

ULTRA HIGH PRECISION Mn-Cr ISOTOPE SYSTEMATICS OF SELECT METEORITES. A. Yamakawa¹, K. Yamashita², and Q. Z. Yin¹, ¹Department of Geology, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA (ayamakawa@ucdavis.edu, qyin@ucdavis.edu), ²Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tushima-naka kita-ku, Okayama 700-8530, Japan (ktv@cc.okayama-u.ac.jp).

Introduction: The ⁵³Mn-⁵³Cr system (half-life: 3.7 ± 0.4 Ma [1]) has been a useful tool for dating a variety of early formed objects, because ⁵³Mn has a suitable half-life for high-resolution chronology for the first ~20 Ma of solar system history. Additional advantage to determine Cr isotope is the anomalies in ⁵⁴Cr isotope. Since each meteorite group preserves its own ⁵⁴Cr isotope value, it can be used as an important tracer to probe the precursor materials.

When chronological study is applied to a sample, it is always important to make cross-calibration with other chronometers. In [2], the age determination of chondrules and metal in CB chondrite Gujba was achieved using Mn-Cr isotopic systematics, and the obtained age was evaluated with other chronometers. Here, we first review the isotopic studies described in [2], and then re-evaluate the relative and absolute age constraints in the light of recent development of angrite age anchor changes due to the newly available ²³⁸U/²³⁵U isotopic composition in angrites [3,4]. Second, we also review the results of the Mn-Cr studies in monomict ureilites reported by [5]. Since ureilites preserve both primitive and igneous signatures, they provide invaluable information about the earliest planetesimal formation.

Samples and Methods: Mn and Cr concentrations and Cr isotope compositions were measured in whole rock and leachate-residue of chondrules and metal in Gujba, and eight whole rock (NWA 766, DaG 340, DaG 868, Dhofar 132, Dhofar 836, and El Gouanem and NWA 1241) and two leachate-residue of monomict ureilites (NWA 766 and NWA 1241).

For Gujba, whole rock chondrule fragments were dissolved in a HF+HNO₃ mixture using Teflon bombs at 190°C (solid circle in Fig. 1), while leaching experiment was performed using 6M-HCl (solid triangle), and then the residue dissolved in Teflon bombs using HF+HNO₃ mixture (solid diamond). The metal grain (solid square) was dissolved in 6M-HCl and 1M-HNO₃.

Since monomict ureilites mainly consist of olivine and pyroxene, Mn/Cr ratios of each mineral are not widely different. To obtain precise age for ureilites, stepwise dissolutions, method modified from [6], was performed to obtain data from phases with various Mn/Cr ratios. In the first two steps, 0.5M-acetic acid (LE 1) and 0.2M- HNO₃ (LE 2) were used to dissolve materials in the vein, such as carbonate. In the third step, the Fe metal on the rims of olivine grains (the

'reduction rim') that has contact with the vein was dissolved using 1M-HCl (LE 3). The main phases of monomict ureilites, olivine and pyroxene, were subsequently dissolved using 6M-HCl (LE 4) and HNO₃+HF mixture (LE 5), respectively. Procedures from LE 1 to LE 5 were carried out using an ultrasonic bath at room temperature. Finally, a small amount of the remaining phases, except for carbon, were completely dissolved in Teflon bomb using HF+HNO₃ mixture at 190°C. An additional experiment was performed for NWA 766, known to contain Cr-rich spinel [7]. Everything except the refractory phase was dissolved using HF+HNO₃ mixture in ultrasonic bath (labeled silicates in Fig. 2a), and the remaining refractory phase was dissolved in a Teflon bomb (labeled Cr-rich spinel in Fig. 2a). The eight whole rock powders were also dissolved using HF+HNO₃ mixture in Teflon bombs at 190°C.

The Cr isotope ratios were measured using a Thermo-Finnigan TRITON-TI thermal ionization mass spectrometer. For the chemical separation and isotope measurement of Cr, and the method for Mn/Cr ratio measurement is described in [8] and [9], respectively.

