

**MERCURY CONCENTRATIONS AND HG ISOTOPE COMPOSITIONS OF CHONDRITES AND EUCRITES.** J. G. Wiederhold<sup>1</sup> and M. Schönbachler<sup>1</sup>, <sup>1</sup>Institute of Geochemistry and Petrology, ETH Zurich, 8092 Zurich, Switzerland (wiederhold@env.ethz.ch, mariasc@ethz.ch).

**Introduction:** Terrestrial planets and meteorites show different degrees of volatile element depletion relative to the Sun and CI chondrites. This bears witness to the abundant thermal processing (i.e. condensation/evaporation) that was a key feature in the early solar system. Processes in the solar nebula (e.g. evaporation of solids, condensation of nebular gas and chondrule formation) and the accretion of planetesimals and planets (impact driven growth, shock heating and thermal metamorphism) involved various kinds of thermal processing, which lead to a loss of volatile elements. These processes generated stable isotope fractionation if condensation/evaporation were incomplete. Mercury isotopes are a promising tool to investigate this issue. Mercury is highly volatile, bridging the gap between ices/gases and volatile elements such as Cd, In and Tl. Interestingly, Cd depletion in unequilibrated ordinary chondrites is accompanied by large Cd isotope variations in the permil range, while such feature is not observed for carbonaceous chondrites [1]. Similar data for Hg are currently not available, except for two meteorites (Murchison and Allende) [2].

Moreover, Hg possesses seven stable isotopes that are produced by different nucleosynthetic processes. The isotope <sup>196</sup>Hg is a *p*-process isotope, while <sup>198,202</sup>Hg are mainly produced by the *s*-process, <sup>199,204</sup>Hg by the *r*-process and <sup>200,201</sup>Hg are of mixed *s*- and *r*-process origin. This renders Hg an ideal element to test the isotopic heterogeneity in the solar system. Early neutron activation work reported large variations in <sup>202</sup>Hg/<sup>196</sup>Hg ratios; newer work, however, did not confirm these variations [2+3].

To address these issues, we present novel Hg concentration and isotope data for meteorites.

**Analytical techniques:** A total of 24 meteorites were analyzed for their Hg concentrations (CI, CM, CR, CV, OC, R-chondrites, eucrites, an acapulcoite, and a lodranite) and Hg isotope ratios were determined for 13 of them (CI, CM, CV, OC and eucrites). Selected terrestrial standard materials were processed in parallel to the meteorite samples (GSD-10, NIST-2711).

**Hg concentration analysis.** Total Hg concentrations were measured by combustion Atomic Absorption Spectrometry (AAS) (LECO AMA 254). Sample powders were combusted in Ni boats at 550°C in an O<sub>2</sub> flow and the released Hg was quantified by AAS. Selected sample boats were analyzed twice, but no measurable Hg signals were obtained during the second analysis, indicating complete Hg release during the first combustion. The reproducibility was assessed by

multiple analyses of GSD-10 during different sessions resulting in a Hg concentration of  $282.6 \pm 7.3 \text{ ng g}^{-1}$  (1SD, n=21). We estimate the precision of the concentration data to about  $\pm 5\%$ . Somewhat larger variations between sample replicates pointed toward the presence of heterogeneities in some of the sample powders.

**Sample preparation for Hg isotope analysis.** A two-stage tube combustion oven coupled with an oxidizing liquid trap was used for the pre-enrichment of Hg prior to isotope analysis. The combustion system was developed and validated in a previous study [4] based on [5]. The first combustion oven was slowly heated over  $\sim 6$  hours to a maximum of 900°C (instead of 600°C in [4]) to achieve complete Hg release from the meteorites, considering that [2] reported the release of some Hg species from meteorites at temperature  $>600^\circ\text{C}$ . The blank of the oven combustion procedure was 0.54 ng Hg, corresponding to  $<1\%$  of the Hg in the sample solutions. The recovery of the oven procedure was assessed by combusting GSD-10, yielding an average Hg recovery of  $102.5 \pm 8.6\%$  (1SD, n=3), similar to our previous studies on soil samples ( $94 \pm 8.5\%$ , n=72; [4]). Using the Hg concentrations of the meteorites measured on a different aliquot by combustion AAS as reference, the recovery of the oven procedure was  $94.0 \pm 37.2\%$  (1SD, n=18). The larger variability compared to GSD-10 is potentially due to heterogeneities in Hg concentration of the meteorite powders.

