METHODS FOR CHEMISTRY AND PREPARATION OF LOW-CL CONCENTRATION SAMPLES FOR STABLE CHLORINE ISOTOPE MEASUREMENTS WITH AMS. Tyler Anderson1,2 and Alan J. Hidy1, Jeremy W. Boyce2, 1Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, 7000 East Ave, L-397, Livermore, CA 94550, *anderson309@llnl.gov, 2NASA-Johnson Space Center, Mail Code XI, Houston, TX 77058, USA

Introduction: Cl is a volatile element and can be lost during formation and evolution of planetary bodies, which can lead to fractionation of its two stable isotopes, $^{35}$Cl and $^{37}$Cl. Stable Cl isotope variations (reported as $\delta^{37}$Cl, in parts per thousand (%), relative to standard mean ocean chloride (SMOC) [1]) have been measured in many lunar samples and have produced a wide range from ~$-4\%$ to $+81\%$ [2-7]. This variation has led to various interpretations of how the fractionation was produced, from degassing during accretion, magma ocean, or volcanic phases of lunar evolution [3, 4].

Chlorine isotope measurements from two methods, SIMS and IRMS, have produced significantly different results, leading to difficulties in interpreting $\delta^{37}$Cl data, which led us to develop a method for high precision ($\sim 1$-$4\%$, with $10 \mu g$ Cl, $2\sigma$) stable Cl isotope measurements using the cesium sputter negative ion source of an accelerator mass spectrometry (AMS) system [8].

This work is the next step in developing the chemistry and methods required to dissolve, separate, and measure samples from highly fractionated, low Cl concentration materials such as those found in astro materials from the Moon, Mars and Vesta [2-7, 9-12]. Here we present progress toward a method that can efficiently extract small amounts of Cl from a silicate matrix. Our approach involves bulking with Br carrier following HF digestion to efficiently scavenge Cl with a Ag(Br+Cl) precipitation. The Ag(Br+Cl) is then re-dissolved and Cl is chemically separated from Br via anion exchange chromatography. This will enable sample preparation with microgram-scale Cl masses, to ultimately prepare samples for measurement using the cesium sputter AMS method [8]. The presented experiments are aimed at establishing a robust column separation procedure, potential sources of Cl contamination, and isotope fractionation in the column.

Methods: Five sets of samples containing 50 micrograms of Cl were created in triplicate to test the column chemistry (Table 1). One drop of 1:1 NH$_4$OH + H$_2$O was added to each solution to more accurately reflect the composition of solutions prepared from dissolved rock samples. The anion exchange resin used (AG 2 X8, 100-200 mesh, chloride form) was rinsed in MQ water 3 times and ‘bad’ beads were decanted off. After being washed, 2ml of the resin was added to 0.8 cm inner diameter gravity flow columns and conditioned with 10 ml of 3 N HNO$_3$ to convert to nitrate form prior to use. After conditioning the columns, they were loaded with each of the 3 sets of samples described above (sets 3-5). Elution began with 4 ml of 0.1 M NH$_3$, 4 ml of 0.05 N HNO$_3$ and 2 ml of 0.3 N HNO$_3$, all of which was drained to a waste reservoir. The next 4 ml of added 0.3 N HNO$_3$ contained the sample Cl and was collected in 15 ml centrifuge tubes filled with ~10 mg of Nb powder. The Cl was precipitated as AgCl with the addition of 0.5 ml of 2% AgNO$_3$ in 2N HNO$_3$, in stochiometric excess, in a low light setting to avoid photodissociation. The samples were then vortexed and allowed to sit overnight in solution.

The AgCl was then vortexed again before being rinsed by centrifuging the tubes for 5 minutes at 3000 RPM to compact the AgCl into a pellet, the supernatant liquid was pipetted out, 2 ml of MQ water was added, and each tube was vortexed and centrifuged again. The majority of the remaining supernatant liquid was removed by pipette, and the AgCl was slurried and transferred to acid-cleaned glass shell vials to dry at 80 degrees C in an oven overnight, depositing AgCl throughout the Nb.

Results: All measurements were on 50 µg of added Cl and had a precision of between $0.1 - 0.8\%$, $2\sigma$. Preliminary results show that this method fractionates stable Cl $\sim 3$-$4\%$ relative to the natural ratio (Figure 1). The Cl samples with 500 µg of added Br showed an addition of a minimum of 2 µg of Cl relative to the control samples (Figure 2). Columns that were re-conditioned and re-used after prior addition of 0.5 – 1 mg samples of natural ratio Cl retained between 35 and 120 µg of sample Cl, significantly inflating the 1:1 Cl toward the natural ratio (Figure 3).

Discussion: We were able to fully separate the 50 µg of added Cl from 500 µg of added Br using anion exchange resin, enabling this method for use in scavenging micrograms of Cl from low mass or low-Cl astromaterials. In a natural sample, the Cl and Br would be co-precipitated together and re-dissolved to be loaded into the anion exchange columns.

Our finding that the column chemistry slightly fractionates the Cl samples can likely be precisely

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quantified and accounted for with further measurements or may not be present with other forms of resin, which will have to be tested.

The current source of Br standard solution adds approximately 2 µg of Cl to the sample, so for smaller Cl masses, either a new Cl-free Br source will be needed, or the Br solution could be cleaned of Cl using this anion exchange method.

We find that the column conditioning using 3.0 N HNO₃ is sufficient to clean the initial Cl present in the Cl form resin, though it is insufficient for re-conditioning of columns after use, suggesting the need for either re-conditioning with higher concentrations and/or volumes of HNO₃, or preparing a new column and new resin for each sample.

Anderson et al. [8] outlined how to measure stable chlorine isotopes using only the Cs sputter source of an AMS facility at high precision. This work represents an important next step to being able to fully dissolve rock samples and scavenge small masses of Cl for stable Cl isotopic measurements of low mass or low-Cl concentration lunar and meteoric samples with AMS.

Future tests will use different chemical forms of resin such as the OH- form to quantify any Cl fractionation or contamination and note any process changes.

**Conclusion:** We have shown the ability to chemically separate Cl from Br, representing important initial steps toward a method for scavenging small Cl masses from natural samples for stable Cl isotope measurements with AMS.

**Acknowledgments:** Prepared in part by LLNL under Contract DE-AC52-07NA27344; LLNL-ABS-858930.