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SAYING SO DOESN'T MAKE IT SO

PAPERS IN HONOUR OF B. FOSS LEACH

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Dating New Zealand Bone By Electron Spin Resonance

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There has been much discussion on dates of Polynesian settlement of New Zealand. An 83-person poll taken at the New Zealand Archaeological Association conference during May 1988 showed a definite split between those who thought that first settlement had occurred around A.D. 800 and those who thought that it took place around A.D. 1000 (Walton 1988: 79). That difference notwithstanding, the poll results indicated that 83% thought that New Zealand had been settled after about A.D. 700, while only 17% suggested earlier dates. A literature search for earlier dates revealed two samples, R2054/1 and R2233/3 from Oturehua Quarry dated to the eighth millennium B.C. (Leach 1969: 52); a date of 1320 ± 200 B.C.; from Poukawa, Hawkes Bay (Pullar 1965: 11); and one of 1525 B.C. from Timpendean moa bone site, which McCulloch and Trotter (1975: 7) dropped from their series since it lay outside the range of their other dates. All these dates were obtained by the radiocarbon method "generally considered to be the final answer for dating" (McFadgen 1982: 379). A different technique, obsidian hydration shell measurement by the tritium exchange method, yielded hydration ages of 1600 years ago for a flake from N57/2 (Kauri Point), and 1400 years ago for one from N65/18 (Ngaroto Swamp Pa) (Lowe *et al.* 1984).

This seems a large number of dates to be simply considered as aberrations. So one must ask, how reliable are any dates obtained? For radiocarbon dating, McFadgen (1982: 379) states that counting errors for more than 70% of New Zealand dates are greater than 50 years and that any two dates cannot distinguish with certainty events closer in time than 140 years. Law (1984) goes further, to say that charcoal and collagen ages of less than 450 years B.P. are useless.

Because of New Zealand's short prehistory as accepted at present, errors are proportionately large, and errors and corrections limit the effectiveness of radiocarbon dates.

A rather more serious problem in the dating of human bone is the destruction of a valuable sample in the interests of obtaining a date which may or may not be accurate. For example, to obtain the minimum 6 g of pure carbon required for conventional radiocarbon dating, 240 g of bone, virtually an entire human femur, would be sacrificed. This technique is destructive and therefore wasteful. A large bone is subject to a greater potential level of contamination; variations in temperature and atmospheric ^{14}C levels over the years are often not detectable; and logistics and expense make the technique unfavourable.

Reduction of sample size has been an important objective of research. Indeed, in radiocarbon dating by the proportional gas counter method, "the New Zealand laboratory was one of the pioneers" (Golson 1955: 130). Further refinement is offered by the tandem, particle accelerator mass spectrometer (TAMS) where 5–20 mg of carbon with ages of up to 60,000 years may be dated in a few hours (Lowe *et al.* 1983), compared with up to 35 hours counting time required by conventional counters. However, no matter what the level of sophistication attained, the system is defeated if there is a long turn-around time at the dating laboratory.

For dating bone, what is needed is a technique that requires a small amount of bone, is non-destructive, reproducible, rapid, accurate, simple to carry out and of low cost.

Electron spin resonance spectroscopy (ESR to the chemists, or electron paramagnetic spectroscopy (EPR) to the solid state physicists) had not been studied as a dating method for New Zealand bone. The principle of this form of spectroscopy is the detection of lattice defects occurring in mineral crystals in the sample material; the number of defects is proportional to the age of the sample. These defects are believed to be the result of radiation damage caused by naturally-occurring isotopes within, or in close proximity to, the material being studied (Ikeya 1986: 59). Therefore, the greater the number of defects, the greater the total dose of natural radiation that the sample has received since interment and the greater the age of the sample. The procedure can be carried out at room temperature and repeated without destroying what is being measured.

A detailed paper by Whitehead *et al.* (1986) has evaluated the use of the technique on Pacific island teeth, with encouraging results. Generally, however, there are many deficiencies in the ESR dating literature, a major one being the lack of description of the methodology used. This paper describes the development of a methodology.

In passing through matter, nuclear radiation gives rise to ionisation, the detachment of electrons from their parent atoms. The amount of ionisation depends on the chemical constitution of the sample and on the type of radiation. An alpha (α) particle per unit track produces 100 times the ionisation of a beta (β) particle and 10,000 times that of a gamma (γ) ray. However, the most energetic α particle has a range of 45 µm in clay soil, while a β particle can travel up to 1 mm, compared to the 40 cm penetration of a γ ray. Most of the electrons recombine with their parent atoms, but some are trapped at defects in the crystal lattice structure. The paramagnetic unpaired electron can be detected directly by microwave spectroscopy.

