Radiation in Art and Archeometry
D.C. Creagh and D.A. Bradley (editors)

AMS dating in archaeology, history and art

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Radiocarbon (^{14}C) dating provides an absolute time scale for human history over the last 50,000 years. Accelerator Mass Spectrometry (AMS), with its capacity to analyse ^{14}C in sub-milligram carbon samples, has expanded enormously the applicability of this dating method. Specific molecular compounds extracted from ancient bones, single seeds and other microscopic carbon-bearing substances of archaeological significance can now be dated, increasing the sensibility and reliability of the chronological determination. Thanks to the very limited invasiveness of AMS, rare artefacts can be sampled for dating without undue damage. The state of the art in AMS dating of objects significant for archaeology, history and art is reviewed with examples from some recent applications.

1. INTRODUCTION

One of the main objectives of archaeology is to chronologically order past events by studying material remains that reflect human behaviour. A versatile array of dating methods is nowadays available. Relative chronologies can be deduced from circumstantial evidence, such as change of style and manufacturing technique. Relative chronological information can also be obtained using methods based on time-dependent geological and chemical changes (eg stratigraphy, sedimentation rate, weathering, hydration, magnetism). Certain kinds of annual phenomena, such as tree rings or varves, will yield very precise chronologies if stringent precautions are followed. Finally, many methods providing absolute chronologies are based on time-dependent phenomena related to natural radioactivity, and include:

1. exponential decay of long-lived cosmogenic radionuclides, as in the radiocarbon method;
2. exponential in-situ production by secondary cosmic rays of long-lived radionuclides, such as ^{10}Be, ^{26}Al and ^{36}Cl, which can be used for dating rock surfaces and stone artefacts;

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3. linear build-up of radiation exposure effects, in thermoluminescence (TL), optically stimulated luminescence (OSL), electron spin resonance (ESR) and fission track dating;
4. exponential build-up of a radiogenic daughter from a primordial radionuclide, in K-Ar, Ar-Ar and U-series dating.

^{14}C is the most widely used of these chronometers. In the late 1940s, the development of radiocarbon dating by detection of the ^{14}C residual activity (Libby, 1946; Arnold and Libby, 1949) revolutionised archaeology providing a precise and direct measurement of the time scale for the development of human activities during the late Quaternary. In particular, radiocarbon dating had a strong impact on the understanding of European prehistory, previously dated only by correlation with the historical chronology of the Near East (Renfrew, 1973)

In the late 1970s (Muller, 1977; Bennett *et al.*, 1977; Nelson *et al.*, 1977), the development of direct atom counting by AMS enhanced more than a million-fold the sensitivity of ^{14}C analysis. Extensive AMS work followed, particularly in the analysis of radiocarbon and other cosmogenic radionuclides for archaeological, geological and environmental applications (Tuniz *et al.*, 1998; Fifield, 1999). Through the non-invasive analysis of famous artefacts and findings such as the Shroud of Turin (see Figure 1; Damon *et al.*, 1989), the Ice Man (Prinoth-Fornwagner and Niklaus, 1994) and the Dead Sea Scrolls (Bonani *et al.*, 1992), AMS has gained widespread public recognition as a dating technique.

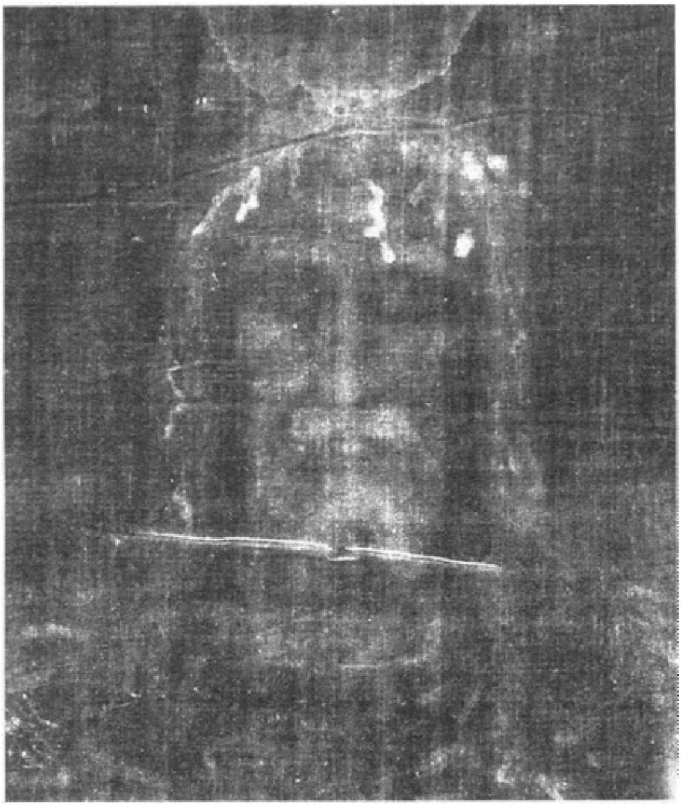

Figure 1. Close up of the facial image of the Shroud of Turin as it appears on a photographic negative (photo: © 1978 Barrie M. Schwortz).

Radiocarbon dating must be applied with due consideration for contamination, bioturbation, natural isotopic fractionation and many other factors that can influence its accuracy. Appropriate procedures to correct for these effects have been established. In the following, AMS dating will be reviewed with some illustrations that draw on the special advantages of this method to determine a precise chronology for human prehistory. The application of AMS dating to authenticate objects and materials of historical and artistic significance will be also discussed.

2. PRINCIPLES OF RADIOCARBON DATING

^{14}C is formed in the atmosphere by nuclear reactions of secondary cosmic neutrons with nitrogen (78 % of the atmosphere consists of N_2) and is quickly distributed throughout the atmosphere as $^{14}CO_2$. In pre-industrial times, the atmospheric isotopic ratio $^{14}C/^{12}C$ was about 1.2×10^{-12}. In a simplified model, which is not strictly correct (see sections 4. and 5.) but is often used to introduce the basic idea, we may argue that living organisms participating to the carbon cycle via metabolic processes are characterised by this radiocarbon concentration. When a living organism dies, the carbon exchange stops. Hence, by measuring the residual ^{14}C concentration in organic samples, if they have not been contaminated by younger material (eg via bacterial action, soil organic acids) or older material (eg geologic calcium carbonate), it is possible to calculate the time elapsed since the material was originally formed. Ages up to about 50,000 BP can be determined by radiocarbon dating.

2.1. Radiocarbon: a gift of nature

The functioning of radiocarbon as a precise natural chronometer in archaeology is due to a number of favourable circumstances. Firstly, the ^{14}C half-life of 5730 years is ideal for studies in the temporal scale characterising the development of human civilisation. Furthermore, the rather rapid and homogeneous mixing in the atmosphere of the freshly produced $^{14}CO_2$ gas attenuates production variations. Hence, the *time zero* point of the chronometer (the initial isotopic ratio in living organisms) is fairly uniform in space and time. Finally, incorporation of ^{14}C within organic molecules permits the extraction of material for dating which is directly derived from the original living organism.

In principle, other natural long-lived radioisotopes could be useful to extend the datable time span in archaeology. In particular, the cosmogenic isotope ^{41}Ca was measured by AMS in modern bones and other terrestrial materials to test the possibility of directly dating archaeological findings with ages of 10^5 - 10^6 years (Middleton *et al.*, 1989). Unfortunately, the variability of the $^{41}Ca/^{40}Ca$ ratio in contemporary materials makes it difficult to establish the *time zero* point for this chronometer.

3. AMS: COUNTING ATOMS RATHER THAN DECAYS

AMS is the analytical technique of choice for the detection of long-lived radionuclides in samples which cannot be practically analysed with decay counting or conventional mass

spectrometry (MS). Its advantage is that the ambiguities in ion identification are practically removed, enabling the analysis of isotopic ratios as low as 10^{-15}, a factor 10^5 lower than in most MS systems. Since the atoms and not the radiation resulting from their decay are directly counted, the sensitivity of AMS is unaffected by the half-life of the isotope being measured and detection limits at the level of 10^6 atoms are possible. Compared to the decay counting technique, the efficiency of AMS in detecting long-lived radionuclides is $10^5 - 10^9$ times higher, the size of the sample required for analysis can be 10^3 - 10^6 times smaller and the measurement can be performed 100 to 1000 times faster. For example, samples having as little as 20 • g carbon are analysed in 30 minutes at the ANTARES AMS centre (see Figure 2). To highlight the difference between decay counting and atom concentration analysis, consider 1 g of modern carbon containing 6 x 10^{10} atoms of ^{14}C, which can be measured by decay counting with 1% precision (10^4 decays detected) in 1000 minutes hours. With a high-intensity ion source, AMS can count 10^4 ^{14}C atoms in one minute, consuming only 100 • g of the source material.

