

Carbon and carbon-14 in lunar soil 14163

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Abstract - Carbon is removed from the surface of lunar soil 14163 size fractions by combustions at 500°C and 1000°C in an oxygen stream and the carbon contents and the carbon-14 activities are measured. The carbon contents are inversely correlated with grain size. A measured carbon content of 198 ppm for bulk 14163, obtained by combining the size fraction results, is modified to 109 ± 12 ppm by a carbon contamination correction. This value is in accord with a previous determination, 110 ppm, for bulk 14163. The small ($< 53 \mu$) grains of 14163 had more combusted carbon-14 activity, 31.2 ± 2.5 dpm/kg, than the large ($> 53 \mu$) grains, 11.2 ± 2.0 dpm/kg. The combusted carbon and carbon-14 are attributed mainly to solar-wind implantation. Melt extractions of carbon-14 from the combusted soil samples gave essentially identical activities, 21.0 ± 1.5 and 19.2 ± 2.0 dpm/kg for the small and large grains, and are attributed to cosmic-ray spallation-produced carbon-14.

DISCLAIMER



1. INTRODUCTION

The carbon in lunar soils, ~ 100 ppm, is large compared to that in lunar crystalline rocks, ~ 10 ppm; the excess carbon in soil can be easily accounted for by solar-wind carbon implantation during four billion years (Moore et al., 1970, 1974; Des Marais et al., 1973; Gibson and Moore, 1973; Epstein and Taylor, 1973; Kaplan et al., 1976). The carbon contents of soil grains increase inversely with grain size (Des Marais et al., 1973) except for agglutinates; the carbon (Filleux et al., 1978) is concentrated on the grain surface. The close association between the carbon and nitrogen abundances in soil suggests a common solar-wind origin (Kerridge and Kaplan, 1978). Studies of fractional carbon releases by dissolution in organic solvents (Cadogan et al., 1972), pyrolyses at different temperatures (Chang et al., 1972; Gibson and Moore, 1973), and hydrolysis (Abell et al., 1971) support the solar-wind implantation hypothesis. Some authors (Gibson and Moore, 1973) state without qualification that the carbon released from soil below 1100°C in pyrolysis extractions is mainly of solar-wind origin.

The carbon studies in lunar soil suggest possibilities for investigations of ^{14}C in the solar wind. Fireman et al. (1976a,b) and Fireman (1978) carried out investigations of this type after Begemann et al. (1972) reported excess ^{14}C not attributable to cosmic-ray interactions on the top of rock 12056 even though Boeckl (1972) did not find such an excess for rock 12002. Fireman (1978) obtained excess ^{14}C in lunar surface soil and, on the basis of the temperature-release pattern and grain-size dependence, concluded that the excess ^{14}C was of solar-wind origin. From these lunar soil results, a $^{14}\text{C}/^1\text{H}$ ratio of $\sim 5 \times 10^{-11}$ was estimated for solar wind averaged over $\sim 10^4$ years. This ratio is much higher than expected on the basis of Wang and Ramaty's interpretation

(1974) of solar gamma-ray measurements (Chupp *et al.*, 1973). Because of the theoretical significance of ^{14}C in the solar wind, it is desirable to improve the measurements. In the earlier lunar ^{14}C work, no effort was made to achieve low carbon blanks. In fact, carrier carbon was introduced to facilitate the ^{14}C extraction. In this experiment, a combustion extraction line with a very low carbon blank (achieved by the use of O-ring stopcocks) is used so that a direct comparison with previous carbon measurements is obtained in addition to the ^{14}C .

There are four ideas in this experiment: (1) to remove the carbon on the surface of soil grains without disturbing the interior silicate material by low temperature combustions; (2) to compare the amount of combusted carbon with previous carbon determinations; (3) to compare the ^{14}C activities in combustions and meltings of fine-grained (< 53 μ size) 14163 with those in large-grained (> 53 μ size) 14163 and with those in (< 53 μ size) Bruderheim material; (4) to compare the count data obtained in two different low-level counting set-ups, one at SAO and one at BNL. The ^{14}C counting of the samples has not yet been done in the BNL low-level set-up.

Although the main effort is on carbon and carbon-14, we also measured the hydrogen contents and are determining tritium activities for the combustion extractions. The hydrogen and preliminary tritium results are given in Appendix I.

2. EXPERIMENTAL PROCEDURE

We received 5.0 g of lunar soil 14163, which was sieved into a 2.94-g fraction (< 53 μ) and a 2.01-g fraction (> 53 μ). The fractional weights are in accord with the measured size distribution (King *et al.*, 1972). A 2.5-g comparison sample was prepared by crushing Bruderheim interior material and sieving it.

