

MANGANESE-CHROMIUM ISOTOPE SYSTEMATICS OF IVUNA, KAINSAZ AND OTHER CARBONACEOUS CHONDRITES. A. Shukolyukov¹, G.W. Lugmair^{1,2}, and O. Bogdanovski² ¹Scripps Institution of Oceanography, University of California, San Diego, La Jolla CA 92093-0212, USA, ²Max-Planck-Institute for Chemistry, Cosmochemistry, PO 3060, 55020 Mainz, Germany.

We have shown earlier [1] that the bulk samples of carbonaceous chondrites [CC] reveal excesses in both ⁵³Cr (⁵³Cr*) and ⁵⁴Cr (⁵⁴Cr*) as compared to the terrestrial standard value. The ⁵³Cr/⁵²Cr ratios in bulk samples of Orgueil (CI), Murray (CM), Allende (CV), and the Bencubbin/CH-like meteorite Hammadah Al Hambra 237 (HH237) are correlated with the respective Mn/Cr ratios [1]. In contrast to CC, HH237 is characterized by a deficit of ⁵³Cr (-0.15±0.10ε) at a low Mn/Cr ratio of 0.07. The HH237 data point, however, falls on the CC line. Here we report new ⁵³Mn-⁵³Cr results for the CC Kainsaz (CO) and Ivuna (CI).

The ⁵³Cr and ⁵⁴Cr excesses in bulk Kainsaz and Ivuna are +0.20±0.13ε and +1.02±0.24ε, and +0.41±0.11ε and +1.59±0.24ε, respectively (La Jolla data). The same sample of Ivuna was measured in Mainz with consistent ⁵³Cr* and ⁵⁴Cr* of +0.42±0.11ε and +1.47±0.20ε. The Ivuna data are the same as those for the other CI chondrite Orgueil (+0.39±0.10ε and +1.51±0.20ε) [1]. All these values have been obtained by repeat measurements of the Cr isotopic composition: 40-90 runs (300 ratios each). The presented uncertainties are 2 σ_{mean}.

The Mn/Cr ratios in bulk CC decrease in the sequence CI - CM - CO - CV. The measured ⁵⁵Mn/⁵²Cr ratios are 0.82 (Ivuna), 0.81 (Orgueil), 0.64 (Murray), 0.54 (Kainsaz), and 0.43 (Allende). This may be due to nebular fractionation caused by volatility controlled Mn loss from hot regions [e.g. 2]. On the other hand, it is also plausible that heating by ²⁶Al already at the planetesimal stage may have been of major importance. Whichever scenario is true, we can assume that the initial Cr isotopic composition and the ⁵³Mn abundance were the same in the zone where the precursor material for these objects formed. Then the ⁵³Cr/⁵²Cr ratios in bulk carbonaceous chondrites should constrain the ⁵³Mn/⁵⁵Mn ratio at the time of Mn/Cr fractionation.

The data points for Ivuna and Kainsaz fall on the HH237-Allende-Murray-Orgueil isochron of [1]. The updated ⁵³Mn/⁵⁵Mn ratio is (8.5±1.5) × 10⁻⁶ with an initial ⁵³Cr/⁵²Cr ratio at the time of Mn/Cr fractionation of ~ -0.21ε. Using this ⁵³Mn/⁵⁵Mn ratio and the angrite LEW86010 as an absolute time marker [3], the time for the Mn/Cr fractionation would be ~4568±1 Ma. This time is ~3 Ma less than the time estimated for the onset of ⁵³Mn decay (4571 Ma [4]) and is very similar to the timing of the Chainpur and Bishunpur chondrule

formation (~4569 Ma; [5]). It appears that this time indicates a period of intense thermal processing of inner solar system material [4].

A remarkable feature of CC is that, in contrast to the other meteorite classes, their bulk samples exhibit clear ⁵⁴Cr excesses. Moreover, these excesses are correlated with the ⁵³Cr excesses (Fig. 1) and, thus, with the Mn/Cr ratios. The primitive Ivuna and Orgueil reveal the largest ⁵³Cr* and ⁵⁴Cr* of ~0.4ε and ~1.5ε, respectively, while the most heavily processed Allende shows the smallest excesses of ~0.1ε and ~0.9ε. HH237 obviously does not follow this trend as its ⁵⁴Cr* is the same as that in Allende, while ordinary chondrites have ⁵³Cr* and ⁵⁴Cr* of ~0.5ε and ~0ε. How can we explain these correlations among CC?

