STABLE CHLORINE ISOTOPE MEASUREMENTS OF ASTROMATERIALS USING THE CS-SPUTTER NEGATIVE ION SOURCE OF AN ACCELERATOR MASS SPECTROMETER

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Introduction: The volatile element Cl can be lost during the formation and evolution of planetary bodies, leading to fractionation of its two stable isotopes ^{35}Cl and ^{37}Cl. Chlorine isotope variations (reported as δ^{37}Cl in parts per thousand (‰) relative to Standard Mean Ocean Chloride, SMOC) [1] are documented to exceed 80‰ [2] between different lunar rock samples and have been variably interpreted as the fingerprint of degassing during accretion, magma ocean, or volcanic portions of lunar history [3,4]. The large *intersample* and *intrasample* variations observed by both bulk isotope ratio mass spectrometry (IRMS) and in-situ secondary ion mass spectrometry (SIMS) methods are difficult to interpret in part because of a paucity of bulk Cl isotope measurements (Figure 1). This lack of high-precision bulk data is due to the relative rarity of IRMS laboratories capable of making these high precision measurements on small samples of precious planetary materials such as those returned by human or robotic exploration. Here we present a new method for performing high precision δ^{37}Cl measurements using the Cs-sputter negative ion source of an existing accelerator mass spectrometer. A brief description of the methods used for this work is followed by the results of our δ^{37}Cl measurements and a discussion of the technique's possible applications.

Methods: Measurements were performed at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL). All measurements were performed using only the pre-acceleration equipment, which includes a high output Cs-sputter Negative Ion Source [9,10], a 90° bending magnet with fast bouncing capability, and a suppressed Faraday cup.

Materials: Three reference materials were produced through a dilution series at LLNL, mixing natural ratio (^{37}Cl/^{35}Cl = 0.320) Weeks Island Halite (δ^{37}Cl ≈ 0‰) [1] with a heavily enriched synthetic reference salt purchased from Oak Ridge National Laboratory (δ^{37}Cl ≈ +94%). Along with WIH, dilution series members D1-A (targeted δ^{37}Cl ≈+9‰), and D1-B (targeted δ^{37}Cl ≈+44‰) were measured.

Chemistry: Between 0.5 and 50 µg of Cl from D1-A, D1-B, or WIH were added to ≈ 12 mg Nb powder and then precipitated as AgCl. The precipitation step was performed with lab ceiling lights turned off to mitigate photo decomposition of AgCl. To avoid loss of significant Cl due to the non-zero solubility of AgCl in water (≈ 2 µg/g) for masses ≤ 2 µg Cl, Cl bearing solutions were added directly to Nb powder then allowed to evaporate, ultimately depositing the Cl throughout the Nb.

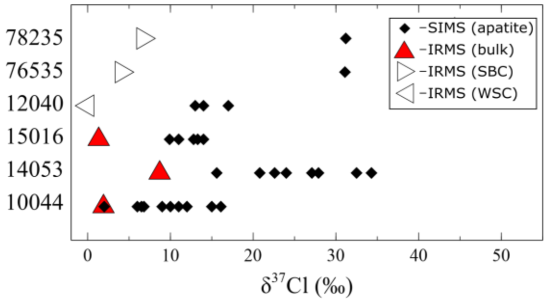

Fig 1. Measurements of δ^{37}Cl by SIMS of apatite (black diamonds) [3, 5-7] and IRMS, where both types of measurements have been made on the same samples. Bulk δ^{37}Cl values are represented by red triangles, whereas samples having only one of structurally bound (SBC) or water soluble Cl (WSC) measurements are indicated by unfilled triangles [8].

Analytical Protocols: The Nb-bulked AgCl samples were loaded into stainless steel cathodes and compacted to ensure a smooth, flat surface. Beam currents were measured on a single suppressed Faraday cup. Fast bouncing of the high voltage applied to the magnet box allowed for the nearly continuous alternating measurement of ^{35}Cl^{-} and ^{37}Cl^{-} beams. Each time a cathode was visited, the sample was measured for approximately four minutes, during which time the ^{37}Cl^{-} and ^{35}Cl^{-} currents were integrated. Each sample had at least one replicate and each of these were typically visited at least three times.