Fig. 1 is a drawing of the combustion system. The sample in a quartz dish is inserted into the line. Runs made by heating empty quartz dishes in the stream of oxygen gave negligible carbon blanks (corresponding to less than 1 ppm of carbon).

The sample is baked out overnight at 100°C to remove atmospheric contaminants. The sample is then heated to 500°C for 3 hours in a stream of oxygen (12-cm Hg pressure). The 500°C combustion removes terrestrial contaminants and approximately one-fourth of the lunar surface carbon (according to the ^{14}C results, which will be discussed in detail later). The stream of oxygen flows across the sample, through a CuO furnace, into a glass spiral trap at liquid N_2 temperature, and then out of the system. The CO_2 and SO_2 collected in the trap are removed at -78°C and circulated over a Ag-Cu furnace, which removes SO_2 but not CO_2 . The CO_2 is measured volumetrically and stored for later ^{14}C counting. The water in the trap is then removed and sealed in a break-off flask. The combustion is carried out for three hours at 1000°C and repeated again at 1000°C. The combusted sample is then removed from this extraction system and placed in another extraction system where it is melted and remelted in the presence of carrier carbon as described (Fireman *et al.*, 1976a, b, 1977). The 1000°C combustion, if carried out for the proper length of time, ~3 hours, should remove completely the surface implanted carbon without disturbing the stony interior. The second 3-hour 1000°C combustion checks this point. The meltings remove completely the ^{14}C produced by spallation within the stony interior.

The extracted CO_2 is put into a low-level proportional mini-counter (Fireman *et al.*, 1976a, b, 1977) for counting the activity. The counters used ranged in volume from 0.7 to 3.0 cm^3 . The CO_2 pressure is kept to 1 atm. or less. Argon is added until the counter pressure is approximately 2 atm. The energy resolution of the

counters is determined by an external ^{55}Fe source. If the energy resolution for the 5.8 KeV x-ray is not 20% or better, the counter filling is removed. The CO_2 and Ar are repurified and then reinserted into the counter. The counter backgrounds as determined with CO_2 from a petroleum source, are approximately 2 counts/day above 5.8 KeV energy for the 0.7 cm^3 volume counter and 5 counts/day for the 3.0 cm^3 volume counters. The counter efficiencies above 5.8 KeV are 30% for the 0.7 cm^3 counters and 50% for the 3.0 cm^3 counters. The counts between 1.0 and 7.0 KeV are recorded on a 100-channel analyzer, the counts above 6.5 KeV energy are recorded on scalars.

The water in the break-off flask is removed and condensed on a Mg amalgam. The water is converted to H_2 by heating the amalgam to $\sim 200^\circ\text{C}$. The H_2 is measured volumetrically; purified by adsorption on vanadium powder at room temperature; released from the vanadium at $\sim 300^\circ\text{C}$; remeasured volumetrically; passed over charcoal at -78°C to remove radon; and then put in a counter. The counters used for the low-level tritium counting have been described (Fireman et al., 1970, 1973).

3. RESULTS

Table 1 gives the carbon contents and ^{14}C activities of the two size fractions of soil 14163 and of the sieved Bruderheim sample. There is an inverse correlation of the carbon contents with 14163 grain size; however, the second 3-hour combustion at 1000°C had essentially identical amounts of carbon for the small and large grains, 12 and 13 ppm. The total combusted carbon is 253 ppm for the small grains and 123 ppm for the large grains. If the combusted carbon contents of the two size fractions are combined according to their fractional weights, then presieved 14163 soil has 198 ppm of carbon. This value is higher than the reported values 110 and 120 ppm. Our

higher value is probably due to carbon handling contamination, which is combusted at 500°C. In Appendix II, we calculate on the bases of the specific activities that ~80% of the 500°C carbon is due to terrestrial contamination. After the contamination correction is applied, our presieved 14163 material has 109 ± 13 ppm of carbon.

The specific activity of contemporary carbon is 0.8×10^{-2} dpm per cc STP of CO_2 . The carbon combusted at 500°C from the Bruderheim sample has a specific activity of $(1.4 \pm 0.6) \times 10^{-2}$ dpm per cc and can be attributed entirely to contemporary carbon. Contamination contributes a negligible amount of activity to all other samples except possibly to the 500°C extraction of the large 14163 grains.

