

AMS DATING OF A LATE QUATERNARY TEPHRA AT GRAHAM'S TERRACE, NEW ZEALAND

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ABSTRACT. The radiocarbon dating of volcanic ash (tephra) deposits in New Zealand has been difficult on sites remote from the eruption, which contain either little carbon or degraded and contaminated charcoal. Although many studies of contamination removal from macroscopic charcoals from tephra sequences have been made, little attention has been paid to those containing no visible charcoal, because of the difficulty of obtaining sufficient carbon for radiometric dating. We report here experiments using accelerator mass spectrometry to establish a reliable method for dating a low-carbon aeolian and peat deposit containing a tephra horizon. Results so far demonstrate that improvements to existing chemical pretreatment methods are possible, and that dates obtained on oxidized fine-grained residues can approach the maximum age determined on good quality charred wood samples.

INTRODUCTION

The Graham's Terrace tephra site is about 9.5 km southeast of Nelson Creek township in the Grey River valley on the South Island of New Zealand (Grid Reference NZMS 260 K32/928588). Mew *et al.* (1986) described the site, and carried out extensive chemical and sedimentological analyses, concluding that the tephra is identical to a widely distributed volcanic ash deposit, variously called Kawakawa, Oruanui, Wairakei or Aokautere. The pooled mean age of four radiocarbon determinations, Q-2665 to -2668, made on carbonized wood fragments, found embedded in non-welded ignimbrite from a major eruption at Taupo in central North Island, New Zealand, is $22,590 \pm 230$ BP. Other dates on materials associated with the same eruption, at both North and South Island sites, range from $20,550 \pm 300$ to $21,300 \pm 460$ BP (Wilson, Switsur & Ward 1988). Acid-washed fine sandy loam from below the tephra layer at the Graham's Terrace site in north western South Island gave an age of $15,600 \pm 250$ BP (NZ-6557, Mew *et al.* 1986). This discrepancy in ages for the supposedly same event gave initial impetus to the work reported here.

Previous work on macroscopic charcoal from Quaternary deposits in New Zealand have demonstrated that contamination by younger organic carbon is common and difficult to remove completely. Bailey and Lee (1972) and Bailey *et al.* (1975) used extraction with 0.5 mol sodium hydroxide, and concluded that the humic-acid fractions in their samples were not age-affecting contaminants, whereas Goh and Molloy (1972) demonstrated that extraction with alkali/pyrophosphate was an effective pretreatment for charcoals. When using soil organic components for dating, in contrast to buried charcoals, Goh and Pullar (1977) showed that alkali/pyrophosphate extraction was not as effective as hydrolysis with either 6 mol HCl or 72% sulfuric acid, and that solvent extraction also gave an increase in age. Goh, Molloy and Rafter (1977) found that the clay-humus fraction physically sorted from loess deposits was younger than charcoal from the same deposit. Goh (1978) and Hammond *et al.* (1991) concluded that 70% nitric acid hydrolysis was the most effective treatment when soil organic components were used for dating, though in some soils, the amounts of carbon left for dating may be insufficient for conventional radiometric dating. According to Goh (1991), chemical pretreatments used for buried charcoals should be different from those used for soil organic components, because of the different nature of contamination in

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these materials. With the availability of accelerator mass spectrometry (AMS) technology, and the consequent small-sample capability allowing substantially improved chemical pretreatment, we approached the problem by dating all fractions from many different chemical extractions.

SAMPLE PRETREATMENT

All samples contained 4.5–5.5% organic carbon when analyzed by a chromate oxidation method (Schollenberger 1945). Before chemical pretreatment, samples of *ca.* 200 g were wet-sieved through a 63- μ m screen, and 10–20 g subsamples of the fine fraction were used for further work. In all cases, more than 95% by weight passed the 63- μ m screen. For the tephra layer itself, some fibrous material was retained on the sieve, and this was processed by standard methods for cellulose preparation (5% NaClO₂ in pH3 HCl at 90°C). For the remaining fine-grained samples, two sets of pretreatment methodologies, and the data resulting from these, are described here – one set was carried out by A. P. Hammond and K. M. Goh at Lincoln University, the other set carried out by Richard Gillespie at the Australian National University (ANU).