A single unpaired electron placed in a magnetic field has a spin, whose axis may line up either parallel or anti-parallel to the magnetic field. In the anti-parallel alignment the energy state is lower than in the parallel alignment. Hence if energy could be absorbed, the spin axis may flip from anti-parallel to parallel. This may occur when a resonance balance is attained between the frequency of microwave power delivered and the strength of the magnetic field.

The sample is placed in an EPR spectrometer (Figure 1), into a microwave cavity between the poles of a magnet. Microwave power of a very precise and constant frequency is delivered to the cavity. When the changing magnetic field strength reaches a value which satisfies the resonance condition, a change in the microwave power level, due to energy absorption by the paramagnetic sample flipping from anti-parallel to parallel alignment, causes a recordable change in the crystal current. Increased sensitivity is obtained by modulating the slowly varying magnetic field. The signal seen on the monitor of the Apple IIe 64 K microcomputer in Figure 1 is therefore a first derivative of the absorption line. The

peak-to-peak amplitude (A_{pp}) of the signal depends on the level of energy absorption, which depends on the number of unpaired electrons which have flipped to the higher energy alignment, which is determined by the level of radiation damage sustained by the sample, which finally is determined by the time elapsed since interment.

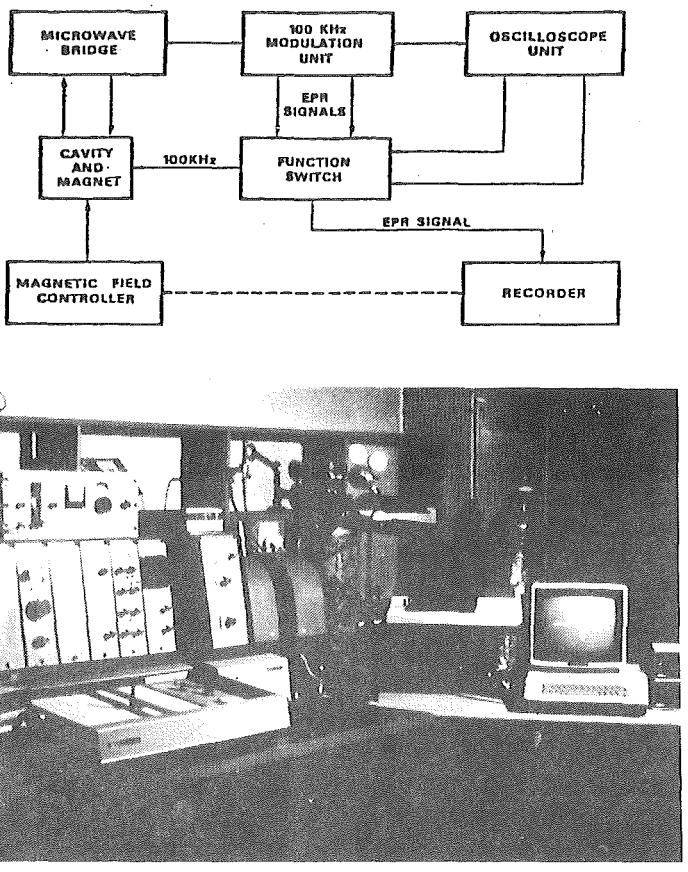


Figure 1: The E-104 EPR Spectrometer. Block diagram (above); photographed with an Apple IIe microcomputer, for interfacing (below).

The administration of additive, artificial irradiation linearly increases the A_{pp} (Figure 2). Extrapolation of the curve to zero gives the archaeological radiation dose which the sample has received. When this value is divided by the 'annual dose rate', the number of years of burial may be found.

To reach this goal, four different aspects have to be considered: the nature of the material being sampled and the way in which it is presented for measurement; operational procedures of the EPR spectrometer; the nature of the radiation and its associated problems; and the determination of the natural, annual dose rate.