The small grains of 14163 have more ^{14}C activity (52.2 dpm/kg) than the large grains (30.4 dpm/kg). The activity difference is in the combustions and not in the melts (cf. Table 1). These results are in accord with those obtained by step-wise pyrolyses of size fractions of soil 10084 (Fireman *et al.*, 1977) and are consistent with the idea that the below melting ^{14}C is solar-wind-implanted and the above-melting ^{14}C is cosmic-ray spallation-produced.

The small grains of Bruderheim had twice as much melt ^{14}C as the 14163 samples. The bulk of Bruderheim's ^{14}C activity is in the melts. The ^{14}C in Bruderheim should be entirely spallation-produced. Twice as much spallation is expected in Bruderheim than in lunar material on the basis of geometrical considerations (solid angle encompassed by the incoming cosmic rays).

Spallation of oxygen and not of carbon produces ^{14}C . In chondrites, such as Bruderheim, practically all oxygen is in silicates and all carbon is in the form of

graphite. The small amount of ^{14}C activity in the 1000°C combustion probably results from a slight disruption of the crystalline lattice of some Bruderheim silicate minerals at this temperature. The oxygen and carbon are similarly distributed in lunar crystalline rocks; lunar silicates are more refractory than those in chondrites. Less disruption of lunar stony material at 1000°C is therefore expected. Even identical crystalline disruptions at 1000°C in Bruderheim and in the lunar material would not account for the ^{14}C observed in the combustions of 14163.

If the ^{14}C combusted from the small grains minus that from the large grains is attributed to solar-wind implantation, then 20.8 ± 3.3 dpm/kg of solar-wind ^{14}C was implanted in soil 14163. The $^{14}\text{C}/^1\text{H}$ ratio estimated for the solar wind from this ^{14}C implantation rate is $\sim 4 \times 10^{-11}$.

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Table 1. C and ^{14}C in soil 14163 and Bruderheim size fractions.

Sample Wgt. (grain size)	Combust. Temp. (°C)	CO ₂ (cc STP)	C (ppm)	C** (ppm)	^{14}C (dpm/kg)	Tot. ^{14}C (dpm/kg)
14163	500	0.780	142	31 ± 17	8.2 ± 0.6	
2.94 g	1000*	0.544	99	99	23.8 ± 2.2	52.2 ± 3.0
(< 53 μ)	1000†	0.069	12	12		
	Melt†	3.35	—	—	21.0 ± 1.5	
14163	500	0.284	75	13 ± 18	3.2 ± 1.0	
2.01 g	1000*	0.132	35	35	8.0 ± 1.5	30.4 ± 3.0
(> 53 μ)	1000†	0.049	13	13		
	Melt†	2.35	—	—	19.2 ± 2.0	
Bruderheim	500	0.860	184	< 30	4.8 ± 2.0	
2.50 g	1000	0.109	23	23	9.6 ± 1.0	51.8 ± 5.0
(< 53 μ)	Melt†	0.696	—	—	38.5 ± 4.0	

* Recombustion at 1000°C.

† C + CO₂ carriers added (sample melted and remelted).

** Corrected for contemporary carbon contamination.

Appendix I: Hydrogen and Tritium

Lunar soil is saturated with solar-wind hydrogen. There is no evidence for solar-wind tritium implantation. In fact, tritium measurements on Surveyor 3 material give an upper limit for the ${}^3\text{H}/{}^1\text{H}$ ratio in the solar wind of 1×10^{-11} (Fireman et al., 1976a). Tritium has been measured in approximately 50 lunar samples (Fireman et al., 1970, 1973; D'Amico et al., 1970, 1971; Bochsler et al., 1971; Stoenner et al., 1970, 1971, 1972, 1974; Niederer et al., 1975). Most of the analyzed samples are from shallow depths and have approximately 300 dpm/kg of tritium. These results are qualitatively explained by galactic and solar cosmic-ray-spallation production. A few lunar samples have anomalously high ${}^3\text{H}$ contents (Bochsler et al., 1971; Stoenner et al., 1972, 1974), e.g., chips from rocks 12053 and 12065 and soil sample 70006. Most or all of the anomalous ${}^3\text{H}$ is loosely bound and can be removed by baking-out the sample at 300°C for several hours or for longer times at lower temperatures. These high ${}^3\text{H}$ results have been attributed to terrestrial contamination that occurred during handling or from contaminated spacecraft instruments.

