

THE ORIGIN OF NUCLEOSYNTHETIC ZIRCONIUM-96 HETEROGENEITIES IN THE INNER SOLAR SYSTEM. W. M. Akram¹, M. Schönbächler¹, H. M. Williams² and A. N. Halliday², ¹School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Oxford Road, M13 9PL, UK (waheed.akram@postgrad.manchester.ac.uk), ²Dept. of Earth Sciences, The University of Oxford, OX1 4BH, UK.

Introduction: Evidence for isotopic anomalies in bulk carbonaceous chondrites relative to other meteorites, the Moon and Earth has been reported for several elements (e.g., Sm, Nd, Ba, Mo, Ti and Cr [1, 2, 3, 4]). The origin of these heterogeneities is not very well understood. The isotopic composition of Zr mainly reflects a mixture of different *s*- and *r*-process nucleosynthetic components. The *s*-process is capable of producing ⁹⁰Zr, ⁹¹Zr, ⁹²Zr and ⁹⁴Zr, while the formation of ⁹⁶Zr requires higher neutron fluxes, rendering the *r*-process a more likely mechanism for producing most of the ⁹⁶Zr. Earlier studies on bulk samples [5] showed that the Zr isotope compositions of various solar system materials (e.g., chondrites, eucrites, Moon and Earth) do not vary outside the analytical uncertainty and the authors concluded that Zr isotopes were distributed evenly in the solar system at the bulk rock and larger scale. However, the data for bulk carbonaceous chondrites hinted at a potential enrichment in ⁹⁶Zr/⁹⁰Zr compared to Earth, but this could not be resolved at the time. The aim of this study is to obtain high-precision Zr isotope data to better characterize potential Zr isotope heterogeneities in our solar system on a bulk rock level.

Samples: A number of bulk carbonaceous chondrites were analyzed: two CV3 (Allende, Grosnaja), three CM2 (Cold Bokkeveld, Murray, Murchison) and one CO (Colony) chondrite. Moreover, Zr isotope data were obtained for one Allende Calcium-Aluminum-rich inclusion (CAI 3529-41), three eucrites (Pasamonte, Sioux County, Juvinas), one ordinary chondrite (Forest Vale), two lunar whole rock (15555, 71566), lunar ilmenite separates from the two high-Ti mare basalts 70035 and 77516, a pyroxene separate from 77516 and the terrestrial USGS standards BHVO2 (basalt) and Cody Shale.

Analytical Technique: Up to 600 mg of carbonaceous chondrites, and 200 mg of eucrite material were processed to obtain one set of measurements. All samples were crushed, and subsequently digested in a Parr[®] bomb for 4½ days at 170° in an HNO₃/HF acid mixture. A two-stage anion exchange separation procedure was applied to separate elements that could interfere with the Zr signal on the ICPMS, notably Mo, Ru, Fe, Cr, and Ti [6].

All five Zr isotopes were analyzed simultaneously on a Nu Plasma MC-ICPMS and the instrumental mass fractionation was corrected using the exponential law relative to ⁹⁴Zr/⁹⁰Zr. A single sample measurement con-

sists of 60 ratios, each with a 5s integration time. Molybdenum and Ru corrections were applied to account for isobaric interferences on ⁹⁶Zr (and ⁹⁴Zr, ⁹²Zr for Mo). Samples were measured using sample-standard bracketing. The Zr isotope compositions are given in epsilon relative to a Zr Alfa Aesar standard solution. For repeat measurements of a sample, the weighted mean and its uncertainty is used, otherwise the two standard deviation is given. The previously reported analytical uncertainty [5, 6] was significantly improved by measuring Zr solutions at higher signal intensity (~ 1.6 x 10⁻¹⁰ A for ⁹⁰Zr). This yielded an external reproducibility (2σ) for an analytical session of better than ± 18 ppm, ± 20 ppm and ± 50 ppm for ⁹¹Zr/⁹⁰Zr, ⁹²Zr/⁹⁰Zr and ⁹⁶Zr/⁹⁰Zr, respectively. This represents an improvement of more than a factor of two for ⁹⁶Zr/⁹⁰Zr compared to previous studies.

