Supplemental Material

The Molecular Environment of Phosphorus in Sewage Sludge Ashes: Implications for Bioavailability

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Supplemental Table S1. Solubility products (-log $K_{sp}$) of selected phosphate minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Equilibrium reaction</th>
<th>-log $K_{sp}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite</td>
<td>$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{H}^+ = 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{H}_2\text{O}$</td>
<td>38.2</td>
<td>Crannell et al., 2000</td>
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<tr>
<td>Chlorapatite</td>
<td>$\text{Ca}_5(\text{PO}_4)_3\text{Cl} = 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{Cl}^-$</td>
<td>46.9</td>
<td>Vieillard and Tardy, 1984</td>
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<td>Low whitlockite</td>
<td>$\beta-\text{Ca}_3(\text{PO}_4)_2 = 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$</td>
<td>32.7</td>
<td>Crannell et al., 2000</td>
</tr>
<tr>
<td>AlPO$_4$</td>
<td>$\text{AlPO}_4 = \text{Al}^{3+} + \text{PO}_4^{3-}$</td>
<td>17.0</td>
<td>Vieillard and Tardy, 1984</td>
</tr>
<tr>
<td>Variscite</td>
<td>$\text{AlPO}_4.2\text{H}_2\text{O} = \text{Al}^{3+} + \text{PO}_4^{3-} + 2\text{H}_2\text{O}$</td>
<td>21.8</td>
<td>Scheffer et al., 2010</td>
</tr>
<tr>
<td>Strengite</td>
<td>$\text{FePO}_4.2\text{H}_2\text{O} = \text{Fe}^{3+} + \text{PO}_4^{3-} + 2\text{H}_2\text{O}$</td>
<td>28.4</td>
<td>Iuliano et al., 2007</td>
</tr>
<tr>
<td>Vivianite</td>
<td>$\text{Fe}_3(\text{PO}_4)_2.8\text{H}_2\text{O} = 3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$</td>
<td>35.7</td>
<td>Al-Borno and Tomson, 1994</td>
</tr>
</tbody>
</table>
Supplemental Fig. S1. X-ray powder diffraction spectra of sewage sludge ashes (SSA) before and after thermo-chemical treatment to remove heavy metals; the SSAs are denoted according to their cation signature resulting from waste water processing prior to incineration and thermo-chemical treatment; a) untreated SSAs (Al-untr, Fe-untr, FeCa-untr and Ca-untr) and b) thermo-chemically treated SSAs (Al-tr, Fe-tr, FeCa-tr and Ca-tr). AlPO₄, ICSD 417475 (Ap). Chlorapatite, ICSD 6192 (Ca). Hydroxylapatite, ICSD 1707 (Ha). Withlockite, ICSD 6190 (W). Anhydrite (A). Calcite (C). Quartz (Q). Iron oxides (i). Silicates other than quartz (s). Internal standard lithium fluoride (LiF)
Supplemental Fig. S2. $^{31}$P solid-state Direct-Polarization Magic-Angle Spinning Nuclear Magnetic Resonance spectra of sewage sludge ashes (SSA) before and after thermo-chemical treatment to remove heavy metals; the SSAs are denoted according to their cation signature resulting from waste water processing prior to incineration and thermo-chemical treatment; a) untreated SSAs (Al-untr, Fe-untr, FeCa-untr and Ca-untr) and b) thermo-chemically treated SSAs (Al-tr, Fe-tr, FeCa-tr and Ca-tr); first spinning sidebands (*)
**Supplemental Fig. S3.** Phosphorus K-edge $k^3$ weighted $\chi(k)$ extended X-ray absorption fine structure spectra of selected reference compounds and sewage sludge ashes (SSA) before and after thermo-chemical treatment to remove heavy metals; the SSAs are denoted according to
their cation signature resulting from waste water processing prior to incineration and thermo-
chemical treatment; untreated SSAs (Al-untr, Fe-untr, FeCa-untr and Ca-untr) and thermo-
chemically treated SSAs (Al-tr, Fe-tr, FeCa-tr and Ca-tr); Phosphorus sorbed to Al hydroxide
(sAl-P), P sorbed to goethite (sFe-P), amorphous calcium phosphate (ACP), β-tricalcium
phosphate (β-TCP), P sorbed to calcite (sCa-P), hydroxyapatite (HA). Background removal was
performed by setting the pre-edge range to -69 to -10 eV and the normalization range to +30 to
+149 eV. A second order polynomial function was applied, k range was limited to 1.0-6.2 Å; k
weighting was 1
**Supplemental Fig. S4.** P K-edge Fourier transforms (uncorrected for phase shift, k weight 3) of X-ray absorption fine structure spectra of sewage sludge ashes (SSA) before and after thermo-chemical treatment to remove heavy metals; the SSAs are denoted according to their cation signature resulting from waste water processing prior to incineration and thermo-chemical treatment; a) untreated SSAs (Al-untr, Fe-untr, FeCa-untr and Ca-untr) and b) thermo-chemically treated SSAs (Al-tr, Fe-tr, FeCa-tr and Ca-tr). Background removal was performed by setting the pre-edge range to -69 to -10 eV and the normalization range to +30 to +149 eV. A second order polynomial function was applied, k weighting was 1 and the spline range was limited to 1.0-6.2 Å. A Kaiser-Bessel window was chosen for Fourier transformation.
Supplemental References


