

Beyond radiocarbon's black hole: ^{14}C dating of old (35-55 ka) charcoal

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For ^{14}C dating, small amounts of contamination in old samples make them appear substantially younger, producing a clustering of contaminated ^{14}C dates between 35 and 45 ^{14}C ka B.P. In fact, measured ^{14}C ages fall within this range with such regularity that geochronologists informally refer to this time period as the “black hole” of radiocarbon dating. In order to obtain reliable ^{14}C ages within and beyond the black hole, two experimental criteria must be met. First, secondary (or contaminant) carbon species must be completely removed from the sample matrix. The standard acid-base-acid (ABA) treatment that is used by all ^{14}C laboratories is sufficient for most organic samples, including charcoal. However, the small amount of contamination (<1%) that is left behind by the ABA treatment results in significant errors for old samples because the impact of contamination increases with age. For example, a sample that is 21,000 years old that is contaminated with 0.5% modern carbon will result in a ^{14}C age that is ~500 years too young. The same amount of contamination will cause a 50,000-year-old sample to appear to be 13,700 years too young! To address this problem, Michael Bird and co-workers developed an aggressive chemical pretreatment technique that consists of acid, base, and wet oxidation steps, known as ABOX. Although the ABOX technique is limited to materials composed of elemental C, specifically charcoal and graphite, it is very effective at removing contaminant carbon species.

The second experimental criteria for ^{14}C dating of old samples is that the inside of the vacuum system used for extracting sample C and converting it to graphite must be completely isolated from other carbon sources, namely atmospheric CO_2 . Moreover, sample cross-talk must be eliminated. At the University of Arizona's Desert Laboratory, we have recently constructed a new vacuum extraction system that is designed and dedicated for ^{14}C dating of old samples. Our new extraction system integrates several features that are above and beyond those found in typical extraction systems, including (1) a backing system that is used to remove atmospheric gases introduced when loading samples, (2) ultra-high-purity (UHP) He that is used to “scrub” the inside of the system between samples, (3) UHP O_2 that is used for all combustion steps, (4) a variable temperature trap that is held at -130°C to remove water vapor, and (5) an inline Cu/Ag trap held at 620°C to remove halides, SO_x , and NO_x species.

Following ABOX treatment, charcoal samples are subjected to stepped-combustion, typically for 1 hour at temperatures of 330°C , 630°C , and 850°C . Secondary carbon species that survive the ABOX treatment evolve and are removed at lower temperatures; original sample C evolves and is collected at higher temperatures. Our graphitization system includes inlet ports that allow us to oxidize and reduce Fe and Zn powders that are used in the catalytic reduction of CO to graphite. Powders are oxidized in UHP O_2 for 2 hours at 330°C , scrubbed with UHP He, and then reduced in UHP H_2 again for 2 hours at 330°C . To ensure replicability, a thermal control

system that uses a servo feedback loop maintains furnace temperatures to within $\pm 5^\circ\text{C}$. At present, the background (or blank) level for our system, including chemical pretreatment, combustion, cleanup, graphitization, storage, and measurement, is 0.04 ± 0.01 pMC (equivalent to an age of ~ 65 ka) based on analysis of ^{14}C -free geological graphite. This represents an improvement by a factor of 7-10 over typical ^{14}C extraction systems and allows us to reliably measure ^{14}C ages of natural charcoal up to ~ 50 ka.