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^{36}Cl accelerator mass spectrometry with a bespoke instrument

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ABSTRACT

Cosmogenic ^{36}Cl analysis by accelerator mass spectrometry (AMS) is a valuable environmental and geological sciences research tool. Overcoming the stable nuclide ^{36}S isobar interfering with measurement is challenging, however. Traditionally this has required large accelerators, but following recent technical advances it is now possible with ~30 MeV ion energies. Consequently 5 MV or even smaller modern bespoke spectrometers are now ^{36}Cl-capable, increasing accessibility and promoting wider and more varied ^{36}Cl use.

However, the technical ability to identify ^{36}Cl ions is quite distinct from demonstrated high-performance AMS. Such is the theme of this paper. We present a systematic analysis of the accurate measurement of sample radioisotope relative to the stable chlorine, the normalisation of the measured ratio and correction for remaining ^{36}S interference, all combined with the use of stable-isotope dilution to determine sample Cl concentration to begin with. We conclude by showing that repeated analyses support our claims for routine 3% ^{36}Cl-AMS data. Accordingly, the modest SUERC spectrometer well competes with the performance of larger longer-established instruments, and the results may be quite generic for modern bespoke instruments.

1. Introduction

In situ cosmogenic nuclei, made by cosmic ray induced nuclear reactions cumulatively on exposed surfaces, are natural chronometers and valuable tools for environmental study. Cosmogenic ^{36}Cl ($t_{1/2} = 3 \times 10^5$ yr) is dominantly produced in spallation reactions on Ca and K and via neutron capture on ^{35}Cl, and so is applicable to a range of lithologies for studying events within the last 1 Myr. The different ^{36}Cl production mechanisms result in versatility but also challenging data interpretation when unravelling the measured ^{36}Cl concentrations [1]. Uncertainties in radionuclide production and sometimes difficult sample preparation for analysis can be additional complications.

However, the main difficulty in utilising the ^{36}Cl signal for environmental research arises from the stable isobar ^{36}S. These two nuclides can, however, be separated based on different rate of energy loss in matter if high enough ion energies are available. This has typically required large (10–15 MV) legacy nuclear physics particle accelerators but recently it has been shown that sufficient separation can be achieved with much lower ion energies than before (~ 30 MeV) [2–6]; the accelerator mass spectrometer detector resolution being improved by using uniform thin (~30 nm) silicon rich nitride membranes that can hold differential pressures between the detector volume and rest of the spectrometer [7,8]. Thin uniform window in front of the detector will minimise energy losses and peak broadening.

Consequently measurements can now be done with 5 MV, or even smaller, modern accelerator mass spectrometers utilising gas stripping to produce the highest possible quality beams. Accordingly, a new class of commercial purpose-built 5–6 MV ^{36}Cl-capable spectrometers is being deployed around the globe, with additional measurement capacity greater than that of the existing legacy accelerators. This should increase accessibility and promote wider and more varied ^{36}Cl use.

This work describes ^{36}Cl measurement on the SUERC 5 MV accelerator mass spectrometer, showing that modern bespoke spectrometers offer a now mature tool for environmental and geological research using ^{36}Cl. Such new spectrometers are comparable to the capabilities of older legacy accelerators and even offer some distinct advantages. In practice, though, these two technologies likely will have their separate uses and in fact be quite complementary.

2. SUERC ^{36}Cl accelerator mass spectrometry

We begin by summarising instrumental aspects of SUERC ^{36}Cl measurement that are already published [2,6]. First, negative ions