The Lincoln University techniques follow more-or-less standard practices presently employed in New Zealand and elsewhere, for the radiocarbon dating of soils and sedimentary charcoals (Goh 1991). These methods employ dilute acid and alkali extractions, often called the acid/base/acid sequence, to remove fulvic- and humic-acid contaminants. This involves extraction of humic material with an alkaline solution containing 0.1 mol sodium hydroxide and tetrasodium pyrophosphate, with subsequent precipitation of the humic-acid component using concentrated hydrochloric acid. The fulvic acid remains in solution and may be recovered by evaporation or dialysis. Also used were strong acid treatments, such as 6 mol hydrochloric acid hydrolysis (Scharpenseel 1979), and 70% nitric-acid hydrolysis (Shultz 1962). A graded-strength organic solvent extraction sequence, using acetone, petroleum spirit, ethanol/benzene and methanol/chloroform under reflux conditions (Hance & Anderson 1963), and the simpler technique of ultrasonic agitation in chloroform (Fowler, Gillespie & Hedges 1986), were used for lipid extractions. We also used a pollen analysis preparation (N. Moar, personal communication 1988) with the sequence:

1. Boiling 10% KOH solution
2. Wet sieving
3. Boiling 10% HCl
4. Digestion in hot 40% HF
5. Hypochlorite bleach
6. Acetolysis with hot concentrate H₂SO₄/acetic anhydride.

At ANU, we explored techniques borrowed from those used to prepare samples for pollen analysis and fire history in Australia (Gray 1965; Clark 1983; Singh & Geissler 1985). These chemical procedures are designed to remove most inorganic and organic materials except pollen and fine charcoal from fine-grained sediments. After some preliminary trials with samples from other sites (Gillespie *et al.* 1991), we developed the following pretreatment sequence:

1. Wet seive to pass 63 μ m, acidify with HCl to ~pH1, centrifuge and wash
2. Extraction with alkali (either hot 10% KOH or cold 0.1 mol NaOH/Na₄P₂O₇)
3. Digestion with hot 40% HF
4. Oxidation with 10% KClO₃ in 35% HNO₃ (dilute Shultze solution (Gray 1965))
5. Extraction with cold 5% ammonia solution
6. Reacidification with HCl.

All operations after the initial sieving are carried out in the same 50-ml polypropylene centrifuge tube to minimize contamination introduced in the laboratory (Gillespie & Hedges 1984), and to allow the use of the hot hydrofluoric acid solution. The alkali solutions remove dark humic materials; several extractions are usually needed, and long centrifuge times are sometimes necessary to spin down all of the fine sediment. One improvement to this scheme might be to perform the hydrofluoric acid digestion before the alkali extraction, since destruction of clay minerals and clay-organic complexes makes the alkali treatment more effective, and centrifugation is faster with the clays removed. Silicates are destroyed in the HF digestion stage, the most significant loss occurring during the first hour of heating in a boiling water bath. Caution is necessary for this step, because some samples react very violently – slow addition of HF, gentle stirring and a resting period to allow any initial reaction to subside should precede heating. For sediments containing calcium or aluminum, it is advantageous to add 10% hydrochloric acid to the hydrofluoric acid solution to avoid precipitation of insoluble fluorides. Oxidation with dilute Schultze solution may also be quite vigorous, requiring similar caution, and no heating is normally required. This oxidation reagent is stronger than the hypochlorite bleach used for the New Zealand sequence above, but does not oxidize pollen. The Schultze oxidation releases more dark humic material; this can be extracted with any alkaline solution, the 5% ammonia solution used here is effective, simple to prepare and volatile.

