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A novel approach to process carbonate samples for radiocarbon measurements with helium carrier gas

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ABSTRACT

Most laboratories prepare carbonates samples for radiocarbon analysis by acid decomposition in evacuated glass tubes and subsequent reduction of the evolved CO_2 to graphite in self-made reduction manifolds. This process is time consuming and labor intensive. In this work, we have tested a new approach for the preparation of carbonate samples, where any high-vacuum system is avoided and helium is used as a carrier gas. The liberation of CO_2 from carbonates with phosphoric acid is performed in a similar way as it is often done in stable isotope ratio mass spectrometry where CO_2 is released with acid in septum sealed tube under helium atmosphere. The formed CO_2 is later flushed in a helium flow by means of a double-walled needle mounted from the tubes to the zeolite trap of the automated graphitization equipment (AGE). It essentially replaces the elemental analyzer normally used for the combustion of organic samples. The process can be fully automated from sampling the released CO_2 in the septum-sealed tubes with a commercially available auto-sampler to the graphitization with the automated graphitization. The new method yields in low sample blanks of about 50000 years. Results of processed reference materials (IAEA-C2, FIRI-C) are in agreement with their consensus values.

1. Introduction

Radiocarbon analysis of carbonates is often applied and may give answers to different questions. Carbonate shells of foraminifera or ostracods can be used for radiocarbon dating sediments, when the reservoir age of the location is known [1–3]. In the marine environment, the reservoir age at a certain location (water depth) is related with the ventilation age of the prevailing water mass. The combination of $^{230}Th/^{234}U$ and ^{14}C dating in deep-sea corals, for example, allows determining the water mass ventilation age at the time of coral growth [4,5]. In continental carbonates ^{14}C measurements have mainly been applied to speleothems [6,7]. The combination of ^{14}C with $^{230}Th/^{234}U$ dating allows extending the radiocarbon calibration curve far beyond 26 kyr, in the marine [8] and also in the continental environment [9].

Conventional AMS radiocarbon analysis of carbonate samples, such as speleothems, foraminifera and corals, requires the extraction of about 1 mg of C (10 mg $CaCO_3$). Most laboratories prepare samples by decomposition of carbonates with phosphoric acid in evacuated glass tubes [10]. The formed CO_2 requires further cleaning and conversion into graphite. The entire processing of carbonate samples to graphite targets is thus labor intensive and time consuming [3,11]. One person normally produces only a few real samples per day because of the slow process to evacuate the glass tubes in which carbonate samples are decomposed. A further time consuming step is the cryogenic separation of CO_2 and water evolved during carbonate hydrolysis.

In a recent work an elemental analyzer (EA) was used for a simplified conversion of carbonates to CO_2 [12]. An advantage is the automated processing of multiple samples with a sample changer in the EA by thermal decomposition. Additionally no vacuum system is required for the decomposition of the carbonates. However, this method carries some disadvantages. The additional instrument is expensive and needs maintenance, but, more importantly, in an EA not only carbonates are converted to CO_2 but also organic material included in the sample material. Carbonate decomposition with acid in contrast allows a material-specific analysis of inorganic carbon and leaves organic substances behind.

Here, we present a new approach for a simplified acid decomposition of carbonates to obtain CO_2 for conversion into AMS graphite targets. The applied method is similar to an approach already used for stable isotope measurements ($\delta^{13}C$, $\delta^{18}O$) of carbonates that are decomposed under a helium atmosphere in septum sealed tubes [13] (Gas bench II, Thermo Fisher, Germany). We then also take advantage of the automated graphitization equipment (AGE) at

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ETH, which accepts CO_2 in a helium flow for the graphitization process [14,15]. A carbonate dissociation line replaces the EA normally used for the combustion of organic samples (Fig. 1).

2. Method

Carbonate samples were first cleaned when necessary [16]. Then preferably 10 mg $CaCO_3$ were weighted into 12 mL vials and closed with screw cap containing a butyl septum (Exetainer® vials, Labco, UK). Air was removed from the vials with a He flow of 100 mL/min using a double-walled needle (Thermo, Germany) inserted through the septum. The time for flushing was set to 10 min after systematical testing. For this, relatively small ^{14}C-free carbonate samples (3 mg $CaCO_3$, IAEA-C1) were analyzed and the radiocarbon content plotted against the flushing time (Fig. 2).

Then 0.5 mL H_3PO_4 heated at 75 °C is added with a gas-tight syringe. Analytical grade phosphoric acids in a concentrations range of 85% to 103% were tested. The samples are kept overnight at 75 °C to ensure complete decomposition of the carbonates (while for most samples 30–60 min would be sufficient).

The formed CO_2 was then flushed with 100 mL/min helium (purity: 99.995%) within 2 min to the AGE by means of the double walled needle (Fig. 1). Any water is retained on a phosphorus pentoxide trap (Merck Sicapent®). The CO_2 is then adsorbed on the zeolite trap (Supelco®, X13, -60 mesh, 200 mg) of the AGE system, while helium is vented to air. Finally, the pure CO_2 is thermally released into a selected reactor of the AGE, where it is converted with hydrogen (purity: 99.999%) to graphite on 4.5 mg iron powder (Alfa Aesar®, reduced iron 99%, −325 mesh) in about 2 h [14]. The graphite targets where then measured on the AMS system MICADAS at ETH [17,18].

