at the expense of lowland cereals ($^{87}Sr/^{86}Sr = 0.7096$). The model uses Eq. (8) and calculates J_i using Ca-weighted values, as per Table IV.

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

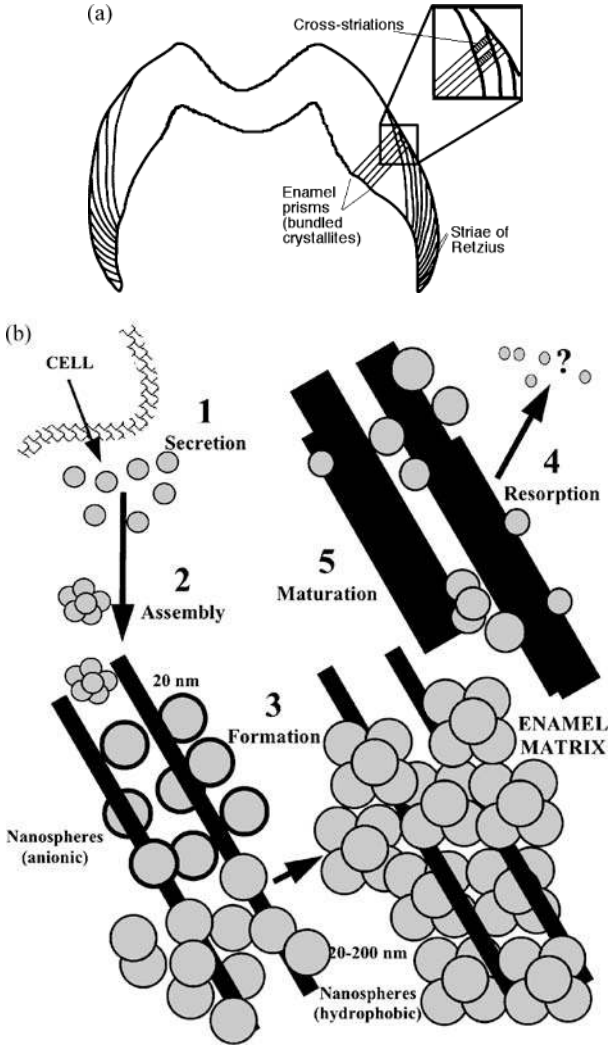

Fig. 18. **(a)**: Schematic molar cross-section showing enamel microstructure. After Smith *et al*. (2003, Fig. 1). **(b):** Schematic diagram by Fincham *et al*. (1999) for enamel biomineralization, under which (1) amelogenins are synthesized and secreted by the ameloblast cell, (2) single amelogenins 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).

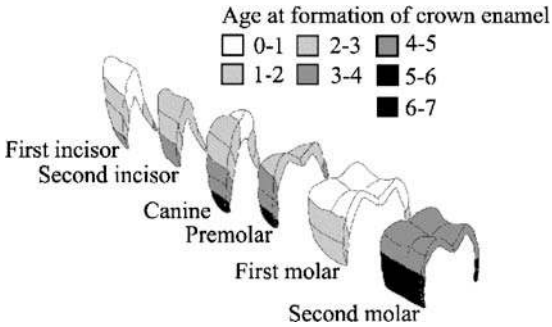

Fig. 19. Permanent crown formation of in human tooth enamel. Ages vary from this guide; more detailed descriptions are available from other sources (e.g., Fincham *et al*., 1999; Hillson, 1997; Reid and Dean, 2006). After Hillson (1986, Fig. 2.4).

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 conclusive microsapmpling 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*.,

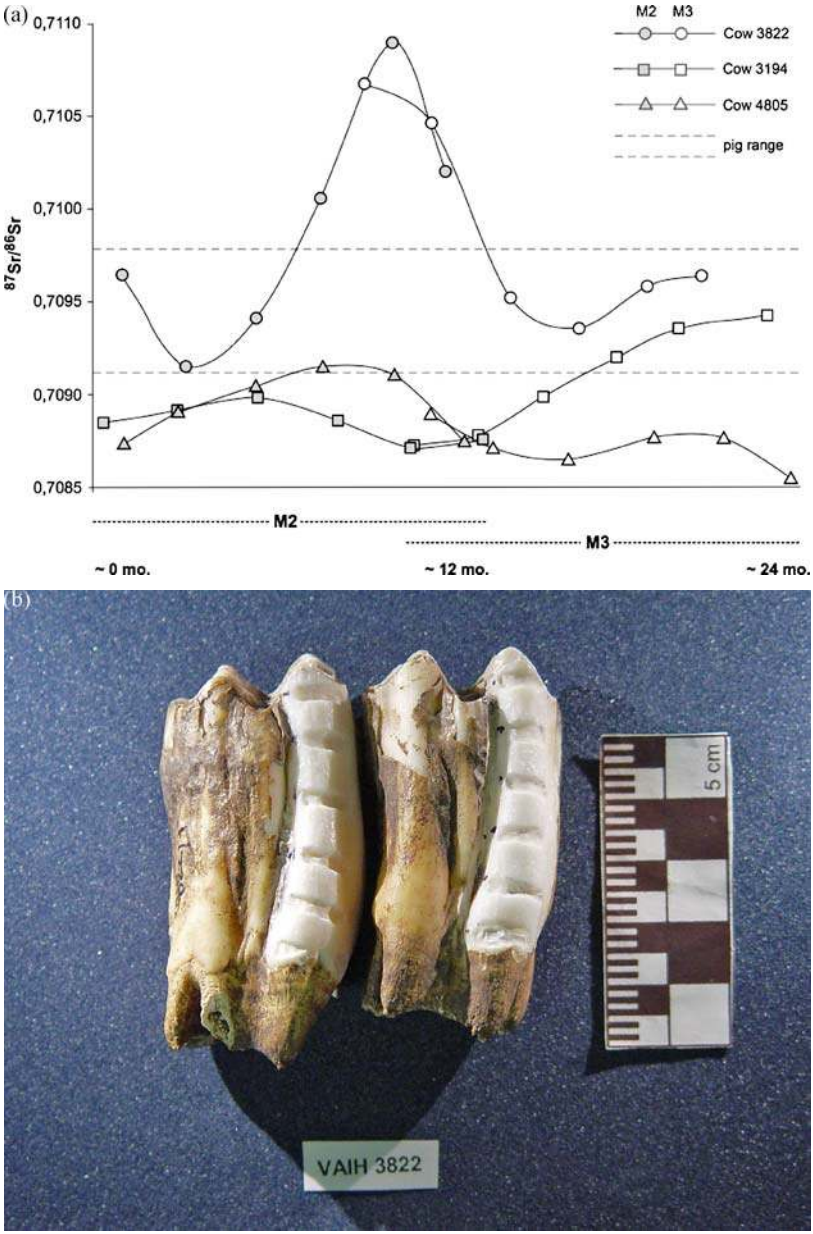

Fig. 20. Sequential sampling of $^{87}Sr/^{86}Sr$ in teeth from three different cows at Vaihingen, Neolithic Germany. Cattle teeth grow at different times after birth, with the second molar (M2) growing from about birth to about ten months, and the third molar (M3) growing from about age 10 months to about 2 years old. After Bentley and Knipper (2005b).

