

## MASS-INDEPENDENT CHROMIUM ISOTOPIC PANORAMA IN CHONDRITES: IMPLICATIONS FOR ORIGIN OF CHONDRITE PARENT BODIES AND EARLY TERRESTRIAL DEPLETION.

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**Introduction:** Chondrites are the oldest cosmic sedimentary rocks, the most pristine of which preserve information about the origin of the Solar System [e.g., 1]. Thus, investigating the chemical and isotopic compositions of chondrites is central to better understand the evolution of the Solar System and planet formation. Chondrites also record large chemical and isotopic variations amongst them [2-4]. Mass-independent chromium isotope variation can provide both timing (<sup>53</sup>Mn-<sup>53</sup>Cr chronometry) and origin (<sup>54</sup>Cr systematics) information about chondrite parent body formation.

Here, we have developed a high-yield (~95%) chemical purification, and employed MC-ICP-MS (that can avoid the potential equilibrium Cr isotope fractionation during evaporation on TIMS [5]) to achieve measurements with higher precision and accuracy for a series of chondrite samples, including CI, CH, CB, CR, CM, CO, CV, CK carbonaceous chondrites (CC), one EH chondrite, Rumuruti (R) chondrites, one Kakangari (K) chondrite and some ungrouped chondrites. The related analytical methods are described in [4,6-8].

**Results and Discussion:** We first tested the data accuracy and external reproducibility using standard samples. Orgueil:  $\epsilon^{53}\text{Cr} = 0.19 \pm 0.00$  and  $\epsilon^{54}\text{Cr} = 1.50 \pm 0.01$  (2SD, N = 2), DTS-1:  $\epsilon^{53}\text{Cr} = 0.05 \pm 0.03$ ,  $\epsilon^{54}\text{Cr} = 0.16 \pm 0.06$  (2SD, N = 5) and Allende:  $\epsilon^{53}\text{Cr} = 0.10 \pm 0.04$  and  $\epsilon^{54}\text{Cr} = 0.92 \pm 0.07$  (2SD, N = 5).

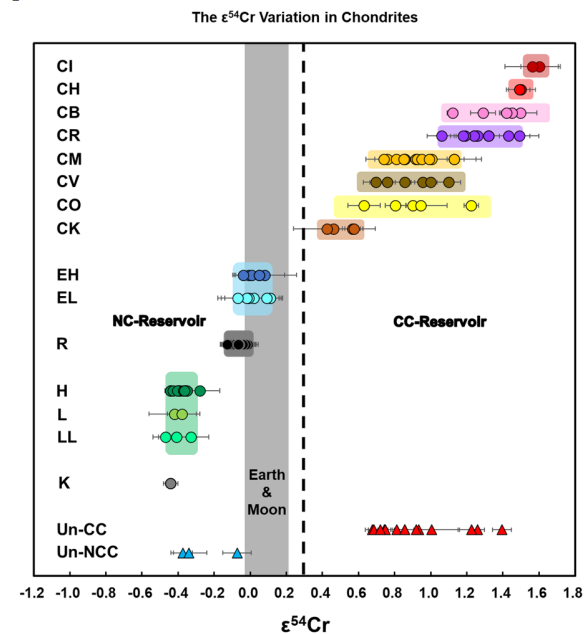
All the R chondrites have average  $\epsilon^{53}\text{Cr} = 0.23 \pm 0.05$  and  $\epsilon^{54}\text{Cr} = -0.06 \pm 0.08$  (2SD, N = 12) that is similar to the enstatite chondrites (EC), aubrites and Earth-Moon system [9, 10], while the LEW 87232 (K) chondrite has a higher <sup>55</sup>Mn/<sup>52</sup>Cr and  $\epsilon^{53}\text{Cr}$  values of 1.32 and  $0.50 \pm 0.02$ , and an ordinary chondrite (OC)-like  $\epsilon^{54}\text{Cr}$  value  $-0.44 \pm 0.04$  (2SE, N = 5).