Pretreated samples were combusted in evacuated and sealed quartz tubes with copper II oxide and silver wire. The purified CO₂ was then converted to graphite, following a method developed by Lowe and Judd (1987). Sample CO₂ is introduced with hydrogen into a quartz reaction vessel containing finely divided iron powder. At 700°C, the CO₂ is reduced to graphite, which is deposited on the iron catalyst. This mixture is pressed into a copper target holder for insertion into the AMS system. All graphite targets were measured in the Nuclear Sciences Group (INS) AMS facility in the same way (Wallace *et al.* 1987). The sample ¹⁴C count rates, normalized to the ¹³C currents, were compared with the normalized count rate from a target prepared from the NBS oxalic acid modern standard. Measurement of each sample target was broken into three runs of 10 min each, with the standard counted at the beginning, middle and end of each sequence. Any drift in the system could be detected and compensated for, during this procedure. Experimental errors assigned to the results are based on counting statistics, with an extra term to account for any non-statistical scatter indicated by applying a chi-square test to the measured values.

In calculating the ¹⁴C ages of the samples, the ¹⁴C count rates were corrected for the different natural carbon isotopic abundances in samples and standard (using δ¹³C values from separate measurements on the same CO₂ used to prepare the graphite target), and then normalized to δ¹³C = -25‰ for samples, and δ¹³C = -19‰ for the modern standard. Dates reported are conventional ¹⁴C ages, as defined by Stuiver and Polach (1977), based on the Libby half-life of 5568 years.

RESULTS AND DISCUSSION

Taking the series of chemically separated fractions, processed at Lincoln University, from Profiles 5 and 7 (Table 1), all acid-soluble preparations yield ages younger than that of an untreated sample (12.57 ± 0.37 ka BP, NZA-262). The fraction insoluble in 6 mol HCl is the same age as the untreated sample, indicating that there is little protein or other easily hydrolyzed organic component in the sediment. The fraction soluble in organic solvents (NZA-239) is older than the untreated sample, but still considerably younger than 22.6 ka, the presumed age of the tephra deposition. In this series, the oldest dates are obtained on the residue after hydrolysis/oxidation with 70% nitric acid, which has previously been an effective pretreatment for soil organic matter in peats (Goh 1978). Hammond *et al.* (1991) have discussed the significance of the other dates in this series.

TABLE 1. AMS Dates From Graham's Terrace, Profiles 5 and 7*

Lab no.	Location	Fraction dated	$\delta^{13}\text{C}$	Age BP
NZA-264	P5, 0–5 cm below tephra	0.1 mol HCl/0.3 mol HF soluble		5975 \pm 250
NZA-258	P5, 0–5 cm below tephra	Fulvic acid, extracted with 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$		7770 \pm 265
NZA-256	P5, 0–5 cm below tephra	6 mol HCl soluble	-27.1	8710 \pm 300
NZA-287	P5, 0–5 cm below tephra	70% HNO_3 soluble	-26.5	12,080 \pm 345
NZA-271	P5, 0–5 cm below tephra	Residue after 6 mol HCl	-28.5	12,525 \pm 170
NZA-262	P5, 0–5 cm below tephra	Untreated		12,565 \pm 365
NZA-327	P7, 0–5 cm above tephra	Residue after hot 1 mol HCl, 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$	-28.6	14,410 \pm 215
NZA-239	P5, 0–5 cm below tephra	Lipids, extracted with the solvent sequence: acetone, petroleum spirit ethanol/benzene, methanol/chloroform		15,205 \pm 240
NZA-335	P5, 0–5 cm below tephra	NZ pollen preparation (see text)	-28.3	15,240 \pm 510
NZA-325	P7, 0–5 cm below tephra	Residue after hot 1 mol HCl, 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$	-28.5	15,490 \pm 250
NZA-371	P5, 0–5 cm above tephra	Residue after 70% HNO_3	-26.7	15,540 \pm 240
NZA-909	P5, 0–5 cm above tephra	Repeat of NZA-371 after second treatment with 70% HNO_3	-29.7	16,740 \pm 230
NZA-270	P5, 0–5 cm below tephra	Residue after 0.1 mol HCl/0.3 mol HF, 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$	-28.7	17,515 \pm 460
NZA-263	P5, 0–5 cm below tephra	Residue after 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$		17,900 \pm 335
NZA-293	P5, 0–5 cm below tephra	Residue after 70% HNO_3	-30.2	18,810 \pm 380
NZA-373	P7, 0–5 cm below tephra	Residue after 70% HNO_3	-28.8	19,170 \pm 480
NZA-372	P5, 50 cm below tephra	Residue after 70% HNO_3	-26.7	20,670 \pm 470

*Samples pretreated at Lincoln University, New Zealand, by Hammond and Goh.