Discussions: In [2] and [5], the initial ⁵³Mn/⁵⁵Mn ratios and Pb-Pb ages of (3.24 ± 0.04) × 10⁻⁶ [10] and 4564.42 ± 0.12 Ma [11] from D'Orbigny, and (1.25 ± 0.07) × 10⁻⁶ [12] and 4558.55 ± 0.15 Ma [11] from LEW 86010 were used for the calculations. Here we re-calculate the "absolute" Mn-Cr ages using updated Pb-Pb ages with newly determined ²³⁸U/²³⁵U ratios [3,4]. For D'Orbigny, ²³⁸U/²³⁵U of 137.776 ± 0.026 was determined by [3], which corresponds to a new Pb-Pb age of 4563.34 ± 0.30 Ma. Using the range of measured ²³⁸U/²³⁵U of 137.763 to 137.802, or 137.783 ± 0.020 by [4] for LEW 86010, the Pb-Pb age changes to 4557.53 ± 0.25 Ma, which includes the ²³⁸U/²³⁵U uncertainty (preliminary result, Amelin personal communication).

Gujba: Data from chondrules and metals in Gujba indicate a correlation slope of ⁵³Mn/⁵⁵Mn = (3.18 ± 0.52) × 10⁻⁶ (Fig. 1). Using the initial ⁵³Mn/⁵⁵Mn ratio and updated Pb-Pb age of D'Orbigny as relative and absolute age anchors, a Mn-Cr age of 4563.2 ± 0.9 Ma is obtained for Gujba. With an initial ⁵³Mn/⁵⁵Mn ratio and [12] updated Pb-Pb age of LEW 86010, a Mn-Cr age of 4562.5 ± 1.1 Ma is also obtained. Both Mn-Cr ages (4563.2 ± 0.9 Ma relative to D'Orbigny anchor, and 4562.5 ± 1.1 Ma relative to LEW 86010) are entirely consistent with the absolute Pb-Pb age of

4562.68 ± 0.49 Ma reported by [13], with the caveat that $^{238}\text{U}/^{235}\text{U}$ in Gujba is yet to be measured. However, this age is also identical to the Hf-W age of 4562.3 ± 2.6 Ma [14] relative to the CAI age anchor with a measured $^{238}\text{U}/^{235}\text{U}$ ratio [15].

In this study, all chondrules and the metal grain of Gujba preserve a uniform $\epsilon^{54}\text{Cr}$ value, a mean of +1.29 ± 0.02. This result is identical within error to the previously reported $\epsilon^{54}\text{Cr}$ value of +1.07 ± 0.27 from metal spherule in the same meteorite [16]. The homogeneous $\epsilon^{54}\text{Cr}$ value of Gujba indicates that both chondrules and the metal grain were derived from an isotopically homogeneous reservoir.

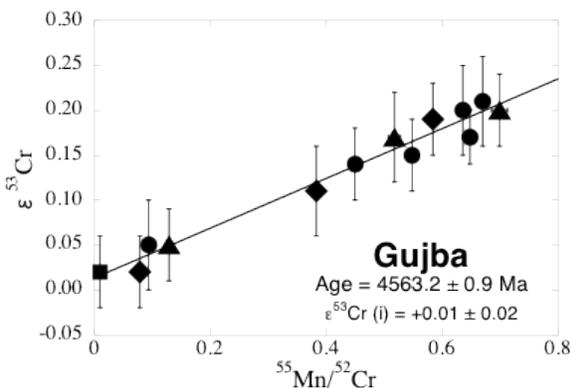


Fig. 1 ^{53}Mn - ^{53}Cr isochron for chondrules (single chondrule fragment: solid circle; leachate: solid triangle; residue: diamond) and metal grain (solid square) extracted from Gujba.