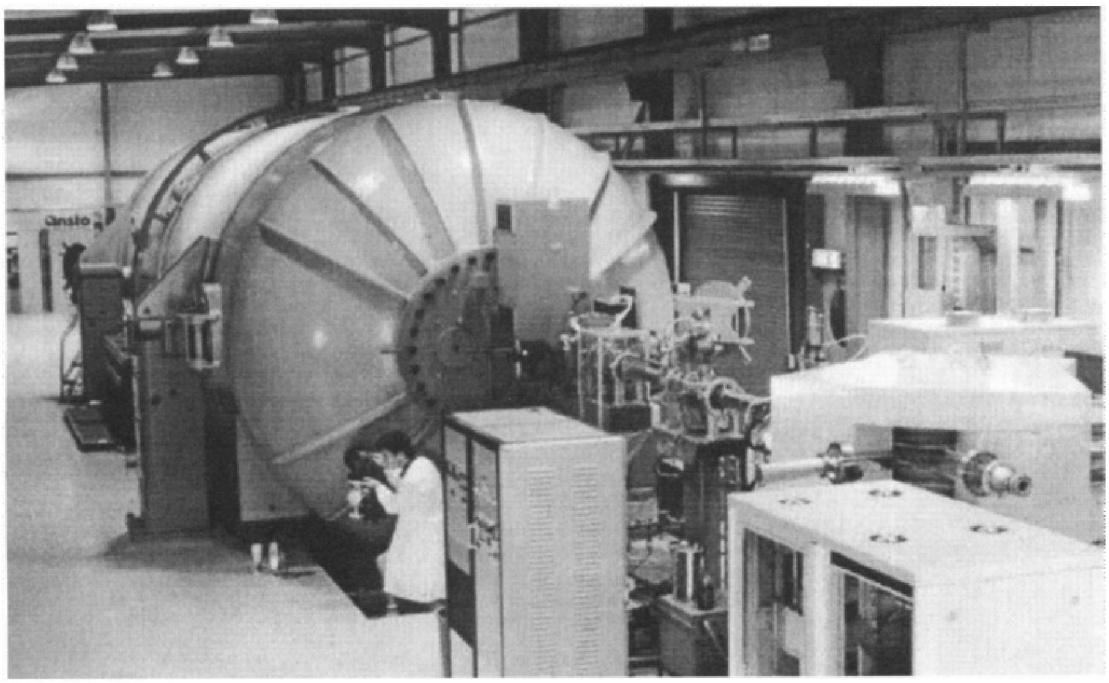

Figure 2. The Tandem Accelerator in use at the ANTARES AMS centre (Australian Nuclear Science and Technology Organisation, Sydney; Tuniz *et al.*, 1995).

3.1. Choice of accelerator

In AMS, the intrinsic analytical properties of ion accelerators are exploited to perform ultra-sensitive isotopic analyses.

Van de Graaff tandem electrostatic accelerators are the optimum choice for a variety of AMS applications. Tandem accelerators working between 0.5 - 3 MV have been specifically designed for ^{14}C analysis (Purser, 1994; Suter, 1999). Large tandem accelerators, originally

developed for nuclear physics research, are also used to analyse a variety of rare radionuclides (Tuniz *et al.*, 1995) with the advantage of allowing higher energies and a more effective separation of isobaric interferences.

Other accelerators, such as cyclotrons, were unsuccessfully used in early attempts to measure long-lived cosmogenic radioisotopes at natural ^{14}C levels. Only recently, an AMS system based on a small cyclotron has been developed to detect ^{14}C at natural abundances (Chen *et al.*, 1999). However, its practical use is limited and further developments will be required to allow precise measurements of isotopic ratios.

3.2. Radiocarbon analysis with tandem Van de Graaff accelerators

A typical AMS set-up is shown in Figure 3. Negative carbon ions are produced in the caesium sputter ion source and, after low-energy mass analysis, are injected into the tandem accelerator. In the case of ^{14}C, isobaric interferences are completely eliminated because ^{14}N does not form stable negative ions. High precision AMS measurements are carried out either by using simultaneous injection or by rapid sequential injection of the isotopes ^{12}C, ^{13}C and ^{14}C. Negative ions are attracted to the positive voltage on the terminal and thereby accelerated to energies between 0.5 - 15 MeV, at which point they pass through a low pressure gas or a thin carbon foil and are stripped of some of their electrons. Multi-charged positive ions are then further accelerated away from the same positive terminal voltage. The stripping process is used to destroy molecular interference which is the main limitation for conventional mass spectrometry. After the acceleration stage, a magnet selects the most probable charge state (typically 3^+ or 4^+, depending on ion energy). Velocity or energy analysers provide additional filtering to remove residual background. Finally, identification of the ^{14}C ions is performed in an ion detector. The isotopic ratio $^{14}C/^{12}C$ (or $^{14}C/^{13}C$) is derived from the ^{14}C counting rate in the detector and the ^{12}C and ^{13}C beam currents measured in Faraday cups. A similar methodology is used to analyse other rare cosmogenic radionuclides, such as ^{10}Be, ^{26}Al, etc.

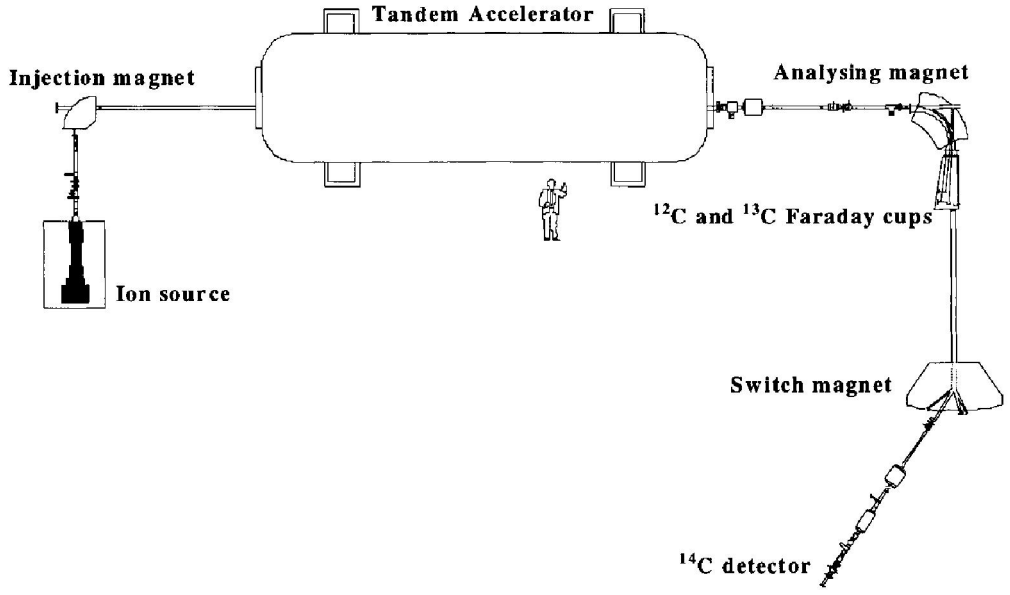

Figure 3. Scheme of the ANTARES AMS facility as used for ^{14}C AMS (Tuniz *et al.*,

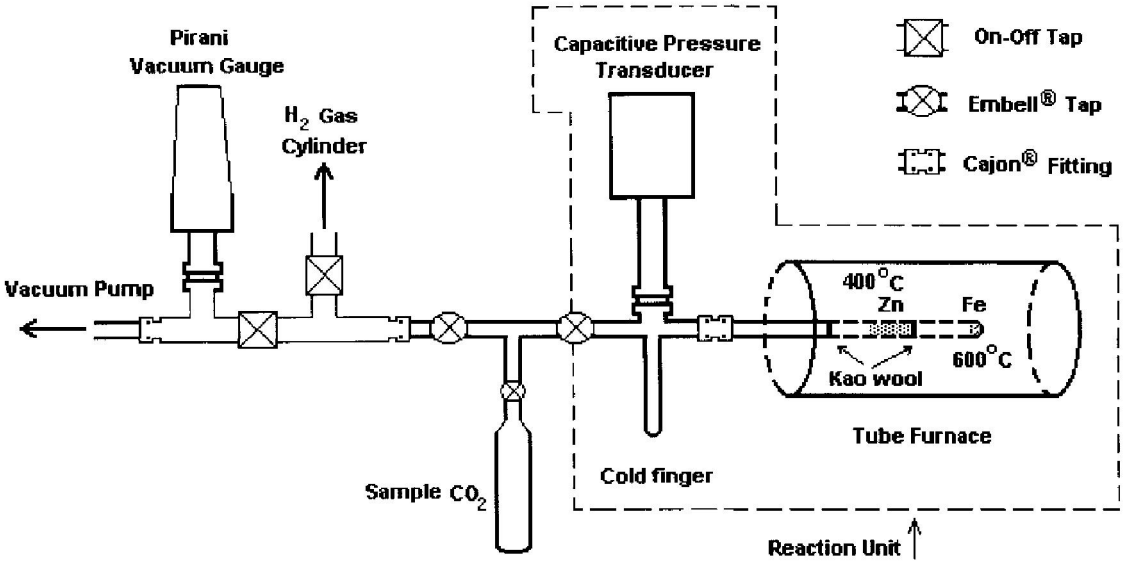

Figure 4. Scheme of the graphitisation line using the Zn/Fe method.

