

**THE CADMIUM ISOTOPIC COMPOSITION OF EARTH AND CARBONACEOUS CHONDRITES.** C. S. Palk<sup>1</sup>, M. Schönbacher<sup>2</sup>, M. Rehkämper<sup>1</sup> and B. J. Wood<sup>3</sup>, <sup>1</sup>Department of Earth Science and Engineering, Imperial College London SW7 2BP, UK (c.palk09@imperial.ac.uk), <sup>2</sup>Institut für Geochemie und Petrologie, ETH Zürich, 8092 Zürich, Switzerland, <sup>3</sup>Department of Earth Sciences, University of Oxford OX1 3AN, UK.

**Introduction:** Cadmium is a highly volatile element with a 50% condensation temperature of 652 K [1]. Cd isotope data for terrestrial rocks and meteorites can hence provide new insights into how volatiles were delivered to the early Earth, and particularly whether the volatile element budget of Earth was provided by a ‘late veneer’ of chondritic material [2].

To this end, we present new Cd isotope data for (i) CI and CM carbonaceous chondrites and (ii) a comprehensive suite of terrestrial rocks from major tectonic settings. These results are supplemented with published Cd isotope data for terrestrial rocks and chondrites to enable a detailed isotopic comparison of these two ‘reservoirs’. In addition, we also carried out four metal-silicate partitioning experiments, to evaluate possible Cd isotope fractionation during core segregation.

**Samples:** For this study, we analyzed the carbonaceous chondrites Ivuna CI and Murchison CM to supplement published results for CI, CM, CR, CV and CO chondrites (Fig. 1). The terrestrial samples analyzed include peridotites, komatiites, mid-ocean ridge basalts (MORB), ocean island basalts (OIB) and loess deposits. These were supplemented by scarce published data for terrestrial rocks of mantle and crustal origin (Fig. 1). The metal-silicate partitioning experiments were carried out at 1360 to 1570°C and 1.5 GPa for about 50 to 70 min in MgO, silica and graphite capsules, using techniques modified from [3, 4]. The experiments hence provide a good indication of whether Cd isotope fractionation is expected for metal-silicate partitioning at conditions relevant for terrestrial core formation.

**Analytical techniques:** The rock and meteorite samples were digested using standard HF-HNO<sub>3</sub>-HCl procedures on a hotplate and in some cases using high pressure vessels for the dissolution of refractory phases. Some MORB chips required mild acid leaching to remove surface Fe-Mn coatings. The metal separates from the partitioning experiments were dissolved in modified aqua regia whilst the silicate separates were digested using concentrated HF-HNO<sub>3</sub>.

Prior to the separation of Cd for mass spectrometry, the sample solutions were mixed with a <sup>111</sup>Cd-<sup>113</sup>Cd double-spike [5], to provide an optimum ratio of spike to sample derived Cd of ~1 [6]. The spiked samples were passed through a two-stage anion exchange chemistry followed by a further stage of extraction chromatography modified from [5, 7]. The separation

procedures were optimized to remove matrix elements present in silicates and chondrites and routinely produced Cd yields of ~85%.

The Cd contents and isotopic compositions of the samples were determined using a Nu Plasma HR MC-ICP-MS by monitoring the ion beams of <sup>111</sup>Cd, <sup>112</sup>Cd, <sup>113</sup>Cd, <sup>114</sup>Cd, <sup>115</sup>In, and <sup>117</sup>Sn, the latter two for correction of isobaric interferences. Sample-standard bracketing techniques were employed and data reduction was carried out offline using iterative procedures [8] to correct for instrumental mass bias, modified for the correction of isobaric interferences [5].

The Cd isotope compositions are reported using the  $\epsilon$ -notation [9] relative to the standard reference material NIST 3108 Cd [10]. The external 2sd reproducibility of bracketing standard analyses was typically  $\epsilon^{114/110}\text{Cd} \approx \pm 0.3$  to  $\pm 0.9$  for solutions with Cd contents of ~60 ppb, a concentration that was employed for most sample analyses.

**Results and Discussion:** With one exception, the peridotites analyzed display a narrow range of Cd isotope compositions with  $\epsilon^{114/110}\text{Cd}$  values of between -2 and 0 (Fig. 1). The exceptional sample (a spinel lherzolite) with  $\epsilon^{114/110}\text{Cd} \approx +8.7$  was most likely altered by metasomatism. Excluding this sample, the peridotites define a mean  $\epsilon^{114/110}\text{Cd} = -0.9 \pm 0.5$  (2se). In comparison to the peridotites, mantle-derived melts, as defined by data for komatiites, MORBs and OIBs, exhibit a greater spread of isotopic compositions and typically slightly more positive  $\epsilon^{114/110}\text{Cd}$  values. Possibly, the greater scatter and more positive  $\epsilon^{114/110}\text{Cd}$  of OIBs relative to MORBs is due to loss of Cd during outgassing [11].

To characterize the continental crust, we have analyzed samples of loess plus an andesite and an island arc basalt. The loess deposits, which best characterize the upper continental crust, display a mean  $\epsilon^{114/110}\text{Cd}$  of  $-0.1 \pm 0.7$  (2se). This average changes only slightly, to  $+0.3 \pm 0.5$ , when all data for samples of the continental crust (including published results for sulfides) are considered.

In summary, it appears that the continental crust and mantle-derived melts have slightly heavier Cd isotope compositions than the mantle, as defined by peridotites. This difference may reflect minor Cd isotope fractionation during partial melting of the mantle. However, as the crust holds only a tiny proportion of the silicate Earth’s Cd budget, the isotope composition

of the bulk silicate Earth (BSE) is best defined by the peridotite mean of  $\epsilon^{114/110}\text{Cd} = -0.9 \pm 0.5$ .

