^{14}C AGES OF 10 YAMATO AND ALLAN HILLS METEORITES

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Abstract: Carbon was extracted from 1 g samples of ten Antarctic chondrites, using stepwise heating. The evolved CO_2 was collected at 1000°C, melt and remelt. The ^{14}C concentrations were measured at the Isotrace AMS facility and were compared with the zero-age ^{14}C concentration of the Bruderheim (L6) chondrite. The Allan Hills meteorite ALH-77231 (L6) yielded a terrestrial age, not corrected for *in situ* production, of 30 ka. The uncorrected terrestrial ages of the 9 Yamato meteorites Y-74014 (H6), Y-74097 (Dio), Y-74191 (L3), Y-75271 (L5), Y-790448 (LL3), Y-791500 (H3), Y-791630 (L4), Y-791717 (C3) and Y-74647 (H5) showed a wide range from 500 a to 30 ka.

1. Introduction

Terrestrial ages of Antarctic meteorites, measured from the radionuclide abundances, are important time markers that can reflect the history of movement of the ice sheet. The radioisotopes which have been used in these studies include ^{14}C ($T_{1/2} = 5740$ years), ^{81}Kr ($2.1 \times 10^{+5}$ years), ^{36}Cl ($3.0 \times 10^{+5}$ years), ^{26}Al ($7.05 \times 10^{+5}$ years), ^{10}Be ($1.6 \times 10^{+6}$ years), ^{53}Mn ($3.7 \times 10^{+6}$ years) and ^{40}K ($1.28 \times 10^{+9}$ years) (NISHIIZUMI, 1986; and references therein). Although ^{14}C has the shortest half life and can consequently only determine the terrestrial ages of relatively young meteorites, its compounds are very stable and should, in the absence of contamination, yield reliable ages up to 100 ka. At the Isotrace laboratory at Toronto, we have pioneered the development of accelerator mass spectrometry (AMS) since 1977 and have been engaged in routine ^{14}C analysis since 1985. At Isotrace all three carbon isotopes are accelerated and measured, allowing complete correction for natural, sample preparation and sputter fractionation. More detailed descriptions of the system and procedures have been presented by BEUKENS *et al.* (1986) and KIESER *et al.* (1986). Figure 1 shows the precision of the dates as a function of the radiocarbon age. The solid line represents the predicted precision for a sample of 1 to 5 mg carbon, which has been analysed for 3 hours. The dots represent the actual dates, showing that most dates cluster around the predicted curve. Often the amount of datable carbon is substantially less than 1 mg and the sample cannot be analysed for the full 3 hours. This results in a somewhat lower precision, reflected by the dots above the curve. If a better precision is required the sample is analysed for more than 3 hours, resulting in the dots below the curve. The apparent age due to system background has been measured to be well over 80000 years BP or $<0.005\%$ of modern. This obviously does not affect the measured ages and is the reason why the results follow the theoretical curve so well at the upper end. The total carbon, extracted from 1 g of a chondrite
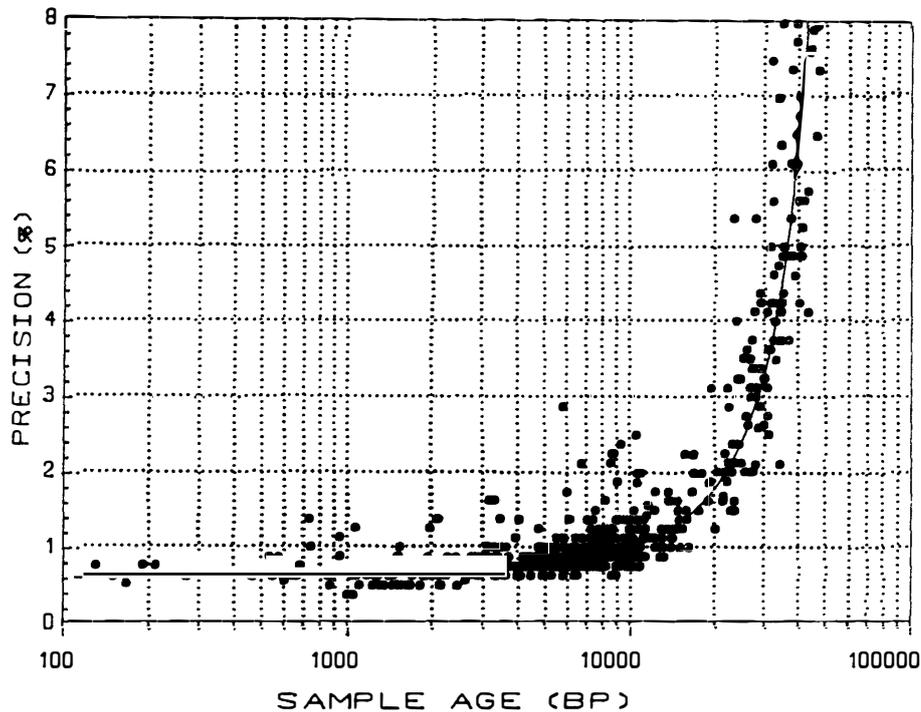
Fig. 1. Precision obtained as a function of the age of samples dated at the Isotrace laboratory. The solid line indicates the expected precision for a 1 to 5 mg carbon sample which has been analysed for 3 hours.