3. Results and discussion

The new carbonate method produces low processing blanks as can be seen on the example of a first measurement sequence (Table 1) with only 0.0023 ± 0.0002 $F^{14}C$ (48800 ± 800 years, n = 7). The blanks are very well reproduced and were confirmed in several independent measurements later (see also Fig. 2).

An important factor for a low processing blank is the He flushing of the sample vials prior to the decomposition of the carbonates with phosphoric acid. While a ^{14}C-free sample of 3 mg results in a nearly 0.02 $F^{14}C$ increased blank when the air is not at all removed
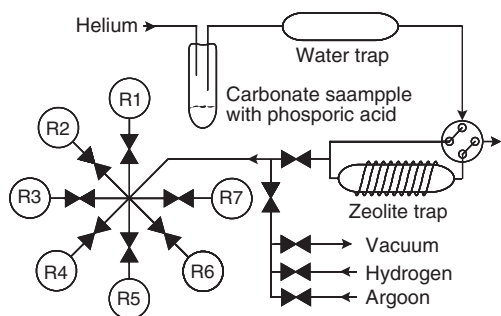

Fig. 1. Schematic arrangement of the carbonate dissociation line connected to the AGE with its zeolite trap and the 7 reactors (R1–R7). After acid decomposition of the carbonates in a septum sealed tube, the CO_2 is flushed with 100 mL/min helium over a water trap to the zeolite trap, where helium flows through and the CO_2 is adsorbed. The CO_2 is thermally released from the trap and transferred to the individual reactors simply by gas expansion. Here, tubing with a small inner diameter of only 0.5 mm are used to keep the volume of the gas lines plus zeolite trap relatively small (400 µL) compared to the reactor with a volume of 4.5 mL. Hydrogen is used for the CO_2 reduction and argon for venting the reactors after reaction is finished.
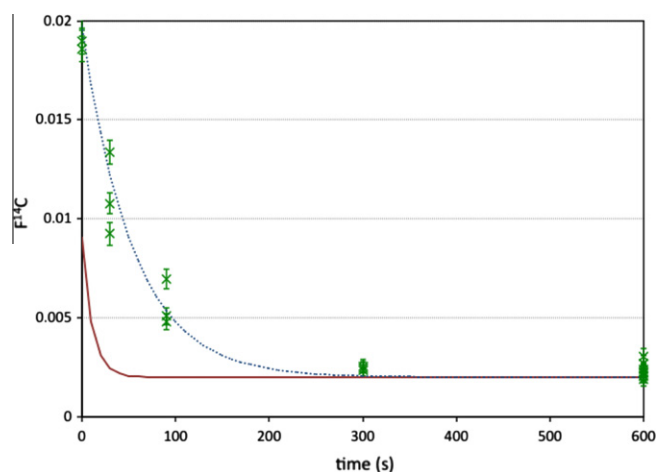

Fig. 2. The measured radiocarbon concentration of 3 mg IAEA-C1 samples (containing no ^{14}C) are plotted over the time septum sealed vials containing the carbonates are flushed with helium (1.5 bar, 100 mL/min) prior to acid decomposition and graphitization. The solid curve shows a theoretical calculation for 100 mL/min helium flushing, assuming at the beginning 1 bar of air containing 400 ppm of CO_2 with 1 $F^{14}C$. The dotted curve is an adaption of the theoretical curve to the measured values by assuming 2.5 times the concentration of CO_2 at the beginning and 5 times reduced flushing rate of only 20 mL/min helium. An offset of the curves of 0.002 $F^{14}C$ was added, assuming to be introduced by the subsequent graphitization process.

from the 12 mL vial, the value of about 0.0025 $F^{14}C$ seems not to change significantly anymore after about 5 min of flushing with 100 mL/min He (see Fig. 2). This is significantly longer than one would expect from a theoretical calculation of the ^{14}C concentration, assuming 12 mL air with 400 ppm CO_2 of 1.04 $F^{14}C$ has to be flushed out (solid curve in Fig. 2):

$$C_t = C_0 \cdot e^{-\frac{Q}{V}t} \tag{1}$$

where c_0 is the starting concentration of ^{14}C, Q is the flow rate (100 mL/min) V is the gas volume (12 mL) and t is the time.

The starting concentration of radiocarbon must obviously be a factor about 2.5 higher and the efficiency of the flushing process is by a factor of 5 lower. While the starting concentration of CO_2 might be somewhat higher in a laboratory because of exhaled air from humans with significantly higher CO_2 concentrations compared than in normal ambient air, a factor of 2.5 seems to be very high, so not very likely. The release of CO_2 adsorbed on the glass walls of the vials is also possible and would explain the relatively low flushing efficiency, as adsorbed CO_2 is not as readily removed as CO_2 in the gas phase.

In contrast to the observation that an extended flushing is required to remove any contamination from the vials, the time to efficiently flush the formed CO_2 after the addition of acid to the trap of the graphitization system is less than 2 min (close to what one would expect from Eq. (1)). Any remaining CO_2 in the vial is <5% (determined on a second extraction). The CO_2 is transferred from the trap to the reactors by gas expansion with an efficiency of >90% [14].

We have also tested the influence of different phosphoric acids concentrations (85%, 99% and 103%) on the processing blank. The 85% H_3PO_4 carries potentially the risk of sample contamination because it contains water and thus may introduce some dissolved CO_2 from ambient air. However, no significant difference in the blank level was observed when only 0.5–1 mL acid was used. This is best shown on measurements performed in a different study where small carbonate samples (<1 mg) were analyzed and an increased blank was only visible on these small samples when more than 1 mL acid 85% acid was used for the carbonate decomposition [19].