3 Bone dating background

Bone is a body tissue composed of bioapatite (mineral, crystalline carbonate–hydroxylapatite inorganic phase 60-70 wt%), collagen (proteins, the organic fraction 20-30 wt%), and water (ca.10 wt%) (Figure 3.1).

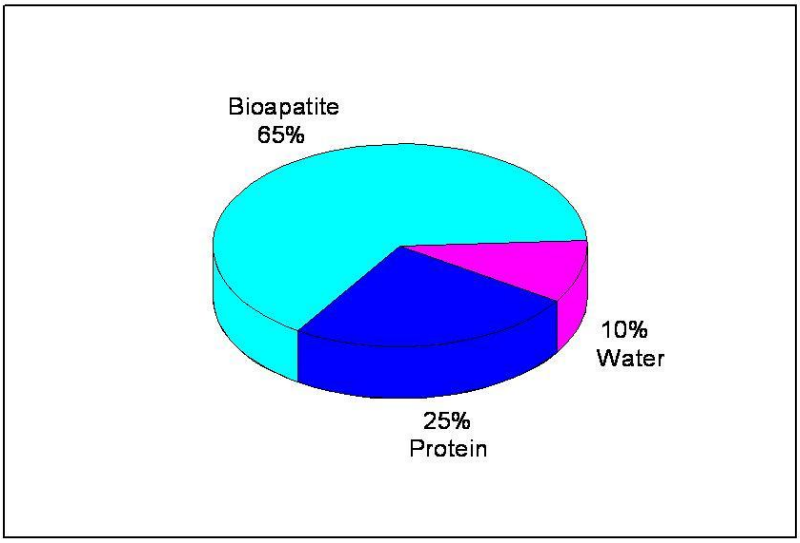

Figure 3.1 Bone composition mineral, crystalline carbonate–hydroxylapatite inorganic phase 60-70 wt%, proteins, the organic fraction 20-30 wt% and circa 10% of water.

Bone collagen is an important substrate for radiocarbon dating (Arnold and Libby, 1951), and stable isotopic analysis (Collins, et al., 2002). In addition, bone is a useful material to date in archaeology as it can be the direct target of the event being dated (i.e. dating a human itself) or closely associated to the event of interest (i.e. animal remains from a site, bone artefacts).

Despite the utility of using bone for radiocarbon dating there are often problems in dating bone from archaeological sites as it is at risk from contamination and it is often degraded. Degradation involves structural alteration and the gradual breakup of the protein chains. Background contamination can then come from the inclusion of exogenous carbonaceous contaminants, either *in situ*, during the excavation, or in the laboratory.

Bones, of course, can be contaminated by old or modern carbon. The shift in radiocarbon age from the true age due to the addition of either of these is illustrated by a series of experiments where I added 10 microgram of either modern or ^{14}C free carbon to 1 mg of the original carbon deriving from different time periods (Table 3.I).

Table 3.I Series of experiments where I have added 10 microgram of either modern or ^{14}C free carbon to 1 mg of the original carbon deriving from different time periods

True age	**Period**	**pmC sample**	**pmC modern added**	**Contam. age**	**Diff. years**	**Weight modern**
42,000	Neanderthal	0.54	1.00	33,545	8455	0.01 mg
25,000	Upper Palaeolithic	4.45	1.00	23,372	1628	0.01 mg
6,000	Neolithic	47.38	1.00	5,832	168	0.01 mg
3,000	Late Bronze age	68.83	1.00	2,884	116	0.01 mg
True age	**Period**	**pmC sample**	**pmC contam.**	**Contam. age**	**Diff. years**	**Weight fossil C added**
35,000	Neanderthal	1.28	1.27	35,080	80	0.01 mg
6,000	Neolithic	47.38	46.91	6,080	80	0.01 mg
3,000	Late Bronze age	68.83	68.15	3,080	80	0.01 mg

As can be seen, a sample dating to 42,000 radiocarbon years, with just 10 micrograms of modern contamination, is shifted to an apparent age of 33,000 years, which is more than 8000 years younger. For an Upper Palaeolithic sample dating to 25,000 years the contamination changes the true age by 1,628 years. For Neolithic and Late Bronze Age samples the shift is smaller, but still much higher than the typical radiocarbon error of 25 to 40 years for these time periods. Adding 1% of fossil material, e.g. from organic solvents of petrochemical origin, shifts all dates to older ages by 80 years. Therefore, fossil contamination is less severe for old samples but for the younger samples it is still larger than the age error. There are a number of real examples of these problems (Conard and Bolus, 2008, Higham, et al., 2006a, Jacobi, et al., 2006).

Initial attempts to date bone apatite largely failed (see review by Surovell, 2000) because carbonates exchange readily with surrounding inorganic carbonate (e.g. dissolved in ground water). In contrast, collagen is much more stable. Longin (1971) proposed a method to isolate bone collagen. This aspect is treated in detail in chapter 6

(introduction of paper (Talamo and Richards, 2011)) As an indicator of contamination and/or degradation of collagen different authors use C:N ratios, $\delta^{13}C$ and $\delta^{15}N$, and amino acid composition (Ambrose, 1990, DeNiro, 1985, Harbeck and Grupe, 2009, Hedges, 2002, Klinken, 1999, Schoeninger, et al., 1989, Strydonck, et al., 2004). Usually it is assumed that contamination is likely when atomic C:N ratio falls outside the range observed for modern animals and humans (2.9-3.6). $\delta^{13}C$ and $\delta^{15}N$ values in bone collagen depends on diet, used to distinguish herbivores from carnivores and furthermore between marine and terrestrial diet. Typical values for animal bone collagen are taken from Strydonck et al.(2004, p.128), and are shown here in table 3.II.

Table 3. II Typical values for animal bone collagen, taken from Strydonck et al. (2004)

Bone collagen from animals having q 100% diet of:	**$\delta^{13}C‰$**	**$\delta^{15}N‰$**
C-3	-21	+5
meat C-3 herbivores	-18	+8
C-4 plants	-7	+5
marine food	-13	+18
river fish	-24	+16
lake fish	-20	+16

An illustrative figure of regional variations in the isotopic values, and of variations among species, is shown in Katzenberg (2008, p.427). The full range of these parameters needs to be considered to determine if collagen extracted from an archaeological bone is of sufficiently good quality (Lee-Thorp, 2008, Richards and Hedges, 1999, Richards and Hedges, 2003, Richards, et al., 2005, Richards, et al., 2000, Richards, et al., 2008). Another simple but important criterion is the quantity of collagen that can be recovered. Usually a limit of 1% weight is considered necessary as a minimum condition (Hedges and Van Klinken, 1992) and samples of lower yield are potentionally problematic (Brock, et al., 2007, Higham, et al., 2006b).

There are advanced techniques to characterize the state of preservation of bone, such as Fourier transform infrared spectroscopy (FT-IR) which gives an index of crystallinity of the bone mineral (Weiner and Bar-Yosef, 1990, Yizhaq, et al., 2005), X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Reiche, et al., 2002).