is substantially lower than 1 mg but ^{14}C is present in adequate quantities. To increase the total carbon to the required amount, approximately 7 cc (STP) of "dead" carbon (carbon, not containing any ^{14}C) is added to the sample. This does not affect the ^{14}C content and therefore not the end result. One g of a recently fallen chondrite such as Bruderheim then yields a ^{14}C/^{12}C ratio close to modern. The extracts with the smallest ^{14}C content (very old meteorites and the remelts) yield apparent ages younger than 30000 years BP, well within the capability of the Isotrace facility. With the current high precision and small sample size capability we decided on a thorough investigation of the possible sources of contamination and the efficiency of the extraction method. Although AMS measurements essentially yield ^{14}C/^{12}C ratios and not ^{14}C content, in this paper we have converted the results to disintegrations per minute (dpm) and disintegrations per minute per kg of meteorite (dpm/kg) to facilitate the comparison with previously reported results.

2. Extraction Method

Radiocarbon isotope measurements of meteorites are complicated by the serious problem of contamination by terrestrial carbon, since exposure to weathering and contamination may add substantial amounts of carbon to the samples (GIBSON and BOGARD, 1978). Stepwise mass spectrometric pyrolysis of meteorites and terrestrial basalts by SIMONEIT et al. (1973) demonstrated a trimodal release pattern for CO and CO_2. A 200–600°C fraction consisting mainly of CO_2, was interpreted as lightly adsorbed atmo-

spheric CO_2. A 700–1000°C CO and CO_2 fraction was interpreted as surface reaction products and chemisorbed species. A 1150–1350°C fraction, consisting mainly of CO, was interpreted as being derived from spallation products. This interpretation of re-action products was assumed by Fireman (1978) to apply equally to ^{14}C and his ex-traction system has been used in this work. The carbon compounds are extracted from a meteorite sample in a heated molybdenum crucible. Prior to extraction the sample and crucible are outgassed overnight at 150°C in vacuum. Low temperature extractions are made at 500 and 1000°C for 4 hours. A high temperature extraction is made at 1600°C where the molybdenum crucible softens and fuses with the sample. The cosmo-genic ^{14}C is then released from this viscous mixture and collected for 4 hours. This fraction is usually called the "melt". After the sample is allowed to cool it is reheated to over 1600°C to extract the remaining ^{14}C. This fraction is usually called the "remelt". After approximately 7 cc of carrier CO_2 is added to the system, the gasses are cycled over hot CuO and the CO_2 condensed in a LN_2 trap.

3. Contamination Studies

The material used as "dead" carrier gas was cylinder CO_2 which originates from the combustion of natural gas. Although natural gas should not contain any ^{14}C, the industrial processes for extracting natural gas, the combustion thereof and the storage of the CO_2 in cylinders are not necessarily free from contamination by other ^{14}C sources. The first analysis was therefore designed to measure the actual ^{14}C content of the CO_2 carrier gas used in these experiments. The measured $^{14}C/^{12}C$ ratio of (3.8 ± 0.3) 10^{-15} (Table 1) is significantly larger than our upper limit for contamination due to sample preparation (Beukens et al., 1986). 7 cc of carrier CO_2 therefore contributes (0.16 ± 0.01) 10^{-3} dpm to a sample. All measurements have been corrected for this small con-tribution but in none of the cases did it significanlty affect the result.

To determine the contribution of the hot CuO to the sample contamination, 7 cc of carrier CO_2 was cycled over hot CuO for 4 hours. After subtracting the ^{14}C content attributed to the carrier gas, the residual ^{14}C of (0.06 ± 0.03) 10^{-3} dpm (Table 1) indicates that the contamination from this source is not significant.

The final contamination test was intended to check as complete as possible the overall contribution of the system by heating to 1600°C a cleaned and baked molyb-denum crucible without a sample. Any gasses which might have evolved and the carrier CO_2 where then cycled for 4 hours over hot CuO. This check was performed twice, on different crucibles. After correcting for the ^{14}C content of the carrier gas, the residuals

Table 1. Contamination measurements.

