THE DISTRIBUTION OF NUCLEOSYNTHETIC BARIUM AND CHROMIUM ISOPE ANOMALIES IN METEORITIC SAMPLES. L. Qin, C. M. O’D. Alexander, R. W. Carlson, and M. Horan. Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road, NW, Washington, DC 20015, USA (E-mail: lqin@ciw.edu)

Introduction: Various short-lived radiometric systems can serve as important chronometers for early Solar System events. Two that have achieved prominence lately are $^{53}$Mn-$^{53}$Cr and $^{146}$Sm-$^{143}$Nd. The use of these chronometers relies on the assumption that the Solar System initially had homogeneous isotopic compositions for the daughter elements and for the abundance of the parent isotopes. Recent developments in mass spectrometry make detections of small isotopic variations possible. With this resolution, planetary-scale isotopic anomalies have been documented for various elements. For some elements, the existence of isotope anomalies clearly indicates a nucleosynthetic origin, and thus may undermine the use of some short-lived chronometers or affect their chronological interpretation. For instance, a recent study [1] reported Ba nucleosynthetic anomalies (strong enrichments in $^{137}$Ba and $^{138}$Ba) for carbonaceous chondrites and one ordinary chondrite and argued that this would affect the interpretation of the $^{142}$Nd difference between chondrites and terrestrial samples [2]. However this result is contradictory to a previous study [3] and several follow-up studies [4-6] that either reported no anomaly or an anomaly with a different pattern (enrichments in $^{135}$Ba and $^{137}$Ba). Several reasons make Ba isotopic analyses of great interest. One is that $^{135}$Ba is the decay product of short-lived $^{135}$Cs (t$_{1/2}$=2 Myr), so it can potentially be used as a cosmochronometer. Another reason is that Ba consists of 7 isotopes produced by different processes of stellar nucleosynthesis, and thus offers a good opportunity to examine the nucleosynthetic contributions to Ba isotopic anomalies.

Another example of nucleosynthetic isotopic variability occurs in $^{54}$Cr [7-10]. In contrast, the observed variability in $^{53}$Cr is usually assumed to reflect decay of $^{53}$Mn. However a recent study shows an apparent correlation between $^{54}$Cr excess and $^{53}$Cr excess in bulk carbonaceous chondrites [9]. Sequential leaching experiments on bulk carbonaceous chondrites revealed that these two Cr isotope excesses are carried in different components [7-10]. Thus it is not clear why the two Cr isotope excesses should be correlated, and whether or not $^{55}$Cr variability partially reflects a nucleosynthetic heterogeneity. These are important questions especially when $^{54}$Mn-$^{53}$Cr has become an increasingly useful and widely applied cosmochronometer (e.g. [11]). Identifying the $^{54}$Cr carrier phase will assist in addressing the relationship, if any, of $^{54}$Cr and $^{53}$Cr variability. The $^{54}$Cr carriers are acid-resistant at low temperature. Our recent study showed that the leachates of acid residues of chondrites show large $^{54}$Cr excesses of 10-100 $\epsilon$ [12]. The excesses decrease in the sequence CM>LL>CV. Since the $^{54}$Cr carrier is acid-resistant, we should be able to concentrate the carrier, examine whether it has the same composition in all chondrites types, and define the degree to which $^{54}$Cr excesses are accompanied by $^{53}$Cr variability.

To address these issues, we report here Cr isotope analyses of leachates of acid residues of Murchison (CM), CR and enstatite chondrites at various temperatures. We also readdress the issue of Ba and Cr nucleosynthetic anomalies in bulk chondrites.

Samples and Methods: Sample dissolution and chemical separation. An important aspect of whole rock analyses of meteorites that contain refractory pre-solar phases is to ensure total dissolution of all the components. Step-wise acid leaching experiments show that different mineral components of meteorites have distinct isotopic compositions of Cr and Ba [3, 7-10]. Some carrier phases of pre-solar Ba and Cr may survive during standard HF-HNO$_3$ digestion, such as silicon-carbide and refractory oxides. Fusion techniques using lithium borates can ensure complete dissolution, but for Ba, the blank level in the flux is unacceptably high, > 1 $\mu$g per gram of flux. To avoid this problem, ~0.6 g of Allende meteorite sample powder was sealed in a platinum tube and heated in air at 1600 °C (above the liquidus of Allende) for 30 minutes in a tube-furnace. After separation from the Pt, the technique for subsequent acid dissolution and chemical separation followed that of [4]. For Cr isotope analyses of bulk meteorites, two different approaches were made. One approach involved heating the sample at 1100 °C in air for 30 minutes followed by acid digestion. In the second approach, the sample was mixed with lithium-borate flux in 1:7 ratio and heated at 1050-1100 °C for 20 minutes. The resulting glass was dissolved in 2 N HNO3. Chemical separation of Cr from the flux and matrix elements was achieved through a two-step cation exchange procedure. In the first step, the lithium flux and most of the matrix elements (except Fe) were removed from the sample solution in HNO$_3$. In the second step, Cr was further purified in HCl following a standard column chemical procedure [8].

The residues of carbonaceous and enstatite chondrites were leached with 6 N HCl at various temperatures for ~12 hours. The leachates were only passed
through the second step of the Cr separation procedure. The isotopic compositions of Ba and Cr were analyzed by TIMS (Triton) at DTM. The instrumental mass fractionation was corrected by assuming constant ratios of $^{134}\text{Ba}/^{136}\text{Ba}$ and $^{50}\text{Cr}/^{52}\text{Cr}$ for Ba and Cr isotope analyses respectively and using the exponential law.

