https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

Technical Note: Stable Chloride Measurements at CAMS

Tyler S. Anderson[1], Alan J. Hidy[1]

[1] Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory Livermore, CA 94550, USA

Correspondence to: Tyler S. Anderson (anderson309@llnl.gov)

Abstract.

We present a new method for preparing silicate samples for stable chloride analysis using the low-energy injection components of an accelerator mass spectrometry (AMS) system. This method uses Nb over AgBr as a bulking agent during sample preparation which drastically reduces background Cl signals (ion source memory) by a factor of ~100 and allows for faster, cheaper, and more precise analyses on low-Cl samples (<10 µg Cl). We demonstrate this approach with measurements of stable chlorine isotope ratios ($^{35}Cl/^{37}Cl$) performed on silicates, prepared in both AgBr and Nb matrices, that characterize chlorine concentrations of samples containing ~1-500 ppm Cl. While this method was developed primarily to interrogate silicates, it performs equally well on other commonly analyzed sample matrices including carbonates and water. This Nb-based method is now the standard procedure at the Center for Accelerator Mass Spectrometry (CAMS) for preparing all stable Cl targets, including those accompanying ^{36}Cl analyses.

1 Introduction

The ratio of chlorine's two stable isotopes, ^{35}Cl and ^{37}Cl, has been studied as a probe for planetary science to understand high temperature planetary processes like volcanism, accretion, or magma oceans (e.g., (Boyce et al., 2015; Greenwood et al., 2017; Boyce et al., 2018; Wang et al., 2019; Day et al., 2017; Sharp et al., 2016; Sarafian et al., 2017; Shearer et al., 2018). For example, low Cl concentrations in astromaterials are often interpreted as the result of extensive volatilization and loss of Cl, with preferential loss of ^{37}Cl through kinetic fractionation, changing the material's $^{35}Cl/^{37}Cl$ ratio. Presently, the two most commonly used techniques for stable Cl analyses are secondary ion mass spectrometry (SIMS), which performs *in situ* analyses of high Cl concentration minerals like apatite, and isotope ratio mass spectrometry (IRMS), which performs bulk analyses and requires at least ~100 µg of Cl. There are, however, relatively few facilities capable of performing these analyses, in part a result of the difficulty of performing measurements on low concentrations or low masses of Cl, which has resulted in a dearth of available data for stable Cl ratios in planetary astromaterials.

When measured with AMS, stable Cl ratio analyses were first performed on large masses of AgCl (> ~10-100 mg), which were primarily analyzed to quantify the radioisotope ^{36}Cl via double isotope dilution (Elmore et al., 1979; Davie et al., 1987). Such a large mass of AgCl was used to cover the face of the sample holder ('cathode'), reducing the interference of the isobar ^{36}S from sputtering of the cathode's metal surface (e.g., Cu, stainless steel). As sensitivity improved and the mass of

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

AgCl required for analysis decreased, the reduction in sulfur was maintained by back-filling cathodes with AgBr, used due to its low sulfur content and chemical compatibility with AgCl, and drilling out a hole where the sample AgCl was loaded.

Recently, CAMS has moved toward analyzing stable Cl separately, prior to ^{36}Cl analysis, in a sample composed of smaller amounts of AgCl embedded in an AgBr matrix that can be packed in drilled stainless steel targets that are regularly used for other isotopes at CAMS (e.g., ^{10}Be and ^{26}Al). This workflow is published in (Lesnek et al., 2024) and comes with multiple benefits. First, it significantly reduces the amount of expensive isotopically enriched Cl carrier that is typically needed to analyze total Cl via isotope dilution. Performing stable Cl analyses before ^{36}Cl analyses allows for Cl concentration determination prior to preparation of the larger ^{36}Cl sample, better informing the required sample mass to digest for optimized ^{36}Cl analyses. The ^{36}Cl sample can then be bulked with cheap natural ratio Cl instead of expensive isotopically enriched Cl spike (particularly ^{37}Cl)—effectively reducing the required enriched Cl carrier mass from ~1 mg to 50 ug per sample (recommended for stable Cl analysis). This method provides additional flexibility because the carrier can be enriched in either ^{35}Cl or ^{37}Cl, and carrier solutions known to contain unacceptably high levels of ^{36}Cl can be used because they are no longer being added to the ^{36}Cl sample. While use of AgBr has been critical for ^{36}Cl analyses, and well suited to the analytical needs for stable Cl analyses of terrestrial samples not limited by mass or Cl concentration, use of AgBr brings with it significant downsides that have until now made analysis of small, rare, or Cl-poor samples – such as meteorites or samples returned from space missions – infeasible due to significant background Cl, matrix volatility, and ion source memory effects (Finkel et al., 2013).

In 2022, Anderson et al. presented a new analytical technique using a Nb powder matrix for stable Cl measurements instead of AgBr, drastically reducing the Cl mass required for stable Cl analyses from ~100 µg to as little as 1 µg with samples precipitated from prepared saltwater solutions. During that developmental work, multiple observations were made that suggested several improvements to the measurement technique could be achieved by switching from Nb to AgBr. These included significantly reduced Cl backgrounds, improved source stability resulting in higher ion beam currents, and very low memory effects, all while allowing high precision measurements (1-4 permille, 1σ) (Anderson et al., 2022). These previously unpublished observations and follow-up experiments are described in this work. Unfortunately, that Nb technique was only applied to Cl precipitated directly from saltwater solutions. While it served to demonstrate the feasibility of low-level Cl analyses performed in Nb, the incompatibility of Nb with existing sample preparation requiring hydrofluoric acid (HF) limited its immediate applicability to silicates until problems with separating and preserving the small masses of Cl from an HF matrix were resolved. Here, we present methods for extracting small amounts of Cl from silicates and preparing AgCl samples in a Nb matrix for high-precision stable Cl analyses with AMS. Based on performance of the Nb method for silicate and other sample matrices and its advantages over AgBr-based preparation methods, stable Cl analyses at CAMS are now exclusively performed on AgCl in Nb.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

1.1 Motivation for switching from AgBr

A key motivation for this work emerged from (Anderson et al., 2022) where a range of ion source cathode voltages were tested for viability. Higher cathode voltages increased the intensity of the produced ion beam (Fig. 1), but the volatility of AgBr limited operation to ~2.5 kV to prevent melting and ion source shorts. This volatility issue is not unique to AgBr; AgCl and other silver halides face similar limitations, which is why lower cathode voltage limits also apply to ^{36}Cl targets that use pure AgCl matrices. Using Nb reduced volatility and allowed operation up to ~5 kV. While the cathode voltage for Nb can be run above 5 kV without shorting CAMS ion sources, current output becomes less stable near this voltage. Thus, a more conservative value of 4.5 kV is considered the nominal operational voltage for stable Cl in Nb targets.

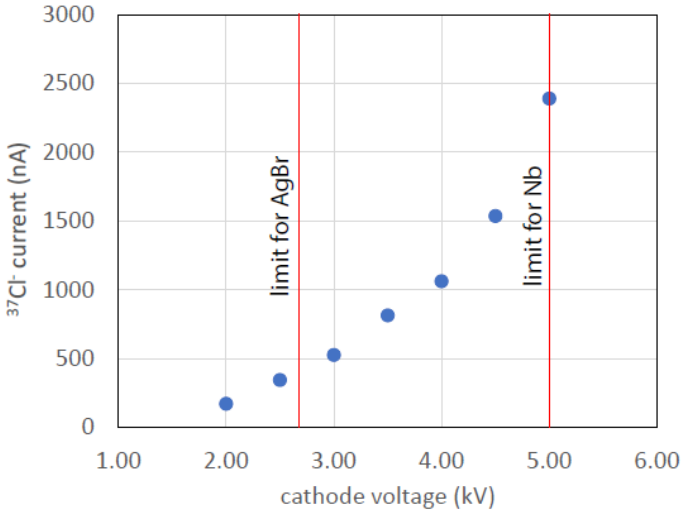

Figure 1: $^{37}Cl^-$ current output for a target containing 50 µg total Cl (at natural abundance ratio) showing operational stability limits for targets prepared in AgBr vs. Nb in CAMS ion sources. Note: Cs pot temperatures for stable Cl are held at a constant range between 142-145°C.