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are created in a Cs sputter source after which they are momentum and energy analysed before being injected into the accelerator. Accelerator transmission is beam current-dependent above 30 μA and so analysis is typically done from ion beams of about 20 μA $^{35}Cl^-$. In the initial acceleration stage negative ions are accelerated towards the positively-biased terminal where they are passed through a thin gas and become positively charged. Positively charged ions are then further accelerated away from the terminal and the 5+ charge state is selected with the following mass spectrometer. Molecules become unstable at high charge states and consequently the method provides effective suppression of molecular interferences. Ion transmission through the accelerator to the detector is about 20%; ions of stable ^{35}Cl and ^{37}Cl are measured at high energy off-axis Faraday cups and ^{36}Cl ions are separated from the interfering ^{36}S ions in a multi anode gas ionisation detector. Machine background for ^{36}Cl/Cl is typically below 10^{-15}. To reduce a ^{36}S signal from the ion source components each AgCl sample is pressed into clean AgBr substrate and a spherical ioniser used to tightly focus the Cs beam at the cathode surface. Cross talk between samples in the ion source is in the order of 10^{-3} and samples with ^{36}Cl/Cl ratios above 10^{-12} are avoided. Consequently samples with ^{36}Cl/Cl ratios down to 10^{-15} can be measured without significant memory effects.

An automated algorithm is used to control the measurement progress allowing continuous unattended operation. Samples are measured in repeated sequence until a sample's analyses are sufficient and it is removed from the sequence; sample analysis continues until both ^{36}Cl counting statistics and standard deviation of the mean of the repeated ^{36}Cl/Cl measurements achieve 3% typically, discarding only early inconsistent measurements. (The algorithm guides data management but is not used as a substitute for the data reduction.) This promotes a reliable quality, and minimises and overcomes ion source memory; high-level samples are quickly measured to completion while measurements of low-level samples automatically continue until significantly unaffected by source memory. Data generation proceeds expeditiously.

To achieve 3% uncertainty within three measurements or more on a single sample each individual measurement proceeds until 400 counts or given time limit (typically 6 min) is reached. For samples with ^{36}Cl/Cl ratio in the range of 10^{-13} the given count limit is reached within a few minutes, and in the absence of surface contamination 3% uncertainty is achieved within three measurements. For lower level samples and blanks, 10 measurements are often required; if typical 1.3 mg Cl was used as a carrier, more than 20 measurements can readily be completed before the sample is exhausted. To finish a wheel of 67 samples takes about 2–3 days depending on the ^{36}Cl/Cl ratios in the samples and desired precision. The sample wheel is divided into groups of about 10 samples and each group is measured to completion in turn. Each group consists of one primary standard and typically two secondary standards allowing effective quality assurance. The ~500 samples/year routinely performed at SUERC require ~1 month of accelerator time divided between several runs.

3. Stable Cl measurement with isotope dilution

3.1. Measurement principles and uncertainties

Given the production of ^{36}Cl via neutron capture on ^{35}Cl, it is imperative to know the stable Cl concentration in the material for ^{36}Cl exposure age dating. Isotope dilution (ID) is typically the preferred method for measuring the Cl concentrations because of the better precision at low concentrations compared, for example, to ion-selective electrode method or Prompt Gamma Activation Analysis (PGAA) [9–13]. In addition ID–AMS allows ^{36}Cl/Cl ratio and Cl concentration to be measured simultaneously from a single AMS target. However, PGAA measurement has advantages as it can be used for determining not only the target elements for ^{36}Cl production (Cl, Ca, K, Ti and Fe) but also neutron absorbers (B, Gd, Sm) and moderators (H) that are required for exposure age calculations. Consequently the Cl measurement with PGAA gives complementary information that can be used for quality assurance and optimisation of the sample preparation [13].

The principle of the isotope dilution method is to alter the isotopic composition of the sample by adding a known amount of isotopically enriched material of know isotopic composition. The resulting change in the isotopic ratio can be used to calculate the concentration of the element in the original sample. In the case of Cl either ^{35}Cl or ^{37}Cl isotopes can be used to alter the stable Cl ratio.