The results for the metal-silicate partitioning experiments indicate no significant Cd isotope fractionation at the 0.5  $\epsilon$ -level. Whilst the data obtained in the four experiments were highly reproducible, further experiments are planned to ascertain that equilibrium was attained. In summary, these results suggest that the Earth's core, and hence the bulk Earth, likely have the same Cd isotope composition as the BSE.

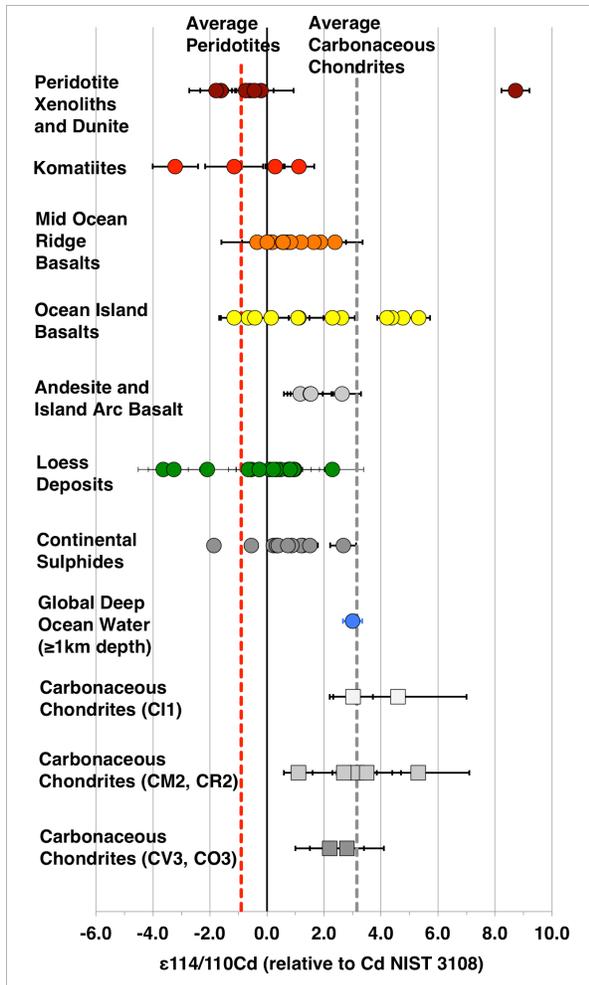


Figure 1 – Cd isotope compositions of the bulk silicate earth and carbonaceous chondrites. Data for all continental sulphides, 2 MORBs, 2 OIBs and 3 loess samples are from [12]. The results for for 7 carbonaceous chondrites are from [13], whilst data for average global deep ocean water are from [14]. The vertical dashed lines represent the average  $\epsilon^{114/110}\text{Cd}$  values for unaltered peridotites ( $-0.9 \pm 0.5$ ) and carbonaceous chondrites ( $+3.2 \pm 0.8$ ). Individual error bars are shown at 2se level.

In comparison, the mean  $\epsilon^{114/110}\text{Cd}$  value for carbonaceous chondrites is  $+3.2 \pm 0.8$  (2se), excluding the strongly fractionated samples of [13], with very posi-

tive  $\epsilon^{114/110}\text{Cd}$ , that were probably affected by thermal processing and/or shock. This implies that there is a small but clearly resolvable difference between the Cd isotopic compositions of the BSE (and the bulk Earth) and carbonaceous chondrites.

**Conclusions:** Taken together, published isotopic data and our new results for both terrestrial rocks (Fig. 1) and samples from partitioning experiments suggest that the bulk Earth and BSE have a common Cd isotope composition of  $\epsilon^{114/110}\text{Cd} \approx -0.9 \pm 0.5$ . In comparison, carbonaceous chondrites have a slightly higher  $\epsilon^{114/110}\text{Cd}$  value of  $+3.2 \pm 0.8$ . This small but resolvable isotopic difference is difficult to explain, if it is assumed that the silicate Earth's budget of Cd was primarily delivered by a 'late veneer' of material with a composition akin to carbonaceous chondrites, as suggested by [2]. The distinct terrestrial Cd isotope composition may hence indicate that the Earth's Cd was sourced from a distinct reservoir, most likely the inner solar system feeding zone of Earth's main accretion phase.

**References:** [1] Lodders, K. (2003) *The Astrophysical Journal*, 591, 1220-1247. [2] Albarede, F. (2009) *Nature*, 461, 1227-1233. [3] Wood, B. J., et al. (2014) *Geochim. Cosmochim. Acta*, 145, 248-267. [4] Bridgestock, L. J., et al. (2014) *Earth Planet Sc Lett*, 400, 153-164. [5] Ripperger, S. and Rehkämper, M. (2007) *Geochim. Cosmochim. Acta*, 71, 631-642. [6] Rudge, J. F., et al. (2009) *Chem Geol*, 265, 420-431. [7] Wombacher, F., et al. (2003) *Geochim. Cosmochim. Acta*, 67, 4639-4654. [8] Siebert, C., et al. (2001) *Geochem. Geophys. Geosyst.*, 2, 1032. [9] Wombacher, F. and Rehkämper, M. (2004) *Geostandards and Geoanalytical Research*, 28, 173-178. [10] Abouchami, W., et al. (2013) *Geostandards and Geoanalytical Research*, 37, 5-17. [11] Norman, M. D., et al. (2004) *Geochim. Cosmochim. Acta*, 68, 3761-3777. [12] Schmitt, A.-D., et al. (2009) *Earth Planet Sc Lett*, 277, 262-272. [13] Baker, R. G. A., et al. (2010) *Earth Planet Sc Lett*, 291, 39-47. [14] Xue, Z., et al. (2013) *Earth Planet Sc Lett*, 382, 161-172.