Nb target preparation was also seen to profoundly reduce background and memory effects compared to AgBr. An example of this is shown in Fig. 2 where background measurements of Cl charge were acquired between AgCl samples and standards analyzed in Nb and AgBr from matrix-blanks measured between Cl-containing targets. The measurements of charge were acquired from targets containing no added Cl and therefore indicate residual memory from previously analyzed targets. These data were produced from sample wheels identical in terms of sample material and chloride content of each target and were run consecutively (the Nb wheel ran first followed by the AgBr wheel). The reduced background from the Nb wheel improved signal to noise by a factor of ~100, and memory effects following samples with high Cl targets also decayed more rapidly in Nb.

Collectively, these early findings demonstrated the potential benefits from using Nb as a matrix for stable Cl isotope analyses of silicates. However, after an initial attempt testing the method with a feldspar sample it became clear that isobaric interference stemming from residual fluoride from HF dissolution was problematic. A mass scan of this feldspar target (Fig. 3) revealed a large peak at mass 19 (fluorine is the only stable isotope at this mass). Because strong oxygen peaks at mass 16 are ubiquitous in Cs sputter sources, interference at mass 35 from $^{16}O^{19}F^-$ is likely and renders accurate $^{35}Cl/^{37}Cl$ ratio determination infeasible. Thus, additional method development was clearly required. Our refined sample preparation method

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

resolving this issue along with two experiments directly comparing AgBr and Nb preparation are described in the sections that follow.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

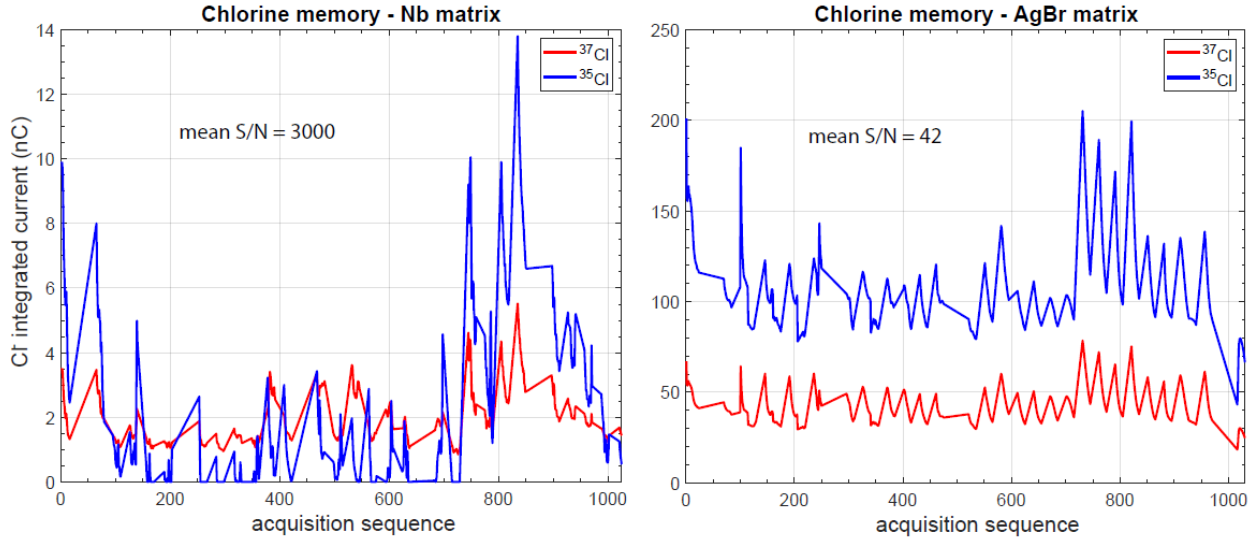

Figure 2: Cl background measurements from identical stable Cl wheels but prepared with different matrices (Nb and AgBr). Note the different scales for the y-axes between the two plots. The average signal to noise ratios (S/N) of integrated currents from unknown targets to respective background are noted on each plot.

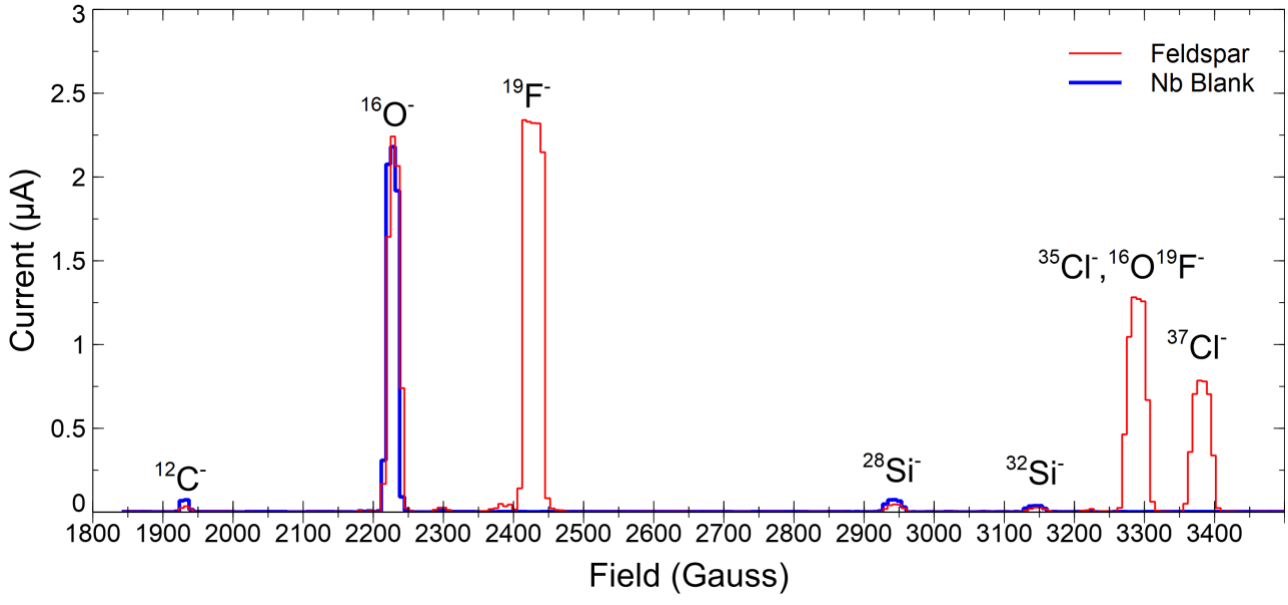

Figure 3: Mass scans for initial test of a 1 g feldspar aliquot enriched with carrier (50 µg Cl; $^{35}Cl/^{37}Cl \sim 1$) and its corresponding Nb blank, prepared following (Anderson et al., 2022). Significant mass peaks are labelled with likely contributing anion species. Scans suggest existing methods are incompatible with silicate samples that require HF digestions as $^{16}O^{19}F^-$ interferes with measurement of $^{35}Cl^-$.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

2 Methods

The methods presented here include 1) an improved chemistry procedure for preparing samples for stable Cl analyses in Nb, with the accompanying former procedure used for AgBr, 2) creation of a dilution series used to compare stable Cl analyses between Nb and AgBr sample matrices, 3) mass spectrometry techniques at CAMS used for stable Cl analysis, including 4) the quantification of background and memory during stable Cl analysis, 5) mass scans used to diagnose potential interferences, and 6) data reduction techniques.