Monomict Ureilites: Since the materials in the reduction rim and vein has been thought as a product of a later process that occurred in the ureilite parent body [17], the data points from LE 1 to LE 3 were eliminated from the age calculation for NWA 766. The $\epsilon^{53}\text{Cr}$ and $^{55}\text{Mn}/^{52}\text{Cr}$ ratios showed a well correlation (Fig. 2a), which calculates the slope of $^{53}\text{Mn}/^{55}\text{Mn} = (3.35 \pm 0.41) \times 10^{-6}$. When the new D'Orbigny age, which corrected for $^{238}\text{U}/^{235}\text{U}$, is applied as an anchor [3,4,11], an absolute Mn-Cr age of 4563.52 ± 0.67 Ma was obtained. This is the most precise age reported for monomict ureilites. It should be also mentioned that this age is identical with the oldest age preserved in other achondrites such as HED and angrites [e.g. 18, 19]. Additionally, eight whole rock samples plot along this line, suggesting their formation from an isotopically uniform reservoir. On the other hand, NWA 1241 showed a relatively young age with an upper limit of <4560 Ma (Fig. 2b). These two ages indicate that ureilite parent body was formed, at least, by 4564 Ma, and the igneous activity was continued for several million years.

The $\epsilon^{54}\text{Cr}$ isotopic data of all fractions, whole rocks and leachate-residue, indicate a homogeneous value of ~ -0.9, widely different from those of carbonaceous chondrites. Although there are similarities in ureilites and carbonaceous chondrites (such as oxygen isotope), the result suggests that genetic relationship between two meteorite groups is less likely.

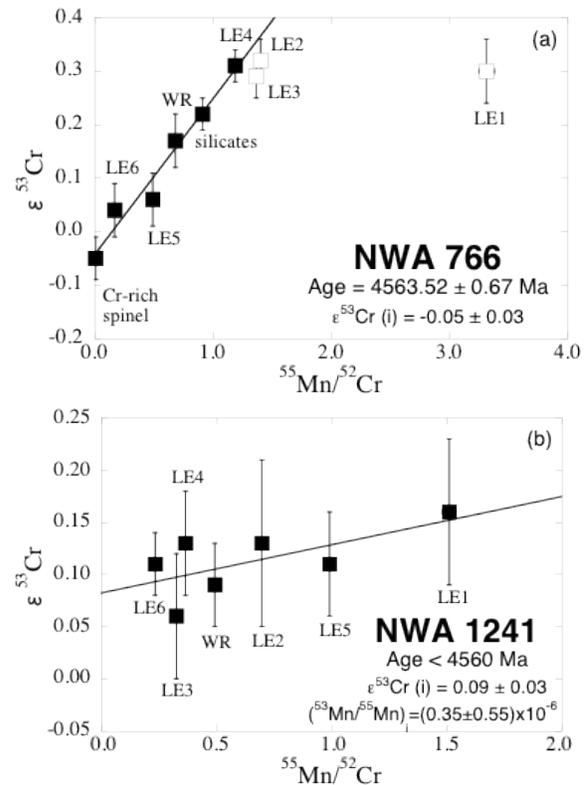


Fig. 2 ^{53}Mn - ^{53}Cr isochron for monomict ureilites: (a) NWA 766 (LE 1 to 3: open circle), and (b) NWA 1241.

References: [1] Honda & Imamura (1971) *Phys. Rev.*, 4, 1182. [2] Yamashita et al. (2011) *ApJ*, 723, 20. [3] Brennecka and Wadhwa (2011) Goldschmidt Abstract A579. [4] Kaltenbach et al. (2011) Goldschmidt Abstract A1137. [5] Yamakawa et al. (2010) *ApJ*, 720, 150. [6] Rotaru et al. (1992) *Nature*, 358, 465. [7] Sikirdji and Warren (2001) *MAPS* 36, A189 (abst.). [8] Yamakawa et al. (2009) *Anal. Chem.*, 81, 9787. [9] Makishima et al. (2010) *Chemical Geology*, 274, 82. [10] Glavin et al. (2004) *MAPS*, 39, 693. [11] Amelin. (2008) *GCA* 72, 221. [12] Lugmair & Shukolyukov (1998) *GCA* 62, 2863. [13] Krot et al. (2005) *Nature*, 436, 989. [14] Kleine et al. (2005) *GCA* 69, 5805. [15] Amelin et al (2010) *EPSL* 300, 343. [16] Trinquier et al. (2008) *GCA* 72, 5146. [17] Walker and Grove (1993) *Meteoritics* 28, 629. [18] Wadhwa et al. (2005) *LPSC* 36th, #2126. [19] Shukolyukov and Lugmair (2007) *LPSC* 38th, #1423.