4. SAMPLES FOR AMS ^{14}C ANALYSIS

Organic samples to be analysed by AMS need to be purified and transformed into a graphite target for the ion source. Most samples require treatment to remove extraneous carbon or to extract fractions containing only original carbon compounds. CO_2 is obtained from the purified sample either by combustion or hydrolysis. Finally, CO_2 is reduced to graphite via a catalytic process with Fe or Co in the presence of Zn (see Figure 4) and/or hydrogen (Jull et al., 1986; Jacobsen *et al.*, 1997). CO_2 rather than graphite can be also used, eliminating the need of converting gas to graphite (Bronk-Ramsey and Hedges, 1997). However, only low ion currents are achievable, considerably limiting the analytical throughput.

4.1. What is being dated?

The degree to which AMS dated samples are representative of a specific past event is crucial to the satisfactory interpretation of the results. Some of the archaeological materials that have been studied illustrate the importance of the small sample capability. In particular

1. individual amino acids extracted from bone or blood can sometimes provide a better basis for radiocarbon dating than the use of all organic material;
2. individual seeds can be directly dated instead of using neighbouring pieces of charcoal;
3. tiny pieces of charcoal, extracted from inclusions in ceramics can directly date the object of interest;
4. a small number of foraminifera shells (or pollen grains) of one species can be selected under a microscope and used to date sediment layers with good time resolution

The interpretation of ^{14}C measurements, including the potential for contamination, depends on the molecular species that are extracted and used to date the original sample. The

small sample capability of AMS increases the need for careful study of the material used for dating and provides the means for making detailed assessments of the differences in ^{14}C content of various molecular species present in a sample.

An important example is the radiocarbon dating of bones. Buried bones are easily contaminated by carbonates from the surrounding soil. A simple extraction of the original organic components such as collagen may not be sufficient, as complex molecules, including proteins present in ground-waters and various soluble carbonaceous materials, may also penetrate the bone. To limit this kind of contamination, methods based on the isolation of carbon atoms forming intact peptide bonds in bone proteins have been developed (Nelson, 1991).

A simpler approach is to date all organic carbon whilst avoiding any inorganic components. For example Russ *et al.* (1990) have developed a method for using a low-temperature (100 °C), low-pressure (4 torr) oxygen plasma to selectively oxidise the organic carbon in small samples of pigments from prehistoric rock paintings to CO_2 for AMS dating.

Nelson *et al.* (1986) reported the use of AMS to obtain radiocarbon dates for blood residues on prehistoric stone tools. In one case, involving blood from a snowshoe hare, the ^{14}C date (1010 ± 90 BP) was in good agreement with measurements on charcoal from a closely associated hearth (1060 ± 160 BP). Only 50 μg of carbon, extracted from high molecular weight proteins, was obtained in the second case of human blood from a chert tool and this proved sufficient to obtain a date (2180 ± 160 BP) compatible with expectations.

Another important issue to consider is the biological aging process. The ^{14}C concentration of living tissues is fixed as it is formed. Thereafter the cells and bone carbonate in animals are renewed very slowly by the metabolic processes, while radioactive decay of the fixed ^{14}C is continuously lowering the initial level. The net result is that the ^{14}C content lags the atmosphere by up to a few decades. In the case of growing trees, cells formation happens only in a narrow zone under the bark, so the innermost wood may already be centuries old before the tree dies. In some but not all species, there is a clear ring boundary corresponding to each year. This forms the basis of dendrochronology and explains why wood is so widely employed for radiocarbon calibration studies.

5. PERFORMANCE AND LIMITATIONS OF AMS ^{14}C DATING

The attributes of AMS ^{14}C dating which are most significant for archaeological applications are sample size, datable time span and dating accuracy.

Table 1. Typical sample size required for ^{14}C dating of archaeologically significant materials.

Material	Quantity*	Material	Quantity*
Wood	5	Shell, Carbonates	10
Bone	500	Paper, textiles	5 – 10
Charcoal	3 – 5	Grass, seeds, leaves, grains	5 – 10
Beeswax	1 – 2	Hair, skin	5 – 7
Pollen	1	Teeth, tusk, ivory	500 – 700

* milligrams for AMS, grams for decay counting

5.1. Sample size

Sample sizes required for AMS, as reported in Table 1 for some archaeologically significant carbonaceous materials, are generally 1000 times smaller than those required for decay counting and samples as small as 20 μg carbon can be processed. While the use of small samples greatly extends the applicability of ^{14}C dating, contamination in the field and during chemistry processing may limit both accuracy and datable time span.

5.2. Datable time span

Oxidation and graphitisation processes are responsible for a background equivalent to about 1 μg modern carbon. This sets an equivalent age limit of about 50,000 BP for 1 mg specimens. On the other hand, measurements carried out with geological (*i.e.* ^{14}C-free) unprocessed graphite give results equivalent to an age of 60,000 to 70,000 BP, and accelerator background (with no sample) is equivalent to an age of 80,000 to 90,000 BP. Hence, the datable time span by AMS ^{14}C could, in principle, be extended beyond the present limits. This extension would be very valuable for studying early activities of *Homo sapiens sapiens* in order to corroborate results from other dating techniques such as OSL and U-series dating (for a comparison of the datable time span for different dating techniques see Figure 5). Recent studies suggest that the use of a stepped combustion technique could further reduce the contamination (Bird *et al.*, 1999). Pre-treatment of the glassware by baking it under streaming oxygen also showed a beneficial effect (Lawson *et al.*, 1999).

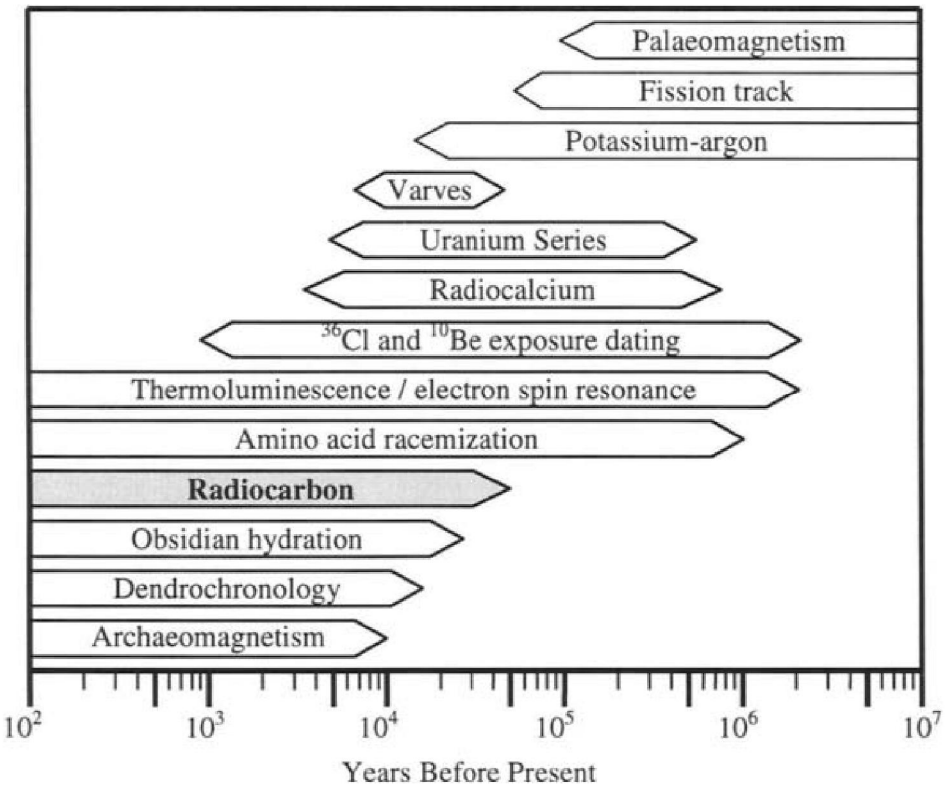

Figure 5. Comparison of the datable time span of different dating techniques.

5.3. Precision and accuracy

The precision of AMS radiocarbon measurements is usually dominated by statistical error. A minimum mass of about 20 μg is necessary to date recent (< 5000 BP) specimens with an error of 1% (~ 80 *a*). With the use of multiple graphite targets obtained from the same material, AMS has demonstrated the capability to provide a precision of 0.2 % (< 20 *a*) for the radiocarbon analysis of modern samples. However, there are a number of systematic effects which must be considered to obtain an accurate age. These effects are briefly discussed in the following.