2.1 Sample preparation for stable Cl analysis

The general procedures for preparing samples for stable Cl measurements are outlined below for both AgBr and Nb matrices and shown in Fig. 4. These are broken up into three sections: 1) digestion of silicates up to the point of fluoride cake removal, 2) preparation to target for stable Cl measurement in AgBr, and 3) preparation to target for stable Cl measurement in Nb. This procedure is designed for sample masses of up to ~1 g but can be scaled to larger masses as appropriate. Note that all preparation steps where Cl exists as precipitated AgCl should be performed in low light or under red/amber lighting to reduce

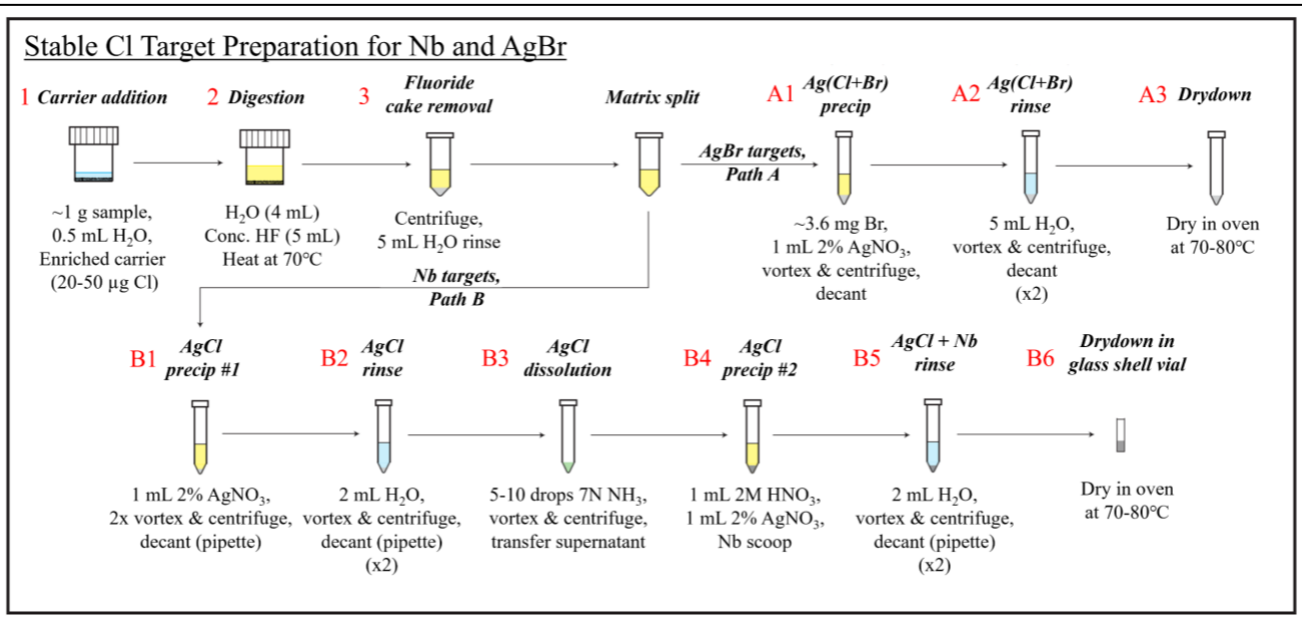

Figure 4: Stable Cl sample preparation procedure for AgBr and Nb target matrices. AgBr targets (path A) follow the workflow of Lesnek et al. (2024); Nb targets (path B) follow recommended workflow modified from (Anderson et al., 2022) which includes additional precipitation and rinsing steps to completely remove trace HF prior to Nb powder addition. Note: Enriched carrier is added in step **1** only for Cl concentration measurements via isotope dilution. AgBr standards and matrix blanks start at step **A1**; Nb standards start at **B4**; Nb matrix blanks start at **B5**, with the Nb addition from step **B4** performed here instead.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

AgCl photodissociation. When Cl concentration of a sample is desired in lieu of its native $^{35}Cl/^{37}Cl$ ratio, an enriched Cl standard with a ratio sufficiently different from natural (e.g., $^{35}Cl/^{37}Cl \sim 1$) is added prior to acid digestion to determine the Cl concentration via isotope dilution.

2.1.1 Silicate digestion

The digestion process is shown in Fig. 4. Silicate samples, nominally between 0.5 – 1 g, are prepared as fine powders, or with particle sizes up to coarse-medium sand. Sample digestions are performed either in Teflon vials, or 50 mL polypropylene centrifuge tubes with plug seal caps. Digestion within centrifuge tubes is conveneient for periodic vortexing during digestion, which helps prevent buildup of thick fluoride cakes that can extend digestion time. When subsampling is necessary (for example when testing a larger ^{36}Cl sample for Cl concentration), we recommend using a riffle splitter, as suggested by (Lesnek et al., 2024) to extract a homogeneous aliquot for samples coarser than ~100 µm. A small amount (~0.5 mL) of Type 1 water is added to the vessel prior to sample addition to help reduce the effects of static on small grains.

Our sample digestion procedure generally follows that established by (Stone et al., 1996), with laboratory methods available online (https://depts.washington.edu/cosmolab/chem.shtml). For each gram of sample, 4 mL of Type 1 water is added as a thermal buffer, then 4-5 mL concentrated HF is added. Initially about half the HF is added slowly while monitoring for reactions. The digestion vessels are left with lids loosely fitted for ~45 minutes to prevent pressure buildup, then sealed tightly and placed on a hotplate at 70°C. Basal heating creates a thermal gradient that drives convection currents, which accelerate the reaction and prevent dense hexafluorisilicic acid (formed from HF-silicate reactions) from settling over the sample and slowing dissolution. Additionally, vessels are agitated frequently to encourage dissolution and prevent grains from being trapped in fluoride solids that may form. This process continues until no grains of the original sample are visible.

Following digestion, contents of the digestion vessels are transferred to 15 mL centrifuge tubes, including any remaining fluoride solids, and centrifuged at 5000 RPM for 5 minutes to compact the fluoride solids at the bottom. The supernatant is then transferred to new 15 mL tubes, leaving fluoride solids (cake) behind.

2.1.2 Path A: AgBr target prep

For AgBr targets, preparation from other common sample types (e.g. water or carbonate) and standards (including matrix-only AgBr blanks) follows an identical post-digestion procedure picking up after the fluoride cake removal step (denoted with '**A1**' on path A of Fig. 4). To ensure sufficient mass for packing, 3.6 mg of Br from a Br solution is added as carrier. Cl and Br are precipitated by adding 1 mL of 2% $AgNO_3$ in 2M HNO_3, then the tube is vortexed and set aside for ~5 minutes to allow flocculation and settling.

After settling, tubes are gently tapped to dislodge any Ag(Br+Cl) adhering to the sides or graduations, allowed to settle, and then centrifuged (1600 RPM, 5 minutes; all subsequent centrifugations use these settings unless otherwise noted). Supernatants are decanted and 5 mL of Type 1 water is added. To rinse, the Ag(Br+Cl) pellet is broken up by vortexing, the tube is tapped and allowed to settle, centrifuged, and the supernatant is decanted (henceforth, this cycle of vortexing, tapping,

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

settling, and centrifuging us referred to as VTSC for brevity). A second identical 5 mL water rinse and VTSC cycle is then performed. After decanting the final supernatant, the tubes are dried without lids in an oven at 70-80 °C (~12 h), and the pellets are ready for AMS target packing.

2.1.3 Path B: Nb target prep

For Nb targets prepared from samples digested in HF, additional steps are required to remove residual fluoride and prevent formation of NbF_5, which is a likely culprit for $^{16}O^{19}F^-$ interference at mass 35. After transfer from the digestion vessel, Cl is precipitated by adding 1 mL of 2% $AgNO_3$ in 2M HNO_3 and immediately followed by a VTSC cycle. Without decanting, a second VTSC cycle is performed; this second cycle ensures effective scavenging of colloidal AgCl for smaller precipitation volumes. Afterward, the supernatant is carefully removed by pipette, and two VTSC rinse cycles are performed with 2 mL of Type 1 water, extracting the supernatants by pipette.

After rinsing, 5-10 drops of 7N NH_3 are added to re-dissolve the AgCl while leaving any fluoride solids undissolved. The tube is vortexed and centrifuged to compact any remaining fluoride solids, then the supernatant is carefully transferred by clean pipette to a new 15 mL tube, leaving any solids behind.