Results and Discussion: The ε⁹¹Zr and ε⁹²Zr data are identical within the analytical uncertainty for all analyzed samples. Terrestrial and lunar samples, three eucrites, and the H4 chondrite Forest Vale also possess a uniform ε⁹⁶Zr (Fig. 1). In contrast, carbonaceous chondrites display a range of positive ε⁹⁶Zr values relative to the terrestrial and lunar samples. The positive shift is most apparent for CAI 3529-41 (+2.4ε ± 0.4). This sample was previously analyzed by [5] and our new result at higher precision is in good agreement with the previous analyses. Repeat high-precision measurements of bulk rock Allende, combined with results from a previous study [6] yield an average ε⁹⁶Zr = +1.1 ± 0.1, which is clearly distinct from the terrestrial value.

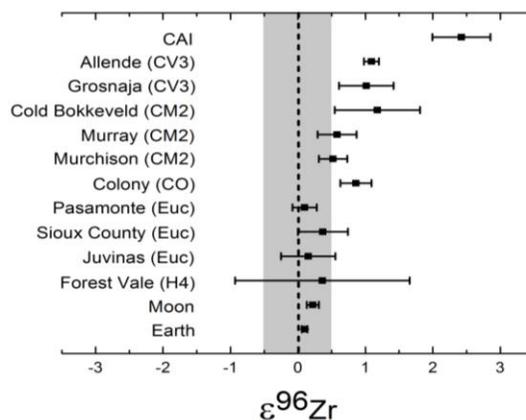


Fig. 1: The ε⁹⁶Zr data for the Earth, Moon and meteorites. Shaded region shows the long-term external reproducibility on the ⁹⁶Zr/⁹⁰Zr ratios.

The positive shift for Murchison ($\epsilon^{96}\text{Zr} = +0.5 \pm 0.2$) is less pronounced, but again different to the Zr isotope composition of the Earth.

For Murchison, an alternate dissolution technique using a hot-plate digestion procedure was also carried out, which revealed a large $\epsilon^{96}\text{Zr}$ excess of $+2.0 \pm 0.3$. This result is clearly higher than the value obtained from the Parr bomb dissolution ($\epsilon^{96}\text{Zr} = +0.5 \pm 0.2$) - a digestion procedure, which is known to attack SiC grains [7]. The CM2 chondrite Murchison possesses a relatively high amount of refractory SiC grains. These grains contain significant amounts of Zr that is enriched in the s-process isotopes ($^{90,91,92,94}\text{Zr}$), but depleted in ^{96}Zr relative to the Earth [8, 9]. The incomplete dissolution of such SiC grains therefore leads to an apparent excess in ^{96}Zr for bulk rock analyses, consistent with our results obtained from the hot-plate dissolution. The relatively low temperatures and pressures experienced during the hot-plate digestion are most likely insufficient for the digestion of SiC grains, thereby explaining the different results for the hotplate and Parr bomb dissolutions. For this reason, all samples were digested in Parr bombs and the quoted Murchison result for the hot plate is excluded from further analysis.

Figure 2 shows the weighted means of $\epsilon^{96}\text{Zr}$ vs. $\epsilon^{92}\text{Zr}$ grouped by meteorite classes, terrestrial and lunar samples. The observed positive shifts in $\epsilon^{96}\text{Zr}$ correlate with fluctuations in $\epsilon^{92}\text{Zr}$ (and $\epsilon^{91}\text{Zr}$ - not shown here). A linear fit to the data (solid line) defines a mixing line between r - and s -process Zr with a slope of 0.031 ± 0.086 , and intercept of -0.042 ± 0.036 (Fig. 2). The dotted line fit is taken from [7] and is defined by acid leachates of the carbonaceous chondrites Orgueil, Murchison and Allende. The line also passes through the SiC data. The slopes and intercepts of both fits are identical, within uncertainty (gradient from [7] = 0.023 ± 0.001 and intercept = 0.022 ± 0.071). This further supports the notion that the Zr isotope composition of our solar system reflects a mixture of s -process and r -process Zr. The low slope (0.031) between the $\epsilon^{96}\text{Zr}$ anomalies with $\epsilon^{92}\text{Zr}$ suggests that carbonaceous chondrites have incorporated different amounts of material that is dominated by a strong ^{96}Zr component (potentially of r -process origin).

