Supporting Information

**Immobilization of Hg(II) by Coprecipitation in Sulfate-Cement Systems**

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**Content:** Description of the elemental analysis of the aqueous solutions, mercury (low concentration) sorption and chemical extractions experiments, S and Hg X-ray absorption spectroscopy (XAS) methods, Hg XAS analysis of samples, and reference compounds, three figures (S1, S2 and S3), and five tables (S1, S2, S3, S4 and S5); fourteen pages.
Analysis of aqueous solutions

Solution pH was measured with a General 757 microelectrode calibrated using commercial pH 4.0, 7.0, and 10.0 buffer solutions. Equilibrium and extraction solutions were filtered (0.45 µm), diluted as needed and analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin-Elmer Optima 5300 DV) or inductively coupled plasma-mass spectrometry (ICP-MS; Agilent 7500cs). Practical limits of detection for ICP-OES were calculated as the standard deviations of the instrument response from 7 repeated analyses of sample matrix that matched blank solutions. Detection limits were 2.2, 21 and 0.6 µg/l for Ca, S, and Fe, respectively. In order to analyze Hg in high ionic strength samples, the ICP-MS was optimized for Hg measurement at low concentrations. The Integrated Sample Introduction System (ISIS) parameters for Hg analysis were: 30 seconds uptake at 0.5 rps, analysis speed = 0.1 rps, constant flow nebulization at ~100 µl/min using Agilent Micro Flow 100 nebulizer, and rinse 30 seconds at 1 rps. Calibration standards were prepared in deionized water acidified to 2% with nitric acid and containing 100 ppb Au to stabilize Hg at low concentration in solution. Standards were prepared at 10, 20, 50, 100, 200 and 500 ppt (parts per trillion) Hg. Limits of detection were calculated as three standard deviations of the instrument response from 10 repeated analyses of sample-matrix-matched blank solutions. From this analysis, a reproducible, practical instrument detection limit of 50 ng/l (ppt) was established. Mercury analyses by ICP-MS were carried out within 48 h after experiments were completed in order to minimize sample exposure time to containers.
Table S1. Element concentrations of coprecipitated solid samples

|                        | Hg-Al-cpt     | Hg-Fe-cpt    |
|------------------------|---------------|--------------|
| Hg$_{\text{exch}}$ (mmol kg$^{-1}$) $^{b}$ | 0.59(0.04)    | 1.04(0.08)   |
| Hg$_{\text{exch}}$ (%) $^{b}$              | 20.10         | 25.15        |
| Hg (mmol kg$^{-1}$)                  | 3.90(0.31)    | 2.64(0.21)   |
| Hg (%)                               | 94.20         | 90.06        |
| Fe (mmol kg$^{-1}$)                  | --            | 566.25(28.31)|
| S (mmol kg$^{-1}$)                   | 2551.07(127.5)| 300.34(15.01)|
| Al (mmol kg$^{-1}$)                  | 1829.92(91.4) | --           |
| Ca (mmol kg$^{-1}$)                  | 4612.71(230)  | 324.74(16.2) |

Standard deviation of replicate measurements in parentheses.

$^{a}$ Solids digested in aqua regia 3:1 HCl:HNO$_3$ and measured by ICP-MS or ICP-OES.

$^{b}$ Mercury exchangeable concentration using 1.0 M MgCl$_2$(aq)$^{1}$.

Table S2. Element concentrations of supernatant solutions (in mmol L$^{-1}$)$^{a}$

|                        | Hg   | Fe   | S    | Al   | Ca   |
|------------------------|------|------|------|------|------|
| Hg-Al-cpt              | 0.0063(0.0009) | n.a. | 28.67(0.97) | 26.13(1.05) | 34.82(0.69) |
| Mass balance (%) $^{b}$ | 70.68 | n.a. | 131.67 | 113.64 | 123.54 |
| Hg-Fe-cpt              | 0.036(0.007)  | 45.22(2.71) | 104.83(7.75) | n.a.   | 218.53(12.45) |
| Mass balance (%) $^{b}$ | 101.50 | 129.98 | 131.80 | n.a.   | 133.74 |

Standard deviation of replicate measurements in parentheses.