The Cl is then reprecipitated by adding 1 mL of 2% $AgNO_3$ in 2M HNO_3 along with ~11 mg of Nb powder (one level scoop from a size 3, 2.5 mm Chalazion curette). After a VTSC cycle, the supernatant is carefully decanted by pipette, leaving a small amount of liquid above the Nb+AgCl surface; this mixture compacts less firmly than Ag(Br+Cl) and is easily disrupted, requiring careful handling to avoid sample loss. The sample then undergoes two VTSC rinse cycles in 2 mL of Type 1 water, each time carefully extracting the supernatant by pipette. After the final centrifugation, ~80-90% of the remaining water is removed by pipette and the sample is ready for transfer.

The remaining ~10-20% of liquid is used to slurry the Nb + AgCl mixture for transfer to a glass shell vial. The solids are suspended by repeatedly aspirating and dispensing with a pipette until most material can be retrieved. Remaining Nb (visually apparent as dark gray particles) is recovered by adding several drops of Type 1 water and repeating the aspiration process. After the transfer to the shell vial is complete, the solids are allowed to settle and excess water is extracted by pipette without disturbing the solids. With the liquid headspace minimized, the vials are placed in a heat block in a dark oven at 70-80°C to dry for ~12 h, and the mixtures are ready for AMS target packing.

For preparation of Nb targets from other common sample types (e.g. water or carbonate) or standards, the post-digestion fluoride removal steps are omitted, and preparation proceeds from step **B4** along path B in Fig. 4. For Nb blanks, no precipitation is required and preparation begins at step **B5**.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

2.2 Experiment #1: Dilution series

A dilution series was prepared by mixing a natural ratio Cl standard (TraceCert Cl, $^{35}Cl/^{37}Cl$ =3.127, [Cl] = 1001 ± 4 µg/ml) with an in-house enriched standard (1:1B, $^{35}Cl/^{37}Cl$ = 1.019, [Cl] = 266.3 ± 0.9 µg/ml) to evaluate whether measurements differ between AgBr and Nb matrices. Samples with $^{35}Cl/^{37}Cl$ ratios of approximately 3.0, 2.5, 2.0, and 1.5, were prepared in both AgBr and Nb matrices. After preparation, 50 µg of Cl from each solution was prepared in triplicate following both the AgBr and Nb preparation paths and measured following our standard mass spectrometry protocols. Details of the sample preparation are listed in Table 1.

Nominal ratio	% TraceCert	% 1:1B	TraceCert Cl mass (g)	1:1B Cl Mass (g)	[Cl] (µg /ml)	Expected mixed ratio
3.127	100	0	0.7456	0	1001	3.127
3.0	97.0	3.0	0.9605	0.1159	978.7	2.994
2.5	82.9	17.1	0.4047	0.3334	875.2	2.479
2.0	64.1	35.9	0.3154	0.7048	737.2	1.976
1.5	37.8	62.2	0.1827	1.2193	543.9	1.484
1.019	0	100	0	1.956	266.3	1.019

Table 1: Dilution series composition showing nominal $^{35}Cl/^{37}Cl$ ratios, proportions and weights of natural ratio and ~1:1 ratio standards used, resulting Cl concentration, and expected ratios.

2.3 Experiment #2: Rock standard measurements

AgBr and Nb matrices were compared for stable Cl extraction from silicates to evaluate measurement reproducibility and ion source memory effects. Sample materials included feldspar, quartz, and three USGS standards (Table 2): BIR-1 (Icelandic basalt), RGM-1 (Glass Mountain Rhyolite), and AGV-1 (Analyzed Andesite, (Jochum et al., 2016)). Four replicates were prepared for each sample type. Approximately 1 g of each material was aliquoted from a larger sample, using a riffle splitter for the larger grained feldspar and quartz samples (150-250 µm) and via spatula for the finer grained USGS standards (<75 µm). Digestion proceeded as described in section 2.1, with a double shot of carrier (~100 µg Cl from 1:1B) added such that split aliquots could be prepared post-dissolution using both the standard AgBr method and the newer Nb method (Figure 4). Samples were digested over 3 days to ensure grains from all samples were fully dissolved. To enable direct intercomparison,

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

Sample	Sample mass (g)	Cl carrier (g)	Cl added (µg)	Est. Sample Cl (ppm)
Feldspar #1	1.0768	0.3935	98	< 10
Feldspar #2	1.0457	0.3945	99	< 10
Feldspar #3	1.0120	0.3948	99	< 10
Feldspar #4	1.0135	0.3951	99	< 10
Quartz #1	1.1456	0.3946	99	Unknown
Quartz #2	1.2223	0.3958	99	Unknown
Quartz #3	1.1761	0.3948	99	Unknown
Quartz #4	1.1233	0.3940	99	Unknown
BIR-1 #1	1.0109	0.3950	99	44
BIR-1 #2	1.0476	0.3951	99	44
BIR-1 #3	1.0871	0.3952	99	44
BIR-1 #4	1.2700	0.3947	99	44
RGM-1 #1	1.0852	0.3951	99	510
RGM-1 #2	1.0091	0.3955	99	510
RGM-1 #3	1.0006	0.3957	99	510
RGM-1 #4	1.1420	0.3956	99	510
AGV-1 #1	1.0865	0.3954	99	133
AGV-1 #2	1.0729	0.3953	99	133
AGV-1 #3	1.0140	0.3963	99	133
AGV-1 #4	1.0157	0.3933	98	133

Table 2: Sample masses, Cl carrier additions prior to splitting, and estimated Cl concentrations (taken from (Jochum et al., 2016) for USGS standards; feldspar estimate from previous analysis). Samples were split equally between AgBr and Nb preparation methods.

replicate samples, blanks, and standards were analyzed on separate wheels in identical sequence for both matrices, including two successive blank measurements for Nb to match the AgBr protocol.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

2.2 Stable Chlorine Measurement with Mass Spectrometry

Measurements were performed at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL) using only low-energy components of the 10 MV FN Tandem AMS system. Following the methods described in (Anderson et al., 2022), stable chlorine isotope measurements are performed using a cesium sputter ion source, a 90-degree magnet with fast high-voltage bouncing capability, and a suppressed Faraday cup with current integrator (Fig. 5). The ^{35}Cl and ^{37}Cl currents are 'bounced' between by rapidly changing a high voltage applied to the magnet, spending 40 ms on each isotope per 200 ms cycle to nearly continuously measure the $^{35}Cl/^{37}Cl$ ratio. One complete measurement 'pass' on a sample consists of 15 successive 12.5 s intervals during which the $^{35}Cl^-$ and $^{37}Cl^-$ charges are collected, lasting about 3 minutes. Nominally Cl-free blank materials and isotopic standard materials with natural and enriched ratios are also regularly measured to correct unknown ratios.

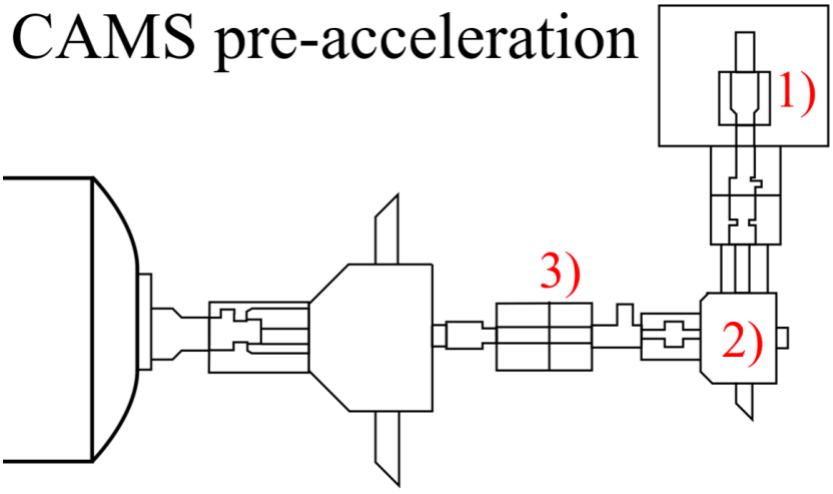

Figure 5: Modified from (Anderson et al., 2022), pre-acceleration components used to measure stable Cl at CAMS: 1) ion source, 2) injection magnet with fast bouncing capability, 3) suppressed Faraday cup.