5.3.1. Contamination

As mentioned above, due to the small mass of material used in AMS measurements, the oxidation and graphitisation processes inevitably lead to contamination by modern CO_2. It is essential to assess the contamination level introduced by each type of procedure by processing a blank material (*eg* coal, graphite, marble etc.). A correction can then be applied (see Figure 6). For contamination of modern origin, the correction is small for recent samples and large for older samples. It ultimately limits the maximum age of the materials which can be dated.

5.3.2. Fractionation

Natural chemical or physical processes can mass fractionate the carbon isotopes during carbon uptake and alter the $^{13}C/^{12}C$ and $^{14}C/^{12}C$ isotopic ratios. Natural mass fractionation is expressed in terms of $\delta^{13}C$ which is a measure (in parts per thousand) of the deviation of the isotope ratio $^{13}C/^{12}C$ from a standard material referred to as PDB, a Cretaceous belemnite, *Belemnitella americana*, from the Pee Dee formation of South Carolina (Olsson, 1970). Typical $\delta^{13}C$ values for environmental materials can vary between +2 permil (eg marine

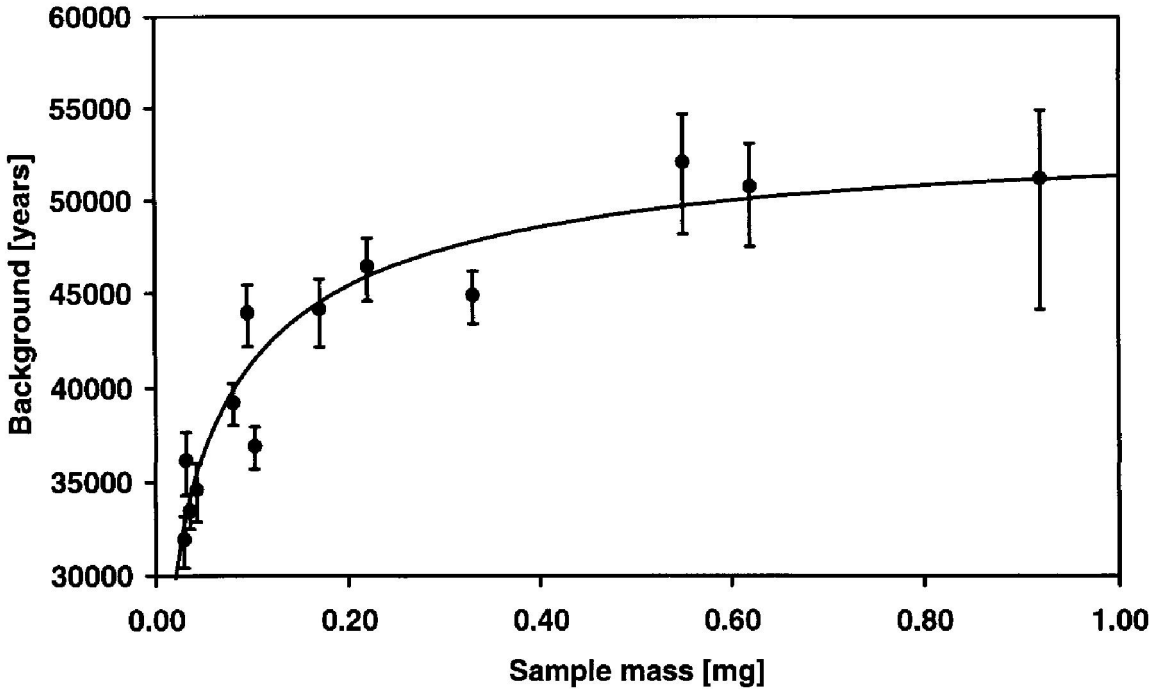

Figure 6. A typical background corresponding to the contamination introduced by the chemical procedures.

carbonate) to -27 permil (eg some kinds of wood). This effect is significant and must be taken into account to obtain accurate ages. The $\delta^{13}C$ value for a material to be radiocarbon dated must be known to correct for the fractionation affecting the ^{14}C isotopic ratio. Additional fractionation may be introduced by chemistry processing of AMS samples (*eg* incomplete graphitisation) and during AMS analysis (*eg* ion sputtering and stripping processes). In general, these effects are corrected by processing and measuring standard materials of known isotopic ratio such as the oxalic acid HOxI (Stuiver, 1983).

5.3.3. Reservoir effects

Organic specimens drawing carbon from reservoirs other than the atmosphere may yield incorrect ages. In the case of marine shells deriving their carbon from seawater, a system not in equilibrium with the atmosphere, the reservoir effect leads to age differences of up to 1000 years (Stuiver *et al.*, 1998b). This difference can be reflected in bones of animals or humans consuming fish. High apparent ages can be found in plants near volcanoes erupting ^{14}C-depleted CO_2. Other small age shifts arise from differences in atmospheric mixing between northern and southern hemispheres, and regional air-sea exchange of CO_2.

5.3.4. Variation in ^{14}C production rate (calibration)

Conventional radiocarbon ages are reported in years before present (BP), where present is 1950 AD, and are calculated using the "Libby" half-life of 5568 years on the assumption that the production of ^{14}C in the past has been constant (Donahue *et al.*, 1990). The difference between conventional radiocarbon ages and calendar ages (*calibrated* ages) has been determined with high precision for all of the Holocene by radiocarbon measurements on tree ring samples (see Figure 7; Stuiver *et al.*, 1998a), which are independently and precisely dated by dendrochronology. Part of this difference derives from the use of the conventional

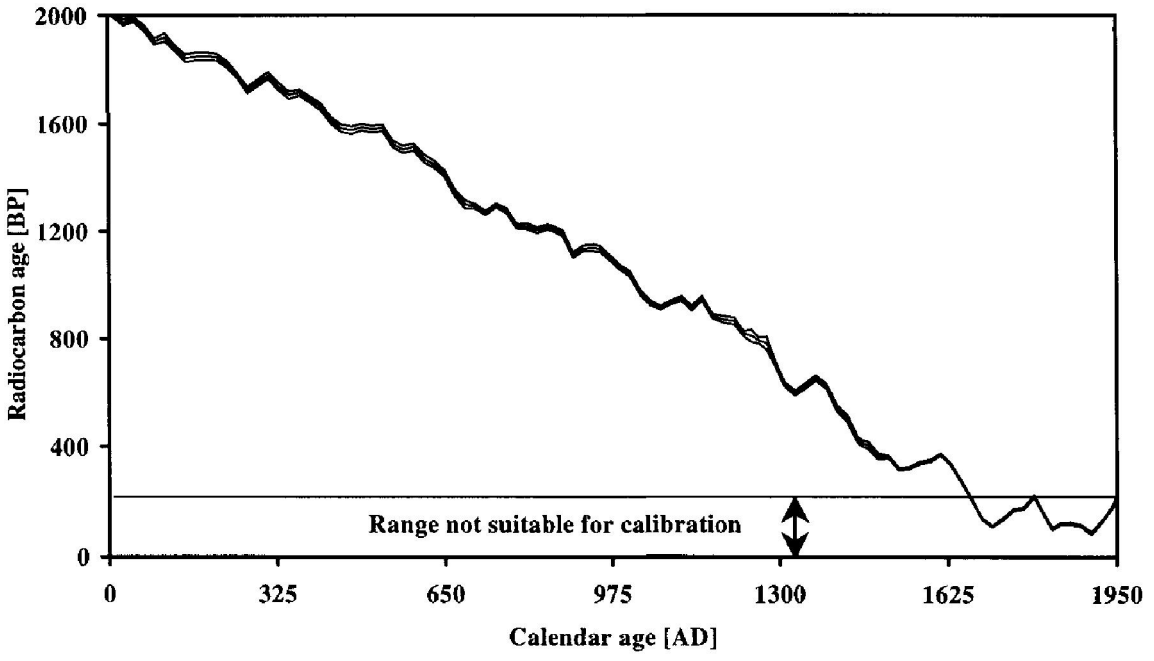

Figure 7. The calibration curve for the last two millennia (Stuiver *et al.*, 1998a).

half-life, which is known to be 3% too small. The remaining difference derives from secular variations of ^{14}C production rate in the atmosphere due to geo- and helio-magnetic effects and global variations in the parameters of the carbon cycle. In the range 1650 – 1950 AD calibrated ages are ambiguous due to fluctuations in atmospheric ^{14}C concentration. Samples with conventional radiocarbon ages of 200 years or less are often reported as 'modern' (Stuiver and Polach, 1977). A radiocarbon calibration for the late Pleistocene has been obtained by comparing radiocarbon results to ages obtained by Uranium/Thorium (Bard *et al.*, 1998) and varve (lacustrine annual sedimentary layers) chronology (Kitagawa and van der Plicht, 1998; Hughen *et al.*, 1998). Radiocarbon ages are younger than calendar ages during the late Pleistocene, with a difference of 1000-2000 years between 15,000 and 10,000 BP.