Bone is a non-uniform material—76.04% being inorganic and consisting of pseudo-hexagonal crystals similar in x-ray diffraction pattern to the mineral hydroxyapatite (although various anions and cations can be associated with the lattice). Of the 23.96%

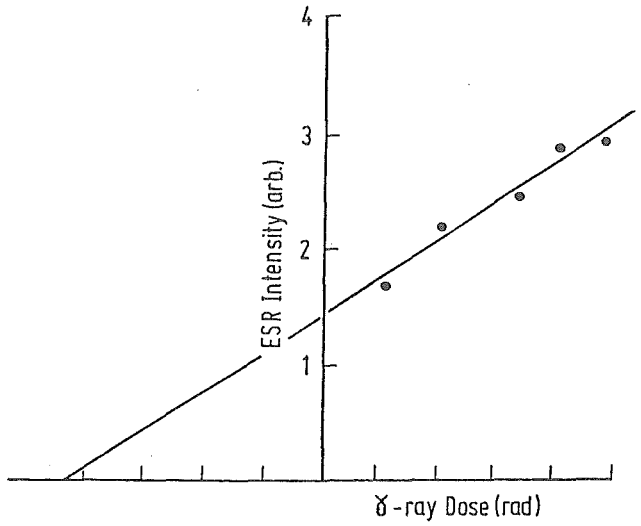


Figure 2: Linear enhancement of A_{pp} by artificial irradiation; and extrapolation.

organic fraction, 88% consists of collagen in fibrils. Since both organic and inorganic components are capable of giving ESR signals, both need to be isolated and studied.

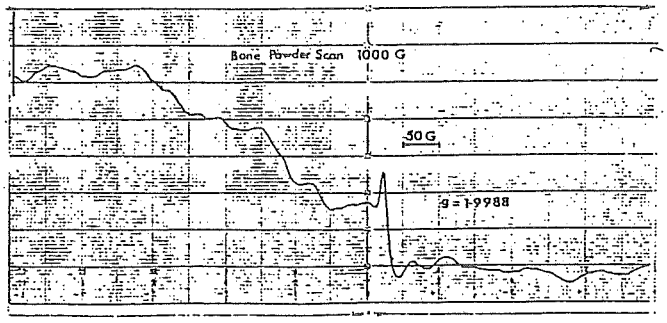
Initially bone slivers, sandpapered to remove the outer 3 mm (thereby removing the effects of α and β radiation) and chiselled to an appropriate size to fit the EPR spectrometer cavity, were used. However it was found that orientation of the sliver within the cavity was critical, the hydroxyapatite crystals causing as much as 4.5% variation in ESR spectral amplitude. Bone powder capable of passing through a 75 µm sieve was used in 200 mg samples, after grinding. Grinding itself produced an ESR signal, both from crystal breakdown and from heat induced by the process. This problem was overcome by grinding under liquid nitrogen and then leaving the powder for several days before processing it further. Finally, to ensure constant density of sample (the more sample in a given volume, the greater the number of defect centres, hence the greater the spectral A_{pp}), cylinders of powder 7.6 mm long by 5.8 mm diameter, were pressed.

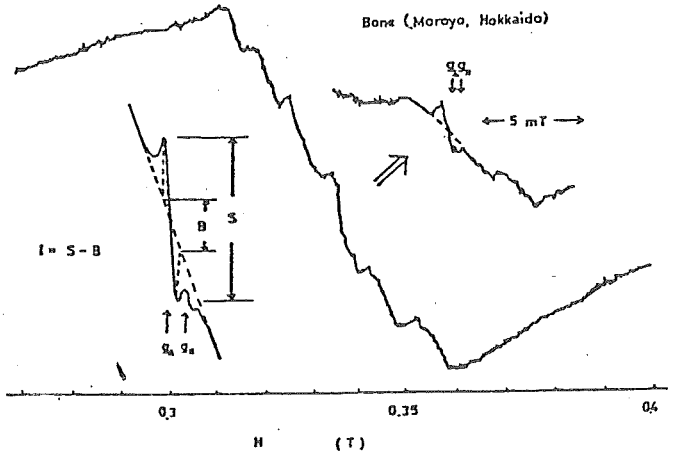
Initially, all sample spectral A_{pp} were normalised against that of the EPR Strong Pitch standard, since variations in ambient temperature and humidity can affect the sample spectral A_{pp}. In order to reduce the error incurred by exchanging samples in the spectrometer cavity, a ruby crystal standard was later imbedded in the sample container base and scanned together with the sample.

Much time was spent in determining the optimal operating parameters for scanning bone in the EPR spectrometer, and then further refinement of computer program ESRI/O, used to record and analyse the spectral data on an Apple IIe 64 K microcomputer (Figure 1), allowed the data to be passed to a VAX computer where more powerful operations were performed.