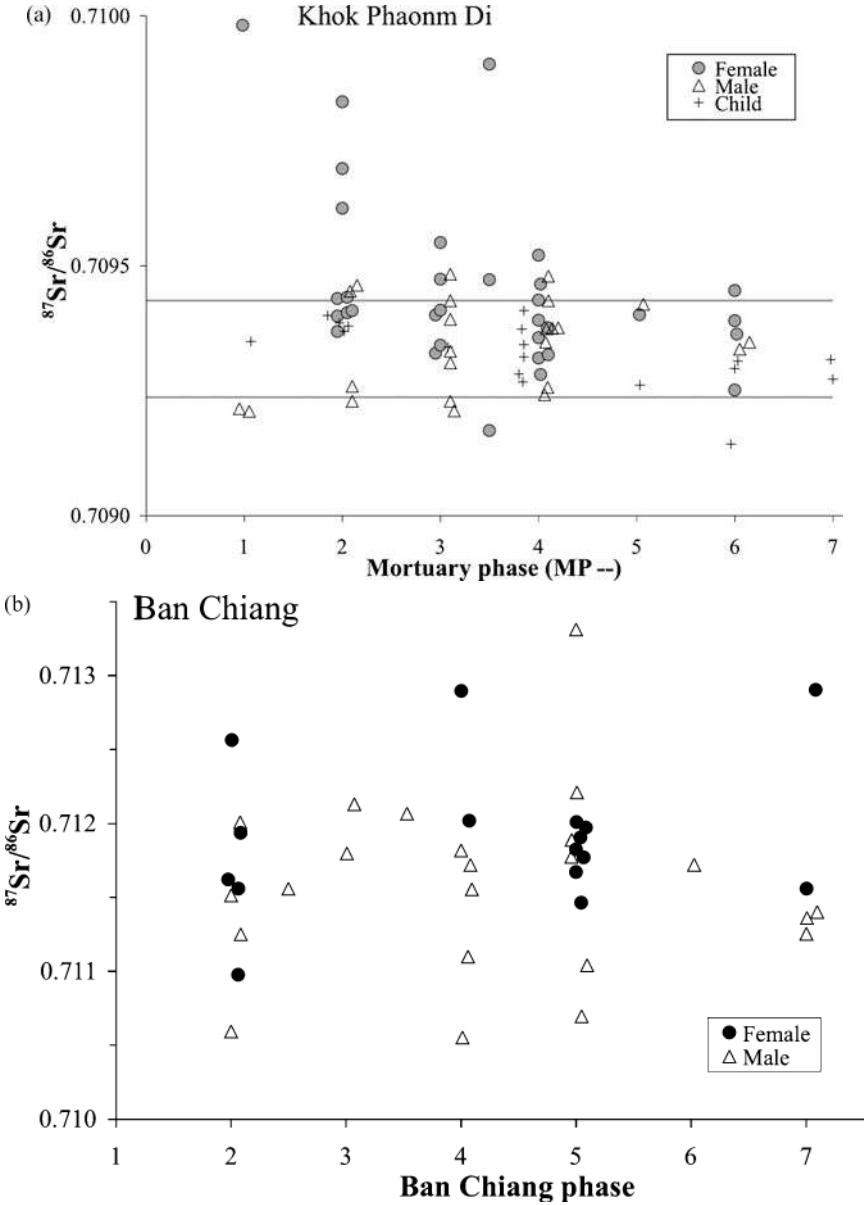

Fig. 21. $^{87}Sr/^{86}Sr$ in human enamel from Ban Chiang (Bentley, *et al*., 2005) and Khok Phanom Di (Bentley, 2004), by chronological phase. Grey dashes: approximate local ranges, which at Khok Phanom Di is consistent with seafood and/or costal resources (and males as fishermen).

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.

ACKNOWLEDGEMENTS

I thank Clark Johnson, Mike Richards and two anonymous reviewers for very helpful comments. I thank Bill White for his invaluable instruction in years past, and James Burton, Martin Kennedy and Janet Montgomery for sharing their considerable knowledge along the way.

REFERENCES CITED

Åberg, G. (1995). The use of natural strontium isotopes as tracers in environmental studies. *Water, Air, and Soil Pollution* **79:** 309–322.

Åberg, G., Fosse, G., and Stray, H. (1998). Man, nutrition and mobility: A comparison of teeth and bone from the Medieval era and the present from Pb and Sr isotopes. *Science of the Total Environment* **224:** 109–119.

Åberg, G., Jacks, G., and Hamilton, P. J. (1989). Weathering rates and $^{87}Sr/^{86}Sr$ ratios: An isotopic approach. *Journal of Hydrology* **109:** 65–78.

Åberg G., Jacks, G., Wickman, T., and Hamilton, P. J. (1990). Strontium isotopes in trees as indicator for calcium availability. *Catena* **17:**1–11.

Arbogast, R.-M. (2000). Zu den Tierknochen aus Vaihingen. In Krause R. (ed.), *Die Bandkeramische Siedlungsgrabung bei Vaihingen an der Enz* (*Krs Ludwigsburg*) *Baden-Württemberg*, Bericht der Römisch Germanischen Kommission 79, 1998, pp. 101–104.

Aubert, D., Probst, A., Stille, P., and Viville, D. (2002). Evidence of hydrological control of Sr behavior in stream water (Strengbach catchment, Vosges mountains, France). *Applied Geochemistry* **17:** 285–300.

Bacon, J. R., and Bain, D. C. (1995). Characterization of environmental water samples using strontium and lead stable-isotope compositions. *Environmental Geochemistry and Health* **17:** 39–49.

Bain, D. C., Midwood, A. J., and Miller, J. D. (1998). Strontium isotope ratios in streams and the effect of flow rate in relation to weathering in catchments. *Catena* **32:** 143–151.

Balasse, M. (2003). Potential biases in sampling design and interpretation of intra-tooth isotope analysis. *International Journal of Osteoarchaeology* **13:** 3–10.

Balasse, M., Ambrose, S. H., Smith, A. B., and Price, T. D. (2002). The seasonal mobility model for prehistoric herders in the south-western cape of South Africa assessed by isotopic analysis of sheep tooth enamel. *Journal of Archaeological Science* **29:** 917–932.

Bashkin, V. N. (2002). *Modern Biogeochemisry*, Kluwer Academic, Dordrecht.