**Results:** *Ba results.* Our preliminary Ba results show that Allende still has small but resolvable enrichments in $^{135}\text{Ba}$ ($17 \pm 7$ ppm) and $^{137}\text{Ba}$ ($14 \pm 12$ ppm), even after the sample was melted at $1600 \degree C$. The shape of this anomaly pattern is consistent with an $r$-process enrichment pattern. An important potential Ba anomaly carrier phase, SiC, is not expected to survive at such a high temperature. Thus these values should reflect the isotopic compositions of the bulk Allende sample. The excesses in $^{135}\text{Ba}$ and $^{137}\text{Ba}$ here are slightly lower than those observed in [5]. This could reflect either incomplete dissolution of the Ba carrier in [5], heterogeneity in the sample, or an unaccounted-for blank contribution during the melting of the sample. The two low-abundance $p$-process isotopes $^{136}\text{Ba}$ and $^{132}\text{Ba}$ did not show a difference from the terrestrial standard at the level of $30$ ppm ($2\sigma$ internal). Two recent studies reported deficits in $p$-process isotopes of Sm and Nd in carbonaceous chondrites [4, 13], but our results provide no evidence that this deficiency extends to Ba.

**Cr results.** Both bulk Allende (CV) and Murchison (CM) show excess in $\varepsilon^{54}\text{Cr}$ of $\sim 1 \varepsilon$. For Allende, the fusion method shows an $\varepsilon^{54}\text{Cr}$ excess of $0.60 \pm 0.14$ ($2\sigma$, internal), equal within error to the value of $1.04 \pm 0.34$ obtained by heating the sample to $1100 \degree C$. The internal precision by the fusion technique is two-fold better than the heating method, most likely as a result of a cleaner Cr fraction after the two-column procedure, making this method useful for characterizing small variations of $^{54}\text{Cr}$ in future studies. Using this method, an $\varepsilon^{54}\text{Cr}$ value of $0.71 \pm 0.12$ was obtained for Murchison. Our results for $\varepsilon^{54}\text{Cr}$ for Allende and Murchison are in good agreement with a recent study [10] that did not use a fusion dissolution. The excesses in $^{54}\text{Cr}$ in bulk carbonaceous chondrites provide evidence for planetary-scale nebular heterogeneity in the early Solar System, consistent with that demonstrated by Ba, Nd and Sm. The $\varepsilon^{54}\text{Cr}$ values for Allende or Murchison are $0.09 \pm 0.07$ and $0.07 \pm 0.06$ respectively. The external precision is $0.14$, so neither of the two show resolvable deviation from the terrestrial standard in $\varepsilon^{54}\text{Cr}$. Our $\varepsilon^{53}\text{Cr}$ result for Allende agrees with [9], but the value for Murchison is lower than that obtained in [9] for another CM-chondrite Murray, which shows an excess of $0.27 \pm 0.09$.

The leachates of acid residues of Murchison show large excess in $\varepsilon^{54}\text{Cr}$, confirming our previous study [12]. The excesses increase from $36 \varepsilon$ to $77 \varepsilon$ when the leaching temperature increases from $60 \degree C$ to $80 \degree C$. This shows that the leachable, isotopically anomalous Cr in the residue increases with temperature. $^{54}\text{Cr}$ excesses are accompanied by small $^{53}\text{Cr}$ deficits, also consistent with our earlier work [12].

We analyzed the acid leachates of one CR and two enstatite chondrites. GRA95229 (CR) shows an interesting large $^{54}\text{Cr}$ excess of $200 \pm 10 \varepsilon$, but the Cr concentration in this sample is relatively low, and the ion signal is small, thus the result needs further verification to make sure no analytical artifact is involved. We obtained good-quality data for the two enstatite samples: PCA91020 (EL) and PCA91238 (EH). The former has a small $^{54}\text{Cr}$ excess of $0.51 \pm 0.15$ and the latter shows essentially terrestrial composition. The small $^{54}\text{Cr}$ excess of PCA91020 is accompanied by a small $^{53}\text{Cr}$ anomaly of $-0.34 \pm 0.07$. The bulk E-chondrites show an average (close to) terrestrial $^{54}\text{Cr}$ composition, indicating an accretion region different from that of C-chondrites [10]. The absence of or small Cr isotope anomalies in the acid residues could reflect that anomalous Cr carrier phases are rare or have only small isotopic anomalies in their accretion region, or have been destroyed by parent-body metamorphism.

**Conclusions:** Our complete sample dissolution method reveals that the CV-chondrite Allende shows small yet resolvable Ba isotopic anomalies, resulting from an excess of $r$-process over $s$-process component in the nebular region of its accretion. Our studies did not find deficits in $p$-process isotopes of Ba outside analytical uncertainty. $^{54}\text{Cr}$ excesses are reproduced for two bulk C-chondrites Allende and Murchison. We did not find $^{53}\text{Cr}$ excesses. Leachates of acid residues of two enstatite chondrites show small or no $^{53}\text{Cr}$ anomalies, in contrast to large excesses observed for those of C- and OC-chondrites. This could reflect that either they were accreted in a different nebular region, or the $^{54}\text{Cr}$ carriers have been destroyed by parent body metamorphism.