Results: The results of our measurements on our Cl standard materials are shown in Figure 2, presented in delta notation relative to SMOC (‰). The average measured value for WIH replicates was normalized to exactly 0‰, and we observed a dispersion around that of ± 0.4‰, 2σ (N=12). Synthetic reference salt D1-A (targeted ≈ +9‰) averaged +9.7 ± 2.3%, 2σ (N=12), and D1-B (targeted ≈ +44‰) averaged +45.2 ± 2.6‰, 2σ (N=22). The weighted mean–calculated using our

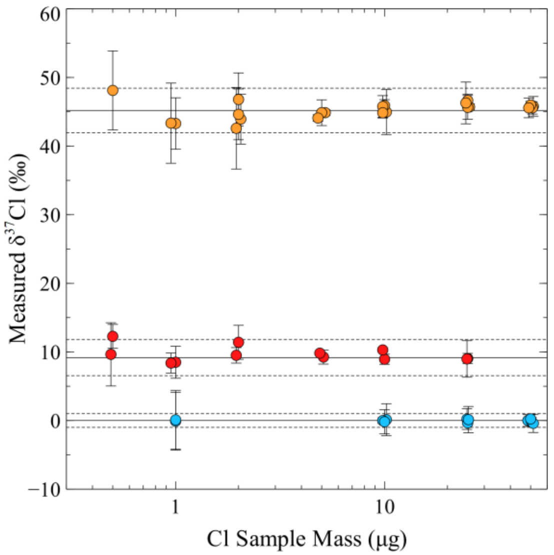

Fig 2. Results from the δ^{37}Cl measurements on materials WIH (blue), D1-A (red), and D1-B (orange). Each point represents a cathode's average δ^{37}Cl value with 2σ error bars, the solid lines represent the sample average measured δ^{37}Cl value for each material, and the dashed lines show 2σ upper and lower bounds. Data points are artificially staggered in mass to reduce overlap for same-mass samples.

δ^{37}Cl values by mass–for D1-A = 9.3 ± 1.6‰, 2σ (MSWD = 0.089, $p(\chi^2) = 0.99$), and for D1-B = 45.4 ± 1.6‰, 2σ (MSWD = 0.13, $p(\chi^2) = 0.99$).

Discussion The data reported here represent successful measurements on samples containing as little as 0.5 µg of Cl. Relative to their respective reference values, 69% of the cathode averages are accurate to within 1‰, and 86% are accurate to within 2‰. The data are considerably more accurate than they are precise, with precision around 1-4‰, similar to published SIMS data [3,5-8], and accuracy around 1‰ (Figure 3), suggesting the analytical uncertainties are overestimated by up to a factor of 4. The technique's precision and accuracy make it ideal for samples with large isotopic variations (more than a few ‰), even if they are small, rare, or Cl-poor; perfectly suitable for measurements of astromaterials from bodies such as the Moon, Mars, and 4 Vesta.

Conclusion: Understanding the role of chlorine and other volatile elements by studying how they are isotopically fractionated in astromaterials can provide insights into the formation of the Moon and other terrestrial bodies. Most measurements of δ^{37}Cl to date are performed in-situ in Cl-rich minerals, like apatite, using SIMS, while far fewer bulk δ^{37}Cl measurements using IRMS have been made. The paucity of bulk chlorine isotope data motivated the development of a method to perform the needed bulk Cl measurements using existing accelerator mass spectrometry facilities. Our measurements have demonstrated the ability to accurately measure δ^{37}Cl values from 0 to +45‰ to within 1‰, in samples with Cl masses as low as 1 µg, with typical precision of 1-4‰. Our hope is that this method will be used to supplement existing techniques, reducing the cost and complexity of bulk Cl measurements, and making urgently needed δ^{37}Cl measurement capabilities more widely accessible.

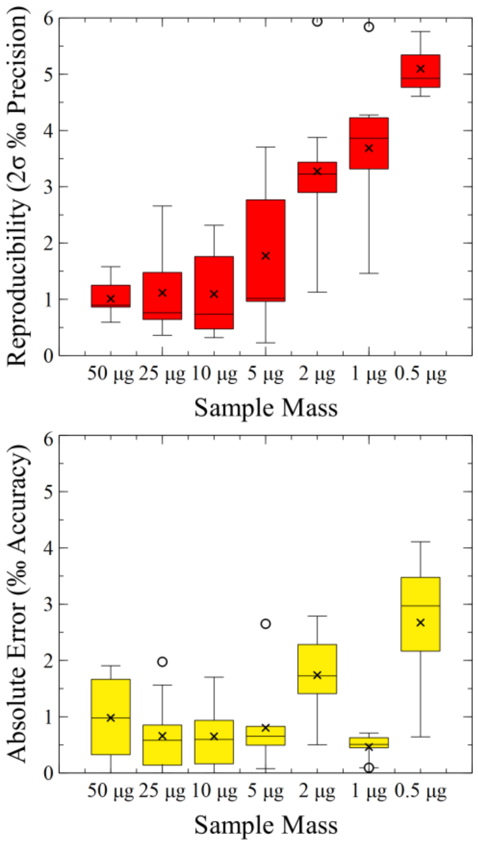

Fig 3. The cathode reproducibility and absolute error for all samples as a function of mass. The data are consistently more accurate than they are precise, suggesting that the reported analytical uncertainties are over-estimated.

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