Background measurements of matrix blank targets are acquired both before and after each sample and standard until $^{35}Cl^-$ and $^{37}Cl^-$ collected charges return to pre-measurement values or plateau. Nb blanks typically require only one 'pass' to return to background compared to two or more 'passes' for AgBr blanks. Standards with precisely known $^{35}Cl/^{37}Cl$ ratios and Cl concentrations (e.g., TraceCert Cl; $^{35}Cl/^{37}Cl$ = 3.127, [Cl] = 1001 ± 4 µg Cl/ml, or 1:1B, $^{35}Cl/^{37}Cl$ = 1.019, [Cl] = 266.3 ± 0.9 µg/ml) are regularly measured to normalize for instrumental mass fractionation. Three natural ratio standards are typically measured every 30-45 minutes to track changes in ion source conditions. To compare relative current output for AgBr and Nb at their maximum operating voltages, natural ratio Cl standards were pre-sputtered for 2 minutes, analyzed for one typical measurement pass lasting ~3 minutes, and the maximum Cl- currents were recorded. AgBr and Nb based samples are always measured separately with matrix-matched blanks and standards.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

Our measured ratios are reported as $^{35}Cl/^{37}Cl$, but can be converted to a commonly used unit $\delta^{37}Cl$, which is reported in parts per thousand or permille (‰), and calculated as follows

$$\delta^{37}Cl = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000,$$

where R_{sample} is the measured $^{37}Cl/^{35}Cl$ ratio of a sample and $R_{standard}$ is the nominal $^{37}Cl/^{35}Cl$ ratio of the standard (relative to Standard Mean Ocean Chloride (SMOC) (Kaufmann et al., 1984)).

2.2.1 Data Reduction

Background charges (nC) for both $^{35}Cl^-$ and $^{37}Cl^-$ beams are determined by linear interpolation between the average of the 5 nearest measured values (out of 12-15 per pass) from matrix blanks run before and after each sample and standard. These background values are subtracted from measured $^{35}Cl^-$ and $^{37}Cl^-$ charges to determine blank-corrected ratios for all Cl-containing targets.

To account for instrumental mass fractionation, all $^{35}Cl/^{37}Cl$ ratios are normalized to the natural ratio measured in standard material by multiplying by a normalization factor defined as

$$F_{norm} = \frac{R_{standard}}{R_{mesaured}},$$

where $R_{standard}$ is the standard's known $^{35}Cl/^{37}Cl$ ratio (3.127) and $R_{measured}$ is the experimentally measured $^{35}Cl/^{37}Cl$ value. Measured standard ratios are typically ~0.3% higher than the natural ratio, resulting in F_{norm} of ~0.997.

Measurement uncertainties are calculated in two ways and, to be conservative on measurement precision, the largest value of the two is used. Method one calculates the *intra*-target standard deviation of the 15 individual analyses that make up one measurement 'pass'; method two calculates the *inter*-target standard deviation from secondary standards that should have the same ratio (e.g., 1:1B). Ratio normalization and uncertainty calculations are performed using "Fudger", an in-house data analysis program that has been in use for reporting other AMS isotopes commonly measured at CAMS (e.g., ^{14}C, ^{10}Be, ^{26}Al, ^{36}Cl) for more than two decades (Ognibene and Vogel, 2005).

2.2.2 Mass scans

Mass scans were performed to validate successful fluoride removal and confirm the absence of $^{16}O^{19}F^-$ interference at mass 35 following the Nb preparation procedure. Scans were conducted on 1) an HF process blank, 2) an Nb matrix blank, 3) a feldspar sample, 4) an enriched ~1:1 ratio Cl standard, 5) two natural ratio standards at lower Cl concentrations (20 and 5 µg Cl), and 6) two silicate lunar meteorites. The feldspar and one lunar meteorite were prepared via the former Nb sample preparation method (after (Anderson et al., 2022); the HF process blank and other lunar meteorite were prepared following the procedure described in section 2.1 (path B). Each mass scan was obtained by increasing the analyzing magnet's field in 300 steps with 4-second settling times to measure ion beam current at each field value. The blanks and feldspar were scanned from

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

~1850 to ~3500 Gauss (~12 to 39 amu) while the Cl standards and meteorites were scanned from ~2200 to ~3750 Gauss (16 to 40 amu).

3 Results

3.1 Mass scans

Mass scans in Figures 6 and 7 demonstrate that the new Nb target preparation procedure successfully removes fluorides and eliminates the $^{16}O^{19}F^-$ interference at mass 35. Figure 6 compares a feldspar sample prepared using the former procedure (top panel; from Figure 3) to a process blank containing 50 µg Cl from the 1:1B standard that underwent HF digestion (bottom panel). The process blank lacks a significant fluoride peak, and the measured $^{35}Cl/^{37}Cl$ ratio is consistent with the added carrier. Similarly, Figure 7 compares lunar meteorite samples analyzed for $\delta^{37}Cl$ prepared using the former procedure (top panel) and the new procedure (bottom panel), confirming complete removal of residual fluoride. Both meteorites were Cl-poor, resulting in lower Cl^- currents, but the absence of the fluoride peak in the bottom panel validates successful interference elimination.

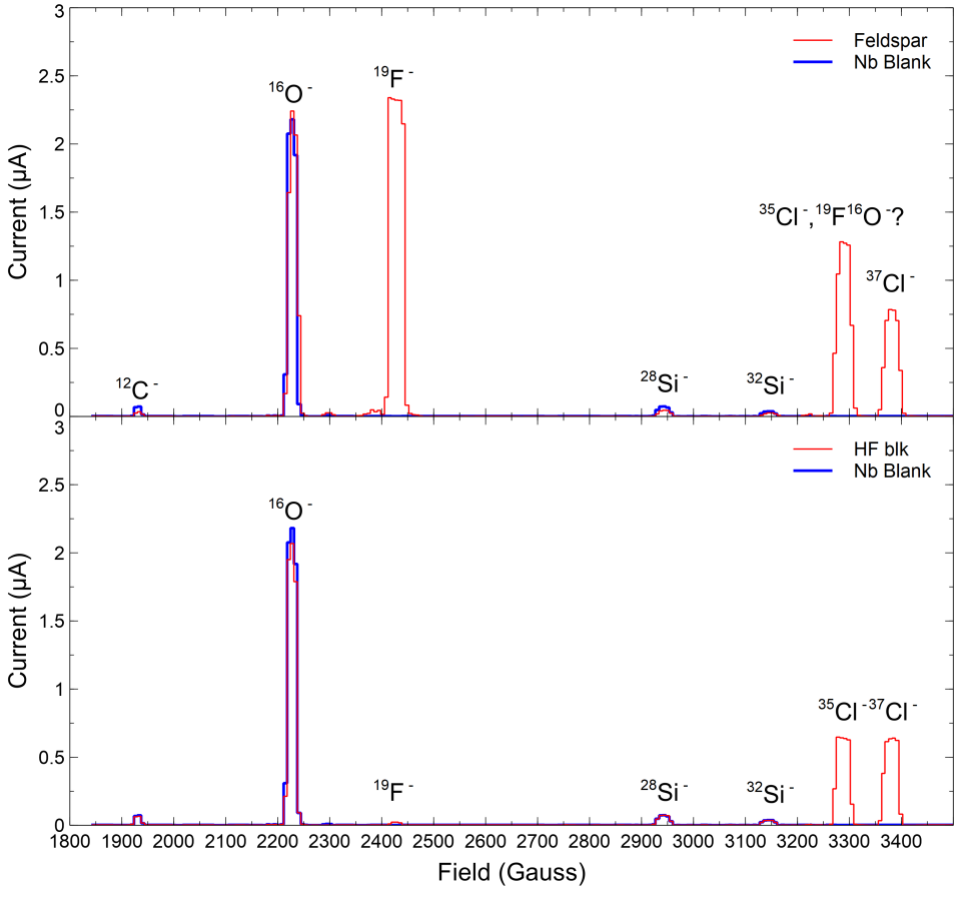

Figure 6: *Top*: Mass scans of feldspar sample and Nb blank from Figure 3, illustrating insufficient fluoride removal prior to adopting new Nb sample prep procedure. *Bottom*: Mass scans of HF process blank with added 1:1B carrier and Nb blank with new target prep procedure and no significant presence of ^{19}F. Measured $^{35}Cl/^{37}Cl$ ratio of ~1:1 is retained.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