All New Zealand samples showed a hugh background iron signal (Figure 3), a situation also found by Ikeya (1986: 106). One approach to resolution of this problem was to make trial and error serial dilutions of ferric chloride solutions containing equal amounts of calcium hydroxide and calcium phosphate and scan these until one was found which gave a

spectrum similar to the natural bone spectrum. This spectrum could then be subtracted from the natural spectrum to produce a 'pure' bone spectrum.





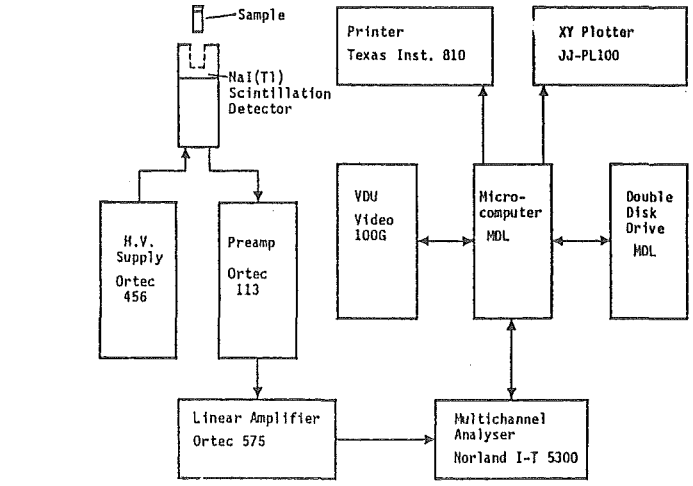
ESR Spectrum of a Bone Approximately 1,000 Years Old from Moroyo, Hokkaido. The contribution from the broad line (B) must be subtracted from the signal height (S), as is shown in the inserted figure

Figure 3: ESR spectrum showing the influence of iron (above); Ikeya's (1986: 106) solution (below).

This part of the study has concentrated on the production of reproducible, 'purified' ESR signals from homogeneous bone samples of constant density.

Powdered surface-lying sheep tibiae from Wairau Bar (New Zealand Archaeological Association Site number S29/7) and a human rib buried in Waihora site (Site number C240/283) on Chatham Island were packed into scintillation vials and placed in the well of a gamma-ray spectrometer where they were counted via a sodium iodide crystal on a multi-channel analyzer, the resulting spectra being dumped to disk storage through an MDL microcomputer linkage (Figure 4), transferred to a VAX computer where programme GAMSOFT calculated the ^{238}U, ^{232}Th and ^{40}K concentrations. Results showed that the levels

of these radionuclides were negligible. Therefore, internal radiation in bone is effectively zero. Hence the total dose received by the sample is contributed by the external dose, from the immediate burial environment plus cosmic radiation.



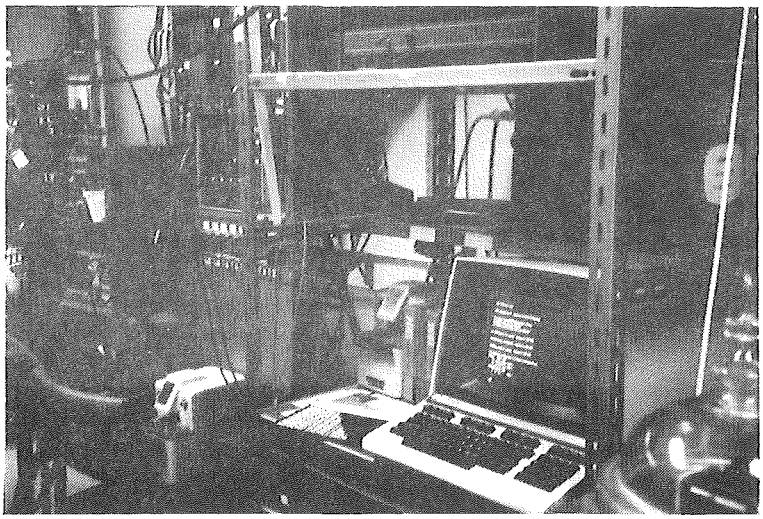


Figure 4: Block diagram of the gamma-ray spectrometer (above); photograph of the same (below).

