Chromium isotopic evidence for an early formation of chondrules from the Ornans CO chondrite

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Introduction: Chondrules are millimeter to sub-millimeter-sized spheres with igneous textures that are believed to have formed as molten droplets during transient heating (up to 2000 K) and rapid cooling (~10-1000 K/h) events in the solar protoplanetary disk [1, 2]. Since they are among the oldest solids in the Solar System [3, 4], chondrules are important records of the chemical and thermal evolution of the early Solar System.

Long-lived (^{207}Pb-^{206}Pb) and short lived (^{26}Al-^{26}Mg) dating systems showed that chondrules formed during the first 5 Myrs of the Solar System [5 and references therein]. However, utilizing of ^{207}Pb-^{206}Pb and ^{26}Al-^{26}Mg chronometry is limited by the unknown U isotope composition of chondrules and potential heterogeneity on the initial ^{26}Al distribution in the Solar System [6], and the two systems usually produce internal isochron ages. On the other hand, the ^{53}Mn-^{53}Cr chronometer ($T_{1/2}$= 3.7 Myr), is suitable and robust for dating early Solar System events [7].

The non-mass dependent variations of the $^{54}Cr/^{52}Cr$ ratio (reported here as $\varepsilon^{54}Cr$, the relative deviation in parts per ten thousand of the internally normalized $^{54}Cr/^{52}Cr$ ratio of the sample relative to the standard) can be used to trace the origins of Solar System materials (including chondrules). This is because it shows widespread heterogeneous $\varepsilon^{54}Cr$ signatures in the Solar System [8, 9]. Therefore, this Cr isotopic study of chondrules from CO3 chondrites (one the of most primitive chondrite group) will contribute to the understanding of the formation timescales and origins of chondrules.

Sample and analytical methods: A ~6g sample of Ornans (CO3.4) was gently crushed and sieved. The fraction that contained grains greater than 500 µm was retained, and the largest chondrules were handpicked from this fraction for analyses. Nine individual chondrules were dissolved in a mixture of $HF+HNO_3$ (2:1) and followed by aqua regia on a hot plate (170 °C). Before chemical separation of Cr, ~15% aliquots were preserved for precise determination of the $^{55}Mn/^{52}Cr$ ratio (using standard addition method) and major element contents by ICP-MS.

The Cr purification protocol is based on the procedure described in [10] involving a two-step cation exchange column protocol. The Cr isotopic compositions of the samples were analyzed by Triton Plus TIMS at State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing. Each sample was run 4-6 times on Re filament. NIST SRM 3112a was used as the standard and all the raw Cr isotopic data were normalized to a $^{50}Cr/^{52}Cr$ ratio of 0.051859 using the exponential law [7].

Results: The $\varepsilon^{53}Cr$ values of Ornans chondrules correlate with their $^{55}Mn/^{52}Cr$ ratios, yielding a slope of 0.63 ± 0.14 (2σ), calculated using the Model 1 fit of Isoplot 4.15 (Figure 1). The Ornans chondrules show large variability in their $\varepsilon^{54}Cr$ values, ranging from +0.20 to +1.22, with an average value of 0.81. Also, the variations in $\varepsilon^{54}Cr$ are correlated with those in $\varepsilon^{53}Cr$ (and $^{55}Mn/^{52}Cr$) (Figure. 2).

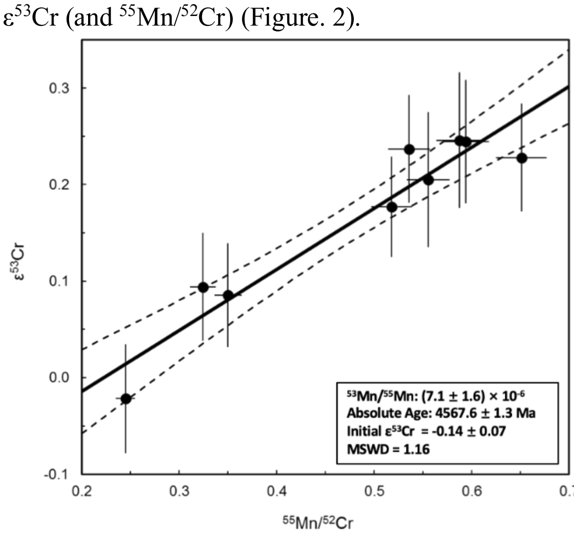

Figure 1 Mn-Cr external isochron for nine chondrules from Ornans (CO3.4) carbonaceous chondrite.