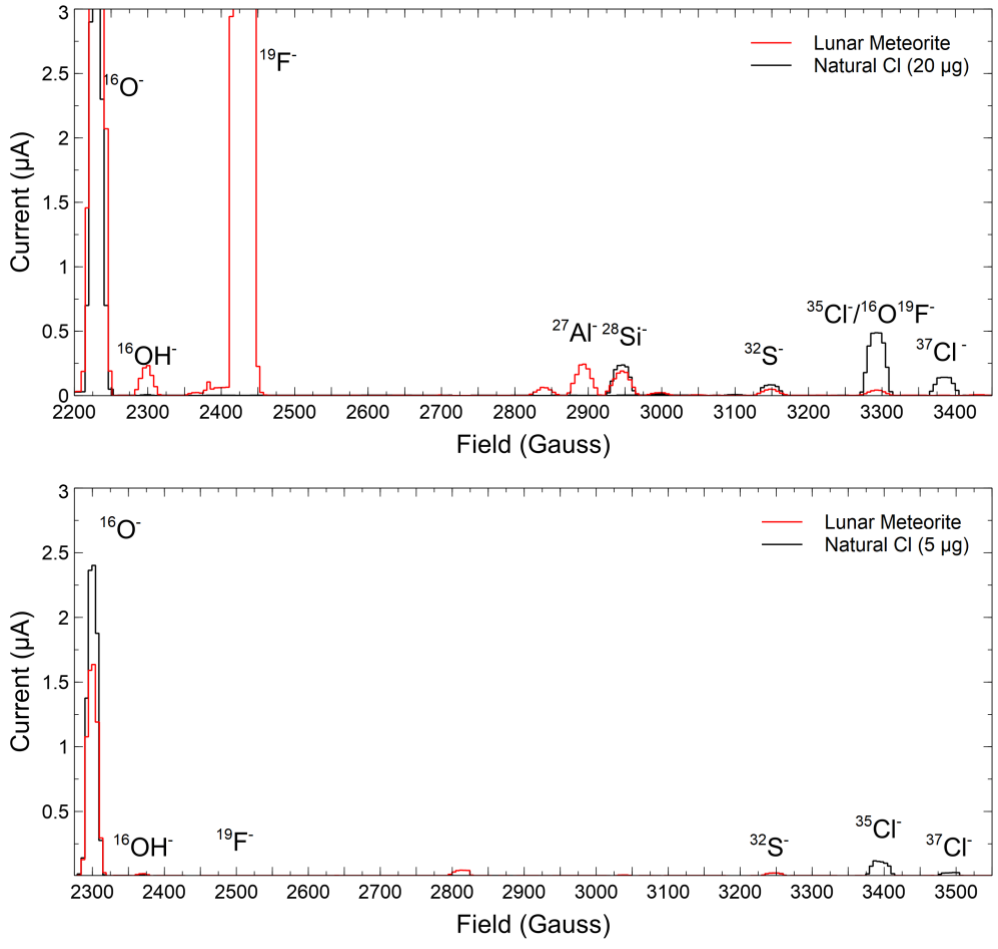

Figure 7: *Top*: Mass scans of natural ratio process blank (TraceCert) and silicate meteorite analyzed for $\delta^{37}Cl$ (no carrier added) prior to adopting new Nb sample prep procedure demonstrating presence of fluoride and interference at mass 35. *Bottom*: Similar mass scans to top panel but following new Nb sample prep procedure demonstrating complete removal of mass 35 isobar. Note: Experiments were performed at different times where there was a difference in the applied magnet voltages which shifted masses to slightly different field values between the two scans.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

3.2 Experiment #1: Dilution series

Measured results from the dilution series prepared in Nb and AgBr are shown in Figure 8, with details listed in Table 2. Matrix-specific linear fits ($y = mx$) indicate excellent agreement across the full sample ratio range with slopes of m = 1.002 for AgBr and m=0.998 for Nb, and reduced chi-squared values of χ_v^2 =1.24 and 1.59, respectively. The permille deviation between the expected ratios and the measured ratios for Nb and AgBr is shown in Fig. 9. Overall, the results indicate larger uncertainties for AgBr than for Nb and suggest that AgBr becomes less accurate as the sample ratio moves further from the natural Cl ratio. This may be related to larger source memory effects from AgBr (see Figure 2), however, the measurements remain consistent with 0 ‰ deviation from the best fit line within uncertainty. The fact that $\chi_v^2 > 1$ for both matrices suggests that the individual uncertainties may be underestimated. The average precision of these measurements was 1.7 ‰ for Nb and 6.5 ‰ for AgBr. The data have nominal excess scatter of 1.5 ‰ for Nb and 0.7 ‰ for AgBr, from which we can infer that the total precision for Nb is ~3.2 ‰ and for AgBr is ~7.2 ‰. Despite this apparent underestimate of uncertainty, the inferred correction still has Nb analyses more than twice as precise as AgBr.

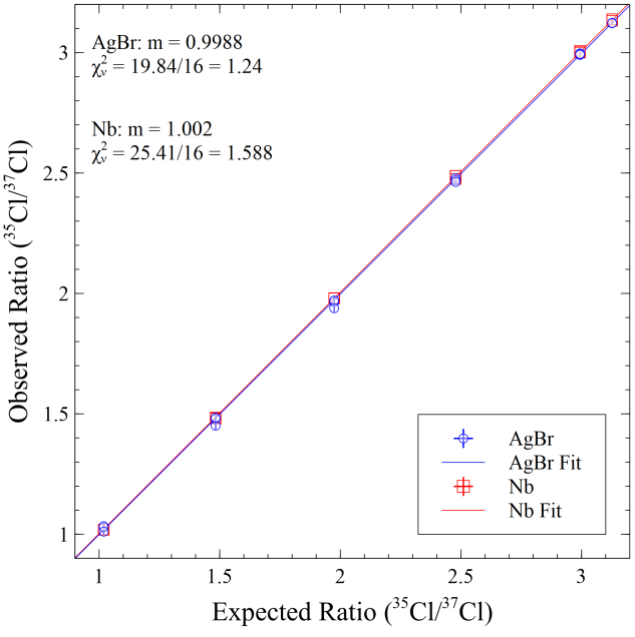

Figure 8: Dilution series measurements and linear fits for identical Nb and AgBr targets. 1σ error bars are plotted, but smaller than the symbol.

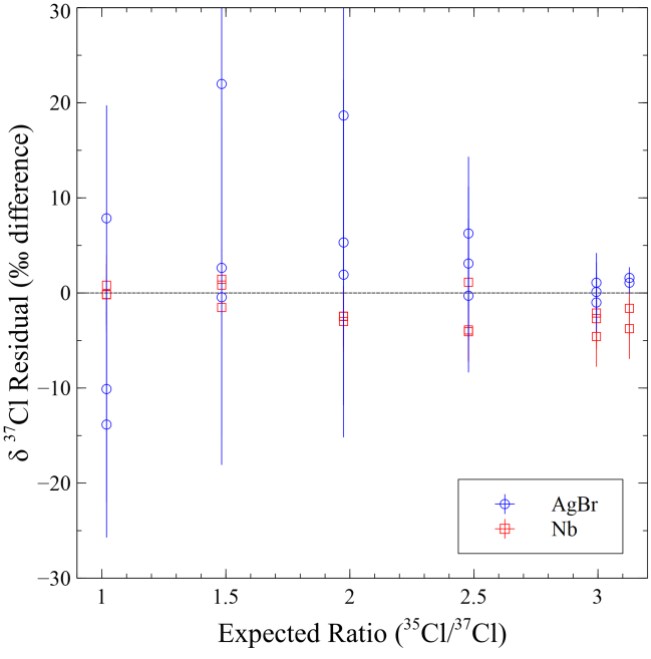

Figure 9: Residuals from the dilution series measurements, in Figure 8.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

3.3 Experiment #2: Rock standard measurements

The silicate measurement results are shown in Table 3 and Fig. 10. Table 3 reports Nb and AgBr measurements in 'raw' form, uncorrected for blank contributions, and as blank-corrected values, with 1σ errors derived from reproducibility across separate measurements and subaliquots. Figure 10 shows the measured Cl concentrations for the five rock types, with replicate measurements averaged into a single value for each sample type in AgBr and Nb. Where available, previous measurements are marked with an X, and estimated concentration ranges are shown with a yellow bar.

