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# PROBLEMS ASSOCIATED WITH THE USE OF COAL AS A SOURCE OF $^{14}$C-FREE BACKGROUND MATERIAL

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ABSTRACT. Many $^{14}$C dating laboratories have established that coal samples exhibit a finite $^{14}$C age, apparently caused by contamination of the specimens before any laboratory preparation is undertaken. In this work, the possibility that the contamination is due to microbial and fungal activity in the coal substrate is considered and some suggestions are made for alternative sources of background test materials for $^{14}$C dating laboratories. Initial results indicate that geologically formed graphites contain little $^{14}$C and are likely to be good background test materials, especially in $^{14}$C AMS laboratories.

## INTRODUCTION

The maximum age that can be determined reliably by the $^{14}$C dating method is limited by several factors, amongst the most important of which is "background." In the case of $^{14}$C dating by accelerator mass spectrometry (AMS), where extremely small samples are used, background problems caused by contamination are proportionally greater than for large samples. Three factors may contribute to the background observed during $^{14}$C determinations using AMS:

1) the limit of detection or machine background
2) contamination of the sample during pretreatment and preparation
3) contamination of the sample prior to any laboratory preparation or analysis.

Vogel *et al* (1987) have provided an excellent analysis of 1) and 2) by separating out the components of contamination introduced during sample combustion and graphitization, as well as the contribution to background by the accelerator system. Some of the background samples tested by Vogel *et al* (1987) were specimens of anthracite coal which showed $^{14}$C concentrations considerably higher than expected due to machine background ages and contamination during sample preparation. When background ages in the vicinity of 50 kyr were expected, the coal samples yielded 40–45 kyr. There are many other unpublished accounts by $^{14}$C laboratories in which the use of coal as a background test material has been investigated. In many cases, the samples were found to contain $^{14}$C, and further studies were discontinued. The AMS and gas counting facilities, DSIR, in Lower Hutt, New Zealand, eg, have observed apparent ages for coal specimens ranging from 25–40 kyr, and the NSF Accelerator Facility at Tucson, Arizona has determined ages of anthracite samples ranging from 30–40 kyr (AJT Jull, pers commun, 1988).

## PROPERTIES OF COAL

Coal represents the accumulation of organic materials in sedimentary strata where it undergoes *in situ* compaction and induration to form various ranks. These vary from lignite, which is only moderately metamor-

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phosed, plant residues still readily apparent, to anthracite, which is very hard and brittle (Wixson *et al,* 1980).

Because coal is formed over geological time scales at depths providing excellent shielding from cosmic rays, its $^{14}C$ content should be insignificant in comparison to the $^{14}C$ introduced by even the most careful sample preparation techniques used in $^{14}C$ dating laboratories. How is it then, that a material, which should show a $^{14}C$ age indistinguishable from that produced by a combination of machine background and contamination during careful sample preparation, routinely produces a finite $^{14}C$ age?

One suggestion is that radium, which is present in some coals at the sub ppm level, as a decay product of the uranium/thorium series, may produce $^{14}C$ during an extremely rare decay event (Rose & Jones, 1984). Jull, Barker and Donahue (1987) have detected $^{14}C$ from this process in uranium/thorium ores. Blendowski, Fliessbach and Walliser (1987) however, have shown that the $^{14}C$ decay mode of $^{226}Ra$ is only of the order of $10^{-11}$ of the preferred $\alpha$ decay channel to $^{222}Rn$. Thus, the amount of $^{14}C$ produced by such events derived from radium in coal must be considered as insignificant.

## MICROBIAL AND FUNGAL ACTIVITY IN COAL

I would like to suggest a simple explanation for the finite $^{14}C$ ages observed for many coal specimens, namely microbial and fungal action in coal substrates.

The action of various kinds of fungi and microbes in coal has been well documented (Paca & Gregr, 1977; Cohen & Aronson, 1987; Greenwell, 1987). Cohen and Gabrielle (1982) first reported that the fungi *Polyporus versicolor* and *Poria montiola* could degrade lignite. The fungus *Polyporus versicolor,* which is the common species involved in the rotting of wood, incorporates atmospheric $CO_2$ during its growth and thereby introduces $^{14}C$ into the coal substrate. Once the coal specimen is contaminated, fungi and microorganisms may be killed by conventional methods such as autoclaving, but the fungal hyphae and waste products, which contain $^{14}C$ derived from atmospheric $CO_2$, will be almost impossible to remove by standard chemical washing procedures. Assuming that a sample of coal contains no $^{14}C$, microbial action only has to result in the deposition of ca 0.1% by weight of modern carbon in the coal to produce an apparent age of 45 kyr for the specimen.

Currently, the electric power industry is very interested in bacteria that can remove organic sulphur, pyrites and other potentially toxic substances from coal (Greenwell, 1987; Olson & Brinckmann, 1986). The bacteria studied so far are related to the microorganisms found feeding on sulphur deposits at submarine hydrothermal vents and obtain their energy by oxidizing reduced iron and sulphur compounds (Singer & Stumm, 1970; Ehrlich, 1981). In moist air, some of these autotrophic species including strains of thiobacillus-like bacteria, oxidize pyrites in coal, incorporate atmospheric $CO_2$ during their growth (Olson & Brinckmann, 1986; Ehrlich, 1981), and deposit products containing $^{14}C$ into the coal. The process is particularly prevalent in warm, damp coal in air, but will still occur at the temperatures and lower relative humidities experienced in $^{14}$C sample preparation laboratories where background coal test specimens have been stored.

## CONCLUSION AND RECOMMENDATIONS

In order to try to prevent microbial and fungal activity in coal, only freshly mined coal, kept dry in a nitrogen atmosphere should be used. However, even with these precautions, considering the ubiquitous occurrence of fungi and microbes (bacteria have been found in a drill hole 3km underground apparently living on granite!), the use of coal samples as routine $^{14}$C laboratory background test samples should probably be avoided.

A better background test material, particularly for $^{14}$C AMS facilities, may be graphite. However, because industrial graphites, which include the synthetic and spectroscopic graphites routinely used in AMS laboratories as background test materials, are usually made by heating mixtures of coking coal and pitch of unknown provenance, these materials should probably also be avoided.

I suggest that a good source of $^{14}$C-free materials for $^{14}$C background and contamination tests is likely to be found by investigating geological deposits of graphite. If these graphites are pure, sulphur-free and stored dry under nitrogen, the possibility of microbial or fungal action should be remote. I recommend that such sources of graphite be evaluated in future studies of factors contributing to $^{14}$C background in dating facilities. Graphite offers the advantage that it can be used directly without laboratory preparation in an accelerator sputter ion source to produce beams of negatively charged carbon ions. The same material can also be combusted, unfortunately with difficulty, to $CO_2$ and regraphitized to provide an unambiguous test of contamination introduced by laboratory target preparation procedures. Initial tests made recently at the New Zealand AMS facility, have shown a 51 kyr background for a geologically formed flake graphite which confirms that "natural graphites" are likely to be a good basis for further study into $^{14}$C-free background materials.

I also suggest that freshly mined dry coal samples be tested for $^{14}$C content and that the $^{14}$C activity be monitored routinely after the samples are stored in laboratory air. The Argonne National Laboratory, eg, maintains a premium coal bank containing eight grades of coal, all of which are stored in an inert atmosphere since mining (Haggin, 1988). Such samples could be used as standards to check for the introduction of $^{14}$C due to microbial activity after exposure of the coal specimen to moisture and air.

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