Beard, B. L., and Johnson C. M. (2000). Strontium isotope composition of skeletal material can determine the birth place and geographic mobility of humans and animals. *Journal of Forensic Sciences* **45:** 1049–1061.

Benson, L., Cordell, L., Vincent, K., Taylor, H., Stein, J., Farmer, G. L., and Futa, K. (2003). Ancient maize from Chacoan great houses: Where was it grown? *Proceedings of the National Academy of Sciences USA* **100:** 13111–13115.

Bentley, R. A. (2001). *Human Migration in Early Neolithic Europe: A Study by Strontium and Lead Isotope Analysis of Archaeological Skeletons*. Ph.D dissertation, Department of Anthropology, University of Wisconsin.

Bentley, R. A. (2004). Characterising human mobility by strontium isotope analysis of the skeletons. In Higham, C. F. W., and Thosarat, R. (eds.), *Khok Phanom Di: Summary and Conclusions*, Oxbow Books, Oxford, pp. 159–166.

Bentley, R. A., and Knipper, C. (2005a). Geographic patterns in biologically-available strontium, carbon and oxygen isotopes signatures in prehistoric SW Germany. *Archaeometry* **47:** 629–644.

Bentley, R. A., and Knipper, C. (2005b). Transhumance at the early Neolithic settlement at Vaihingen (Germany). *Antiquity* 79 (December: "Online Project Gallery").

Bentley, R. A., Pietrusewsky, M., Douglas, M. T., and Atkinson, T. C. (2005). Matrilocality during the prehistoric transition to agriculture in Thailand? *Antiquity* **79:** 865–881.

Bentley, R. A., Price, T. D., and Stephan, E. (2004). Determining the 'local' $^{87}Sr/^{86}Sr$ range for archaeological skeletons: A case study from Neolithic Europe. *Journal of Archaeological Science* **31:** 365–375.

Bentley, R. A., Krause, R., Price, T. D., and Kaufmann, B. (2003). Human mobility at the early Neolithic settlement of Vaihingen, Germany: Evidence from strontium isotope analysis. *Archaeometry* **45:** 471–486.

Bentley, R. A., Price, T. D., Lüning, J., Gronenborn, D., Wahl, J., and Fullagar, P. D. (2002). Human migration in early Neolithic Europe. *Current Anthropology* **43:** 799–804.

Bern, C. R., Townsend, A. R., and Farmer, G. L. (2005). Unexpected dominance of parent-material strontium in a tropical forest on highly weathered soils. *Ecology* **86:** 626–632.

Birchall, J., O'Connell, T. C., Heaton, T. H. E., and Hedges, R. E. M. (2005). Hydrogen isotope ratios in animal body protein reflect trophic level. *Journal of Animal Ecology* **74:** 877–881.

Blum, J. D., Taliaferro, E. H., Weisse, M. T., and Holmes, R. T. (2000). Changes in Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$ ratios between two forest ecosystems in the northeastern USA. *Biogeochemistry* **49:** 87–101.

Blum, J. D., Taliaferro, H., and Holmes, R. T. (2001). Determining the sources of calcium for breeding migratory songbirds using stable strontium isotopes. *Oecologia* **126:** 569–574.

Bocherens, H., Brinkman, D. B., Dauphin, Y., and Mariotti, A. (1994). Microstructural and geochemical investigations on Late Cretaceous archaeosaur teeth from Alberta, Canada. *Canadian Journal of Earth Science* **31:** 783–792.

Böhlke, J. K., and Horan, M. (2000). Strontium isotope geochemistry of groundwaters and streams affected by agriculture, Locust Grove, MD. *Applied Geochemistry* **15:** 599–609.

Borg, L. E., and Banner, J. L. (1996). Neodymium and strontium isotopic constraints on soil sources in Barbados, West Indies. *Geochimica et Cosmochimica Acta* **60:** 4193–4206.

Bowring, S. A., Williams, I. S., and Compston, W. (1989). 3.96 Ga gneisses from the Slave Province, Northwest-Territories, Canada. *Geology* **17:** 971–975.

Budd, P., Montgomery, M., Barreiro, B., and Thomas, R. G. (2000). Differential digenesis of strontium in archaeological human dental tissues. *Applied Geochemistry* **15:** 687–694.

Budd, P., Millard, A., Chenery, C., Lucy, S., and Roberts, C. (2004). Investigating population movement by stable isotope analysis: A report from Britain. *Antiquity* **78:** 127–140.

Buikstra, J. D., Price, T. D., Burton, J. H., and Wright, L. E. (2003). Tombs from the Copan acropolis: A life history approach. In Bell, E., Canuto, M., and Sharer, R. J. (eds.), *Understanding Early Classic Copan*, University of Pennsylvania Museum Publications, Philadelphia, pp. 185–206.

Burton, J. H., and Price, T. D. (1990). The ratio of barium to strontium as a a paleodietary indicator of consumption of marine resources. *Journal of Archaeological Science* **17:** 547–557.

Burton, J. H., and Wright, L. E. (1995). Nonlinearity in the relationship between bone Sr/Ca and diet: paleodietary implications. *American Journal of Physical Anthropology* **96:** 273–282.

Burton, J. H., Price, T. D., and Middleton, W. D. (1999). Correlation of bone Ba/Ca and Sr/Ca due to biological purification of calcium. *Journal of Archaeological Science* **26:** 609–616.

Burton, J. H., Price, T. D., Cahue, L., and Wright, L. E. (2003). The use of barium and strontium abundances in human skeletal tissues to determine their geographic origins. *International Journal of Osteoarchaeology* **13:** 88–95.

Capo, R. C., Stewart, B. W., and Chadwick, O. A. (1998). Strontium isotopes as tracers of ecosystem processes: Theory and methods. *Geoderma* **82:** 197–225.

Chadwick, O. A., Derry, L. A., Vitousek, P. M., Huebert, B. J., and Hedin, L. O. (1999). Changing sources of nutrients during four million years of ecosystem development. *Nature* **397:** 491–497.

Chamberlain, C. P., Blum, J. D., Holmes, R. T., Feng, X., Sherry, T. W., and Graves, G. R. (1997). The use of isotope tracers for identifying populations of migratory birds. *Oecologia* **109:** 132–141.

Chiaradia, M., Gallay, A., and Todt, W. (2003). Differential lead and strontium contamination styles of prehistoric human teeth at a Swiss necropolis (Sion, Valais). *Applied Geochemistry* **18:** 353–370.

Collins, M. J., and Riley, M. S. (2000). Amino acid racemization in biominerals, the impact of protein degradation and loss. In Goodfriend, G. A., Collins, M. J., Fogel, M., Macko, S., and Wehmiller, J. F. (eds.), *Perspectives in Amino Acid and Protein Geochemistry*, Oxford University Press, Oxford, pp. 120–142.