**Acid digestion.** For meteorites with high Hg contents, an acid digestion method using aqua regia [6] was used in parallel to the oven combustion. Aqua regia generally achieves complete dissolution of Hg-bearing phases from geological materials [7].

**Hg isotope ratio analysis.** Stable Hg isotope ratios were determined by cold vapor multicollector inductively coupled plasma mass spectrometry (CV-MC-ICP-MS) using previously described methods [8]. Briefly, a CV introduction system (Cetac HGX-200) was coupled to a Nu Plasma MC-ICPMS. Additionally, a desolvation nebulizer (Apex) was used to introduce a Tl standard (NIST-997), which was admixed to the Hg vapor prior to plasma injection. All seven Hg isotopes and the two Tl isotopes were measured simultaneously. Potential Pt and Pb interferences were monitored, but found to be negligible. Mass bias was corrected by a combination of Tl addition (using  $^{205}\text{Tl}/^{203}\text{Tl} = 2.38714$  and the exponential fractionation law) and sample standard bracketing with the NIST-3133 Hg standard solution. Samples were matched in concentration to within  $\pm 10\%$ . The results are reported

for mass-dependent fractionation (MDF):  $\delta^{202}\text{Hg} = [({}^{202}\text{Hg}/{}^{198}\text{Hg})_{\text{sample}}/({}^{202}\text{Hg}/{}^{198}\text{Hg})_{\text{NIST-3133}}] - 1$  and mass-independent fractionation (MIF) e.g.,  $\Delta^{199}\text{Hg} = \delta^{199}\text{Hg} - (\delta^{202}\text{Hg} \times 0.2520)$ . The reproducibility was assessed by multiple analyses of our in-house standard (ETH Fluka Hg) relative to NIST-3133 in the same analytical sessions. The results ( $\delta^{202}\text{Hg} = -1.33 \pm 0.13\text{‰}$ ;  $\Delta^{199}\text{Hg} = 0.07 \pm 0.06\text{‰}$ ;  $\Delta^{200}\text{Hg} = 0.03 \pm 0.13\text{‰}$ ;  $\Delta^{201}\text{Hg} = 0.02 \pm 0.07\text{‰}$ ;  $\Delta^{204}\text{Hg} = 0.08 \pm 0.21\text{‰}$ , 2SD,  $n = 11$ ) were in excellent agreement with previous studies [4].

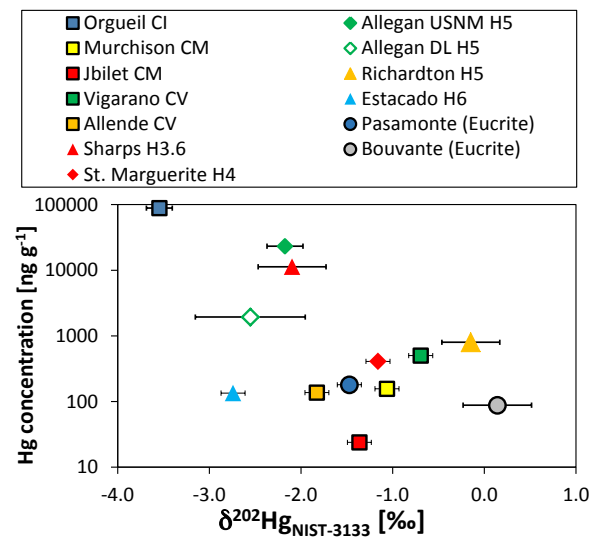
**Results and Discussion: Hg concentrations.** The investigated meteorites yielded a wide range of concentrations from  $2.8 \text{ ng g}^{-1}$  (NWA 2714, lodranite) to  $88420 \text{ ng g}^{-1}$  (Orgueil, CI) (Fig. 1). There was no systematic variation with meteorite class and the depletion pattern did not follow that of other volatile elements such as Cd, which show systematic depletions in carbonaceous chondrites (CV>CM>CI). Different chips from selected meteorites (e.g., Allegan USNM and DL (Fig. 1) and two Allende chips with 137 and  $24.5 \text{ ng g}^{-1}$ , not shown) were analyzed multiple times, and exhibited clear differences in Hg content. This points toward a heterogeneous distribution of Hg-bearing phases in these meteorites. This is supported by petrographic observations, which report heterogeneously distributed HgS as the only so far identified carrier of Hg in chondrites (Tieschitz H/L3.6 [9], Allende CV3 [10], Mighei CM2 [11]) apart from some metallic Hg nano-globules [9]. Previous work also suggested terrestrial contamination as the source for the high Hg content in some meteorites. However, [2] showed with Hg vapor experiments that it is very difficult to pervasively contaminate meteorites in order to generate the observed variations. Heterogeneous distribution of Hg-bearing phases in chondrites can also explain the widely varying Hg concentrations found in previous studies (e.g., [2], [11]).