6. THE *IN SITU* METHOD

Long-lived radioisotopes such as ^{14}C, ^{10}Be (1.50 Ma half-life), ^{26}Al (720 ka), ^{36}Cl (310 ka) and ^{41}Ca (103 ka) are produced *in situ* in the shallow horizons of the Earth by interaction of secondary cosmic rays (mainly neutrons and muons) with suitable target nuclides in rocks and soil. Typical production rates at sea level and high latitudes are discussed in Tuniz *et al.* (1998). AMS is used to determine the radioisotope concentration and subsequently estimate the exposure age of the rock surface. The in-situ method works best on the time period from 5 ka to 5 Ma. The lower limit is set by the sensitivity of AMS. In principle, this method could be used to set an upper limit to the age of rock carvings or paintings. However, the practical limits are determined by the strong dependence on geographic location (latitude and altitude), on shielding conditions and on erosion rates. The analysis of the depth profile of a radionuclide or the measurement of the concentration of two radionuclides with different half lives can be used to determine erosion rate, exposure age and history of a surface.

One of the first archaeological applications of the *in situ* method was the determination of a limit age of the petroglyphs found in the Côa Valley in Portugal (Phillips *et al.*, 1997). ^{36}Cl exposure ages showed that the rock panels were available for engraving during the Palaeolithic, supporting the Palaeolithic origin inferred by the archaeologists (Zilhão, 1995). The *in situ* method was also applied to the dating of the Tabun Cave, Mt. Carmel in Israel (Boaretto *et al.*, 1999). The sediments in the cave are of aeolian origin and are rich in quartz. To study the burial history, ^{26}Al and ^{10}Be concentrations were measured in sediment samples and flint tools.

7. AMS ^{14}C DATING IN PREHISTORY

Radiocarbon dates are the main source of the time perspective in prehistory. Although AMS ^{14}C dating cannot access the earliest human developments occurring at the order of 100,000 BP and beyond, it can reach a highly significant era in human prehistory. It was during the last 50,000 years that *Homo sapiens sapiens*, or modern humans, colonised large habitable parts of our planet. In the following we briefly discuss the contribution of AMS ^{14}C dating to the construction of a chronology for the spread of modern humans, including the

early manifestations of civilisation, *viz.* the capacity of representing and interpreting the reality through rock pictographs.

7.1. Early human migrations

When *Homo sapiens sapiens* colonised America, Europe and Australia is a matter for controversy at present.

The study of human bones in North American sites originally provided a wide range of dates from less than 20,000 BP up to 70,000 BP, with many of these results obtained by amino-acid racemisation and ^{14}C decay counting. It must be noted that radiocarbon dating of ancient bones is unreliable unless specific amino acids are extracted. AMS dating of such minute components extracted from the same bones gave results around 11,000 BP at the oldest (Taylor, 1987). This strengthened the common view that the north American continent was populated not much before the Holocene period, when an ice-free land corridor was opened across the Bering Strait at the end of the last ice age. More work is needed to support these theories as the validity of AMS ^{14}C dates on poorly preserved fossil bones remains questioned (Stafford *et al.*, 1990). In recent years, the debate has been re-opened and many archaeologists now accept the date 12,500 BP for the far southern site of Monte Verde in Chile (Adovasio and Pedler, 1997).

Palaeoanthropologists are interested in the origins of *Homo sapiens sapiens* in Europe and its relation to the hominids of Neanderthal type. AMS has been used to date bones from the Upper Pleistocene to reconstruct the human evolution in this part of the world (Stringer, 1986). The Mousterian - Aurignacian boundary has been dated at about 37,000 BP in Spain (Bischoff *et al.*, 1994) by AMS ^{14}C analysis of charcoal fragments. These dates are at the fringes of the radiocarbon method but they have been confirmed by U-series dating on the enclosing carbonate. The latter method yields a date of about 43,000 BP, a difference which may be partly explained by ^{14}C production variations due to geomagnetic field fluctuations and climatic changes. The evolutionary fate of the Neanderthals and the spread *of Homo sapiens sapiens* has been recently reviewed by Pettitt *et al.* (1999).

Concerning the first colonisation of Australia, many archaeologists agree on the idea that the first humans entered via the north of the continent, Cape York, Arnhem Land or the Kimberley. Much less agreement exists on the time frame of this colonisation. Until recently, the most ancient radiocarbon dates for the human presence in Australia corresponded to less than 40,000 BP, as shown by AMS dates from the Kimberley region (O'Connor, 1995) and from Chillagoe in the Cape York peninsula (David *et al.*, 1997). On the other hand, optically stimulated luminescence yields dates corresponding to 50,000-60,000 BP for sites in the Northern Territory (Roberts *et al.*, 1994). In addition, ESR and U-series dating investigations on the Lake Mungo 3 human skeleton yielded a date of 62,000 ± 6000 BP, in good agreement with OSL age estimates on the sediments into which the skeleton was buried (61,000 ± 2000 BP) (Thorne *et al.*, 1999). This is arguably the earliest known human presence in Australia. The difference between the dates inferred by radiocarbon and other dating methods for the earliest presence of humans in Australia is too large and it cannot be explained by astrophysical or environmental effects on ^{14}C concentration in the atmosphere during the late Pleistocene. Various theories have been advanced to explain this discrepancy, including the hypothesis that Australia was colonised in two or more separate human migrations (Allen and Holdaway, 1995). The association between rising seas in the Austral region, around 60,000,

80,000 and 100,000 years ago, and human occupation of the Australian continent, have also been considered (Chappell, 1993). Recent ^{14}C AMS dates show that the Devil's Lair site in South Western Australia was occupied by aboriginal people 48-49 ka BP, supporting the hypothesis of an early human colonisation of Australia (Turney *et al.*, 2000).

7.2. Prehistoric rock art

Dating rock art is essential to building archaeological models describing the evolution of prehistoric civilisation. The antiquity of European cave paintings was qualitatively established since last century. Relative chronologies were developed using stylistic criteria and the status of the pigments or the presence of Figures, such as extinct fauna, of known antiquity. Some indirect chronological information was then obtained by radiocarbon dating of human occupation remains found near the paintings. However, the real test was to date actual pigments or, better still, organic components of pigments which are likely to have derived from the painters or other contemporary carbon. However, location and extraction of material that has not been contaminated since its original application, which carries a radiocarbon signature unique to that moment, and which has not become part of a complex sequence of updates or overpainting is an enormous challenge. Only recently, direct dating of the charcoal used for the drawings was possible thanks to the sensitivity of AMS ^{14}C dating.

Dates in the range 12,900 - 14,000 BP (Valladas *et al.*, 1992) were obtained for pictures of bison in the Spanish caves of Altamira and El Castillo and in the French Pyrenean cave of Niaux. On the other hand, remains of human occupation in the same caves range approximately from 5,000 to 18,000 BP.

Some very sophisticated Palaeolithic paintings were discovered in 1994 in the Ardèche Valley in France (Chauvet-Pont d'Arc cave). Between 300 and 400 animals are depicted with advanced techniques (including the use of perspective), such as rhinoceros, lions, mammoths, horses and bison. AMS radiocarbon dating using microscopic samples of charcoal from the paintings yield a consistent age of about 31,000 BP for several of these animals (Clottes *et al.*, 1995). Pieces of charcoal found on the ground in the cave yield dates of 22,000 - 29,000 BP, suggesting human incursions for extended periods of time. The radiocarbon dates obtained are the oldest found for prehistoric rock art and confirm that *Homo sapiens sapiens* created elaborate forms of art long before the Upper Palaeolithic.

7.2.1. Australian rock art

The Australian program in AMS dating of rock art includes research into the probable age of the rock art of Chillagoe and Laura (North Queensland), the Kimberley (Western Australia) and Olary District (South Australia). A variety of materials is being analysed, including pigments, oxalate minerals, silica coatings, plant fibres, carbonised plant matter, fatty acids, beeswax and mud-wasp nests. Different sample processing techniques are being explored, including low-pressure plasma techniques and laser extraction methods. Laser-induced combustion and AMS have been used to date single laminae in 2 mm thick rock surface accretions, a very useful method to study prehistoric paintings and engravings (Campbell *et al.*, 1996). AMS dating on charcoal drawings from Chillagoe yield ages of less than 1000 years, supporting the hypothesis of population increase and intensified use of this region during the late Holocene (David *et al.*, 1999).

