A PROCEDURE TO DETERMINE THE COORDINATED CHROMIUM AND CALCIUM ISOTOPIC COMPOSTION OF ASTROMATERIALS INCLUDING THE CHELYABINSK METEORITE.

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Introduction: The isotopic compositions of elements are often used to characterize nucelosynthetic contributions in early Solar System objects. Coordinated multiple middle-mass elements with differing volatilities may provide information regarding the location of condensation of early Solar System solids. Here we detail new procedures that we have developed to make high-precision multi-isotope measurements of chromium and calcium using thermal ionization mass spectrometry, and characterize a suite of chondritic and terrestrial material including two fragments of the Chelyabinsk LL-chondrite.

Analytical Procedure: Powders of whole-rock samples (Chelyabinsk, Allende) and silicate mineral separates (Akermanite NMNH 103104, Augite NMNH 164905) were dissolved in concentrated $HF+HNO_3$ using Parr digestion vessels heated to 180°C for 48 to 72 h. Chromite separates (Lundsgård L6 chondrite, Winona primitive achondrite, NMNH 117075) were dissolved in loosely-capped precleaned 3mL Savillex beakers using $HCl+HNO_3$ (3:1) placed within Parr digestion vessels and heated to 180°C for 48 h. All samples were visually inspected using a microscope to ensure complete dissolution. If undissolved material remained the procedure was repeated.

Chemical separation of Cr: Dissolved Cr sample solutions, either Cr eluted from the TODGA columns described below or the dissolved chromite samples (not processed for Ca) are evaporated, dissolved in HCl and fluxed at 180°C for 12 h to ensure complete reduction prior to chemical separation. Cr is separated via a two-stage micro column procedure based off previous work [1]. The 1st stage anion exchange resin (Bio-Rad AG1-X8 200-400 mesh) separates Fe, the 2nd stage cation exchange resin (Bio-Rad AG 50W-X8 200-400 mesh) purifies Cr. The combined Cr yield of this procedure is ~85%.

Chemical separation of Ca: Following dissolution, sample solutions are evaporated, and concentrated HNO_3 was added to samples dissolved using HF. This solution is ultrasonicated, fluxed, evaporated, and repeated 3 times to ensure no precipitation of fluoride compounds. Samples are then dissolved in dilute HNO_3 and processed using a single-step procedure using Eichrom TODGA resin cartridges and a vacuum box. The method, developed using the elemental distribution coefficients from [2], was designed to specifically separate and purify Ca while also maintaining high Cr yield. Ca yield from this column is consistently >95% for the wide range of sample compositions investigated (including a range of whole-rock compositions, oxides, refractory ceramics, Fe-Mg silicates, and framework silicates).

Isotope Analysis: All isotope measurements are made using a Thermo Scientific TRITON mass spectrometer housed in the Center for Isotope Cosmochemistry and Geochronology, ARES, NASA-JSC.

Cr isotope measurements: Cr samples are loaded in dilute HCl on outgassed single Re filaments along with silica gel and saturated boric acid. Sample load sizes are generally estimated to be 1 μg, though some experimentation was conducted using smaller load sizes. Cr is analyzed using a multi-line method modified from [1]. This method is preferred over a static analysis due to the ability to monitor Faraday cup degradation. Each sample was loaded on 2-3 filaments and each filament was analyzed 2-3 times per session. A single run consists of 21 blocks of 10 ratios through 4 cup settings for a total of 840 ratios per analysis. Virtual amplifier rotation and baseline calibration is preformed preceding each block. The ^{52}Cr beam intensity is normally between 5-10 V using a 10^{11} Ω resistor. Instrumental mass fractionation is corrected using an exponential law and a $^{50}Cr/^{52}Cr$ value of 0.051859 [3]. Isobaric interfering elements are monitored on ^{49}Ti, ^{51}V, and ^{56}Fe, respectively, using an ion counter prior to the analysis. Normally, only ^{56}Fe requires a correction.

Ca isotope measurements: Purified Ca is dissolved in dilute HCl and loaded in 2-3 μg aliquots with dilute H_3PO_4 on outgassed Re filaments. A Parafilm dam is applied to the filament prior to loading the sample in an effort to reduce spreading and improve the consistency of loading. Filaments are slowly heated to evaporate loading acid and residual Parafilm. Ca is analyzed using a multi-dynamic method, which is preferred to better understand cup degradation effects. One standard (SRM 915a) is run for ~ every 2 unknowns; normally 3 standards per barrel. A single run consists of 7 blocks of 15 ratios through four cup settings. Virtual amplifier rotation and baseline calibration are preformed preceding each block. The ^{40}Ca beam intensity is usually between 20-30 V using a 10^{11} Ω resistor. Instrumental mass fractionation is corrected using an exponential law and a $^{42}Ca/^{44}Ca$ value of

0.31221 [4]. Isobaric interfering elements are monitored on ^{39}K and ^{47}Ti during the analysis, and a correction is made for K.