$^{a}$ Measured by ICP-MS or ICP-OES.

$^{b}$ Element mass balance determined respect to element concentration in coprecipitated samples (Table S1)

n.a.: not applicable

total Hg = 0.25 mM

**Mercury sorption experiments and chemical extractions**

A set of Hg batch sorption experiments was performed by mixing solid amendments (Portland cement + FeSO$_4$) with total Hg = 0.01 mM (HgCl$_2$ solution) in 1:10 solid:solution ratio (duplicates). The HgCl$_2$ solution was prepared in synthetic seawater$^2$. Suspensions were shaken in a reciprocal shaker (50 rpm) for time periods of 1, 7 and 30 d at 25 ºC. At the end of each reaction time, suspensions were centrifuged (10000 rpm for 10 min) and supernatant solutions removed, filtered (0.45 µm PTFE syringe filter), and analyzed for Hg using ICP-MS, and ICP-OES for major elements (Ca, S, Fe, Al). At the end of each reaction time, solid products (0.5 g) were resuspended in 5 ml of 0.1 M MgCl$_2$(aq) at pH 11 and shaken for 1 h, and centrifuged at 8000 rpm at 10 ºC for 20 min to extract exchangeable Hg $^{3}$. The supernatant solution was filtered
(0.45 μm PTFE syringe filter) and acidified. Following to the exchangeable fraction, the solid sample was resuspended in 0.2 M acidic ammonium oxalate solution (AAO) (4 h at pH 3 on a reciprocal shaker in the dark) to extract poorly crystalline precipitates. The samples were centrifuged at 8000 rpm at 10 °C for 20 min, and the supernatant solution was acidified.

Table S3. Mercury sorption experiment analysis.a

| Time (days) | 1        | 7        | 30       |
|------------|----------|----------|----------|
| pH         | 10.29    | 11.94    | 12.05    |
| Total sorbed (mmol kg⁻¹) b | 0.253 (9.5 x 10⁻⁵) | 0.244 (2.0 x 10⁻⁵) | 0.265 (7.1 x 10⁻⁴) |
| Residual (mmol kg⁻¹) c | 0.249 (9.5 x 10⁻⁵) | 0.239 (2.0 x 10⁻⁵) | 0.263 (7.1 x 10⁻⁴) |
| Exchangeable (mmol kg⁻¹) c | 0.002 (5.7 x 10⁻⁴) | 0.002 (3.9 x 10⁻⁴) | 0.0007 (7.1 x 10⁻⁸) |
| Exchangeable (%) d | 0.78      | 0.82      | 0.29     |
| AAO (mmol kg⁻¹) c | 0.0028 (1.5 x 10⁻⁴) | 0.0024 (7.7 x 10⁻⁴) | 7.2 x 10⁻⁴ (4.9 x 10⁻⁵) |
| AAO (%) d | 1.13      | 0.99      | 0.29     |

Standard deviation of replicate measurements in parentheses.

a Measured by ICP-MS or ICP-OES.
b Determined as the difference between total (= 0.01 mM) and measured concentration in solution.
c Determined as the difference between total sorbed concentration and the sum of exchangeable and AAO-extracted Hg.
d Calculated respect to the total Hg sorbed concentration.

Table S4. Equilibrium reactions used for modeling coprecipitate experiments.