One possibility is that ⁵⁴Cr* is also radiogenic (like ⁵³Cr*) and formed by the decay of the short-lived radionuclide ⁵⁴Mn. This implies that both parent nuclides ⁵³Mn and ⁵⁴Mn were generated in spallation reactions on Fe (and Mn etc.) during an early period of an active Sun (T-Tauri phase). This scenario, however, meets certain difficulties. The first is the very short half-life of ⁵⁴Mn (312 days). It is rather difficult to construct a physical scenario in which its daughter product, ⁵⁴Cr*, will be correlated with ⁵³Cr* from the decay of ⁵³Mn (T_{1/2}=3.7 Ma), with the Mn/Cr fractionation occurring ~2-3 Ma after the onset of ⁵³Mn decay (see above). In addition, according to a study of the Cr isotopic composition in Orgueil leaches [6], ⁵³Cr* and ⁵⁴Cr* reside in different phases and appear to be decoupled. It may be possible that these difficulties can be somehow overcome but an overall plausibility of this scenario has to be thoroughly tested.

Another suggestion [6] is that ⁵⁴Cr* in the carbonaceous chondrites is due to the presence of a component of presolar origin with a nucleosynthetic signature as may be expected from Type Ia supernovae. Progressive chemical and physical separation of Orgueil material revealed phases with varying degrees of ⁵⁴Cr enrichments up to ~200ε while the ⁵³Cr variations are comparatively small [6]. However, as would be expected, no associated enrichments in isotopes of Ca, Fe, and Zn were found. In addition, this scenario does not explain the presence of the observed correlations from a bulk sample perspective between ⁵⁴Cr*, ⁵³Cr* and Mn/Cr ratios.

One of the suggested explanations for the ⁶³Cu excess recently found in chondrites [7] is that the nuclide

^{63}Cu is a daughter product of the short-lived ^{63}Ni ($T_{1/2}=100$ y), which formed by irradiation during the T-Tauri phase of the Sun. These ^{63}Cu excesses are coupled with the ^{16}O excesses that may also be generated within the solar system [8,9], or may be inherited from anomalous presolar material.

We have noted earlier [10] the rather unexpected relation between $^{54}\text{Cr}^*$ and ^{16}O excesses. All studied samples that plot on the oxygen isotope diagram along the CAI line have $^{54}\text{Cr}^*$: CAI [e.g. 11,12], CC, the Eagle Station pallasite (most likely formed from CV3 type-material [13]), and HH237 and QUE94411 [10]. In contrast, all other studied meteorite classes with normal $^{54}\text{Cr}/^{52}\text{Cr}$ ratios (at least within an uncertainty of ~ 0.1 - 0.3ϵ) plot relatively close to the terrestrial fractionation line. It is not yet clear what all these correlations actually mean or the reason for their existence. At present we are not able to give preference to either the irradiation and/or the presolar scenarios. More data and assessments of data are necessary.

In addition to the bulk Ivuna sample we studied the Cr isotopic composition in two Ivuna phases. The bulk sample was treated with a HF/HNO₃ mixture at room temperature. This dissolution left behind a tiny acid-resistant residue highly enriched in Cr, most likely a chromite-spinel phase. This residue was dissolved in a bomb at 180°C. The Cr isotopic compositions in these samples are presented in Fig. 2. The $^{50}\text{Cr}/^{52}\text{Cr}$ ratio is assumed to be normal. The residue comprises $\sim 18\%$ of total rock Cr. Its Mn/Cr ratio is low: 0.15. The residue exhibits a moderate deficit of ^{53}Cr ($-0.90\pm 0.09\epsilon$) and a large $^{54}\text{Cr}^*$ ($+13.2\pm 0.20\epsilon$). This isotopic composition is reminiscent of that found in 'normal' CAI (moderate ^{53}Cr deficits and $^{54}\text{Cr}^*$ of $\sim 7\epsilon$ [11,12]), although $^{54}\text{Cr}^*$ in the Ivuna residue is almost twice as high. The soluble phase that contains most of the Cr has a moderate $^{53}\text{Cr}^*$ of $+0.57\pm 0.18\epsilon$ and a moderate ^{54}Cr deficit of $-0.66\pm 0.32\epsilon$. Thus, an elevated $^{54}\text{Cr}/^{52}\text{Cr}$ in the total rock is due to the mixing of an abundant component(s) with a moderate deficit of ^{54}Cr and a rare phase with high excess ^{54}Cr . This is consistent with the results obtained in [6]. It is unlikely that a low $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of -0.9ϵ represents a solar system initial: this would imply an unreasonably long time-scale for the early solar system. Rather, it is more likely that the carbonaceous chondrites contain a presolar component(s) with an anomalously low abundance of ^{53}Cr [3].