Data reduction: For each element, instrumental mass fractionation, and interference corrections for Fe and K, respectively, are performed during acquisition using Thermo software. For both ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios, the value for a single run is calculated as the cycle average of the four lines and the sample mean is taken as the average of all of the analyses during a session. For Ca, we empirically determined that the exponential law does not properly account for instrumental mass fractionation outside of a narrow range (0.315-0.310) of ^{42}Ca/^{44}Ca values, which is similar to what has been found by others [5]. To account for this poor correction, we exclude data collected during cycles that yield values outside of this range. For ratios measured on multiple lines, ^{40}Ca/^{44}Ca and ^{43}Ca/^{44}Ca, we perform an offline multidynamic calculation which we report as the mean for a run. The normalized cycle values of the remaining Ca ratios (^{46}Ca/^{44}Ca, ^{48}Ca/^{44}Ca) are reported as the mean. For each sample we report the weighted mean of *n* replicates for each ratio, and 2σ uncertainty on the weighted mean. All ratios are presented in epsilon notation (ε) which is calculated as the deviation from session-averaged standard value in parts per 10,000.

Cr isotopic results: Two chromium standards, in-house legacy standard Cr Std 361 and SRM 3112a, were run in each session. Due to commercial availability and more widespread use, SRM 3112a was used as the reference here. The results we report here for the Chelyabinsk, Lundsgård, and Allende samples agree well with data previously reported [6-8]. Interestingly, an observable difference was measured between the two standards. We attribute this discrepancy to be the result of residual uncorrected isotopic fractionation, either produced during production of the standard [7], or during the analysis as has been observed in earlier studies [1,7,9].

Ca isotopic results: Recent comprehensive studies of oceanic basalts and peridotites [10,11] indicate an observable excess of 0.78ε between the ε40Ca value of the standard (SRM 915a) and that of Earth's mantle, thus here we reference our samples to the mantle value [10,11].

Nearly all measured Ca ratios yield mantle values. Both samples of the Chelyabinsk meteorite yield positive ε40Ca values, even when accounting for radiogenic ingrowth. These values agree well with previously reported values for other LL chondrites [11]; consistent with the material originating in a similar source region. All ε48Ca measurements, including those for Chelyabinsk samples, are within uncertainty of the mantle.
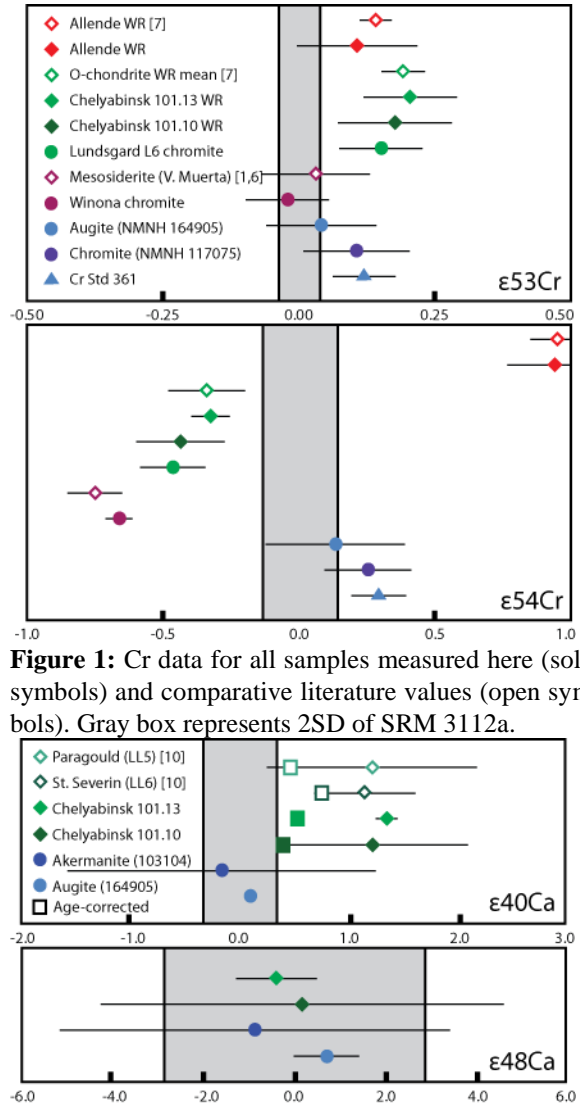

Figure 1: Cr data for all samples measured here (solid symbols) and comparative literature values (open symbols). Gray box represents 2SD of SRM 3112a.

Figure 2: Ca data for all samples measured here (solid symbols) and comparative literature values (open symbols). Gray box represents 2SD of SRM 915a. Square symbols are corrected for radiogenic ingrowth.

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