In previous lunar tritium studies, the hydrogen was extracted by pyrolysis and the grain size dependence in soil was not investigated. For comparison purposes, it is desirable to extract hydrogen by combustions. In the lunar soil tritium studies, there was more scatter in the experimental data than was anticipated. The scatter in the data could have been caused by tritium mobility and its redistribution among different types of soil grains. A study of the ${}^3\text{H}$ grain size dependence might be helpful in interpreting the ${}^3\text{H}$ fluctuations observed.

Table I-1 gives the amounts of hydrogen recovered from the combusted water. In sharp contrast to the carbon contents, there is more hydrogen in the large grains than in the small grains. Evidently hydrogen diffusion plays an important role on the lunar surface. It is also interesting to note that more hydrogen was combusted from lunar soil at 1000°C than at 500°C; the hydrogen of the sieved Bruderheim sample exhibited the reverse behavior. Terrestrial hydrogen in Bruderheim dominates, probably solar-wind hydrogen dominates in the lunar samples.

Preliminary tritium results are also given in Table I-1. Sample 14163 was collected on February 5, 1971; the ^3H decay correction factor is 0.56. In the small (< 53 μ size) 14163 grains, less than 10 dpm/kg was observed for the 500°C combustion and only 10 ± 3 dpm for the 1000°C combustion. This is much less than would be expected on the basis of decay. Either tritium diffusion loss is very important for small grains or the tritium was not completely extracted by the combustions. Very preliminary results indicate that there are significant amounts of ^3H in the large grains.

Table I-1. H_2 and 3H in soil 14163 and sieved Bruderheim.

Sample Wgt. (grain size)	Combust. Temp. (°C)	H_2 cc (STP)	H_2 ppm	3H (dpm/kg)
14163	500	0.57	17	< 10
2.94 g ($< 53 \mu$)	1000	1.21	37	10 ± 3
14163	500	1.00	59	in progress
2.01 g ($> 53 \mu$)	1000	1.51	89	~90
Bruderheim	500	0.83	30	in progress
2.50 g ($< 53 \mu$)	1000	0.53	19	in progress

Appendix II: Terrestrial Carbon Contamination

The specific ^{14}C activity of contemporary terrestrial carbon is 0.8×10^{-2} dpm per cc of CO_2 . The noncontaminated carbon combusted at 500°C is assumed to have the specific activity of the 1000°C combusted carbon, i. e., $(11.4 \pm 1.0) \times 10^{-2}$ dpm per cc of CO_2 for the $< 53\mu$ 14163 sample, $(8.9 \pm 1.5) \times 10^{-2}$ dpm per cc of CO_2 for the $> 53\mu$ 14163 sample, and $(22 \pm 2) \times 10^{-2}$ dpm per cc of CO_2 for the sieved Bruderheim sample.

Let x equal the volume of contaminant CO_2 obtained in the 500°C combustion. The sum of the contaminant and noncontaminant activities equals the total activity observed in the 500°C combustion. Equations (1), (2), and (3) express this relation for the three 500°C combustions. For the ($< 53\mu$) 14163 sample

$$0.8 \times 10^{-2} x + (11.4 \pm 1.0) \times 10^{-2} [0.780 - x] = (8.2 \pm 0.6) (2.94 \times 10^{-3})$$

$$\therefore x = 0.61 \pm 0.09 \text{ cc} \quad (1)$$

and the percentage of contamination is

$$\left(\frac{0.61 \pm 0.09}{0.780} \right) (100\%) \text{ or } (78 \pm 12) \% .$$

For the ($> 53\mu$) 14163 sample

$$0.8 \times 10^{-2} x + (8.9 \pm 1.5) \times 10^{-2} [0.284 - x] = (3.2 \pm 1.0) (2.01 \times 10^{-3})$$

$$\therefore x = 0.23 \pm 0.07 \text{ cc} \quad (2)$$

and the percentage of contamination is

$$\left(\frac{0.23 \pm 0.07}{0.284}\right) (100\%) \text{ or } (82 \pm 25) \% .$$

For the Bruderheim sample

$$0.8 \times 10^{-2} x + (22 \pm 2) \times 10^{-2} [0.860 - x] = (4.8 \pm 2.0) (2.50 \times 10^{-3})$$

$$\therefore x = 0.83 \pm 0.15 \text{ cc}$$

and the percentage of contamination is

$$\left(\frac{0.83 \pm 0.15}{0.860}\right) (100\%) \text{ or } (96 \pm 18) \% .$$

FIGURE CAPTION

Figure 1. Vacuum line for CO₂ and H₂O combustion.

VACUUM LINE FOR CO₂ AND H₂O COMBUSTION