	CO_2 (cc STP)	$^{14}C/^{12}C$	^{14}C DPM $(\times10^{-3})$
Carrier CO_2		$(0.38\pm0.03)10^{-14}$	0.16 ± 0.01[†]
Effect of CuO combustion	0.19	$(0.51\pm0.26)10^{-13}$	0.06 ± 0.03
Contribution by crucible #1	0.35	$(1.48\pm0.05)10^{-12}$	3.21 ± 0.10
Contribution by crucible #2	0.03	—	2.25 ± 0.06

† Calculated contribution to a sample with 7 cc of CO_2 carrier.

showed significant contributions of (3.21 ± 0.10) 10^{-3}dpm and (2.25 ± 0.06) 10^{-3}dpm (Table 1). The ^{14}C/^{12}C ratio of the first measurement is close to that of modern air CO_2. This suggests that this contribution is mainly due to adsorbed CO_2 and that the baking procedure is not adequate. For the second measurement the gas collection appears to have been less complete. Although no step wise extractions have been performed so far, it is expected that the majority of the contamination is extracted in the low temperature fractions. This is supported by the fact that several melts and remelts of meteorites yield an order of magnitude less ^{14}C.

4. Zero Age ^{14}C Concentration

The terrestrial age of a chondrite is obtained by comparing its ^{14}C concentration with that of a recently fallen chondrite. For this purpose the ^{14}C content of the Bruderheim (L6) chondrite, which fell in 1960, has been measured by a number of researchers. Here we present two measurements on ≈ 1 g samples of this meteorite (Table 2).

Table 2. ^{14}C content of the Bruderheim chondrite.

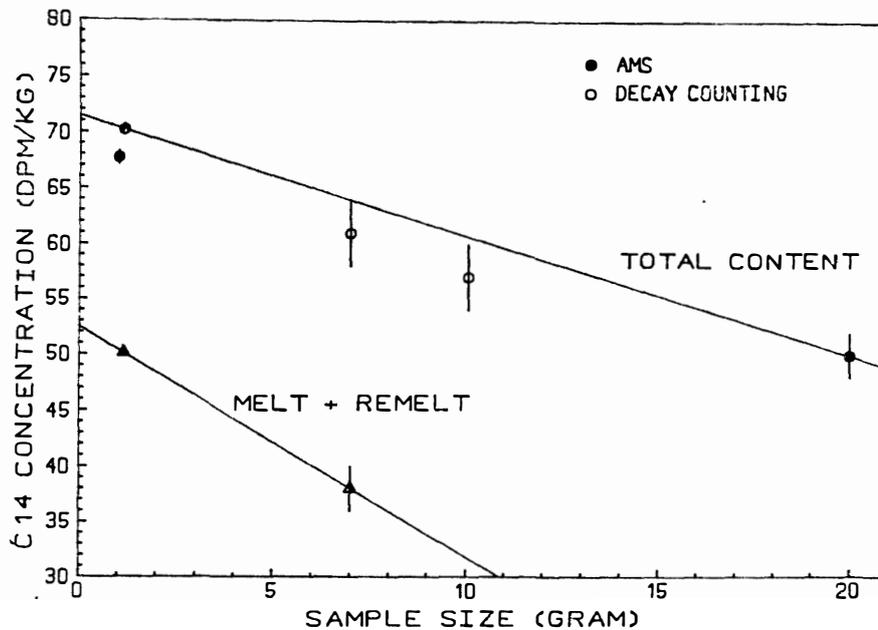|		Sample # 1	Sample # 2
Sample size	(g)	1.148	1.001
Fraction	1000°C	22.3±0.2 dpm/kg	
	melt	47.6±0.3 dpm/kg	67.7±0.6 dpm/kg
	remelt	2.5±0.1 dpm/kg	not measured

Fig. 2. Measurements of the ^{14}C concentration of the Bruderheim chondrite as a function of sample size, using the same extraction system. References for the measurements on samples larger than 1g are: FIREMAN (1978), FIREMAN and NORRIS (1981), and BROWN et al. (1984).

For sample ♯ 1 the 1000°C, melt and remelt fractions were measured for a total ¹⁴C concentration of 72.4±0.4 dpm/kg. For sample ♯ 2 only the total ¹⁴C content was measured and no remelt was done. The measured ¹⁴C concentration of 67.7±0.6 dmp/ kg is in good agreement however with the sum of the 1000°C and melt fractions of 69.9±0.4 dpm/kg for sample ♯ 1. Figure 2 compares our results with previous work on much larger samples, using the same extraction system. This comparison shows a disturbing relationship with sample size. The most likely explanation is that for larger samples, the fusing of the molybdenum crucible with the sample is incomplete, resulting in a lower carbon extraction efficiency. The two melt+remelt measurements in Fig. 2 show a similar relationship. As Bruderheim is a recent fall, it has always been assumed that no ¹⁴C should evolve at 1000°C as no weathering products should be present, and that the cosmogenic ¹⁴C is only extracted in the high temperature fraction. Figure 2 shows however very clearly that a substantial component (30%) of the cosmogenic ¹⁴C is extracted at 1000°C. The 1000°C fraction of antarctic chondrites is therefore also expected to contain, in addition to the weathering products, a similar component of cosmogenic ¹⁴C. The terrestrial age of an antarctic chondrite is obtained by comparing its melt+remelt concentration with the zero age ¹⁴C concentration. This zero age concentration is therefore taken to be the melt-remelt concentration of 50.1±0.3 dmp/kg, measured on Bruderheim sample ♯ 1, and not the total concentration as used by previous authors.