Collins, M. J., Nielsen-Marsh, C. M., Hiller, J., Smith, C. I., and Roberts, J. P. (2002). The survival of organic matter in bone: a review. *Archaeometry* **44:** 383–394.

Comar, C. L., Russel, R. S., and Wasserman, R. H. (1957). Strontium-calcium movement from soil to man. *Science* **129:** 485–492.

Cox, G., and Sealy, J. (1997). Investigating identity and life histories: Isotopic analysis and historical documentation of slave skeletons found on the Cape Town foreshore, South Africa. *International Journal of Historical Archaeology* **1:** 207–224.

Dasch, E. J. (1969). Strontium isotopes in weathering profiles, deep-sea sediments and sedimentary rocks. *Geochimica et Cosmochimica Acta* **33:** 1521–1522.

DeNiro, M. J., and Epstein, S. (1978). Influence of diet on the distribution of carbon isotopes in animals. *Geochimica et Cosmochimica Acta* **42:** 495–506.

DePaolo, D. J. (2004). Calcium isotopic variations produced by biological, kinetic, radiogenic and nucleosynthetic processes. *Reviews in Mineralogy and Geochemistry* **55:** 255–288.

Dickin, A. P. (1995). *Radiogenic Isotope Geology*, Cambridge University Press, New York.

Dijkstra, F. A., Van Breemen, N., Jongmans, A.G., Davies, G. R., and Likens, G. E. (2003). Calcium weathering in forested soils and the effect of different tree species. *Biogeochemistry* **62:** 253–275.

Dolphin, A. E., Kang, D., Goodman, A. H., and Amarasiriwardena, D. D. (2003). Microspatial analyses of intra- and intertooth variations in the distribution of trace elements. *American Journal of Physical Anthropology Supplement* **36:** 90.

Driessens, F. C. M., and Verbeeck, R. M. H. (1990). *Biominerals*, CRC Press, Boca Raton, FL.

Elias, R. W., Hirao, Y., and Patterson, C. C. (1982). The circumvention of the natural biopurification of calcium along nutrient pathways by atmospheric inputs of industrial lead. *Geochimica et Cosmochimica Acta* **46:** 2561–2580.

Ericson, J. E. (1985). Strontium isotope characterization in the study of prehistoric human ecology. *Journal of Human Evolution* **14:** 503–514.

Ericson, J. E. (1989). Some problems and potentials for strontium isotope analysis for human and animal ecology. In Rundel, P. W., Ehleringer, J. R., and Nagy, K. A. (eds.), *Stable Isotopes in Ecological Research*, Springer Verlag, New York, pp. 252–259.

Ezzo, J. A. (1994a). Zinc as a paleodietary indicator—an issue of theoretical validity in bone-chemistry analysis. *American Antiquity* **59:** 606–621.

Ezzo, J. A. (1994b). Putting the chemistry back into archaeological bone chemistry analysis—modeling potential paleodietary indicators. *Journal of Anthropological Archaeology* **13:** 1–34.

Ezzo, J. A., Johnson, C. M., and Price, T. D. (1997). Analytical perspective on prehistoric migration: A case study from east-central Arizona. *Journal of Archaeological Science* **24:** 447–466.

Ezzo, J. A., and Price, T. D. (2002). Migration, regional reorganization, and spatial group composition at Grasshopper Pueblo, Arizona. *Journal of Archaeological Science* **29:** 499–520.

Faure, G. (1986). *Principles of Isotope Geology*, John Wiley, New York.

Fincham, A. G., Moradian-Oldak, J., and Simmer, J. P. (1999). The structural biology of the developing dental enamel matrix. *Journal of Structural Biology* **126:** 270–299.

Fricke, H. C., and O'Neil, J. R. (1996). Inter- and intra-tooth variation in the oxygen isotope composition of mammalian tooth enamel phosphate: implications for palaeoclimatological and palaeobiological research. *Palaeogeography, Palaeoclimatology, Palaeoecology* **126:** 91–99.

Gallet, S., Jahn, B. M., Lanoe, B. V., Dia, A., and Rossello, E. (1998). Loess geochemistry and its implications for particle origin and composition of the upper continental crust. *Earth and Planetary Science Letters* **156:** 157–172.

Ghazi, A. M. (1994). Lead in archaeological samples - an isotopic study by ICP-MS. *Applied Geochemistry* **9:** 627–636.

Gilbert, C., Sealy, J., and Sillen, A. (1994). An investigation of barium, calcium and strontium as palaeodietary indicators in the southwestern Cape, South Africa. *Journal of Archaeological Science* **21:** 173–184.

Gilbert, M. T. P., Wilson, A. S., Bunce, M., Hansen, A. J., Willersley, E., Shapiro, B., Higham, T. F. G., Richards, M. P., O'Connell, T. C., Tobin, D. J., Janaway, R. C., and Cooper, A. (2004). Ancient mitochondrial DNA from hair. *Current Biology* **14:** 463–464.

Goldstein, S. J., and Jacobsen, S. B. (1987). The Nd and Sr isotopic systematics of river-water dissolved material: Implications for the sources of Nd and Sr in seawater. *Chemical Geology* **66:** 245–272.

Gosz, J. R., Brookins, D. G., and Moore, D. I. (1983). Using strontium isotope ratios to estimate inputs into ecosystems. *Bioscience* **33:** 23–30.

Graustein, W. C. (1989). $^{87}Sr/^{86}Sr$ ratios measure the sources and flow of strontium in terrestrial ecosystems. In Rundel, P. W., Ehleringer, J. R., and Nagy, K. A. (eds.), *Stable Isotopes in Ecological Research,* Springer-Verlag, New York, pp. 491–512.

Graustein, W. C., and Armstrong, R. (1983). The use of $^{87}Sr/^{86}Sr$ ratios to measure atmospheric transport into forested watersheds. *Science* **219:** 289–292.

Greenfield, H. J. (1988). Bone consumption by pigs in a contemporary Serbian village: Implications for the interpretation of prehistoric faunal assemblages. *Journal of Field Archaeology* **15:** 473–479.

Gregg, S. A. (1988). *Foragers and Farmers: Population Interaction and Agricultural Expansion in Prehistoric Europe*, University of Chicago Press, Chicago.

Grupe, G., Price, T. D., and Söllner, F. (1999). A reply to the comment by Peter Horn and Dieter Müller-Sohnius. *Applied Geochemistry* **14:** 271–275.

Grupe, G., Price, T. D., Schröter, P., Söllner, F., Johnson, C. M., and Beard, B. L. (1997). Mobility of Bell Beaker people revealed by strontium isotope ratios of tooth and bone: A study of southern Bavarian skeletal remains. *Applied Geochemistry* **12:** 517–525.