Figure 11 shows replicate variability for the four splits of each sample type in AgBr and Nb. Each value is background- and memory-corrected and normalized to the average value for each split across both matrices. Eror bars are 1σ and based on reproducibility of acquisitions (n=15) and estimated uncertainty from source memory correction. On average, AgBr and Nb solution splits agree within 0.8%, with a maximum difference of 1.7%.

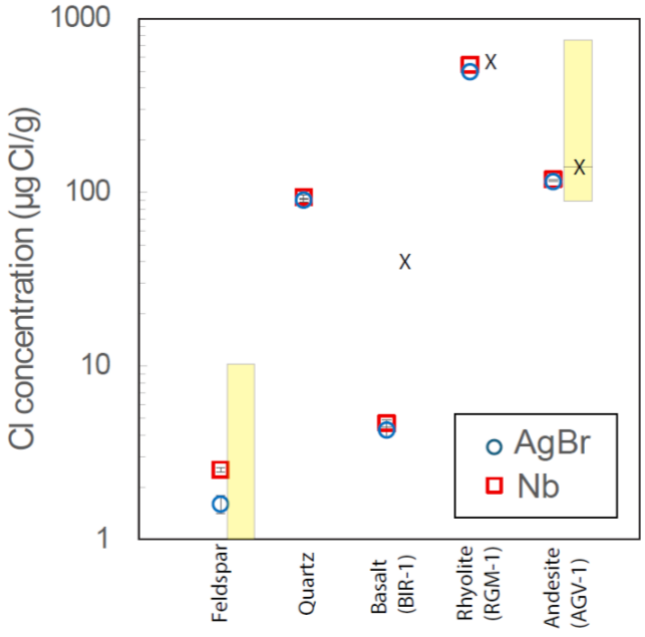

Figure 10: Average of quadruplicate measured chloride concentrations from Experiment #2 silicate samples. Previously reported (or measured) concentrations for samples are shown with an X, and yellow boxes indicate 1σ uncertainties (if available).

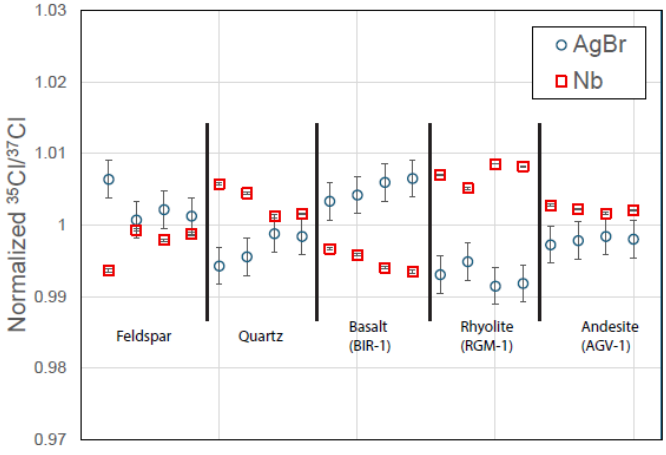

Figure 11: Measured $^{35}Cl/^{37}Cl$ ratios for solution duplicates in AgBr and Nb. Ratios are corrected for source memory and, for plotting purposes, are normalized to the average value measured in each split.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

Sample ID	Nb (raw)		Nb (corr.)		AgBr (raw)		AgBr (corr.)		Expected Value	
	µg Cl/g	±1σ	µg Cl/g	±1σ	µg Cl/g	±1σ	µg Cl/g	±1σ	µg Cl/g	±1σ
Feldspar	2.56	0.08	2.53	0.08	2.07	0.08	1.61	0.18	<10	NA
Quartz	94.2	2.3	94.0	2.3	91.4	1.9	90.4	1.9	NA	NA
BIR-1	4.77	0.25	4.68	0.24	4.70	0.28	4.29	0.3	44	?
RGM-1	546	6	545	6	512	2	496	1	510	?
AGV-1	119.3	0.2	118.9	0.2	115.9	0.5	115.5	0.3	133	41

Table 3: Chlorine concentrations measured in Experiment #2 samples in Nb and AgBr, presented in µg Cl/g (ppm Cl), with 1σ errors.

4 Discussion

As shown in Fig. 1, AgBr is limited to cathode voltages of ~2.5 kV, whereas Nb can be operated at ~ 5.0 kV, due to its lower volatility. At higher voltages, AgBr may melt and fall from the cathode, causing shorts and increasing memory in subsequent analyses. The higher voltage tolerated by Nb produces approximately five times greater Cl^- beam current, improving signal-to-noise ratio relative to AgBr.

Background in AgBr is ~100 times higher than in Nb, based on collected charge (see Fig. 2). Memory effects are also more pronounced in AgBr, particularly after high Cl samples, and decay more rapidly in Nb. Together with the higher beam current available in Nb, these effects yield an almost 100-fold improvement in signal-to-noise ratio relative to AgBr, making Nb the preferred matrix for stable Cl isotope analysis (especially for samples containing ~20 µg of Cl or less). At very low Cl masses (~1 µg), the analytical signal may be only about 10x larger than background, even in Nb, so the higher background and memory with AgBr substantially degrades accuracy (as illustrated in Fig. 10 and Table 3). Consistent with this, AgBr blanks require roughly twice the duration needed for Nb blanks to return to baseline, increasing the total measurement time to at least 6 minutes before and after each sample, compared with 3 minutes or less for Nb.

For high-Cl samples, one might counterintuitively experience a reduction in precision because of 1) large current differences between standard and sample, 2) the need for a higher current integrator scale setting (which may also have higher background values), 3) more frequent discontinuous current spikes from sputtering of larger AgCl chunks, and 4) rapid current fluctuations that can differentially affect the $^{35}Cl^-$ and $^{37}Cl^-$ signals.

Figure 6 shows that residual fluoride can produce a mass 35 interference when rinsing is insufficient after HF digestion. In contrast, two rinses prior to Nb addition reduces the fluoride signal to near background and recovers the expected $^{35}Cl/^{37}Cl$ ratio. This confirms that the revised preparation protocol is critical for reliable and accurate stable Cl analysis of HF-digested silicates.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

The dilution series shows that both AgBr and Nb matrices track the expected ratios well across the full range tested. The near-unity fitted slopes indicate good accuracy for both matrices, while the reduced chi-squared values suggest that the stated uncertainties may be slightly underestimated. However, AgBr measurements carry larger uncertainties than Nb and become less reliable as the sample ratio departs from the natural Cl ratio, consistent with stronger matrix-dependent memory and background effects. While we can infer potential corrections to our quoted uncertainties, we will wait to adopt these new values fully until more data is gathered to enable the most robust and accurate uncertainty determination possible.