| Minerals | Reactions | Log K | Ref. a |
|----------|-----------|-------|--------|
| Calcite  | CaCO₃(s) + H⁺ = Ca²⁺ + HCO₃⁻ | 1.84  | [y][z] |
| Magnesite| MgCO₃(s) + H⁺ = Mg²⁺ + HCO₃⁻ | 2.04  | [y][z] |
| Anhydrite| CaSO₄(s) = Ca²⁺ + SO₄²⁻ | -4.30 | [y] |
| Gypsum   | CaSO₄.2H₂O(s) = Ca²⁺ + SO₄²⁻ + 2H₂O | -4.48 | [y] |
| Syngentite| K₂Ca(SO₄)₂.2H₂O(s) = Ca²⁺ + 2K⁺ + 2SO₄²⁻ + 2H₂O | -7.6  | [y] |
| C-S-H solid solutions, portlandite |              |       |        |
| Tobermorite-I | (CaO)₁₀(SiO₂)₂.2(H₂O)₁₂ + 4 H⁺ = 2Ca²⁺ + 2.4SiO₂(aq) + 5.2H₂O | 15.4  | [x] |
| Tobermorite-II | (CaO)₁₀(SiO₂)(H₂O)₁₂ + 1.66 H⁺ = 0.83Ca²⁺ + 1.05SiO₂(aq) + 2.17 H₂O | 11.18 | [x] |
| Jennite | (CaO)₁₀.₆(SiO₂)(H₂O)₁₂ + 3.3H⁺ = 1.67Ca²⁺ + 1.05SiO₂(aq) + 3.7H₂O | 29.25 | [x] |
| Portlandite | Ca(OH)₂ + 2H⁺ = Ca²⁺ + 2H₂O | 22.55 | [y] |
| AFt-phases |              |       |        |
| Al₂Ettringite | Ca₆Al₄(SO₄)₁₂(OH)₁₂.26H₂O(s) + 12 H⁺ = 6Ca²⁺ + 2Al³⁺ + 3SO₄²⁻ + 38H₂O | 56.84 | [x] |
| Fe₂Ettringite | Ca₆Fe₂(SO₄)₁₂(OH)₁₂.26H₂O(s) + 12 H⁺ = 6Ca²⁺ + 2Fe³⁺ + 3SO₄²⁻ + 38H₂O | 55.2  | [x] |
| Tricalciumaluminate | Ca₆Al₂(CO₃)₆(OH)₁₂.26H₂O(s) + 15H⁺ = 6Ca²⁺ + 2Al³⁺ + 3HCO₃⁻ + 38H₂O | 65.3  | [x] |
| AFm-phases |              |       |        |
| Ca₃Al₂(OH)₆.6H₂O |              |       |        |
| Ca₁₉Fe₂(OH)₁⁴ | 6H₂O | 104.34 | [x] |
| Ca₃Al₂(OH)₁₂.12H₂O |              |       |        |
| Ca₃Fe₂(OH)₁₀.₆H₂O |              |       |        |
| 2CaOAl₂O₃SiO₂8H₂O | 2CaO Al₂O₃SiO₂8H₂O(s) + 10H⁺ = 2Ca²⁺ + 2Al³⁺ + 13H₂O | 45.3  | [x] |
| 2CaOFe₂O₃SiO₂8H₂O | 2CaO Fe₂O₃SiO₂8H₂O(s) + 10H⁺ = 2Ca²⁺ + 2Fe³⁺ + SiO₂(aq) + 13H₂O | 40.28 | [x] |
| 3CaOAl₂O₃CaSO₄(OH)12H₂O | 3CaOAl₂O₃CaSO₄(OH)12H₂O(s) + 12H⁺ = 4Ca²⁺ + 2Al³⁺ + SO₄²⁻ + 18H₂O* | 72.48 | [x] |
| 3CaOFe₂O₃(CaSO₄)12H₂O(s) | 3CaOFe₂O₃(CaSO₄)12H₂O(s) + 12H⁺ = 4Ca²⁺ + 2Fe³⁺ + 18H₂O + SO₄²⁻ | 66   | [x] |
| 3CaOAl₂O₃(CaCO₃)11H₂O | 3CaOAl₂O₃(CaCO₃)11H₂O(s) + 13H⁺ = 4Ca²⁺ + 2Al³⁺ + 17H₂O + HCO₃⁻ | 80.59 | [x] |
| 3CaOFe₂O₃(CaCO₃)11H₂O | 3CaOFe₂O₃(CaCO₃)11H₂O(s) + 13H⁺ = 4Ca²⁺ + 2Fe³⁺ + 17H₂O + HCO₃⁻ | 73.98 | [x] |
| 3CaOAl₂O₃(Ca(OH)₂)o.5 | 3CaOAl₂O₃(Ca(OH)₂)o.5(CaCO₃)0.11.5H₂O(s) + 13.5H⁺ = 4Ca²⁺ + 2Al³⁺ | 91.77 | [x] |
(CaCO₃)₀.₅₁₁·H₂O
3CaFe₂O₄(Ca(OH)₂)₀.₅(CaCO₃)₀.₅₁₁·H₂O
+0.5HCO₃⁻ +13.5H₂O
3CaO Fe₂O₃(Ca(OH)₂)₀.₅(CaCO₃)₀.₅₁₁·H₂O(s) + 13.5H⁺ +4Ca²⁺ +2Fe³⁺ 85.26 [x]