Haak, W., Forster, P., Bramanti, B., Matsumura, S., Brandt, G., Tänzer, M., Villems, R., Renfrew, C., Gronenborn, D., Alt, K. W., and Burger, J. (2005). Ancient DNA from the first European farmers in 7500-year-old Neolithic sites. *Science* **310:** 1016–1018.

Hall-Martin, A. J., Van Der Merwe, N. J., Lee-Thorp, J. A., Armstrong, R. A., Mehl, C. H., Struben, S., and Tykot, R. (1993). Determination of species and geographic origin of rhino horn by isotopic analysis and its possible application to trade control. In Ryder, O. A. (ed.), *Rhinoceros Biology and Conservation*, Zoological Society of San Diego, San Diego, pp. 123–135.

Hare, P. E., Fogel, M. L., Stafford, T. W., Mitchell, A. D., and Hoering, T. C. (1991). The isotopic composition of carbon and nitrogen in individual amino acids isolated from modern and fossil proteins. *Journal of Archaeological Science* **18:** 277–292.

Hatté, C., Antoine, P., Fontugne, M., Rousseau, D.-D., Tisnérat-Laborde, N., and Zöller, L. (1999). New chronology and organic matter $\delta\ ^{13}C$ paleoclimatic significance of Nuβloch loess sequence (Rhine Valley, Germany). *Quaternary International* **62:** 85–91.

Heaton, T. H. E. (1999). Spatial, species, and temporal variations in the $^{13}C/^{12}C$ ratios of C_3 plants: Implications for paleodiet studies. *Journal of Archaeological Science* **26:** 637–649.

Hedges, R. E. M. (2002). Bone diagenesis: An overview of processes. *Archaeometry* **44:** 319–328.

Hedges, R. E. M., Stevens, R. E., and Koch, P. L. (2006). Isotopes in bone and teeth. In Leng, M. J. (ed.), *Isotopes in Palaeoenvironmental Research*, Springer, pp. 117–146.

Hill, P. A. (1998). Bone remodeling. *British Journal of Orthopaedics* **25:** 101–107.

Hillson, S. (1986). *Teeth*, Cambridge University Press.

Hillson, S. (1997). *Dental Anthropology*, Cambridge University Press, Cambridge.

Hodell, D. A., Quinn, R. L., Brenner, M., and Kamenov, G. (2004). Spatial variation of strontium isotopes ($^{87}Sr/^{86}Sr$) in the Maya region: A tool for tracking ancient human migration. *Journal of Archaeological Science* **31:** 585–601.

Hofmann, A. W. (1988). Chemical differentiation of the Earth: The relationship between mantle, continental crust, and oceanic crust. *Earth and Planetary Science Letters* **90:** 297–314.

Hoogewerff, J., Papesch, W., Kralik, M., Berner, M., Vroon, P., Miesbauer, H., Gaber, O., Kunzel, K. H., and Kleinjans, J. (2001). The last domicile of the iceman from Hauslabjoch: A geochemical approach using Sr, C and O isotopes and trace element signatures. *Journal of Archaeological Science* **28:** 983–989.

Hoppe, K. A. (2004). Late Pleistocene mammoth herd structure, migration patterns, and Clovis hunting strategies inferred from isotopic analyses of multiple death assemblages. *Paleobiology* **30:** 129–145.

Hoppe, K. A., Koch, P. L., Carlson, R. W., and Webb, D. S. (1999). Tracking mammoths and mastodons: Reconstruction of migratory behavior using strontium isotope ratios. *Geology* **27:** 439–442.

Hoppe, K. A., Koch, P. L., and Furutani, T. T. (2003). Assessing the preservation of biogenic strontium in fossil bones and tooth enamel. *International Journal of Osteoarchaeology* **13:** 20–28.

Horn, P., Hölzl, S., and Storzer, D. (1994). Habitat determination on a fossil stag's mandible from the site of *Homo heidelbergensis* at Mauer by use of $^{87}Sr/^{86}Sr$. *Naturwissenschaften* **81:** 360–362.

Horn, P., and Müller-Söhnius, D. (1999). Comment on 'Mobility of Bell Beaker people revealed by Sr isotope ratios of tooth and bone: A study of southern Bell Beaker skeletal remains.' *Applied Geochemistry* **14:** 163–169.

Howland, M. R., Corr, L. T., Young, S. M. M., Jones, V., Jim, S., Van Der Merwe, N. J., Mitchell, A. D., and Evershed, R. P. (2003). Expression of the dietary isotope signal in the compound-specific ^{13}C values of pig bone lipids and amino acids. *International Journal of Osteoarchaeology* **13:** 54–65.

Hurley, P. M., Hughes, H., Faure, G., Fairbairn, H. W., and Pinson, W. H. (1962). Radiogenic strontium-87 model of continent formation. *Journal of Geophysical Research* **67:** 5315–5334.

Hurst, R. W., and Davis, T. E. (1981). Strontium isotopes as tracers of airborne fly ash from coal-fired power plants. *Environmental Geology* **3:** 363–397.

Jørgensen, N. O., Morthorst, J., and Holm, P. M. (1999). Strontium isotope studies of 'brown water' (organic-rich groundwater) from Denmark. *Hydrogeology Journal* **7:** 533–539.

Jowsey, J. (1961). Age changes in human bone. *Clinical Orthopaedics* **17:** 210–218.

Jury, R. V., Webb, M. S., and Webb, R. J. (1960). The spectrochemical determination of total strontium in bone, milk and vegetation. *Annalytica Chemica Acta* **22:** 145–152.

Kang, D., Amarasiriwardena, D., and Goodman, A. H. (2004). Application of laser ablation–inductively coupled plasma-mass spectrometry (LA–ICP–MS) to investigate trace metal spatial distributions in human tooth enamel and dentine growth layers and pulp. *Analytical and Bioanalytical Chemistry* **378:** 1608–1615.

Katzenberg, M. A., and Krause, H. R. (1999). Application of stable isotope variation in human tissues to problems in identification. *Canadian Society of Forensic Science Journal* **22:** 7–19.

Kawasaki, A., Oda, H., and Hirata, T. (2002). Determination of strontium isotope ratio of brown rice for estimating its provenance. *Soil Science and Plant Nutrition* **48:** 635–640.

Kelly, S., Heaton, K., and Hoogewerff, J. (2005). Tracing the geographical origin of food: The application of multi-element and multi-isotope analysis. *Trends in Food Science and Technology* **16:** 555–567.

Kennedy, M. J., and Derry, L. A. (1995). Lack of importance of bedrock weathering in supplying base cations to unpolluted forests: Evidence from Sr isotopes. *Geological Society of America Abstracts* **27:** A235.

Kennedy, M. J., Chadwick, O. A., Vitousek, P. M., Derry, L. A., and Hendricks, D. M. (1998). Changing sources of base cations during ecosystem development, Hawaiian Islands. *Geology* **26:**1015–1018.