7.2.1.1. Bradshaw rock art

The Bradshaws are Australian Aboriginal rock paintings with a unique style characterised by elegant and graceful Figures with many ornaments and accoutrements. An example is shown in Figure 8. Paintings of this style are found in the Kimberley region in the north west of the state of Western Australia. The paint colour is usually a light mauve or mulberry. These Figures were first reported by early explorer Joseph Bradshaw who, accompanied by his brother, surveyed this region in 1891. The paintings are so unusual and distinctive that there has been much speculation and debate concerning their origins and meanings. Some researchers have gone as far as to suggest origins other than the ancestors of modern indigenous Australians.

Despite the considerable interest no scientific attempts to date the paintings were made until 1997, primarily because of the difficulties inherent in dating rock paintings. The ANTARES AMS team was involved in two separate investigations. Watchman *et al.* (1997) dated carbon-bearing material scraped from on or near paintings. The conclusion was that the Bradshaw paintings are at least 4,000 years old.

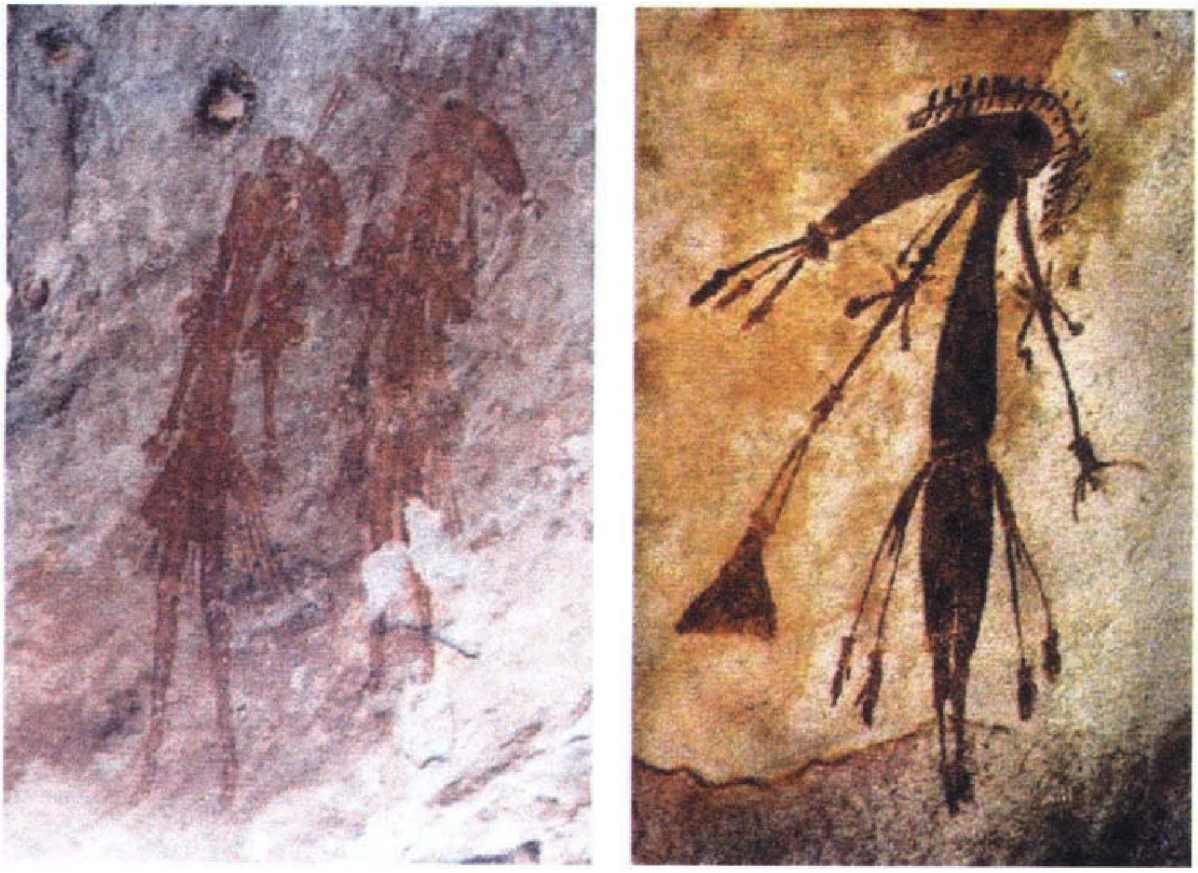

Figure 8. Computer enhanced "Tassel" Bradshaw Figures showing their ornate form of dress with rear triple tassels, bangles, elbow bands, cummerbund waistbands with pubic aprons and complicated head-dresses. A mud-wasp nest can be seen on the rock face just above the left hand Figure. Photo: courtesy of Graham Walsh, Takarakka Rock Art Research Centre.

These dates are somewhat at odds with the findings of the second investigation in which Roberts *et al.*, (1997) made use of the nests of mud-wasps to provide a limit for the age of a Bradshaw painting. Two measurement techniques were involved in this investigation – radiocarbon AMS and OSL. The investigators found a minimum age of 17,000 BP. So the origins of the Bradshaw paintings are still unknown and further (perhaps many) measurements to establish their ages will be required.

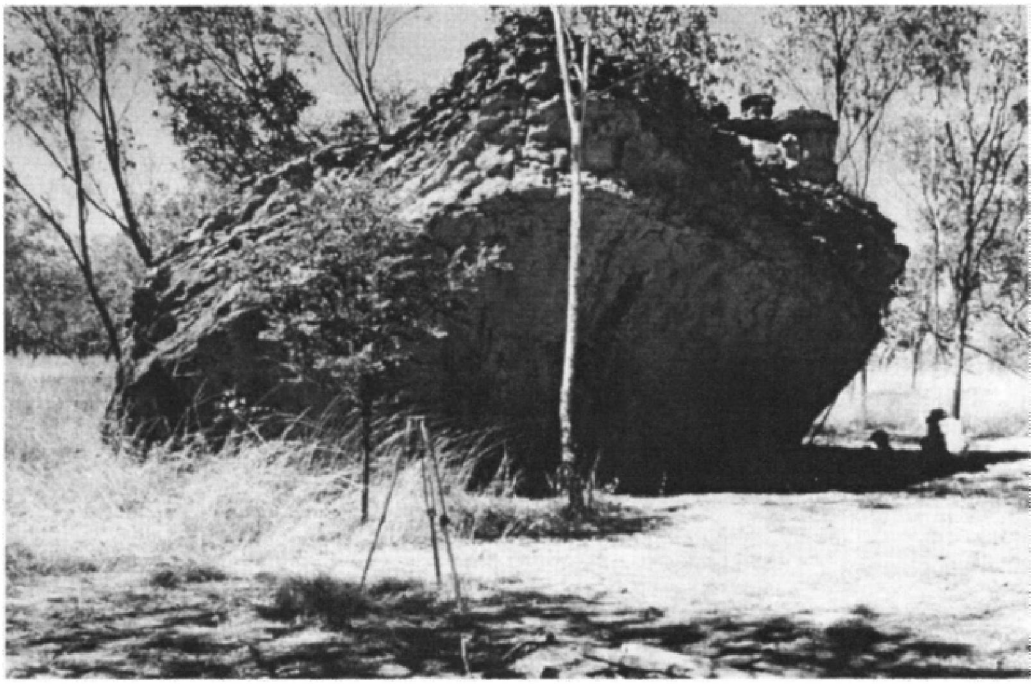

Fig. 9. The Jinmium rock shelter. Photo: courtesy of Richard Roberts, La Trobe University.

7.2.1.2. Jinmium

The Jinmium rock shelter is located in the northern region of Australia under a tilted block of sandstone (see Figure 9). Circular engravings (pecked cupules) have been carved by the early inhabitants of this remote area. Thermoluminescent dating provided ages of 50,000 – 70,000 BP for the quartz sand associated with the buried engravings. Dates between 116,000 and 176,000 BP were provided by TL for the quartz sands of the artefact bearing sedimentary deposits near the rock shelter (Fullagar *et al.*,1996).

These results were subsequently contradicted using other dating techniques. Optically Stimulated Luminescence (OSL) applied to single sand grains indicated that the Jinmium deposits are younger than 10,000 BP. AMS ^{14}C dating of the carbon fragments in the deposits provided similarly young ages (Roberts *et al.*, 1998).

7.3. The ice man

The mummy of a human body (see Figure 10) was discovered in September 1991 in a glacier, at 3210 m on the Ötzal Alps, Alto Adige Region, Italy. The find is now displayed at the South Tyrol Museum of Archeology (Bozen, Italy) and includes shoes, clothes, a copper axe and a quiver of arrows. AMS was used to date a variety of samples from this find, including grass from the shoes and tissue specimens from the body. Results obtained at a number of laboratories concord on a radiocarbon age of 4546 ± 17 BP (Prinoth-Fornwagner and Niklaus, 1994), corresponding to a calendar age between 3100 and 3350 BC. This result and the style of the artefacts found with the body support the hypothesis that the Ice Man belonged to the Remedello culture present in the northern part of the Italian peninsula during this period.