Hydrogarnets
3CaO Al₂O₃ 6H₂O
CaO Al₂O₃ 10H₂O
3CaO 11.5H₂O +0.5HCO₃⁻ +13.5H₂O
3CaO Al₂O₃ 6H₂O(s) + 12H⁺ = 3Ca²⁺ +2Al³⁺ +12H₂O 72.42 [x]
CaO Al₂O₃ 10H₂O(s) + 8H⁺ =Ca²⁺+2Al³⁺+14H₂O 38.25 [x]

Al(OH)₃(am.)
Fe(OH)₃(am.)
Hydrogarnets
3CaO 3Ca(OH)₂(s) 0.₅(CaCO₃)₀.₅₁₁·H₂O
+0.5HCO₃⁻ +13.5H₂O
3CaO Al₂O₃ 6H₂O(s) + 12H⁺ = 3Ca²⁺ +2Al³⁺ +12H₂O 72.42 [x]
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Fe(OH)₃(am.)
Hydrogarnets
3CaO 3Ca(OH)₂(s) 0.₅(CaCO₃)₀.₅₁₁·H₂O
+0.5HCO₃⁻ +13.5H₂O
3CaO Al₂O₃ 6H₂O(s) + 12H⁺ = 3Ca²⁺ +2Al³⁺ +12H₂O 72.42 [x]
CaO Al₂O₃ 10H₂O(s) + 8H⁺ =Ca²⁺+2Al³⁺+14H₂O 38.25 [x]

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CaO Al₂O₃ 10H₂O(s) + 8H⁺ =Ca²⁺+2Al³⁺+14H₂O 38.25 [x]

Sulfur and Hg X-ray absorption spectroscopy (XAS) methods

Sulfur K-edge X-ray absorption spectra were collected on beamline 4-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). Samples were collected at ambient temperature with a Si(111) monochromator crystal in fluorescence mode with either a N₂(g)-filled Lytle detector or a solid-state diode detector. A second mirror was used to reject higher order harmonic reflections. Dried, powdered samples were finely ground and dusted as a thin layer on S-free mylar adhesive tape. Energy was calibrated by assigning the first peak maximum in the S K-edge spectrum of Na₂S₂O₃ 5H₂O to 2472.02 eV. Multiple scans (3-6) for each sample were collected and averaged over the energy range 2370-2815 eV.

Mercury X-ray absorption spectra were collected at the SSRL (beamline 4-1 or 11-2). Samples were loaded undiluted into Teflon sample holders, sealed with Kapton tape, and held in a liquid-He cryostat (at 5–20 K) during data collection. A HgCl₂(aq) reference solution (0.75 mM) was injected into a Teflon sample holder with Kapton windows and quench-frozen in liquid
N₂. Fluorescence spectra were collected using a 30-element Ge detector (3 elements not working) and a Si(220) monochromator crystal on BL 11.2. Solid Hg reference compounds were diluted in BN, packed into Teflon holders, and sealed with Kapton tape. Absorption spectra were collected in transmission using N₂(g)-filled ion chambers and a Si(220) monochromator crystal on BL 4-1. Energy was calibrated using Au foil, assigning the first inflection point on the absorption edge to 11919 eV. Two or three scans were collected and averaged for Hg standards in transmission and up to 16 scans for samples in fluorescence (38 min/scan).