5. Results

Following the procedures outlined above, one Allan Hills and nine Yamato chondrites were analysed. Table 3 shows the ¹⁴C concentrations and the resulting ¹⁴C terrestrial ages. The errors are determined only by the ¹⁴C counting errors and errors in the ¹²C and ¹³C current measurements. This is most likely an underestimate of the real errors. The largest contribution to the error probably arises from the assumptions which have been made to obtain these results. The first assumption is that the zero age

Table 3. Terrestrial ages of 10 antarctic chondrites.

Meteorite		Weight (g)	Melt (dpm/kg)	Remelt (dpm/kg)	Melt+remelt (dpm/kg)	Terrestrial[†] age (y)
Yamato Mountains						
Y-74014	H6	1.054	12.04±0.13	0.82±0.04	12.86±0.14	11,240±100
Y-74097	Dio	1.112	14.69±0.10	0.54±0.03	15.22±0.10	9,850±70
Y-74191	L3	1.066	5.77±0.09	0.76±0.04	6.53±0.11	16,850±140
Y-74647	H5	1.002	30.05±0.21	2.89±0.06	32.94±0.22	3,470±70
Y-75271	L5	1.123	38.39±0.25	1.24±0.04	39.63±0.25	1,930±70
Y-790448	LL3	1.113	0.84±0.04	0.49±0.04	1.34±0.05	29,940±310
Y-791500	H3	1.151	1.29±0.04	0.47±0.02	1.76±0.05	27,680±240
Y-791630	L4	1.093	45.55±0.31	1.55±0.05	47.10±0.35	510±80
Y-791717	C3	1.073	25.16±0.19	0.58±0.04	25.74±0.19	5,510±80
Allan Hills						
ALH-77231	L6	1.071	0.76±0.04	0.44±0.03	1.20±0.05	30,850±350

† Not corrected for *in situ* produced ¹⁴C.

concentration in all chondrites is the same. This is not necessarily correct as variations in the oxygen content should produce different equilibrium ¹⁴C concentrations. KOHMAN and GOEL (1963) have observed variations in the ¹⁴C concentration in recent falls from 47 to 78 dpm/kg. It has also been assumed in this work that the percentage of cosmogenic ¹⁴C extracted at 1000°C is the same as for Bruderheim. Currently no information is available to determine the accuracy of this assumption. Neither of these considerations significantly alters the following conclusions.

As has been observed by FIREMAN (1978), FIREMAN and NORRIS (1981), FIREMAN (1983), BROWN et al. (1984) and JULL et al. (1984), most Allan Hills chondrites yield relatively old ages. This has been attributed to very low ice velocities in this relatively small ice field. The young ages for some of the Yamato chondrites indicate a much higher ice velocity for this area, while the older ages on some of the samples suggest that the ice field, which acts as the collection area, is large.

The oldest ¹⁴C terrestrial ages are however substantially younger than the terrestrial ages, determined by other radioisotopes. In fact, the non-finite ¹⁴C terrestrial ages, reported by FIREMAN and NORRIS (1981), FIREMAN (1983) and JULL et al. (1984) are more the result of large background and/or contamination corrections than low ¹⁴C content. Although this can be attributed, in part to sample selection, it is now clear that in situ production of ¹⁴C plays a major role (LAL, 1987). FIREMAN (1983) first attempted to measure the ¹⁴C content of two field rock samples but failed to detect finite quantities. We have recently repeated this measurement on a volcanic glass sample from the Allan Hills region. Finite ¹⁴C concentrations of 0.93 ± 0.02 and 0.59 ± 0.01 dpm/kg were detected for the melt and remelt fractions. Corrections for in situ produced ¹⁴C of the terrestiral ages reported in Table 3 will have to wait until other samples have been analysed and the production as a function of chemical composition is better understood. However, the observed concentrations are nearly identical to those observed for Y-790448, Y-791500 and ALH-77231, implying that the actual terrestrial ages of these meteorites are substantially older than indicated in Table 3 and are most likely outside the datable range of ¹⁴C.

Acknowledgments

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