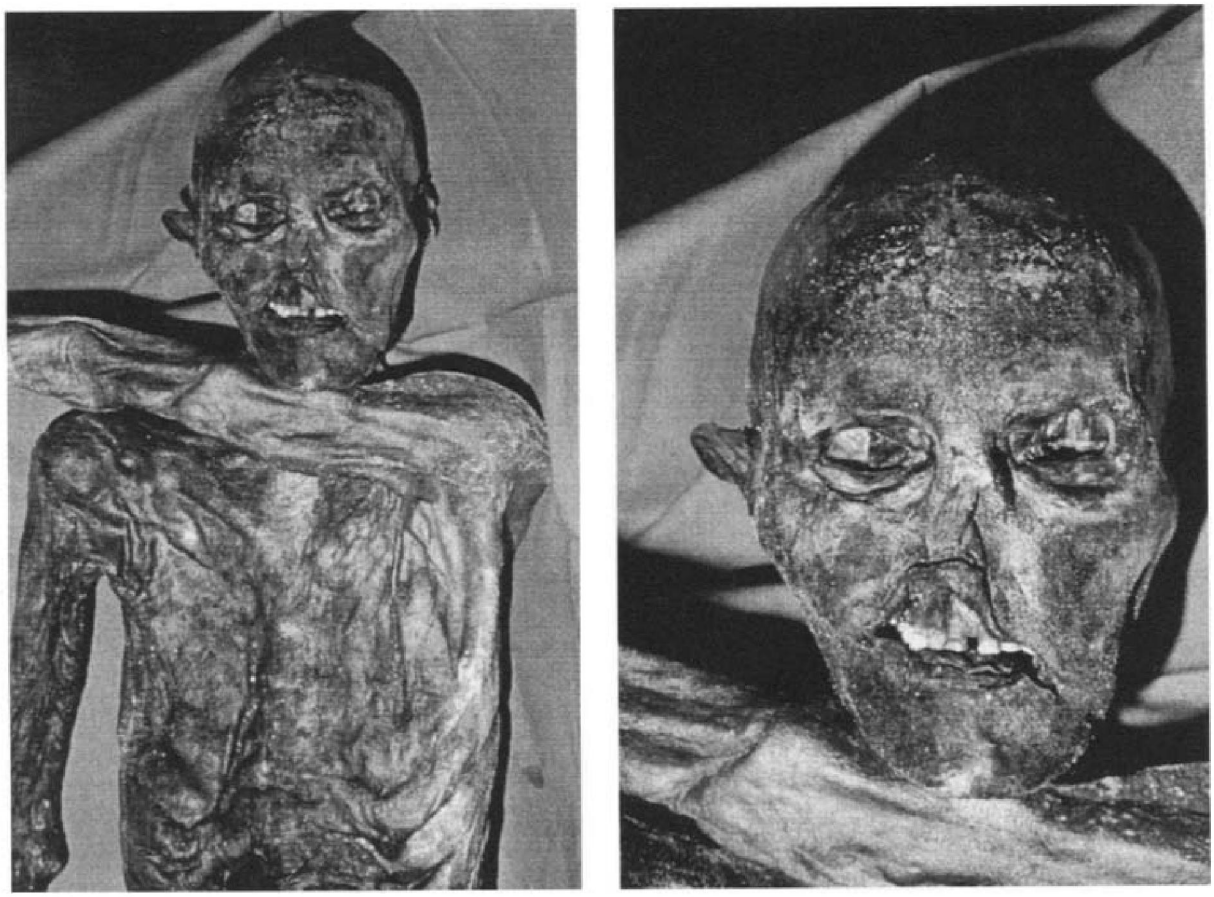

Figure 10. The mummified corpse discovered in 1991. (photo: Marco Samadelli; © South Tyrol Museum of Archaeology, Bozen, Italy)

8. AMS IN HISTORY AND ART

8.1. The Shroud of Turin

The shroud of Turin (Figure 1), held in a church in Turin (Italy), is an object of devotion for many Catholics. The image of a crucified man appears on the textile, considered by the believers to be the burial cloth of Jesus Christ. In 1988, a 10 mm by 70 mm strip of linen was cut, divided in three postage stamp-size samples and distributed to the AMS laboratories in Zurich, Oxford and the University of Arizona in Tucson. The results from the three laboratories agreed on a medieval date, 1290 – 1360 AD, at 90% confidence (Damon *et al.*, 1989). This is close to 1353, the first appearance of the Shroud in historical records. The possibility that the AMS ^{14}C date does not reflect the true age of the Shroud is still being debated. A number of causes, including the 1500s fire and the effect of bacteria and microorganisms, have been considered to explain the younger age. The historical details on the AMS dating of the Shroud of Turin have been given by Gove (1996).

8.2. The Dead Sea Scrolls

The Dead Sea Scrolls are a collection of 1200 parchment and papyrus manuscripts found in 1947 in cave locations close to the Dead Sea. It is believed that they have been written by the Essenes, a religious group belonging to Judaism who lived in the Quman site until the occupation by the Romans in 68 AD. Several manuscripts were dated by means of the ^{14}C AMS technique (Bonani *et al.*, 1992; Jull *et al.*, 1995). The measured ages were in good agreement with the dates on the manuscripts (when present) and/or the ages derived by means of palaeographic estimates.

8.3. The Venafro chessmen

The Venafro chessmen, discovered in 1932 in the southern Italian necropolis of Venafro, are among the most controversial chess-related archaeological finds of this century. For more than 60 years, archaeologists have formulated a variety of hypotheses to explain how bone chess pieces of Arabic shape were discovered in a tomb of Roman age. Some scholars claimed that the chessmen were indeed of Roman origin. The chess pieces are preserved in the Archaeological museum of Naples, where a bone fragment of 2 grams was collected for AMS analysis. Radiocarbon measurements carried out at the ANTARES AMS Centre yielded a calibrated age of 885-1017 AD (68 % confidence level) (Terrasi *et al.*, 1994), supporting the view that this game was introduced to Central Italy during the Saracen invasions of the 10th century AD.

8.4. Charlemagne's crown

The Iron Crown (see Figure 11) of the first Holy Roman Emperor, Charlemagne, is held in the Cathedral at Monza, near Milan in Italy. The origin and age of the crown, later used to crown Napoleon Bonaparte, are uncertain. Historical records place its origin between the Roman and Middle Ages, a spread of several centuries. In 1996, it was discovered that the precious stones were held in place by a mixture of clay and beeswax, which provided enough carbon for AMS radiocarbon dating. The analysis performed at ANTARES yielded an age between 700 and 780 AD (Milazzo *et al.*, 1997), consistent with the historical date for the crowning of Charlemagne, 800 AD, on Christmas Night.

8.5. Donatello's glue

The Annunciazione Cavalcanti (Cathedral of Santa Croce, Florence) is one of the best known creations of the Italian sculptor Donatello (1386-1466 AD). The sculpture is decorated with a group of terra-cotta cherubs. The base of one of these Figures has large cracks that had been subsequently repaired with a resin glue. It is not known when the accident occurred. The ANSTO results for the glue, 1331-1429 AD (68 % confidence level), proved that the restoration had been performed during the lifetime of the artist. The breakage and repair may therefore have happened when the work of art was created. Italian scholars believe that the cherub cracked because it was not hollowed out before firing and that the repair was carried out by Donatello himself, after damaging the statue in the kiln.

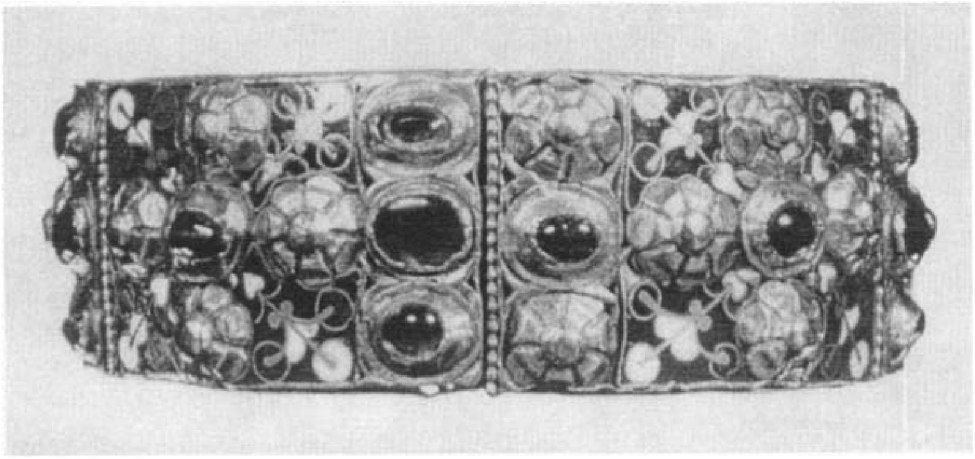

Figure 11. Charlemange's Crown.