Kennedy, M. J., Hedin, L. O., and Derry, L. A. (2002). Decoupling of unpolluted temperate forests from rock nutrient sources revealed by natural $^{87}Sr/^{86}Sr$ and ^{84}Sr tracer addition. *Proceedings of the National Academy of Sciences USA* **99:** 9639–9644.

Knudson, K. J., Price, T. D., Buikstra, J. E., and Blom, D. E. (2004). The use of strontium isotope analysis to investigate Tiwanaku migration and mortuary ritual in Bolivia and Peru. *Archaeometry* **46:** 5–18.

Knudson, K. J., Nystrom, K. C., Tung, T. A., Price, T. D., and Fullagar, P. D. (2005). The origin of the Juch'uypampa cave mummies: Strontium isotope analysis of archaeological human remains from Bolivia. *Journal of Archaeological Science* **32:** 903–913.

Koch, P. L., Heisinger, J., Moss, C., Carlson, R. W., Fogel, M. L., and Behrensmeyer, A. K. (1995). Isotopic tracking of change in diet and habitat use in African elephants. *Science* **267:** 1340–1343.

Koch, P. L., Halliday, A. N., Walter, L. N., Stearley, R. F., Huston, T. J., and Smith, G. R. (1992). Sr isotopic composition of hydroxyapatite from recent and fossil salmon: The record of lifetime migration and diagenesis. *Earth and Planetary Science Letters* **108:** 277–287.

Koch, P. L., Fogel, M. L., and Tuross, N. (1994). Tracing the diets of fossil animals using stable isotopes. In Lajtha, K., and Michener, R. H. (eds.), *Stable Isotopes in Ecology and Environmental Science*, Blackwell Scientific, Oxford, pp. 63–92.

Koch, P. L., Tuross, N., and Fogel, M. L. (1997). The effects of sample treatment and diagenesis on the isotopic integrity of carbonate in biogenic hydroxylapatite. *Journal of Archaeological Science* **24:** 417–429.

Kohn, M. J. (1996). Predicting animal $\delta\ ^{18}O$: Accounting for diet and physiological adaptation. *Geochimica et Cosmochimca Acta* **60:** 4811–4829.

Kohn, M. J., Schoninger, M. J., and Barker, W. W. (1999). Altered states: Effects of diagenesis on fossil tooth chemistry. *Geochimica et Cosmochimica Acta* **63:** 2737–2747.

Kolodny, Y., Luz, B., Sander, M., and Clemens, W. A. (1996). Dinosaur bones: Fossils or pseudomorphs? The pitfalls of physiology reconstruction from apatitic fossils. *Palaeogeography, Palaeoclimatology, Palaeoecology* **126:** 161–171.

Lee-Thorp, J. A. (2002). Two decades of progress towards understanding fossilization processes and isotopic signals in calcified tissue minerals. *Archaeometry* **44:** 435–446.

Lee-Thorp, J. A., and Sponheimer, M. (2003). Three case studies used to reassess the reliability of fossil bone and enamel isotope signals for paleodietary studies. *Journal of Anthropological Archaeology* **22:** 208–216.

Lengemann F. W. (1963). Over-all aspects of calcium and strontium adsorption. In Wasserman, R. H. (ed.), *The Ttransfer of Calcium and Strontium Across Biological Membranes*, Academic Press, New York, pp. 85–96.

McArthur, J. M., Howarth, R. W., and Bailey, T. R. (2001). Strontium isotope stratigraphy: LOWESS Version 3: Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *The Journal of Geology* **109:** 155–170.

McClellan, R. O. (1964). Calcium-strontium discrimination in miniature pigs as related to age. *Nature* **202:** 104–106.

Miller, E. K., Blum, J. A., and Friedland, A. J. (1993). Determination of soil exchangable-cation loss and weathering rates using Sr isotopes. *Nature* **362:** 438–441.

Mitchell, R. L. (1957). The trace element content of plants. *Research* (*London*) **10:** 357.

Montgomery, J., Budd, P., and Evans, J. (2000). Reconstructing the lifetime movements of ancient people: A Neolithic case study from southern England. *European Journal of Archaeology* **3:** 370–386.

Montgomery, J., Evans, J. A., and Roberts, C. A. (2003a). The mineralization, preservation and sampling of teeth: Strategies to optimise comparative study and minimise age-related change for lead and strontium analysis. *American Journal of Physical Anthropology Supplement* **36:** 153.

Montgomery, J., Evans, J. A., and Neighbour, T. (2003b). Sr isotope evidence for population movement within the Hebridean Norse community of NW Scotland. *Journal of the Geological Society* **160:** 649–653.

Montgomery, J., Evans, J. A., Powlesland, D., and Roberts, C. A. (2005). Continuity or colonization in Anglo-Saxon England? Isotope evidence for mobility, subsistence practice and status at West Heslerton. *American Journal of Physical Anthropology* **126:** 123–138.

Montgomery, J., and Evans, J. A. (2006). Immigrants on the Isle of Lewis - combining traditional funerary and modern isotope evidence to investigate social differentiation, migration and dietary change in the Outer Hebrides of Scotland. In Gowland, R., and Knüsel, C. (eds.), *The Social Archaeology of Funerary Remains*, Oxbow, Oxford, pp. 122–142.

Montgomery, J., Evans, J. A., and Cooper, R. E. (n.d.). Resolving archaeological populations with $^{87}Sr/^{86}Sr$ mixing diagrams. *Applied Geochemistry*, submitted.

Mulhern, D. M., and Van Gerven, D. P. (1997). Patterns of femoral bone remodeling dynamics in a medieval Nubian population. *American Journal of Physical Anthropology* **104:** 133–146.

Müller, W., Fricke, H., Halliday, A. N., McCulloch, M. T., and Wartho, J.-A. (2003). Origin and migration of the Alpine Iceman. *Science* **302:** 862–866.

Négrel, P., and Deschamps, P. (1996). Natural and anthropogenic budgets of a small watershed in the Massif Central (France): Chemical and strontium isotopic characterization of water and sediments. *Aquatic Geochemistry* **2:** 1–27.

Négrel, P., Casanova, J., and Aranyossy, J. F. (2001). Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: The Vienne Case (France). *Chemical Geology* **177:** 287–308.

Nelson, B. K., DeNiro, M. J., Schoeninger, M. J., DePaolo, D. J., and Hare, P. E. (1986). Effects of diagenesis on strontium, carbon, nitrogen, and oxygen concentration and isotopic composition of bone. *Geochimica et Cosmogeochimica Acta* **50:** 1941–1949.

Nielsen-Marsh, C. M., and Hedges, R. E. M. (2000a). Patterns of diagenesis in bone I: The effects of site environments. *Journal of Archaeological Science* **27:** 1139–1150.