**Mercury XAS analysis**

Analyses of the Hg EXAFS spectra were performed with the program EXAFSPAK. Background subtraction was done using a linear fit through the pre-edge region and a cubic spline through the spectrum above the absorption edge. Spectra were fit quantitatively using the shell-by-shell method over a k-range of 1.5 to 13-15 Å⁻¹ (depending on data quality) with theoretical single- and multiple-scattering reference functions calculated by the program FEFF 8.0 using atomic clusters from crystalline reference Hg compounds calculated with the program ATOMS (see below). In fits to the HgCl₂(aq) spectrum, N was fixed but R and σ² were varied. All other samples were treated as unknowns, and therefore N and R were varied while σ² and S₀² (= 0.9) were fixed on values determined from reference compound fits. A sensitivity analysis was performed to estimate the variation in N for a range of values of σ² derived from the analyses of reference Hg compounds. This analysis indicated a variation in fitted N of 20-30% in the unknown spectra. Photoelectron threshold energy difference (ΔE₀) was fit as a single parameter for all shells.

**Mercury XAS analysis of reference compounds**
In order to demonstrate the ability of EXAFS analysis to determine the coordination around Hg atoms in unknown systems, the EXAFS spectra of crystalline reference compounds (HgO(s), HgCl₂(s) and Hg₃(SO₄)O₂(s)) were analyzed based on their known crystallographic structures (Figure S3). Because of the strong correlation in EXAFS between N (number of atoms) and \( \sigma^2 \) (Debye–Waller factor) for a set of backscattering atoms at distance (R), the analyses of known Hg structures using shell-by-shell fits provided estimates of \( \sigma^2 \) for the analysis of unknown spectra for which N was unknown. The identity of the reference compounds was confirmed by powder XRD (data not shown) and no impurities were found. In normalized Hg XANES spectra (Figure S2), the three reference compounds are characterized by a prominent absorption feature with similar intensity at 12282-12284 eV near the mid-point of the main absorption edge, but different small adsorption features near the absorption maxima. The energy and shape of these absorption features were distinctive for each mineral and are best observed in the first-derivative spectra (Figure S2). In the case of HgO(s), a wide inflection was found at 12296 eV, compared to a much sharper inflection for HgCl₂(s) at 12292 eV. In addition, another inflection at 12314 eV was observed in the HgO(s) first-derivative spectrum. For Hg₃(SO₄)O₂(s), the inflection points appear at 12294 eV and the presence of a smaller inflection at 12310 eV is different from that of the other compounds.

Analysis of the bulk EXAFS spectra of the reference compounds indicated excellent agreement with interatomic distances calculated from crystal structures reported in the literature (Table S5). The EXAFS spectra of HgO(s) and HgCl₂(s) are dominated by linear coordination of Hg with either O or Cl in both samples. The crystal structure of HgO(s) consists of Hg-O linear chains with two O atoms at 2.03 Å and a second O shell (4 atoms) at 2.83 Å. Eight more Hg shells from the local coordination environment of Hg in HgO(s)\(^{13}\) had sufficient amplitude to be
included in the HgO(s) EXAFS fit (Table S5). In the HgCl₂(s) crystal structure, Hg is bonded linearly to two first-shell Cl atoms a distance of 2.28 Å\(^{14,15}\). Two more Cl shells were included in the fit at distances of 3.24 Å (2 Cl) and 3.40 Å (4 Cl), as well as four Hg backscattering shells at 4.31, 4.46, 4.85 and 5.85 Å. In Hg₃(SO₄)O₂(s), Hg shows a [2+4] coordination, with two O atoms at a distance 2.06 Å and four more O atoms at longer distances (2.53 Å). This [2+x] coordination with two short Hg-O bonds and almost linear O-Hg-O angle is a frequently observed structural unit of Hg(II) oxo-complexes\(^{16}\). Quantitative EXAFS fits identified 2 S shells at 3.38 and 3.68 Å and three more Hg shells at 3.52, 3.74 and 3.83 Å. Although single-scattering paths (SS) between the absorber and backscattering atoms generally have higher amplitude than multi-scattering (MS) paths in EXAFS, MS may contribute significantly to the EXAFS for linear paths between absorber and backscattering atoms\(^{12,17}\). Analysis of MS paths for HgO(s) and HgCl₂(s) showed improvements in best-fits when linear MS paths were included (Table S5, Figure S3). The three-legged paths (Hg→O→O→Hg) and (Hg→Hg→Hg→Hg), and the three-legged path (Hg→Cl→Cl→Hg) were included in HgO(s) and HgCl₂(s) fitting, respectively.
Table S5. Results of Hg EXAFS shell-by-shell fits for Hg reference compounds.