8.6. The conquest of Peru

The manuscripts "*Historia et Rudimenta Linguae Piruanorum*" and "*Exsul Immeritus Blas Valera populo suo*", which were found in the family papers of Neapolitan historian Clara Miccinelli, are commonly known as the "Miccinelli documents". They discuss events and people associated with the Spanish conquest of Peru (see Figure 12).

As well as containing details about reading literary *quipus* (documents which were written using a combination of textile ideograms and knots) "*Historia et Rudimenta Linguae Piruanorum*" (History and Rudiments of the Language of the Peruvians; Laurencich Minelli *et al.*, 1995) makes the incredible claims that Pizarro conquered the region after having Inca generals poisoned with arsenic-tainted wine and then condemned the Inca emperor, Atahuallpa, to death instead of granting him an audience with the King of Spain. The account departs markedly from the long-held version of the event - that Atahuallpa was put to death for ordering the execution of his brother and rival. Furthermore, the manuscript suggests that the chronicler Guamán Poma de Ayala (1538?-1620?), author of one of the most important works on Inca Peru, the "*Nueva*

Corónica y Buen Gobierno" (New Chronicle and Good Government) written sometimes before 1618, merely lent his name to a work actually written by the Jesuit priest Blas Valera.

Fig. 12. Pizarro on his way to Peru, as portrayed in one of the scenes of a painted panorama in the frieze of the Rotunda of the U.S. Capitol Building (Washington DC).

Valera is also believed to be the author of the manuscript "*Exsul Immeritus Blas Valera populo suo*", an account of his own actions. According to this document dated May 10, 1618, Valera was forced to fake his own death in 1597 and, under a false name, was able to live in Peru between 1599 and 1618 and write the "*Nueva Corónica y Buen Gobierno*". Attached to "*Exsul Immeritus Blas Valera populo suo*" there were:

1. a letter from Francisco de Chaves (Laurencich Minelli *et al.*, 1998), a *conquistador* and chronicler on Pizarro's expedition; (the letter, dated August 5, 1533, was addressed to Charles V, King of Spain, and is the source of the accusations already suggested in "*Historia et Rudimenta Linguae Piruanorum*" and "*Exsul Immeritus Blas Valera populo suo*");
2. a wax box containing a fragment of a letter from Columbus and the contract between Guamán Poma de Ayala and Blas Valera; (under the agreement, Ayala lent his name to Valera after payment of a horse and a chariot);
3. a few literary *quipus*.

The historical significance of the discovered material is immense and historians considered it to be of primary importance to verify the authenticity. As a part of a worldwide research collaboration ANSTO performed the radiocarbon dating of five samples associated with the Miccinelli documents (Zoppi *et al.*, 1999). The results showed that, with a high degree of confidence, the wax used to seal the letter to the King of Spain originated earlier than 1533 (see Figure 13), the date on the letter. Similarly, the wax used for the box containing the

agreement allowing Valera to write "*Nueva Corónica y Buen Gobierno*" under a false name, most probably originated before 1618, the accepted completion date of this document.

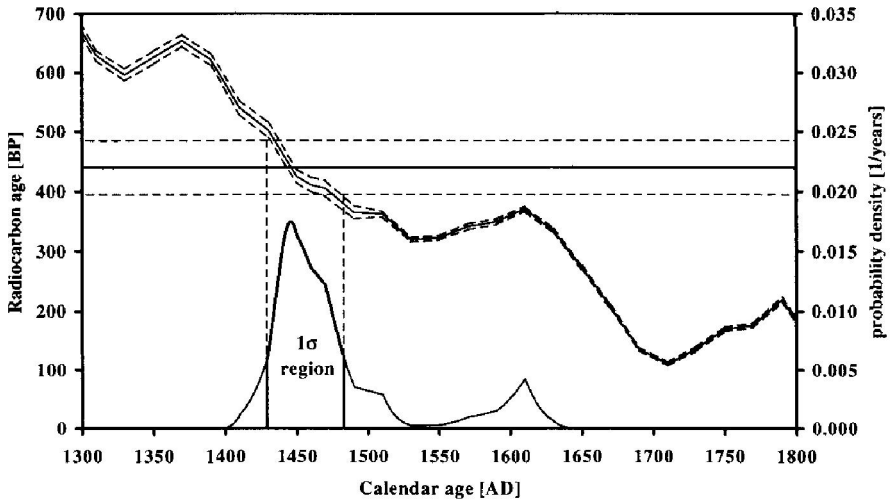

Fig. 13. The calibration of the wax sample from the seal of the letter to the King of Spain.

9. DATING WITH THE BOMB PULSE

Atmospheric nuclear weapons tests during the 1950s and early 1960s produced a rapid increase in ^{14}C. In the northern hemisphere, the 1963-1964 ^{14}C concentration reached a level nearly 100% higher than the pre-bomb level (see Figure 14). Since the Nuclear Test Ban Treaty came into effect in 1963, the atmospheric ^{14}C concentration has been decreasing due to exchange with the biosphere and the oceans (with minor perturbations due to sporadic nuclear tests). Presently, the ^{14}C level has declined to about 110 percent of the pre-bomb level. The shape and intensity of this *bomb pulse* has been determined by measuring ^{14}C in atmospheric CO_2 (Levin *et al.*, 1994; Manning and Melhuish, 1994) tree rings (Hua *et al.*, 1999a&b) and ice cores (Levchenko *et al.*, 1997). The decrease of atmospheric ^{14}C is presently about 80 times faster than radioactive decay.

This well determined temporal change of ^{14}C provides a clock for dating biological materials formed since 1955 AD, and leads to interest in forensic applications. For example, it was shown that it is possible to determine the time of death of humans by using the lipid fraction of bones, which is the most suitable component for dating purposes, thanks to its fast turnover (Wild *et al.*, 1998).

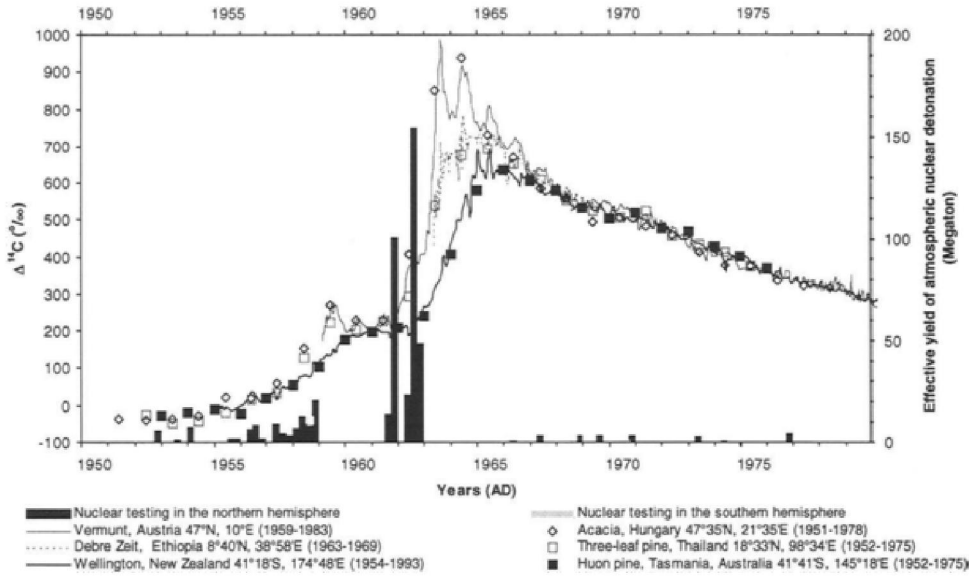

Fig. 14. ^{14}C in tree rings (points) vs atmospheric radiocarbon records (lines) at similar latitudes. Bars represent the magnitude of atmospheric nuclear detonation for 3 month periods. For a review of radiocarbon data from atmospheric and tree-ring samples for the period 1945-1997 AD see Hua *et al.* (1999a&b).

10. CONCLUSIONS

AMS ^{14}C dating is having a tremendous impact on studies in prehistory thanks to a 1000-fold reduction in sample size. Accurate dating is possible by extracting only the most reliable fraction or by minimising sample contamination. Presently, the age limit is around 45,000 - 50,000 BP, with potential for an extension to 60,000 BP. AMS ^{14}C can play an important role in the verification of other dating techniques, such as optically stimulated luminescence and U-series dating, which allow a further extension of the datable time span. Alternative AMS radionuclides with longer half-lives have been considered for archaeological dating but ^{14}C remains a unique chronometer to reconstruct the sequence of prehistoric events.

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