Acknowledgments. We thank Ch. MacIsaac for his help in the lab. Supported by NASA grant NAG 5-4145.

References. [1] Shukolyukov and Lugmair (2001) *Meteoritics&Planet. Sci.* **26**, A188. [2] Palme et al. (1988) in *Meteorites and the Early Solar System* (eds. J.F. Kerridge and M.S. Matthews), pp. 436-461. [3] Lugmair and Shukolyukov (1998) *GCA* **62**, 2863. [4] Lugmair and Shukolyukov (2001) *Meteoritics&Planet. Sci.* **36**, 1017. [5] Nyquist et al. (2001), *Meteoritics&Planet. Sci.* **36**, 911. [6] Podosek et al. (1997) *Meteoritics & Planet.Sci.* **32**, 617. [7] Luck et al. (2003) *Geochim. Cosmochim. Acta* **67**, 143. [8] Clayton (2002) *LPSC XXXIII*, abstr. #1326. [9] Thiemens (1999) *Science* **283**, 341. [10] Shukolyukov and Lugmair (2000) *Meteoritics&Planet. Sci.* **35**, A146. [11] Papanastassiou (1986) *Astrophys. J.* **308**, L27. [12] Birck and Lugmair (1988) *EPSL* **90**, 131. [13] Shukolyukov and Lugmair (2001) *LPSC XXXII*, abstr. #1365.

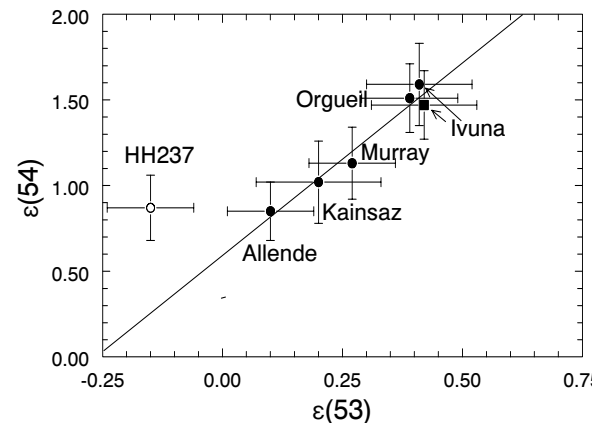


Fig. 1 Correlation between ^{53}Cr and ^{54}Cr excesses in bulk samples of carbonaceous chondrites.

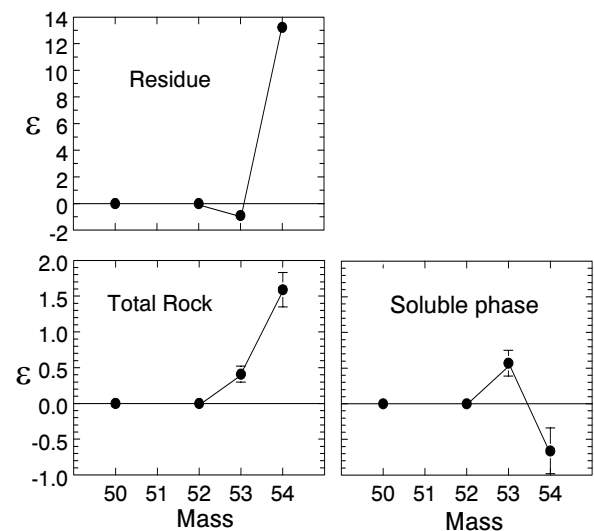


Fig. 2. Cr isotope diagrams for the residue, the soluble phase and the total rock samples of the CI chondrite Ivuna.