

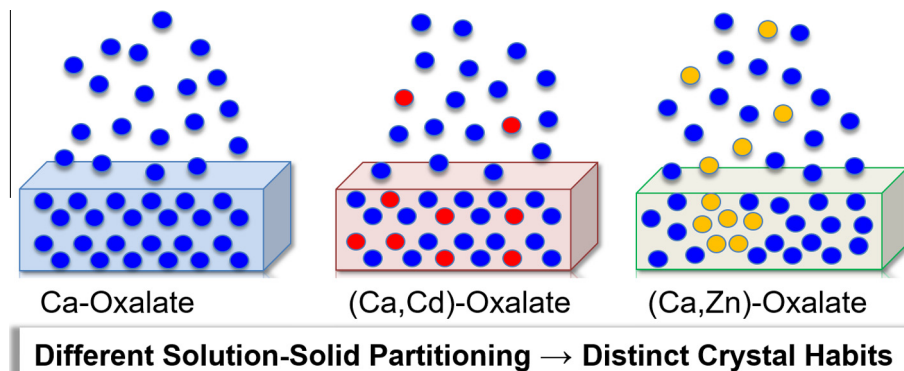


Short Communication

Solubility, structure, and morphology in the co-precipitation of cadmium and zinc with calcium-oxalate

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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 September 2016

Accepted 29 September 2016

Available online 30 September 2016

Keywords:

Oxalate

Biomaterial

Metal sequestration

Zinc

Cadmium

ABSTRACT

Calcium-oxalates (Ca-Ox), which are widely produced by microorganisms and plants, are ubiquitous and persistent biominerals in the biosphere. We investigated the potential trapping of two phytotoxic metals, cadmium (Cd) and zinc (Zn) by isomorphous substitution into the crystalline structure of Ca-Ox precipitated over a wide range of $\text{Cd}^{2+}/\text{Ca}^{2+}$ or $\text{Zn}^{2+}/\text{Ca}^{2+}$ ratio in solution. We employed atomic absorption spectroscopy, X-ray diffraction (XRD), and optical microscopy to evaluate our hypotheses that favorable solid-solution conditions and structural framework of crystal habits promote selective metal trapping within Ca-Ox precipitates. Chemical analysis demonstrated more effective Cd-Ox/Ca-Ox than Zn-Ox/Ca-Ox co-precipitate formation at the same trace metal mole fraction in solution. The XRD results revealed sequestration of Cd, but not Zn, within Ca-Ox monohydrate (whewellite). Comparative chemical analysis with Cd-Ox formation in the absence of Ca-Ox showed that the whewellite solid-solution formation lowered the solubility of Cd^{2+} below that of pure Cd-Ox. The XRD patterns indicated that Zn^{2+} precipitated as a separate pure Zn-Ox crystal that is largely excluded from the Ca-Ox structure. Furthermore, the presence of Zn^{2+} in solution favored the formation of the less stable Ca-Ox dihydrate (weddelite) over whewellite. In agreement with the XRD data, visualization of the co-precipitates by optical microscopy illustrated combined mineral phases of Cd-Ox with Ca-Ox whereas Zn-Ox and Ca-Ox exhibited two distinct mineral morphologies. Our findings shed light into the structural factors that are most critical in facilitating the trapping of toxic trace metals within Ca-Ox crystals.

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1. Introduction

Ca-oxalate (Ca-Ox) minerals (whewellite and weddellite) are abundantly found in plants, soils, sediments, animals, and humans and are second only to Ca-carbonates as the most common biominerals on Earth [1–4]. The Ca-Ox precipitate is relatively insoluble, with the monohydrate (whewellite), dihydrate (weddellite), and trihydrate reported to have solubility product constants of 1.45×10^{-9} , 3.80×10^{-9} , and 4.68×10^{-9} , respectively [5]. Other insoluble oxalates of trace metals including Cd and Zn can also be formed naturally, for example, by soil fungi [6–8]. The solubility product constants of these trace metal oxalates can be above or below that of Ca-Ox, with values of 1.42×10^{-8} for Cd-oxalate (Cd-Ox) trihydrate and 1.38×10^{-9} for Zn-oxalate (Zn-Ox) dihydrate [9]. These trace metals and others have been shown to substitute readily into Ca-Ox crystallites [10,11], raising the possibility that Ca-Ox biominerals could both limit their leaching in soils and promote their detoxification processes in plants or other cellular environments. However, the mechanisms underlying the dependence of this phenomenon on the solubility and physical properties of the specific trace metal are not well understood.

Mazen and Maghraby [12] found evidence for Cd and Pb sequestration within Ca-Ox crystals in the tissues of the aquatic plant *Eichhornia crassipes*. By contrast, there was no indication that Mn co-precipitated into the Ca-Ox crystals present in the leaves of *Persea Americana* (avocado) [13]. Instead, these leaves hyperaccumulated Mn as soluble Mn-oxalate complexes and also possibly Mn-phosphate [13]. The lower solubility of Cd-oxalate (Cd-Ox) and Pb-oxalate (9.59×10^{-10} [14] or 7.41×10^{-12} [15]) than that of Mn-oxalate (1.70×10^{-7} [7]) may explain the selective ability of Ca-Ox to immobilize Cd and Pb preferentially. Sarret et al. [16] reported that lichens exposed to high Zn can reduce its toxic effect by synthesizing higher levels of oxalate to form insoluble Zn-oxalate (Zn-Ox). On the other hand, using an electron microprobe method, Franceschi and Schueren [17] found that the duckweed *Lemna minor* grown on nutrient solutions containing soluble Ba, Cd, Co, Mn, or Sr, incorporated only Sr at measurable levels into oxalate raphide crystals whereas the other metals were not detected in the crystals. Taken collectively, these previous findings imply that the precipitation of Ca-Ox found in many plant species at high levels could have a role in detoxifying toxic trace metals.