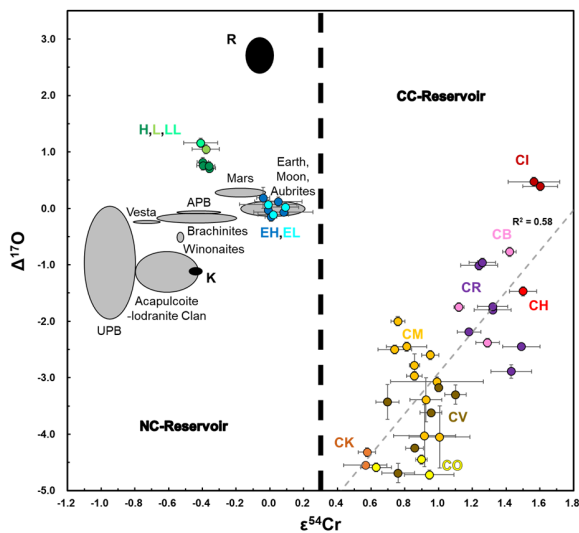
All the ungrouped CCs (N = 14) have  $\epsilon^{54}\text{Cr}$  values > 0.3, ranging from  $0.68 \pm 0.04$  to  $1.40 \pm 0.05$ , while all the ungrouped non-CCs (NCC) (N = 3) have  $\epsilon^{54}\text{Cr} < 0.3$ , ranging from  $-0.37 \pm 0.05$  to  $-0.07 \pm 0.08$ . Combining the data of these ungrouped CCs with the R and K chondrites (both NCCs), confirms the isotope dichotomy in the Solar System materials [10,11].

Combined with the literature data [6,8-10,12-15 and more references], we have updated the  $\epsilon^{54}\text{Cr}$  sequence in chondrites:  $\text{CI} = \text{CH} \geq \text{CB} \geq \text{CR} \geq \text{CM} \approx \text{CV} \approx \text{CO} \geq \text{CK} > \text{EC} = \text{RC} > \text{OC} = \text{KC}$  (**Figures 1 and 2**). Our high-precision data show that the average  $\epsilon^{54}\text{Cr}$  values for bulk CV ( $0.89 \pm 0.12$ ; 2SE, N = 6) and CK chondrites ( $0.51 \pm 0.08$ , 2SE, N = 4) are different, suggesting that they do not originate from the same parent body. CB-CH and CM-CO types have the similar  $\epsilon^{54}\text{Cr}$  values within uncertainty, respectively. CB, CM, CV, CR and CO chondrites have intra-group  $\epsilon^{54}\text{Cr}$  heterogeneities that are likely caused by unrepresentative sampling or heterogeneous accretion of chondrite parent bodies.

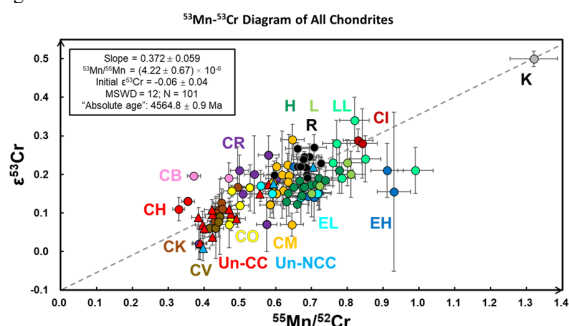
**Figure 1** The  $\epsilon^{54}\text{Cr}$  variations in different groups of chondrites. The colorful shade behind the points are the 2SD uncertainty. Un: ungrouped (triangles); the grey bar: Earth and Moon; the dashed line: the boundary of CC and NC reservoirs ( $\epsilon^{54}\text{Cr} \approx +0.3$ ).

In this study, the two CB chondrites (MIL 05082 and QC 001) have <sup>55</sup>Mn/<sup>52</sup>Cr ratios of 0.37-0.47 and  $\epsilon^{53}\text{Cr}$  values of  $0.20 \pm 0.01$  (2SD, N = 2) that are indistinguishable from CI chondrites ( $0.21 \pm 0.04$ ; 2SD, N = 2). Therefore, there is no valid Mn-Cr isochron in CCs. In **Figure 3**, there is a broad Mn-Cr correlation for all the chondrites, but it is mostly reflecting a mixing process instead of an isochron.





**Figure 2** The  $\epsilon^{54}\text{Cr}$  and  $\Delta^{17}\text{O}$  values of the CCs, OCs, ECs, RCs and KC (filled circles), as well as achondrites, terrestrial and lunar samples (gray ellipses). APB: angrite parent body; UPB: ureilite parent body. The colored circles represent the same samples that are shown in Figure 1.