For the samples processed at ANU from 5 cm above and below the tephra layer in Profile 4B (Table 2), we observe the same younger ages for acid- or alkali-soluble fractions, but the oldest fraction (NZA-323: 21 ka) is now the residue after the full sequence of alkali extraction, hydrofluoric-acid digestion, chlorate oxidation and a second alkali extraction. Investigations on other sites (Gillespie 1990; Gillespie *et al.* 1992) have shown that the second alkali extraction removes humic-type material solubilized by the oxidation treatment, and which is similar in age to the standard humic-acid fraction. Residues were examined microscopically and at 400 \times magnification. It is clear that hot 70% nitric acid destroys pollen and other non-charred botanical debris, whereas the 35% nitric acid/10% potassium chlorate solution, when used at room temperature, leaves most pollen intact. Neither oxidant destroys the fine-grained black material, although a significant amount of carbon is lost with both reagents. Samples over- or underlying the tephra, from Profiles 4B, 5 and 7, were treated with hot 70% nitric acid, followed by cold 6 mol nitric acid. Material soluble in this reagent gave 12,080 \pm 345 BP (NZA-287), an age almost identical to the untreated material. The insoluble fractions range in age from 15,540 \pm 240 to 19,635 \pm 330 BP (NZA-293, -329, -371, and -373). Goh (1991) has shown that this reagent gives maximum ages for buried soils and sediments, whereas the ages at this site are inconsistent. However, the maximum date overlaps with that from the full sequence (with chlorate oxidation) on the same material. The alkali extraction of humic acid is not carried out in the 70% nitric-acid treatment, which probably accounts for the younger, more variable ages on fractions insoluble in this reagent. For those with appropriate laboratory facilities, the full sequence of extractions has several attractions. The 70% nitric-acid treatment is simpler to perform and useful for fieldworkers.

We have a conceptual problem with this “black stuff” – we have not positively identified it as charcoal at Graham's Terrace, although it is convenient to think of it in this way. In some sedi-

TABLE 2. AMS Dates From Graham's Terrace Profile 4B*

Lab no.	Location	Fraction dated	$\delta^{13}\text{C}$	Age BP
NZA-248	Tephra layer	Cellulose, after $\text{NaClO}_2/\text{HCl}$ bleach of fibrous material sieved out	-27.2	10,485 \pm 810
NZA-238	0-5 cm above tephra	Humic acid, extracted with 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$		11,265 \pm 175
NZA-328	0-5 cm above tephra	Untreated	-28.2	11,870 \pm 120
NZA-232	Tephra layer	Humic acid, extracted with 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$		12,170 \pm 160
NZA-234	Tephra layer	Residue after hot 1 mol HCl, 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$	-28.3	12,685 \pm 210
NZA-241	Tephra layer	Residue after 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$, 40% HF, 35% HNO_3 /10% $\text{KClO}_3, \text{NH}_3$	-29.5	15,780 \pm 370
NZA-236	0-5 cm below tephra	Humic acid, extracted with 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$		16,025 \pm 210
NZA-329	0-5 cm above tephra	Residue after 70% HNO_3	-30.3	19,635 \pm 330
NZA-247	0-5 cm above tephra	Residue after 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$, 40% HF, 35% HNO_3 /10% $\text{KClO}_3, \text{NH}_3$	-28.5	20,240 \pm 450
NZA-323	0-5 cm below tephra	Residue after 0.1 mol NaOH/0.1 mol $\text{Na}_4\text{P}_2\text{O}_7$, 40% HF, 35% HNO_3 /10% $\text{KClO}_3, \text{NH}_3$	-28.9	21,010 \pm 395

*Samples pretreated at the Australian National University by Gillespie

ments, it is charcoal and has a similar size range to pollen (Clark 1983). For other sediments, such as the ones we used here, the black particles are smaller (generally $<10 \mu\text{m}$), and require further study to determine their origin and structure. However, both the pollen and the black particles probably arrive in the sediments by similar processes (notably wind or water deposition) at similar times, and the black particles are certainly very resistant to chemical attack.