Nielsen-Marsh, C. M., and Hedges, R. E. M. (2000b). Patterns of diagenesis in bone II: Effects of acetic acid treatment and removal of diagenetic CO_3. *Journal of Archaeological Science* **27:** 1139–1150.

Palmer, M. R., and Edmond, J. M. (1989). The strontium isotope budget of the modern ocean. *Earth and Planetary Science Letters* **92:** 11–26.

Pate, D., and Brown, K. (1985). The stability of bone strontium in the geochemical environment. *Journal of Human Evolution* **14:** 483–491.

Phillips, D. L., and Koch, P. L. (2002). Incorporating concentration dependence in stable isotope mixing models. *Oecologia* **130:** 114–125.

Poszwa, A., Dambrine, E., Pollier, B., and Atteia, O. (2000). A comparison between Ca and Sr cycling in forest ecosystems. *Plant and Soil* **225:** 299–310.

Poszwa, A., Dambrine, E., Ferry, B., Pollier, B., and Loubet, M. (2002). Do deep tree roots provide nutrients to the tropical rainforest? *Biogeochemistry* **60:** 97–118.

Poszwa, A., Ferry, B., Dambrine, E., Pollier, B., Wickman, T., Loubet, M., and Bishop, K. (2004). Variations of bioavailable Sr concentration and $^{87}Sr/^{86}Sr$ ratio in boreal forest ecosystems: Role of biocycling, mineral weathering and depth of root uptake. *Biogeochemistry* **67:** 1–20.

Price, T. D. (1989). Multi-element studies of diagenesis in prehistoric bone. In Price, T. D. (ed.), *The Chemistry of Prehistoric Human Bone*, Cambridge University Press, Cambridge, pp. 126–154.

Price, T. D., Schoeninger, M. J., and Armelagos, G. J. (1985). Bone chemistry and past behavior: An overview. *Journal of Human Evolution* **14:** 419–447.

Price, T. D., Grupe, G., and Schröter, P. (1998). Migration in the Bell Beaker period of central Europe. *Antiquity* **72:** 405–411.

Price, T. D., Blitz, J., Burton, J. H., and Ezzo, J. (1992). Diagenesis in prehistoric bone: Problems and solutions. *Journal of Archaeological Science* **19:** 513–529.

Price, T. D., Johnson, C. M., Ezzo, J. A., Burton, J. H., and Ericson, J. A. (1994). Residential mobility in the prehistoric Southwest United States. A preliminary study using strontium isotope analysis. *Journal of Archaeological Science* **24:** 315–330.

Price, T. D., Manzanilla, L., and Middleton, W. H. (2000). Residential mobility at Teotihuacan: A preliminary study using strontium isotopes. *Journal of Archaeological Science* **27:** 903–914.

Price, T. D., Bentley, R. A., Gronenborn, D., Lüning, J., and Wahl, J. (2001). Human migration in the Linearbandkeramik of Central Europe. *Antiquity* **75:** 593–603.

Price, T. D., Burton, J. H., and Bentley, R. A. (2002). The characterisation of biologically-available strontium isotope ratios for investigation of prehistoric migration. *Archaeometry* **44:** 117–135.

Price, T. D., Tiesler, V., and Burton, J. H. (2006). Early African diaspora in colonial Campeche, Mexico: Strontium isotopic evidence. *American Journal of Physical Anthropology*, in press.

Price, T. D., and Gestsdóttir, H. (2006). The first settlers of Iceland: An isotopic approach to colonisation. *Antiquity* **80:** 130–144.

Probst, A., Viville, D., Fritz, B., Ambroise, B., and Dambrine, E. (1992). Hydrochemical budgets of a small forested granitic cathment exposed to acid deposition: The Strengbach catchment case study (Vosges Massif, France). *Water, Air, and Soil Pollution* **62:** 337–347.

Probst, A., El Gh'mari, A., Aubert, D., Fritz, B., and McNutt, R. (2000). Strontium as a tracer of weathering processes in a silicate catchment polluted by acid atmospheric inputs, (Strengbach, France). *Chemical Geology* **170:** 203–219.

Radosevich, S. (1989). Geochemical techniques applied to bone from South Asia and Alaska: Neither God's truth nor hocus-pocus. In Kenoyer, J. M. (ed.), *Old Problems and New Perspectives in the Archaeology of South Asia*, Department of Anthropology, University of Wisconsin, Madison, pp. 93–102.

Reid, D. J., and Dean, M. C. (2006). Variation in modern human enamel formation times. *Journal of Human Evolution* **50:** 329–346.

Richards, M. P., Fuller, B. F., and Hedges, R. E. M. (2001). Sulphur isotopic variation in ancient bone collagen from Europe: Implications for human palaeodiet, residence mobility, and modern pollutant studies. *Earth and Planetary Science Letters* **191:** 185–190.

Robinson, S., Nicholson, R. A., Pollard, A. M., and O'Connor, T. P. (2003). An evaluation of nitrogen porosimetry as a technique for predicting taphonomic durability in animal bone. *Journal of Archaeological Science* **30:** 391–403.

Sanusi, A., Wortham, H., Millet, M., and Mirabel, P. (1995). Chemical composition of rainwater in eastern France. *Atmospheric Environment* **30:** 59–71.

Schweissing, M. M., and Grupe, G. (2003). Stable strontium isotopes in human teeth and bone: A key to migration events of the late Roman period in Bavaria. *Journal of Archaeological Science* **30:** 1373–1383.

Schoeninger, M. J. (1979). Diet and status at Chalcatzingo: Some empirical and technical aspects of strontium analysis. *American Journal of Physical Anthropology* **51:** 295–310.

Schoeninger, M. J. (1985). Trophic level effects on $^{15}N/^{14}N$ and $^{13}C/^{12}C$ ratios in bone collagen and strontium levels in bone mineral. *Journal of Human Evolution* **14:** 515–525.

Schoeninger, M. J., DeNiro, M. J., and Tauber, H. (1983). Stable nitrogen isotope ratios of bone collagen reflect marine and terrestrial components of prehistoric human diet. *Science* **220:** 1381–1383.

Schoeninger, M. J., and Moore, K. M. (1992). Bone stable isotope studies in archaeology. *Journal of World Prehistory* **6:** 247–296.

Sealy, J. C., and Sillen, A. (1988). Sr and Sr/Ca in marine and terrestrial foodwebs in the southwestern Cape, South-Africa. *Journal of Archaeological Science* **15:** 425–438.

Sealy, J. C., Van Der Merwe, N. J., Sillen, A., Kruger, F. J., and Krueger, W. H. (1991). $^{87}Sr/^{86}Sr$ as a dietary indicator in modern and archaeological bone. *Journal of Archaeological Science* **18:** 399–416.

