

An update on *in situ* cosmogenic ^{14}C analysis at ETH Zürich

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ABSTRACT

We present the improved performance of the modified *in situ* cosmogenic ^{14}C extraction system at ETH Zürich. Samples are now processed faster (2 days in total) and are measured with a high analytical precision of usually <2% using the gas ion source of the MICADAS AMS facility. Measurements of the PP-4 standard sample show a good reproducibility and consistency with published values. Procedural blanks are very low at currently $\sim 4.0 \times 10^4$ ^{14}C atoms. Analyses of samples from a ~ 300 y old rock avalanche prove that we can successfully apply *in situ* ^{14}C exposure dating to very young surfaces. Additionally, we present a modified calculation scheme for *in situ* ^{14}C concentrations which differs from that used for conventional radiocarbon dating. This new approach explicitly accounts for the characteristics of *in situ* ^{14}C production.

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1. Introduction

Terrestrial cosmogenic nuclides are widely applied in Quaternary geochronology and Earth surface process studies. With its short half-life (5730 y) *in situ* cosmogenic ^{14}C is of special interest, as it is particularly sensitive to fast and/or recent landscape changes that cannot be detected by the long-lived radionuclides (^{10}Be , ^{26}Al , ^{36}Cl). Combined with a long-lived isotope, *in situ* ^{14}C provides the opportunity to reconstruct short episodes of surface burial, to distinguish recent exposure from pre-exposure of surfaces [1] or to determine the timing of sediment storage in a fluvial system [2]. However, the often low *in situ* ^{14}C concentrations in terrestrial rocks and the contamination by atmospheric ^{14}C make routine *in situ* ^{14}C analyses difficult. With the development of *in situ* ^{14}C extraction systems based on high-temperature sample heating or melting, significant progress has been made during the past decade [3–7].

The *in situ* ^{14}C extraction system at ETH Zürich has been first described by Hippe et al. [4]. Since then the system has been routinely running and further improved. Most importantly, the blank ^{14}C contribution has been strongly reduced. By now a good database of system blanks, quartz and standard sample analyses has been acquired that allows an evaluation of the long-term analytical performance. Here, we present a summary of these data and

discuss the analytical reproducibility and accuracy. We further describe our revised and more efficient analytical protocol and propose a new approach in data reduction that accounts for the differences between *in situ* produced ^{14}C and conventional radiocarbon. Finally, the capability of *in situ* ^{14}C for exposure dating of very young surfaces will be shown and discussed on ^{14}C data obtained for a ~ 300 y old rock avalanche.

2. Methods

2.1. Modifications of the *in situ* ^{14}C extraction system

Three main features characterize the ETH *in situ* ^{14}C extraction system: (1) the all-metal tubing system, (2) the omission of sample graphitization, and (3) the extraction furnace heated by electron bombardment. The latter allows the extraction of ^{14}C from a quartz sample without using a flux agent. We argue that the extraction without flux and the lack of a graphitization step leads to less ^{14}C contamination and thus lower ^{14}C blanks than systems and procedures using those other techniques. While the system setup in general has remained unchanged, the extraction furnace has seen minor, yet important changes. The tantalum tube inside the furnace (see Fig. 1 in [4]) was replaced by a tungsten tube, which is physically more stable at high temperatures. Furthermore, the control grid bars were re-shaped providing the originally flat bars with a V-profile to prevent constant bending. Both modifications significantly increased the reliability of the extraction furnace.

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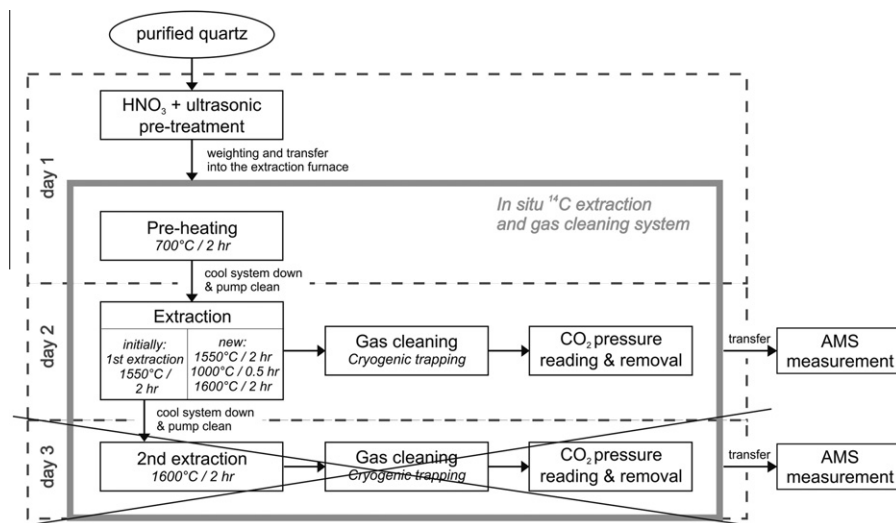


Fig. 1. Illustration of *in situ* ^{14}C analysis as performed at ETH Zürich. The initial 3-day procedure has been recently shortened by including the former second extraction step into an expanded total extraction step. Sample processing can now be accomplished within 2 days.