| Sample          | Hg EXAFS | XRD<sup>d</sup> |
|-----------------|----------|-----------------|
|                 | A-B<sup>a</sup> | N | R (Å) | $\sigma^2$ (Å<sup>2</sup>) | $\Delta E_0$ (Å) | $\chi^2$ | N | R (Å) | R (Å) |
| HgO(s) (Montroydite) | Hg-O     | 2<sup>c</sup> | 2.03 | 0.0014 | -4.19 | 0.46 | 2 | 2.03, 2.06 |
|                 | MS<sup>b1</sup> | 1<sup>c</sup> | 4.11 | 0.0014 |  |  | 4 | 4.07 |
|                 | Hg-O     | 4<sup>c</sup> | 2.83 | 0.0156 |  |  | 4 | 2.80-2.86 |
|                 | Hg-Hg    | 2<sup>c</sup> | 3.30<sup>c</sup> | 0.0026 |  |  | 2 | 3.30 |
|                 | MS<sup>b2</sup> | 1<sup>c</sup> | 6.56 | 0.0026 |  |  | 4 | 6.61 |
|                 | Hg-Hg    | 2<sup>c</sup> | 3.52 | 0.0020 |  |  | 2 | 3.52 |
|                 | Hg-Hg    | 4<sup>c</sup> | 3.64 | 0.0039 |  |  | 4 | 3.58-3.61 |
|                 | Hg-Hg    | 4<sup>c</sup> | 3.74<sup>c</sup> | 0.0079 |  |  | 4 | 3.738 |
|                 | Hg-Hg    | 4<sup>c</sup> | 4.86 | 0.0064 |  |  | 4 | 4.80, 4.85 |
|                 | Hg-Hg    | 2<sup>c</sup> | 5.52<sup>c</sup> | 0.0089 |  |  | 2 | 5.52 |
|                 | Hg-Hg    | 4<sup>c</sup> | 5.82<sup>c</sup> | 0.0065 |  |  | 2 | 5.82 |
|                 | Hg-Hg    | 8<sup>c</sup> | 6.16 | 0.0083 |  |  | 8 | 6.06-6.12 |
| HgCl<sub>2</sub>(s) | Hg-Cl    | 2<sup>c</sup> | 2.28 | 0.0039 | -6.07 | 0.57 | 2 | 2.25, 2.26<sup>1</sup> | 2.27, 2.29<sup>4</sup> |
|                 | MS<sup>b3</sup> | 1<sup>c</sup> | 4.52 | 0.0039<sup>9</sup> |  |  | 4 | 4.51<sup>4</sup> | 4.56<sup>2</sup> |
|                 | Hg-Cl    | 2<sup>c</sup> | 3.24 | 0.0047 |  |  | 2 | 3.23, 3.24<sup>4</sup> | 3.36<sup>4</sup> |
|                 | Hg-Cl    | 4<sup>c</sup> | 3.40 | 0.0082 |  |  | 4 | 3.40-3.54<sup>4</sup> | 3.39, 3.44, 3.47 |
|                 | Hg-Hg    | 2<sup>c</sup> | 4.31 | 0.0038 |  |  | 2 | 4.32<sup>4</sup> | 4.33<sup>2</sup> |
|                 | Hg-Hg    | 2<sup>c</sup> | 4.48 | 0.0038 |  |  | 2 | 4.40<sup>4</sup> | 4.41<sup>4</sup> |
|                 | Hg-Hg    | 4<sup>c</sup> | 4.85<sup>c</sup> | 0.0077 |  |  | 4 | 4.85<sup>4</sup> | 4.85<sup>2</sup> |
|                 | Hg-Hg    | 4<sup>c</sup> | 5.85<sup>c</sup> | 0.0067 |  |  | 4 | 5.85<sup>4</sup> | 5.85<sup>4</sup> |
| Hg<sub>3</sub>(SO<sub>4</sub>)O<sub>2</sub>(s) (Schuetteite) | Hg-O     | 2<sup>c</sup> | 2.06 | 0.0044 | -6.13 | 0.36 | 2 | 2.07, 2.12 |
|                 | Hg-O     | 4<sup>c</sup> | 2.53 | 0.0150 |  |  | 4 | 2.46-2.75 |
|                 | Hg-S     | 1<sup>c</sup> | 3.38<sup>c</sup> | 0.0047 |  |  | 1 | 3.38 |
|                 | Hg-S     | 1<sup>c</sup> | 3.68<sup>c</sup> | 0.0110 |  |  | 1 | 3.68 |
|                 | Hg-Hg    | 3<sup>c</sup> | 3.52 | 0.0043 |  |  | 3 | 3.49-3.56 |
|                 | Hg-Hg    | 2<sup>c</sup> | 3.74 | 0.0063 |  |  | 2 | 3.71, 3.76 |
|                 | Hg-Hg    | 1<sup>c</sup> | 3.83<sup>c</sup> | 0.0093 |  |  | 1 | 3.83 |