Discussion: The slope of the isochron gives an initial $^{53}Mn/^{55}Mn$ ratio of $(7.1 \pm 1.6) \times 10^{-6}$ and the intercept gives an initial $(^{53}Cr/^{52}Cr)_0$ of -0.14 ± 0.07. The initial $^{53}Mn/^{55}Mn$ ratio corresponds to an absolute age of 4567.6 ± 1.3 Ma (2σ) when anchored to the angrite D'Orbigny (U-corrected). Different volatility of Mn and Cr [12] suggests the variability observed in the Mn/Cr ratios between chondrules could be caused by a thermal process. The Mn-Cr age of Ornans chondrules is similar within error to the Pb-Pb age of CV CAIs 4567.30 ± 0.16 Ma [3], which suggests that Mn/Cr fractionations that were preserved in the CO chondrule precursors were established at about the same time as the formation of the CV CAIs. The source of heat responsible for fractionating Mn from Cr in the chondrule precursors may be related to the active young Sun [13] and associated with FU Orionis outbursts [14].

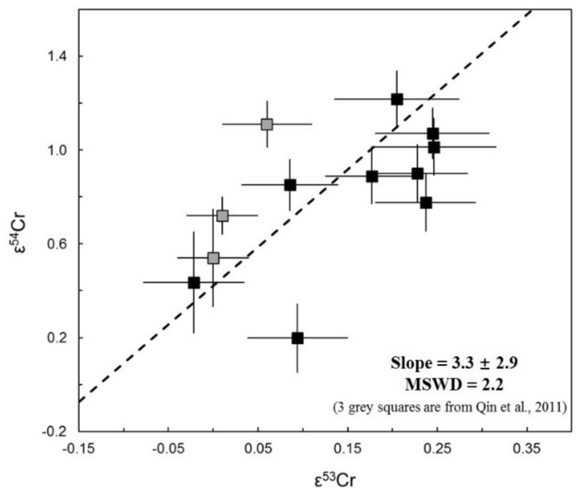

Figure 2 ε^{53}Cr vs. ε^{54}Cr values of the chondrules from the Ornans (CO3.4) carbonaceous chondrite. Three more data of Ornans chondrules (grey) are from [11].

The heterogeneous ε^{54}Cr values which correlate with ε^{53}Cr values and Mn/Cr ratios likely reflect a mixing process of 2 reservoirs, i.e. silicates (excluding CAIs) in CAI region and CI chondrites. Materials that formed in the CAI-forming region, which is generally assumed to have been formed close to the Sun (<0.5 AU [15], would have had low Mn/Cr ratios, as have been observed for CAIs that have ^{55}Mn/^{52}Cr ratios lower than 0.1 [16]. Typically, CAIs have high ε^{54}Cr values (~6) [17], and the reservoir would have been complementary to these CAIs that would then have had low ε^{54}Cr values (mostly the silicate components in CAI forming region). CI chondrites, a CC group composed mostly of matrix, have a bulk ^{55}Mn/^{52}Cr ratio of 0.851 and a bulk ε^{54}Cr value of 1.65 ± 0.07 [10], which is higher than those of all the chondrules analyzed in Ornans. Assuming that CI chondrites represent the most primitive material in the CC forming region (located in the outer Solar System, beyond the orbit of Jupiter) [18], our results are consistent with a large-scale transportation of materials from the inner to the outer Solar System in the early protoplanetary disk.

In addition, chondrules from chondrites with the highest CAI contents (e.g., CV and CO chondrules) exhibit larger ε^{54}Cr variations than chondrules from those containing fewer CAIs (e.g., CB and CR chondrules) (Figure 3), which suggests a grand transportation from inner to outer Solar System, and CV and CO chondrite accretion regions should receive more material transported from the CAI-forming region.

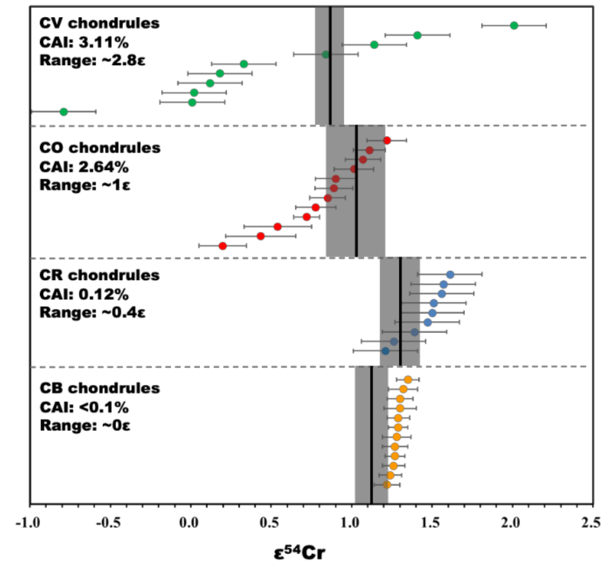

Figure 3 ε^{54}Cr of chondrules (circles) and CAI contents in Vigarano (CV, green), Ornans (CO, red), NWA 801 (CR, blue) and Gujba (CB, orange) chondrites, with the ε^{54}Cr of bulk chondrites (Vigarano for CV, Ornans for CO, GRA 06110 for CR, and Bencubbin for CB (Black lines with uncertainty of grey bars).

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