2.2. Current analytical procedures

About 5 g of quartz are used for an *in situ* ^{14}C analysis. Once loaded into the extraction furnace, the quartz sample is pre-heated at $\sim 700^\circ\text{C}$ (calibrated with a pyrometer) for 2 h under a flow of ultra-high-purity (UHP) O_2 to remove atmospheric contamination. The temperature of 700°C was chosen based on stepped-heating experiments showing that 500°C is sufficient to remove atmospheric ^{14}C [3] but that the *in situ* component is not released below 900°C [4]. This pre-heating step is crucial because the amount of contaminant ^{14}C can be similar or even higher than the *in situ* ^{14}C amount. Next, the furnace is cooled to room temperature and the large amounts of water and other gases released during pre-heating are pumped off (usually overnight) until the system pressure is about 10^{-7} – 10^{-6} Pa. For *in situ* ^{14}C extraction the sample is then heated under a UHP O_2 -flow to 1550 – 1600°C for 2×2 h. The quartz is not melted under these conditions but slight sintering was observed for a few samples. Following extraction, the gas is cleaned and taken off for AMS analysis as previously described [4].

In our initial procedure, two high-temperature heating steps of 2 h duration each were made to guarantee complete extraction of *in situ* ^{14}C from the quartz. The second extraction step was performed the next day after the furnace had been cooled to room temperature overnight. In our modified procedure, samples are heated at 1550 – 1600°C for 2 h, cooled to 1000°C for 30 min, and heated again for 2 h at 1550 – 1600°C . With the additional 1000°C step the quartz crosses the tridymite-cristobalite transformation temperature at 1470°C twice more. The associated transformation of the quartz crystal lattice may help to promote the release of any remaining *in situ* ^{14}C .

The entire extraction (incl. gas cleaning) now requires ~ 10 h and is accomplished in 1 day. Fig. 1 compares present and previous sample processing procedures.

2.3. AMS measurement

The purified CO_2 gas can be measured without graphitization at the MICADAS AMS system at ETH using the gas ion source [8–11]. The current setup of the gas feeding system allows CO_2 amounts equivalent to $\sim 45 \mu\text{g}$ carbon to be released into the ion source. Typically, our samples yield sufficient CO_2 (~ 5 – $30 \mu\text{g}$ carbon) to be measured without further CO_2 -addition. Procedural blanks, however, yield only little CO_2 (1 – $2 \mu\text{g}$ carbon) and therefore re-

quire the addition of ^{14}C -free CO_2 to provide sufficient gas for AMS analysis (Table 1). Samples containing more than $40 \mu\text{g}$ carbon are split into separate breakseal tubes before being taken off the extraction system.

The $^{14}\text{C}/^{12}\text{C}$ ratios obtained from a quartz sample are usually significantly higher than ratios measured, e.g., for modern organic samples. This creates a good signal-to-background ratio and allows a high analytical precision. An example of a ^{14}C measurement from a quartz sample on the MICADAS system is given in Fig. 2. Due to the small sample size ($5.1 \mu\text{g}$ carbon) the $^{14}\text{C}/^{12}\text{C}$ ratio is ~ 7 times the modern ratio and is measured with a counting error lower than 1%.

2.4. Data processing

AMS radiocarbon data are commonly reported as $F^{14}\text{C}$ (or F_m), the measured fraction modern carbon, normalized to a $\delta^{13}\text{C}$ of $-25\text{‰}_{\text{VPDB}}$ and AD 1950 [12,13]. Radiocarbon ages are typically calculated based on this value. The same procedure has so far also been applied to calculate concentrations of *in situ* ^{14}C in quartz. However, the main purpose of a $\delta^{13}\text{C}$ correction is to compensate for natural isotopic fractionation in biochemical processes. The normalization to AD 1950 accounts for the anthropogenic release of ‘bomb’ ^{14}C in the atmosphere. Both effects are not relevant for the production of *in situ* ^{14}C in quartz. As such, we argue that normalization to these parameters is not correct and changes the ‘true’ $^{14}\text{C}/^{12}\text{C}$ ratio of the sample.

Because raw data for *in situ* ^{14}C analyses are often obtained from the AMS laboratories in the same way as classical radiocarbon data, we will describe in the following how we determine the absolute (‘true’) $^{14}\text{C}/^{12}\text{C}$ ratio from reported $F^{14}\text{C}$ and $\delta^{13}\text{C}$ values. Additionally, as an easier way, we calculate the absolute $^{14}\text{C}/^{12}\text{C}$ ratio directly from the measured raw $^{14}\text{C}/^{12}\text{C}$ data. We propose that this procedure should be used for *in situ* ^{14}C data reduction. Below, the subscripts S and OX refer to sample and the oxalic acid standard OX-I, respectively.

The $F^{14}\text{C}$ is defined as the ratio of the sample activity to the standard activity [14], which is equivalent to the ratio of the sample $^{14}\text{C}/^{12}\text{C}$ (or $^{14}\text{C}/^{13}\text{C}$) ratio to the standard $^{14}\text{C}/^{12}\text{C}$ (or $^{14}\text{C}/^{13}\text{C}$) ratio [12,13]. By definition, the standard $^{14}\text{C}/^{12}\text{C}$ ratio is 95% of the specific activity of the international standard oxalic acid (OX-I), in AD 1950 and normalized to $\delta^{13}\text{C} = -19\text{‰}_{\text{VPDB}}$ [14]. To calculate today’s absolute $^{14}\text{C}/^{12}\text{C}$ ratio of a sample, the $\delta^{13}\text{C}$ fractionation correction included in the $F^{14}\text{C}_S$ is undone again using the mea-

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