In this short communication, we shed light on the mechanisms underlying the potential role of Ca-Ox crystals in trapping Zn and Cd. These two metals were chosen because of their common occurrence as anthropogenic metal contaminants in agricultural soils [18]. Furthermore, the different ionic radii of Cd^{2+} (0.95 Å) and Ca^{2+} (1.00 Å) compared to Zn^{2+} (0.74 Å) allowed us to probe the possible influence of ionic potential (charge/radius). We evaluated two main hypotheses: (1) favorable solid solution conditions are required to promote the formation of the co-precipitates and (2) the structural framework of the resulting co-precipitates with respect to the pure Ca-Ox crystals possesses sites amenable to the selective trapping of trace metals. We conducted laboratory experiments that explore the co-precipitation of Ca-Ox crystals with Cd or Zn. The speciation of the solid solution was analyzed and the resulting co-precipitates were characterized by X-ray diffraction (XRD) and optical microscopy. The findings from the present study provide structural insights on how co-precipitation with Ca-Ox crystals may provide a means of trapping certain trace metals within plants and environmental matrices.

2. Experimental methods

2.1. Sample preparation

Trials were performed in duplicates with different volume ratios of 5.0 mM CdCl_2 or ZnCl_2 to 5.0 mM CaCl_2 combined with 100 ml of freshly prepared 5.0 mM Na-oxalate to make up a total volume of 200 ml in Erlenmeyer flasks. Mole fractions $[\text{M}/(\text{M} + \text{Ca})]$ were 0.00, 0.01, 0.05, 0.10, 0.25, 0.50 and 1.0 (where M = Zn or Cd). The Na-oxalate was added following the mixing of CdCl_2 or ZnCl_2 with CaCl_2 , and precipitation was allowed to occur overnight in the absence of light at 22 °C. The same experiments were also run with 10 mM concentrations of the reagents with the same mole fractions in order to increase precipitate yields for subsequent analysis of the crystalline oxalates. The final pH of the aqueous solution was in the range of 6.2–6.8, likely due to some buffering by carbonic acid during the course of the experiment. To test the possible effect of acidic pH, a trial was performed with CdCl_2 pre-acidified to ~pH 4 and Cd-Ox co-precipitates were achieved at all Cd/(Cd + Ca) mole fractions (results not shown).

2.2. Trace metal removal from solution

To evaluate the efficiency of Cd or Zn removal from the solution at environmentally-relevant low concentrations wherein the solution is under saturated with respect to Cd- or Zn-oxalate, experiments similar to those described above were performed in duplicates at a wider range of ratios of Ca/Cd or Ca/Zn up to Ca/M = 500. The oxalate precipitates were separated from the solution phase by filtration (Whatman #42 filter paper). Dissolved concentrations of Cd or Zn in following removal of the precipitated solids were monitored in order to determine the fraction of Cd and Zn removed from solution over a wide range of Ca/Cd and Ca/Zn ratios. A control experiment with Na acetate replacing Na-oxalate over the same range of Ca/Cd ratios confirmed the lack of precipitation of Cd in the absence of oxalate, thus ascertaining that precipitated Cd was in the form of oxalates. The filtered solutions were prepared at appropriate dilutions using 1 M HNO_3 prior to Cd or Zn analysis by Flame Atomic Absorption (FAA) spectrophotometry.

Due to the exceptional removal efficiency of Cd from solution by Ca-Ox (See Results and Discussion), we conducted an additional experiment to determine the solubility of Cd in the presence of excess oxalate, but in the absence of any co-precipitating Ca-Ox. This experiment was conducted by preparing CdCl_2 solutions from 0.01 to 5.0 mM and combining 50 ml of these solutions with 50 ml of 5.0 mM Na-oxalate in Erlenmeyer flasks. The flasks were placed on a reciprocal shaker for 48 h, then filtered through 0.8 μm cellulosic membrane filters. The filtrates were analyzed for dissolved Cd by FAA as described above. These Cd measurements allowed the final equilibrium solutions to be tested for saturation with respect to Cd-oxalate (Cd-Ox) precipitation based on the reported solubility product of Cd-Ox trihydrate of 1.42×10^{-8} [9]. The Visual MINTEQ (version 3.0. Stockholm Royal Institute of Technology (KTH), Stockholm) speciation software was used to calculate expected dissolved Cd (free cationic plus oxalate-complexed) concentrations in the solutions in the absence of precipitation. Subsequently, it was determined which solutions were under- and over-saturated with respect to Cd-Ox trihydrate.

2.3. Analysis of precipitates

The oxalate precipitates collected on the filter papers from the above experiments were washed with deionized water and dried.

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