<sup>a</sup> A–B is the absorber-backscatterer pair; N is the number of backscattering atoms at distance (R); $\sigma^2$ (Debye Waller term) is the absorber–backscatterer mean-square relative displacement; $\Delta E_0$ is the energy shift in the least-squares fit; $\chi^2$ is a reduced least-squares goodness-of-fit parameter ($=(F\text{-factor})/(\# \text{ of points } \cdot \# \text{ of variables})$). Amplitude reduction factor ($S_0^2$) was allowed to vary during fitting with fixed N in order to estimate a value for $S_0^2$ for unknown samples.

<sup>b</sup> Spectrum fit with a multiple scattering path: a three-legged path (Hg→O→O→Hg, (b1), a three-legged path (Hg→Hg→Hg→Hg, (b2) and a three-legged path (Hg→Cl→Cl→Hg). N for MS was fixed to 1.

<sup>c</sup> Parameter fixed in least-squares fit. <sup>d</sup>Parameter linked in fit to the parameter directly above.

<sup>d</sup> Crystallographic distances for Hg reference compounds from published X-ray diffraction studies. HgO(s) from Aurivillius<sup>13</sup>, HgCl<sub>2</sub>(s) from Wyckoff<sup>14</sup> and<sup>15</sup> and Hg<sub>3</sub>(SO<sub>4</sub>)O<sub>2</sub> from Weil<sup>18</sup>.
**Figure S1.** XRD patterns of coprecipitate samples Fe-cpt, Hg-Fe-cpt, Al-cpt and Hg-Al-cpt. The wavelength of the radiation transformed to cobalt K-alpha = 1.789 Å
Figure S2. Mercury L(III)-edge XANES and corresponding first-derivative spectra of Hg reference spectra HgCl$_2$(s), HgO(s) and schuetteite(s) (Hg$_3$(SO$_4$)O$_2$).
Figure S3. Mercury L(III)-edge EXAFS and Fourier transforms (FT) of Hg reference spectra HgCl₂(s), HgO(s) and schuetteite(s) (Hg₃(SO₄)O₂). Deconvolution of single- and multiple-
scattering (ms) paths are shown in EXAFS and FT. Shading in FT shows the fraction of EXAFS amplitude associated with ms components, if present. Solid lines are data and dashed lines are non-linear least-squares fits (numerical fit results are shown in Table S5).

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