For silicate materials, Nb and AgBr give comparable precision at higher Cl concentrations and agree with prior values. In practice, the two matrices are comparable at higher Cl concentrations, but Nb is preferable for low-Cl samples because the blank correction is smaller and more stable. At lower Cl concentrations, AgBr increasingly underestimates Cl. We suspect this is because background and memory become a larger fraction of the signal such that assuming a linear interpolation of memory between background measurements is less valid for AgBr than it is for Nb. We note that for each sample lithology type, the matrix splits exhibit a systematic difference (i.e., results from one matrix are always higher or lower); this observation is consistent with systematic under- or over-correction of Cl memory, which would be most probably when correcting the AgBr splits. The scatter in replicates within each matrix type may reflect incomplete homogenization and sample heterogeneity related to solid phase splitting of the original aliquots. In all cases, this scatter is <1%, which is consistent with expectations of reproducible aliquoting with a riffle splitter (Gerlach et al., 2002).

5 Conclusions

We have developed and implemented a Nb-based preparation method for stable chlorine analysis at CAMS that solves the problem of using Nb for silicate samples prepared by HF digestion—an important sample class for planetary and geochemical applications. With the revised chemistry, use of Nb enables reliable stable Cl analysis of silicates while retaining the benefits previously demonstrated for other sample matrices. Compared with the traditional AgBr approach, Nb 1) substantially reduces background Cl and ion source memory, 2) improves the signal-to-noise ratio for Cl^- beam current measurements, and 3) enables more precise and repeatable analyses of Cl-poor materials.

Nb-packed targets reproduced the stable Cl results obtained with AgBr while also reducing background and memory between analyses. This allows blanks to return to baseline more quickly and shortens acquisition time between samples. Although Nb requires a more involved preparation workflow, its performance gains outweigh the added complexity. The method is applicable to other common sample types as well, including carbonates and water, and supports accurate isotope dilution measurements for samples containing as little as ~1 µg of Cl.

For these reasons, Nb is now the preferred target matrix for all stable Cl analyses at CAMS, while AgBr is retained only for ^{36}Cl analyses where minimizing sulfur contamination remains essential.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

6 Data availability

All raw data can be provided by the corresponding authors upon request.

7 Code availability

The data analysis program Fudger is published and available for anyone to access.

8 Author contributions

TA and AH designed and carried out the experiments; TA performed the measurements with assistance from AH, TA and AH analyzed the data; TA wrote the manuscript draft; AH reviewed and edited the manuscript.

9 Competing interests

The authors declare that they have no conflict of interest.

10 Acknowledgements

The authors thank Ariana Wu for her consistent curiosity and dedication to meteoritic studies, diligent assistance in sample preparation, and regular willingness to serve as a sounding board for ideas that were highly valuable to this research. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and was supported by the LLNL-LDRD Program under Project No. 25-LW-101. This is LLNL-JRNL-2020541.

References

Anderson, T. S., Hidy, A. J., Boyce, J. W., McCubbin, F. M., Tumey, S., Dudley, J.-M., Haney, N. C., Bardoux, G., and Bonifacie, M.: Development towards stable chlorine isotope measurements of astromaterials using the modified Middleton source of an accelerator mass spectrometer, International Journal of Mass Spectrometry, 477, 116849, 10.1016/j.ijms.2022.116849, 2022.

Boyce, J. W., Kanee, S. A., McCubbin, F. M., Barnes, J. J., Bricker, H., and Treiman, A. H.: Early loss, fractionation, and redistribution of chlorine in the Moon as revealed by the low-Ti lunar mare basalt suite, Earth and Planetary Science Letters, 500, 205-214, 10.1016/j.epsl.2018.07.042, 2018.

Boyce, J. W., Treiman, A. H., Guan, Y., Ma, C., Eiler, J. M., Gross, J., Greenwood, J. P., and Stolper, E. M.: The chlorine isotope fingerprint of the lunar magma ocean, Science Advances, 1, e1500380, 10.1126/sciadv.1500380, 2015.

https://doi.org/10.5194/egusphere-2026-4091
Preprint. Discussion started: 27 July 2026

Davie, R., Bird, J., Calf, G., Topham, S., Fifield, L., Ophel, T., Allison, G., and Chivas, A.: The chlorine-36 measurement program at the ANU, Fifth Australian conference on nuclear techniques of analysis: proceedings, 6-9,

Day, J. M. D., Moynier, F., and Shearer, C. K.: Late-stage magmatic outgassing from a volatile-depleted Moon, Proceedings of the National Academy of Sciences, 114, 9547-9551, 10.1073/pnas.1708236114, 2017.

Elmore, D., Fulton, B. R., Clover, M. R., Marsden, J. R., Gove, H. E., Naylor, H., Purser, K. H., Kilius, L. R., Beukens, R. P., and Litherland, A. E.: Analysis of 36Cl in environmental water samples using an electrostatic accelerator, Nature, 277, 22-25, 10.1038/277022a0, 1979.

Finkel, R., Arnold, M., Aumaître, G., Benedetti, L., Bourlès, D., Keddadouche, K., and Merchel, S.: Improved 36Cl performance at the ASTER HVE 5MV accelerator mass spectrometer national facility, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 294, 121-125, 10.1016/j.nimb.2012.05.019, 2013.

Gerlach, R. W., Dobb, D. E., Raab, G. A., and Nocerino, J. M.: Gy sampling theory in environmental studies. 1. Assessing soil splitting protocols, Journal of Chemometrics, 16, 321-328, 10.1002/cem.705, 2002.

Greenwood, J. P., Sakamoto, N., Itoh, S., Warren, P. H., Singer, J. A., Yanai, K., and Yurimoto, H.: The lunar magma ocean volatile signature recorded in chlorine-rich glasses in KREEP basalts 15382 and 15386, GEOCHEMICAL JOURNAL, 51, 105-114, 10.2343/geochemj.2.0453, 2017.

Jochum, K. P., Weis, U., Schwager, B., Stoll, B., Wilson, S. A., Haug, G. H., Andreae, M. O., and Enzweiler, J.: Reference Values Following <scp>ISO</scp> Guidelines for Frequently Requested Rock Reference Materials, Geostandards and Geoanalytical Research, 40, 333-350, 10.1111/j.1751-908x.2015.00392.x, 2016.

Kaufmann, R., Long, A., Bentley, H., and Davis, S.: Natural chlorine isotope variations, Nature, 309, 338-340, 10.1038/309338a0, 1984.

Lesnek, A. J., Licciardi, J. M., Hidy, A. J., and Anderson, T. S.: Technical note: Optimizing the in situ cosmogenic ³⁶Cl extraction and measurement workflow for geologic applications, Geochronology, 6, 475-489, 10.5194/gchron-6-475-2024, 2024.

Ognibene, T. and Vogel, J.: A GUI-based AMS data analysis program [poster], The 10th International Conference on Accelerator Mass Spectrometry, Berkeley, California, 5-10,

Sarafian, A. R., John, T., Roszjar, J., and Whitehouse, M. J.: Chlorine and hydrogen degassing in Vesta's magma ocean, Earth and Planetary Science Letters, 459, 311-319, 10.1016/j.epsl.2016.10.029, 2017.

Sharp, Z., Williams, J., Shearer, C., Agee, C., and McKeegan, K.: The chlorine isotope composition of Martian meteorites 2. Implications for the early solar system and the formation of Mars, Meteoritics & Planetary Science, 51, 2111-2126, 10.1111/maps.12591, 2016.

Shearer, C. K., Messenger, S., Sharp, Z. D., Burger, P. V., Nguyen, A. N., and McCubbin, F. M.: Distinct chlorine isotopic reservoirs on Mars. Implications for character, extent and relative timing of crustal interactions with mantle-derived magmas, evolution of the martian atmosphere, and the building blocks of an early Mars, Geochimica et Cosmochimica Acta, 234, 24-36, 10.1016/j.gca.2018.04.034, 2018.

Stone, J. O., Allan, G. L., Fifield, L. K., and Cresswell, R. G.: Cosmogenic chlorine-36 from calcium spallation, Geochimica et Cosmochimica Acta, 60, 679-692, 10.1016/0016-7037(95)00429-7, 1996.

Wang, Y., Hsu, W., and Guan, Y.: An extremely heavy chlorine reservoir in the Moon: Insights from the apatite in lunar meteorites, Scientific Reports, 9, 5727, 10.1038/s41598-019-42224-8, 2019.