Sealy, J. C., Armstrong, R., and Schrire, C. (1995). Beyond lifetime averages: Tracing life histories through isotopic analysis of different calcified tissues from archaeological human skeletons. *Antiquity* **69:** 290–300.

Shackleton, J., and Elderfield, H. (1990). Strontium isotope dating of the source of Neolithic European Spondylus shell artifacts. *Antiquity* **64:** 312–315.

Sharp, Z. D., Atudorei, V., and Furrer, H. (2000). The effects of diagenesis on oxygen isotope ratios of biogenic phosphates. *Science* **300:** 222–237.

Sillen, A. (1986). Biogenic and diagenetic Sr/Ca in Plio-Pleistocene fossils in the Omo Shungura Formation. *Paleobio* **12:** 311–323.

Sillen, A. (1989). Diagenesis of the inorganic phase of cortical bone. In Price, T. D. (ed.), *The Chemistry of Prehistoric Human Bone*, Cambridge University Press, Cambridge, pp. 211–229.

Sillen, A. (1992). Strontium-calcium ratios (Sr/Ca) of Australopithecus robustus and associated fauna from Swartkrans. *Journal of Human Evolution* **23:** 495–516.

Sillen, A., and Kavanagh, M. (1982). Strontium and paleodietary research: A review. *Yearbook of Physical Anthropology* **25:** 67–90.

Sillen, A., and Sealy, J. C. (1995). Diagenesis of strontium in fossil bone: A reconsideration of Nelson *et al*. (1986). *Journal of Archaeological Science* **22:** 313–320.

Sillen, A., Hall, G., and Armstrong, R. (1995). Strontium calcium ratios (Sr/Ca) and strontium isotopic ratios ($^{87}Sr/^{86}Sr$) of *Australopithecus robustus* and *Homo* sp. from Swartkrans. *Journal of Human Evolution* **28:** 277–285.

Sillen, A., Hall, G., Richardson, S., and Armstrong, R. (1998). $^{87}Sr/^{86}Sr$ ratios in modern and fossil food-webs of the Sterkfontein Valley: Implications for early hominid habitat preference. *Geochimica et Cosmochimica Acta* **62:** 2463–2478.

Smith, T. M., Martin, L. B., and Leakey, M. G. (2003). Enamel thickness, microstructure and development in *Afropithecus turkanensis*. *Journal of Human Evolution* **44:** 283–306.

Stewart, B. W., Capo, R. C., and Chadwick, O. A. (2001). Effects of rainfall on weathering rate, base cation provenance, and Sr isotope composition of Hawaiian soils. *Geochimica et Cosmochimica Acta* **65:** 1087–1099.

Teitelbaum, S. L. (2000). Bone resorption by osteoclasts. *Science* **289:** 1504.

Tieszen, L. L. (1991). Natural variations in the carbon isotope values of plants: Implications for archaeology, ecology, and paleoecology. *Journal of Archaeological Science* **18:** 227–248.

Tieszen, L. L., Boutton, T. W., Tesdahl, K. G., and Slade, N. A. (1983). Fractionation and turnover of stable carbon isotopes in animal tissues: Implications for the $\delta\ ^{13}C$ analysis of diet. *Oecologia* **57:** 32–37.

Tricca, A., Stille, P., Steinmann, M., Kiefel, B., Samuel, J., and Eikenberg, J. (1999). Rare earth elements and Sr and Nd isotopic compositions of dissolved and suspended loads from small river systems in the Vosges mountains (France), the river Rhine and groundwater. *Chemical Geology* **160:** 139–158.

Trickett, M. A., Budd, P., Montgomery, J., and Evans, J. (2003). An assessment of solubility profiling as a decontamination procedure for the $^{87}Sr/^{86}Sr$ analysis of archaeological human skeletal tissue. *Applied Geochemistry* **18:** 653–658.

Tuross, N., Behrensmeyer, A. K., and Eanes, E. D. (1989). Strontium increases and crystallinity changes in taphonomic and archaeological bone. *Journal of Archaeological Science* **16:** 661–672.

Van Der Merwe, N. J. (1982). Carbon isotopes, photosynthesis, and archaeology. *American Scientist* **70:** 596–606.

Van Der Merwe, N. J., Lee-Thorp, J. A., Thackeray, J. F., Hall-Martin, A., Krueger, F. J., Coetzee, H., Bell, R. H. V., and Lindeque, M. (1990). Source-area determination of elephant ivory by isotopic analysis. *Nature*, **346:** 744–746.

Van Der Merwe, N. J., Williamson, R. F., Pfeiffer, S., Thomas, S. C., and Allegretto, K. O. (2003). The Moatfield ossuary: Isotopic dietary analysis of an Iroquoian community, using dental tissue. *Journal of Anthropological Archaeology* **22:** 245–261.

Vanhaeren, M., d'Errico, F., Billy, I., and Grousset, F. (2004). Tracing the source of Upper Palaeolithic shell beads by strontium isotope dating. *Journal of Archaeological Science* **31:** 1481–1488.

Vitousek, P. M., Kennedy, M. J., Derry, L. A., and Chadwick, O. A. (1999). Weathering versus atmospheric sources of strontium in ecosystems on young volcanic soils. *Oecologia* **121:** 255–259.

Vogel, J. C., and Van Der Merwe, N. J. (1977). Isotopic evidence for early maize cultivation in New York State. *American Antiquity* **42:** 238–242.

Vogel, J. C., Eglington, B., and Auret, J. M. (1990). Isotope fingerprints in elephant bone and ivory. *Nature* **346:** 747–749.

Walczyk, T., and von Blanckenburg, F. (2002). Natural iron isotope variations in human blood. *Science* **295:** 2065–2066.

Wang, Y., and Cerling, T. E. (1994). A model for fossil tooth and bone diagenesis: Implications for paleodiet reconstructions from stable isotopes. *Palaeogeography, Palaeoclimatology, Palaeoecology* **107:** 281–288.

Whipkey, C. E., Capo, R. C., Chadwick, O. A., and Stewart, B. W. (2000). The importance of sea spray to the cation budget of a coastal Hawaiian soil: A strontium isotope approach. *Chemical Geology* **168:** 37–48.

White, C. (1993). Isotopic determination of seasonality of diet and death in ancient Nubian hair. *Journal of Archaeological Science* **20:** 657–666.

White, W. M. (n.d.). *Geochemistry*. To be published at Johns Hopkins University Press, currently online at: http://www.imwa.info/Geochemie/Chapters.html.

White, W. M., Schilling, J.-G., and Hart, S. R. (1976). Evidence for the Azores mantle plume from strontium isotope geochemistry of the Central North Atlantic. *Nature* **263:** 659–663.

White, W. M., and Hofmann, A. W. (1982). Sr and Nd isotope geochemistry of oceanic island basalts and mantle evolution. *Nature* **296:** 821–825.