**Hg isotopes.** Samples of Orgueil, Allegan and Sharps were processed with both the acid digestion and the oven combustion procedure yielding identical isotope compositions within the analytical uncertainty thereby validating the methods.

**Hg isotopes (MDF).** Our data exhibited a range of  $\delta^{202}\text{Hg}$  values from  $-3.55\text{‰}$  (Orgueil) to  $+0.14\text{‰}$  (Bouvante). The  $\delta^{202}\text{Hg}$  data was not correlated with Hg concentrations (Fig. 1) indicating a more complicated history than a single fractionation process that led to the various Hg isotope compositions. Moreover, as for the concentration data, the isotope data did not correlate with the meteorite class. Cinnabar in Mighei (CM2) is considered to be the product of aqueous alteration, because it occurs in veins cutting through altered chondrules [11], while its occurrence in Allende and Tieschitz was interpreted to be the result of

low-temperature condensation and sulfidation in the solar nebula under a high sulfur fugacity [9+10]. This shows that diverse local processes can influence the occurrence of HgS and therefore its isotopic composition. If it is correct that HgS is heterogeneously distributed in meteorites, this also implies that it is very challenging to obtain the true bulk Hg content and isotope composition for a meteorite.

**Hg isotopes (MIF).** We did not observe isotopic anomalies in  ${}^{196}\text{Hg}$  that would support the previously reported extreme  ${}^{196}\text{Hg}/{}^{202}\text{Hg}$  ratios, in line with the findings of [2] and [3]. However, small correlated effects in  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  were observed ( $\Delta^{199}\text{Hg}$  range:  $-0.11$  to  $0.15\text{‰}$ ,  $\pm 0.06\text{‰}$ , 2SD), which were consistent in sign and magnitude with the nuclear volume effect, predicted to go along with the observed MDF ( $\delta^{202}\text{Hg}$ ). Our data shows no evidence for the presence of nucleosynthetic isotope anomalies. This further corroborates the idea that nucleosynthetic isotope anomalies are only preserved for more refractory elements because volatile elements were present in the gas phase in the nebula and thus well homogenized.



**Figure 1:** Hg concentration vs  $\delta^{202}\text{Hg}$ . Error bars represent 2SD of either sample replicate analyses or standard reproducibility in same session if a sample was only measured once.

**References:** [1] Wombacher F. et al. (2008) *GCA*, 72, 646-667. [2] Lauretta D. S. et al. (2001) *GCA*, 65, 2807-2818. [3] Kumar P. et al. (2001) *Geochem. J.*, 35, 101-116. [4] Jiskra M. (2014) *ETH Zurich, PhD Thesis No.* 22330. [5] Biswas A. et al. (2008) *ES&T*, 42, 8303-8309. [6] Wiederhold J. G. et al. (2013) *ES&T*, 47, 6137-6145. [7] Bloom N. (2003) *Anal. Chim. Acta*, 479, 233-248. [8] Wiederhold J. G. et al. (2010) *ES&T*, 44, 4191-4197. [9] Caillet Komorowski C. et al. (2012) *EPSL*, 349-350, 261-271. [10] Kurat G. et al. (1989) *Z. Naturforsch.*, 44a, 988-1004. [11] Lauretta D. S. et al. (1999) *EPSL*, 171, 35-47.