The ^{37}Cl/^{35}Cl ratio in the isotopically enriched sample can be written as

$$R_{\mathrm{sample}} = \frac{^{37}\mathrm{Cl}_{\mathrm{rock}} + {}^{37}\mathrm{Cl}_{\mathrm{spike}}}{^{35}\mathrm{Cl}_{\mathrm{rock}} + {}^{35}\mathrm{Cl}_{\mathrm{spike}}} \tag{1}$$

where $R_{\mathrm{sample}} = \left(\frac{^{37}\mathrm{Cl}}{^{35}\mathrm{Cl}}\right)_{\mathrm{sample}}$. The subscript 'sample' refers to the pure AgCl that is used for the ID–AMS measurement and is a combination of the original dissolved material 'rock' that has natural ^{37}Cl/^{35}Cl ratio and 'spike' that is the isotopically enriched material added to the sample. These are atom ratios and, for example, $^{37}\mathrm{Cl}_{\mathrm{rock}}$ refers to the number of ^{37}Cl atoms dissolved from the rock. Similarly $R_{\mathrm{rock}} = \left(\frac{^{37}\mathrm{Cl}}{^{35}\mathrm{Cl}}\right)_{\mathrm{rock}}$ and $R_{\mathrm{spike}} = \left(\frac{^{37}\mathrm{Cl}}{^{35}\mathrm{Cl}}\right)_{\mathrm{spike}}$, and Eq. (1) can be rearranged to

$$\frac{^{35}\mathrm{Cl}_{\mathrm{rock}}}{^{35}\mathrm{Cl}_{\mathrm{spike}}} = \frac{R_{\mathrm{sample}} - R_{\mathrm{spike}}}{R_{\mathrm{rock}} - R_{\mathrm{sample}}} \tag{2}$$

On the basis of Eq. (2) the Cl concentration in the rock can be calculated from the measured (R_{sample}) and known values $(R_{\mathrm{rock}}, R_{\mathrm{spike}})$. However, this equation represents an ideal situation with no Cl contamination. By preparing a laboratory 'blank' samples that have gone through similar sample preparation chemistry and have equal amount of spike added as the real samples, the Cl contamination can be monitored. Laboratory blanks are prepared alongside the real samples. So Eq. (2) now becomes

$$\frac{^{35}\mathrm{Cl}_{\mathrm{rock}}}{^{35}\mathrm{Cl}_{\mathrm{blank}}} = \frac{R_{\mathrm{sample}} - R_{\mathrm{blank}}}{R_{\mathrm{rock}} - R_{\mathrm{sample}}} \tag{3}$$

where

$$R_{\mathrm{blank}} = \frac{^{37}\mathrm{Cl}_{\mathrm{spike}} + {}^{37}\mathrm{Cl}_{\mathrm{cont.}}}{^{35}\mathrm{Cl}_{\mathrm{spike}} + {}^{35}\mathrm{Cl}_{\mathrm{cont.}}}. \tag{4}$$

Here $^{35}\mathrm{Cl}_{\mathrm{cont.}}$ and $^{37}\mathrm{Cl}_{\mathrm{cont.}}$ refer, respectively, to the number of contaminating ^{35}Cl and ^{37}Cl atoms. The total number of ^{35}Cl atoms in the blank can subsequently be written as

$$^{35}\mathrm{Cl}_{\mathrm{blank}} = \left[1 + \frac{R_{\mathrm{blank}} - R_{\mathrm{spike}}}{R_{\mathrm{cont.}} - R_{\mathrm{blank}}}\right] {}^{35}\mathrm{Cl}_{\mathrm{spike}} \tag{5}$$

Now, according to Eqs. (3) and (5) we can calculate the blank corrected number of ^{35}Cl atoms in the rock. However, the above is valid only for a situation where the amount of spike added to the sample and chemistry blank is equal. This is typically the case and consequently the following error propagation is done based on this assumption. In addition, we assume that the Cl contamination has natural ^{37}Cl/^{35}Cl ratio and $R_{\mathrm{cont.}} = R_{\mathrm{rock}}$.

3.1.1. Stable Cl uncertainties

The calculated Cl concentration uncertainties are a combination of measurement uncertainties, the relation of the spike and sample