Thirty-five gram soil samples from Wairau Bar and several other New Zealand sites, as well as Thailand and several Pacific Island sites were processed in a similar manner to the bone samples. The variation in radionuclide concentrations in various soil types was quite marked. Independent analysis of the uranium and thorium contents of some of the samples by neutron activation analysis at Lucas Heights, Australia (Walls, pers. comm.) corroborated the gamma-ray spectroscopy results.

In conjunction with this aspect of the study, thermoluminescence dosimeters were placed in undisturbed soil adjacent to where the soil samples were taken at Wairau Bar. Eight

months later these were removed and counted at the National Radiation Laboratory, Christchurch (Randle, pers. comm.) From these results an annual dose rate for soil was calculated. The value of 950 mrads/year for a typical Wairau Bar soil sample was in good agreement with the approximate 1 rad/year for bone at an open sandy site reported by Ikeya and Miki (1980: 978) and reiterated by Mascarenhas *et al.* (1982: 415). This value was placed into program GAMSOFT to convert the radionuclide concentrations directly to a dose rate. The greater part of this dose rate is contributed by α and β particles. With the outer 3 mm of bone sample removed, only the γ component need be considered. Therefore the dose rate received by a bone sample would be of the order of 98 mrads/year.

The final step in the methodology was the irradiation of samples. As we were dealing with such small dose rates, the use of a commercial ^{60}Co Theratron unit, capable of delivering 300 rads of γ radiation per minute, would lead to too great an error in the level of dose administered.

A ^{137}Cs source capable of delivering 38 rads/hour was housed within a cannibalised beta scintillation counter, surrounded by 5.5 cm thick lead shielding. An electric motor brought the source into position to irradiate bone pellet samples attached to the chamber doors. The irradiated samples were then scanned by the EPR spectrometer.

Initially, no change in ESR signal A_{pp} was observed, even after 1972 rads had been delivered to the sample. It was realised that with relatively recent bone, still containing organic material, organic decomposition was producing an ESR signal. This was confirmed by the use of a perylene radical cation as an ESR calibration standard. Therefore, the radiation damage signal was being swamped and masked.

At this point, program FIT was acquired from the Physics and Engineering Laboratory, DSIR (Devine, pers. comm.). The program fitted a first derivative curve by iteration to the natural ESR spectrum. The fitted curve was then subtracted by program SUBTRACT, and the area beneath the pure radiation damage spectrum was measured. Thus in one move both the iron background ESR signal and the organic decomposition signal had been stripped away to expose, for the first time in archaeologically recent bone, the radiation damage ESR signal.

Figure 5 shows a typical graph of area beneath the radiation damage spectrum plotted against administered radiation dose. The growth in area is non-linear and shows a tendency towards saturation. However, there appears to be some indication of a general increase in area with radiation dose.

In contrast to overseas sites, in New Zealand we are dealing with archaeologically recent bone, still containing a decomposing organic component which gives rise to an ESR signal. This signal has been removed. New Zealand bone contains intrusive iron, giving rise to a huge ESR signal. This signal has been removed. We now have a 'pure' radiation damage ESR signal to work with. We have not yet obtained any dates. There is still much refinement of technique to be carried out before the curve can be extrapolated to the baseline (Figure 2) and divided by the dose rate to achieve a date. But at this point the approach looks promising.

ACKNOWLEDGEMENTS

I would like to pay tribute to Foss, for his skills in the radiation aspect of this study, for the provision of so much computer software, his boundless enthusiasm, his friendship and his encouragement when progress was difficult.

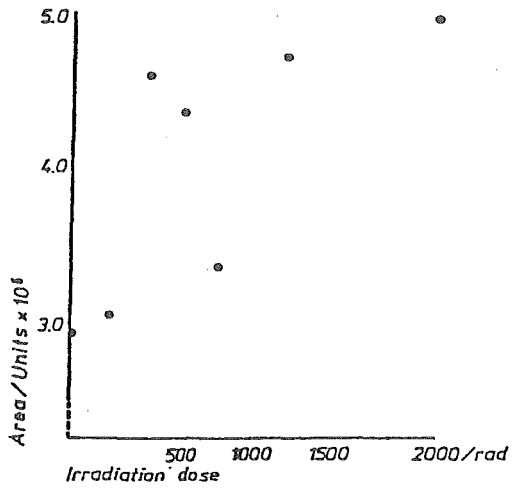


Figure 5: Graph of area beneath the residual spectrum after subtraction, plotted against the artificial radiation received.

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