We have not been able to obtain maximum dates for the tephra layer, itself, because it does not appear to contain the same quantity of residual fine charcoal as the peaty soils over- and underlying it. The tephra layer does, however, contain some probable root material and the same amount of soluble humic material as the peaty soils above and below it. Both of these fractions gave a falsely young age for the deposit.

Questions remain about the different approaches to dating tephra and other deposits with little carbon. Campbell (1986) obtained dates of 21,300 \pm 450 (NZA-7144) and 21,300 \pm 460 (NZA-7373) for peat over- and underlying the Kawakawa Tephra at Howard's River, near Nelson, using gas proportional radiometric ^{14}C with minimal pretreatment (acid wash only), whereas AMS dates obtained by one of us (A.P.H.), using the 70% nitric-acid pretreatment on samples from the same sampling intervals as Campbell, gave 18,920 \pm 420 (NZA-907) and 19,660 \pm 280 (NZA-908). These two sets of data are significantly different, and the samples given a supposedly good pretreatment are younger than untreated samples. Several possible reasons for this difference remain unexplored:

1. Calibration and background subtraction procedural differences between the radiometric and AMS laboratories, which could invalidate the comparisons
2. Unaccounted laboratory contamination introduced during the pretreatment of AMS samples, which may add modern carbon to the measured sample
3. Incomplete combustion of low-carbon samples, which could result in a bias toward the younger, more volatile components not removed during pretreatment, and perhaps most likely,

4. Difficulties of association of samples with the event to be dated when the site is remote from that event (subsequent AMS dating of the same samples dated radiometrically by Campbell gave $20,490 \pm 340$ and $21,040 \pm 335$ BP) (Table 3).

TABLE 3. Other Dates From Kawakawa Tephra Sites*

Lab no.	Location	Fraction dated	$\delta^{13}\text{C}$	Age BP
Q-2665 to Q-2668	Within ignimbrite at four sites near source of eruption	Acid- and alkali-washed charred wood (pooled mean of four determinations)	-23.2	$22,590 \pm 230$
NZ-7373 NZA-2066	Above tephra	Peat, acid-washed AMS date on same sample	-28.1	$21,300 \pm 460$ $21,040 \pm 335$
NZ-7144 NZA-2067	Below tephra	Peat, acid-washed AMS date on same sample	-27.4	$21,300 \pm 450$ $20,490 \pm 340$
NZA-908	Below tephra	Peaty soil after 70% HNO_3	-29.8	$18,920 \pm 420$
NZA-907	Above tephra	Peaty soil after 70% HNO_3	-29.6	$19,660 \pm 280$
NZ-6557	Below tephra	Acid washed fine sandy loam	-	$15,600 \pm 250$

*Q-dates on charred wood from North Island sites, NZ dates on peat from Howard's River, South Island, discussed by Wilson, Switsur and Ward (1988); NZA dates from same Howard's River site, pretreated by Hammond

CONCLUSIONS

The commonly used acid/base/acid extraction techniques for removing contaminants before ^{14}C dating of soils do not yield acceptable dates for the sediments in the Graham's Terrace sequence. Maximum ages are only obtained by treatment with hot 70% nitric acid, or with a more complicated sequence involving chlorate oxidation. Although the samples contain 4–5% organic carbon, most of this is present as younger contaminants, particularly humic materials, which, in these fine-grained sediments, are resistant to the standard pretreatment methods. Some mineral destruction seems to be necessary to remove organic material associated with the fine silt/clay fraction, before oxidation can have the desired effect of rendering soluble the alkali-resistant humic carbon. Given these findings, it was possible to achieve dates within a few percent of the known age defined by measurements on well-preserved, uncontaminated charred wood. Because there are good reasons why we would expect dates on soil or peat organic components to be younger than equivalent charcoal, we view this as a significant success. The concept of dating silt-sized charcoal and pollen has the potential to provide reasonable ages for fine-grained sediments containing very little carbon, and is being further explored at other sites in alluvial, lacustrine and aeolian environments (Gillespie 1990; Gillespie *et al.* 1991, 1992).

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