

THE CHEMICAL PREPARATION OF AgCl FOR MEASURING ^{36}Cl IN POLAR ICE WITH ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. A method of chemical separation and purification of chloride from relatively small samples (500 to 2100g) of glacial ice is presented. With this procedure the first successful measurements of pre-bomb levels of ^{36}Cl in Greenland ice have been made. Emphasis is placed on methods of reducing sulfur, which causes interference in the accelerator mass spectrometry, and in maximizing the yield. Data regarding the selection of materials for sample holders and the use of metal powders for extending the lifetime of the sample are also presented.

INTRODUCTION

Since 1978 when accelerator mass spectrometry of ^{36}Cl in natural samples was first demonstrated (Elmore *et al*, 1979), close to 700 samples have been measured. The chemical preparation of groundwater samples, where tens of liters are usually available (Bentley *et al*, 1985), and the chemical preparation of meteorite samples, where the ^{36}Cl content is relatively high, (Nishiizumi *et al*, 1983) has been very successful, although many of the details have not been recorded in the literature. The measurement of ^{36}Cl in Greenland ice cores has been the most difficult attempted because of the small samples and $^{36}\text{Cl}/\text{Cl}$ ratios that are low as a result of adding carrier. We present here the method of chemical preparation used for these ice cores. The samples produced have been demonstrated to be adequate for better than 7% precision at the $^{36}\text{Cl}/\text{Cl} = 50 \times 10^{-15}$ level.

In order to achieve this level of performance, we had to develop a chemical preparation procedure that satisfied three requirements. First, the sulfur had to be reduced to a level such that ^{36}S interference counting rates were below 2000 counts per second and preferably below 500 counts per second (Elmore *et al*, 1984a, b). We can estimate that this requirement is ca 1ppm sulfur which is equivalent to a part per 10^{10} ^{36}S , or less. Because the cesium beam eventually sputtered through the sample material, this requirement of low sulfur also put restrictions on the purity of the sample holder.

Second, the chemical yield had to be kept as high as possible in order to maintain an adequate amount of sample material. To keep the $^{36}\text{Cl}/\text{Cl}$ ratio well above background, the smallest amount of ^{36}Cl -free chloride carrier was added which was consistent with the third requirement that the sample must give strong and steady beam currents for several hours. Care was needed in the chemistry. In early trials ammonium nitrate was not washed out sufficiently, which resulted in low negative ion currents. Adequate drying of the sample was found to be important; on several occasions poorly dried samples produced weak beam currents. For samples where the yield

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TABLE 1
Sulfur counting rates for sample holder materials

Material	^{36}S counting rate (counts/sec)
99.95% tantalum	100
99.97% molybdenum	200
Single crystal silicon	500
Ultra-pure aluminum	2000
Aluminum alloy	>2000
Stainless steel	>2000

was low, a metal powder was added to the sample to extend the time adequate currents could be obtained.

REDUCTION OF ^{36}S INTERFERENCE

Sulfur is an abundant and ubiquitous element that is difficult to reduce to part per million levels. Reducing the sulfur content in the sample posed the greatest problem in measuring natural levels of ^{36}Cl in polar ice. To minimize sulfur the liquid reagents used in the chemistry were purified by distillation, and a Gelman Water I was used to produce the deionized water. All glass and plastic ware was washed with soap and rinsed with deionized water, distilled nitric acid, distilled ammonium hydroxide, and again with deionized water. Clean gloves were worn at all times. To further reduce the chance of contamination, the sample material was transferred only when necessary. Water washes and one or more barium precipitations were also done to reduce the sulfur content of the sample. The barium addition results in the precipitation of sulfates, the most abundant form of sulfur in ice, as barium sulfate.

A fairly comprehensive search for sample holder materials was undertaken to find a material with the acceptable machining properties, extremely low sulfur negative ion yield, and an affordable price. A list of sulfur counting rates for various materials is given in Table 1. These are the counting rates after 5 minutes of sputtering during which time any surface contamination was removed. High purity aluminum was used in early runs, and later an improvement was made by using single crystal silicon prepared for the semiconductor industry. Silicon had the disadvantage of being diffi-

TABLE 2
Sulfur counting rates for binders

Material	^{36}S counting rate (counts/sec)
99.9999% Au	100
99.98% Ta	700
99.99% Ag	1500
99.999% Mo	3500
99.999% Ni	3500
99.999% Fe	5000
99.999% Co	>>5000

cult to machine. The best material was later found (Wölfli, pers commun) to be 99.95% purity tantalum obtained from Johnson & Matthey Inc.

Although not needed to hold the sample in place, the use of a metal binder was found to extend the run time of extremely small samples without greatly reducing the chlorine beam current. Only after diluting the sample by >50% by volume does one see an appreciable drop in beam current. A test for a suitable binder was undertaken to find one that contributed as little as possible to the ^{36}S counting rate. Table 2 lists the ^{36}S counting rates resulting from the use of several binders with a low sulfur standard. The most appropriate binder was found to be 99.9999% purity gold powder from Johnson & Matthey Inc.