Conclusions: The uniformity in the Zr isotope composition of the Earth, Moon and eucrites has been confirmed in this study using high precision Zr analyses, suggesting that the inner solar system was well mixed in terms of Zr, except for the region where carbonaceous chondrites formed. At the improved level of precision, positive shifts in $\epsilon^{96}\text{Zr}$ are resolved in some bulk carbonaceous chondrites. A trend between CAI content of each type of carbonaceous chondrites (CV >

CM > CO [10]) as a function of $\epsilon^{96}\text{Zr}$ is observed, with the single CAI at one extremity (Fig. 2). This supports previous studies, where CAIs were proposed as carrier phases of ^{96}Zr [5].

Similar results were reported for the neutron-rich isotopes ^{50}Ti and ^{54}Cr , which also show positive enrichments in carbonaceous chondrites correlated with CAIs content [2, 3]. For Allende, mass balance calculations allow for $\epsilon^{96}\text{Zr}$ excesses due to CAIs of up to $+1.15 \epsilon$ relative to the Earth, which is sufficient to account for the observed anomaly reported in this study. This provides evidence for a heterogeneous distribution of CAIs in the solar system and suggests that the Earth acquired less (or no) CAIs compared to carbonaceous chondrites.

The exact astrophysical production site of ^{96}Zr is yet to be determined, and as with ^{50}Ti and ^{54}Cr , ^{96}Zr most likely formed in neutron-rich stellar environments. If this is the case, the heterogeneity in the solar nebula could be the result of a late injection of neutron-rich nuclei from a supernova explosion.

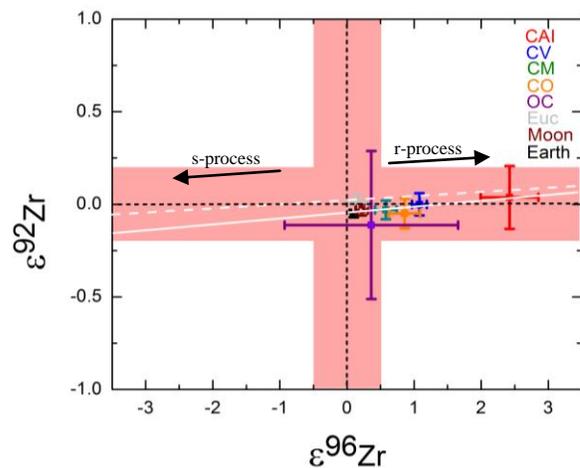


Fig. 2: Correlation between $\epsilon^{96}\text{Zr}$ and $\epsilon^{92}\text{Zr}$ for different meteorite classes and terrestrial / lunar data.

References: [1] Andreasen R. and Sharma M. (2007) *Astrophys. J.*, 665, 874–883. [2] Trinquier A. et al. (2009) *Science*, 324, 374–376. [3] Leya I. et al. (2008) *Earth Planet Sci. Lett.*, 266, 233–244. [4] Dauphas N. et al. (2002) *Astrophys. J.*, 565, 640–644. [5] Schönbachler M. et al. (2003) *Earth Planet Sci. Lett.*, 216, 467–481. [6] Schönbachler M. et al. (2004) *The Analyst*, 129, 32–37. [7] Schönbachler M. et al. (2005), *Geochim. Cosmochim. Acta*, 69, 5113–5122. [8] Nicolussi G. et al (1997) *Science*, 277, 1281–1283. [9] Davis A. M. et al. (1999) Heavy element isotopic compositions of single circumstellar grains from meteorites. In *Nuclei in the Cosmos V*, eds. Prantzos N and Harissopulos S., Editions Frontières, pp563–566. [10] Hezel D., et al. (2008) *MAPS*, 43, 1879 – 1894.