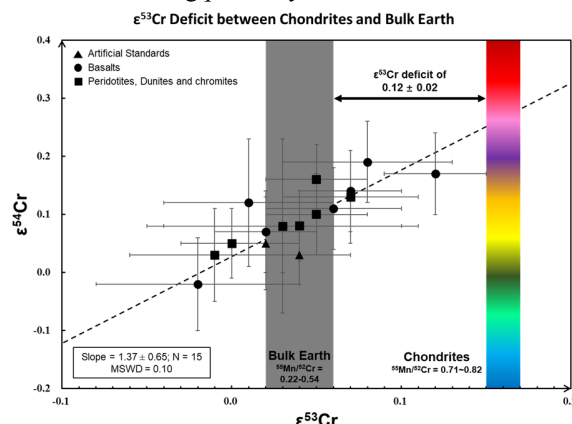


**Figure 3** All of the  $^{55}\text{Mn}/^{52}\text{Cr}$  and  $\epsilon^{53}\text{Cr}$  data for the different chondrite groups. The data (of which symbols are the same as those in Figures 1 and 2) are regressed by Model 3, *Isoplot R*.

There are several likely reasons to argue this is a mixing line instead of an isochron: (1) Unlike other CCs, the CH and CB chondrites probably formed via impacts that postdated the formation of other CCs, i.e., ~5 Ma after CAIs [16]. (2) Different chondrite groups have distinct photochemical and/or nucleosynthetic isotope anomalies (**Figures 1-2**) reflecting variability in the makeup of their precursors and/or their formation environments within the protoplanetary disk. (3) Chondrites are complex assemblages of chondrules, matrix, CAIs, AOs and metals that formed at different times and under varying conditions [17]. These chondritic components do not all have the same ages and/or source regions (initial  $\epsilon^{53}\text{Cr}$  values).

Compared to the NIST 979 Cr standard, bulk (silicate) Earth is characterized by  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values of  $0.04 \pm 0.02$  and  $0.09 \pm 0.03$  (2SE) (**Figure 4**). These correlated and slightly positive values for terrestrial samples potentially reflect a non-kinetic

isotopic fractionation relative to the NIST SRM 979 Cr standard. The lower  $\epsilon^{53}\text{Cr}$  value of the bulk (silicate) Earth compared to chondrites ( $0.16 \pm 0.01$ ; 2SE,  $N=88$ ) requires early volatile loss of Earth's precursor materials. Based on the half-life of  $^{53}\text{Mn}$  (3.7 Ma), this volatile loss likely occurred within 3 Ma of Solar System formation. Therefore, our data suggest that the terrestrial volatile depletion more likely occurred during the formation of Earth precursors as opposed to later volatile loss during planetary evolution.



**Figure 4** The  $\epsilon^{53}\text{Cr}$  and  $\epsilon^{54}\text{Cr}$  values for terrestrial rocks and chondrites. The black circles, squares and triangles are terrestrial crustal, mantle rocks and artificial standards, respectively. The gray (left) and colorful (right) bars indicate the average  $\epsilon^{53}\text{Cr}$  values (with 2SE uncertainty) for bulk silicate Earth (BSE;  $N=15$ ) and chondrites (including CCs, OCs, ECs and RCs;  $N=88$ ), respectively. There is a  $\epsilon^{53}\text{Cr}$  difference of  $0.12 \pm 0.02$  between Bulk Earth and chondrites, which likely indicates an early volatile fractionation of the Mn/Cr ratio (decreasing both the Mn/Cr ratios and  $\epsilon^{53}\text{Cr}$  values) of the proto-Earth.

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**References:** [1] Krot, A.N., et al. (2014) *Treatise on Geochemistry (Second Edition)*, 1-63. [2] Alexander, C.M.O.D. (2019) *GCA*, 254, 246-276. [3] Alexander, C.M.O.D. (2019) *GCA*, 254, 277-309. [4] Zhu, K. et al. (2021) *GCA*, 293, 598-609. [5] Bourdon, B. and Fitoussi C. (2020) *ACS-Earth and Space Chemistry*, 4, 1408-1423. [6] Schiller, M., et al. (2014) *JAAS*, 29, 1406-1416. [7] Zhu, K. et al. (2020) *ApJ*, 888, 126. [8] Perderson S.G. et al. (2019) *MAPS*, 54, 1215-1227. [9] Mougél, B. et al. (2018) *EPSL*, 481, 1-8. [10] Trinquier, A. et al. (2007) *ApJ*, 655, 1179-1185. [11] Warren, P.H. (2011) *EPSL*, 311, 93-100. [12] Qin, L. et al. (2010) *GCA*, 74, 1122-1145. [13] Trinquier, A. et al. (2008) *GCA*, 72, 5146-5163. [14] Williams, C.D. et al. (2020) *PNAS*, 23426-23435. [15] Bischoff, A. et al. (2021) *GCA*, 293, 142-186. [16] Krot, A.N. et al. (2005) *Nature*, 436 989-992. [17] Connelly, J.N. et al. (2012) *Science*, 338, 651-655.