ADDITION OF CARRIER

The ice cores processed ranged in size from 500 to 2100g. Since ice from Camp Century has roughly 100ppb of chloride (Herron, 1980), these quantities of ice contain 50 to 200 μg of chloride. This amount of sample material would not last long in the ion source and would be very difficult to handle. Up to some limit, there is no disadvantage to adding carrier since accelerator mass spectrometry can measure very low $^{36}\text{Cl}/\text{Cl}$ ratios. For a typical sample of 1500g of ice, 2.7mg of ^{36}Cl -free chloride was found to be an appropriate amount of carrier. This reduced the radioisotope ratios to ca 100×10^{-15} , a value high enough to require only a small background correction. Also, this amount of carrier yielded enough material, ca 8mg of AgCl, to give several hours of steady beam currents. The intensity of the cesium beam was lowered to increase the lifetime of the samples. A solution of Week's Island halite (NaCl), provided by the University of Arizona Hydrology Department, was used as carrier. Samples of this material processed identically to the unknowns were measured to have ratios between 1 and 7×10^{-15} . These measurements were used to correct the unknowns for background resulting from the chemical preparation and measurement of samples.

EXTRACTION OF CHLORIDE AS AgCl

The first step of the sample preparation was to rinse the ice with 18M Ω deionized water. This was done to reduce surface contamination. The washed ice was then covered to keep out contaminants and left to melt. A hot plate or microwave oven was sometimes used to save time. After melting, an aliquot of water was removed for measuring the concentration of stable chloride in the ice. Carrier was then added. The mass of carrier and the volume of water were measured to better than 0.5% accuracy. The solution was acidified with ca 1ml of concentrated nitric acid. For a sample of 1500g, 0.85mg of beryllium carrier was also added at this time for future ^{10}Be measurements. Concentrating the solution to ca 250ml by vacuum distillation was found to simplify the subsequent chemistry and to increase yields.

The target material used for ^{36}Cl experiments is AgCl since it readily precipitates out of solution and provides high and steady chlorine beam currents. Following the volume reduction a 10% excess of AgNO_3 was

added to the solution. AgCl was seen immediately as a white precipitate. AgCl is photochemically active and was stored in the dark to prevent decomposition. The covered solution was left for several hours or overnight to allow time for the precipitate to form and settle. The solution was then decanted or pipetted, and saved for the beryllium chemistry. The precipitate was suspended in deionized water, transferred to a centrifuge tube, and spun down to a clean white pellet. Next, the AgCl pellet was dissolved in 2ml of distilled NH_4OH and ca 20ml of deionized water. A vortex mixer was used to speed up the dissolution. One ml of saturated $\text{Ba}(\text{NO}_3)_2$ solution was added to the AgCl solution, which was still in the centrifuge tube. The sample was stored for several hours while the BaSO_4 formed. The solution was centrifuged and pipetted into another centrifuge tube leaving the precipitate behind. The solution was acidified with 10 or 15 drops of concentrated nitric acid. As before the AgCl precipitate formed readily. After waiting several hours the precipitate was centrifuged. Again a clean white pellet formed. The AgCl was twice resuspended in deionized water and centrifuged, completing the chemistry. The yield of the chemistry was typically 50 to 75%. The samples, still in centrifuge tubes, were wrapped in aluminum foil to protect them from light and placed in an oven at ca 120°C for several hours to dry.

MEASURING THE SAMPLE

The samples were loaded into holes in the sample wheel immediately prior to measurement on the accelerator. The sample wheel is 23mm in diameter and has 18 holes spaced 5mm apart. The holes used for the ice samples were 1.2mm in diameter and 1.1mm deep. Samples under ca 4mg of AgCl were mixed with ca 3mg of -22 mesh gold powder. A special stainless steel funnel was used to direct the material into the hole and keep it from entering the neighboring holes. A firm hand pressure on a tamper was used to press the samples in place. There was no tendency for the samples to fall out as with amorphous carbon or beryllium oxide.

Of 27 samples attempted to date 25 were successfully measured. Values of $^{36}\text{Cl}/\text{Cl}$ ranged from 40 to 130×10^{-15} , with uncertainties from 7 to 20%. In several cases the samples or binders were contaminated with sulfur making it necessary to scrape the sample out of the sample wheel for reprocessing. In the reprocessing all the steps after the first AgCl precipitation were repeated. That reprocessing was successful attests to the high yield of the procedure and its ability to work with small samples. In five cases when reprocessing was done to lower the uncertainty of measurements, the second measurement was in agreement with the first. One sample was run for a total of 5 hours and nearly 500 ^{36}Cl events were recorded. This means that uncertainties of the order of 4.5% are possible.

CONCLUSION

After over two years of work on developing a procedure for measuring small samples, we are confident that polar ice samples can be measured routinely. It is hoped that measurements of ^{36}Cl will serve to improve our understanding of the production and transport of cosmogenic radio-

isotopes as well as provide a means of dating old ice with the $^{10}\text{Be}/^{36}\text{Cl}$ ratio (Nishiizumi *et al*, 1983).

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