# Zinc isotopic fractionation in *Phragmites australis* in response to toxic levels of zinc

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## Abstract

Stable isotope signatures of Zn have shown great promise in elucidating changes in uptake and translocation mechanisms of this metal in plants during environmental changes [1] [2]. Here this potential was tested by investigating the effect of high Zn concentrations on the isotopic fractionation patterns of *Phragmites australis* (Cav.) Trin. ex Steud [3]. Plants were grown for 40 d in a nutritive solution containing 3.2 mM (sufficient) or 2 mM (toxic) Zn. The Zn isotopic composition of roots, rhizomes, shoots, and leaves was analysed. Stems and leaves were sampled at different heights to evaluate the effect of long-distance transport on Zn fractionation. During Zn sufficiency, roots, rhizomes, and shoots were isotopically heavy ($\delta^{66}Zn_{JMCLyon}$ = 0.2‰) while the youngest leaves were isotopically light (–0.5‰). During Zn excess, roots were still isotopically heavier ($\delta^{66}Zn$ = 0.5‰) and the rest of the plant was isotopically light (up to –0.5‰).

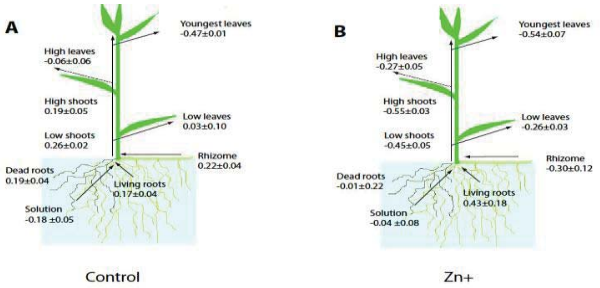

**Figure: Isotopic signature of the studied plant sections compared to solutions.**

## Conclusion

The enrichment of heavy isotopes at the roots was attributed to Zn uptake mediated by transporter proteins under Zn-sufficient conditions and to chelation and compartmentation in Zn excess. The isotopically lighter Zn in shoots and leaves is consistent with long-distance root to shoot transport. The tolerance response of *P. australis* increased the range of Zn fractionation within the plant and with respect to the environment

[1] Weiss et al. (2005) *New Phytol* **165**, 703–710. [2] Arnold et al. (2010) *Plant Cell Environ* **33**, 370–381. [3] Caldelas et al. (2011) *J Exp Bot* **62**, 2169-2178.

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# Interaction of Pb with calcite (104) surface in the presence of EDTA

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The incorporation of metals in calcite is important for understanding many geological and environmental processes but is still incompletely understood. Calcite (104) cleavage surfaces were reacted with Pb-EDTA aqueous solution (0.09 mM Pb, 0.11 mM EDTA, 0.5 mM Ca, pH 8.35) at room temperature for times ranging from minutes to hours. Freshly cleaved calcite was placed in a flow-through cell, and reacted first with calcite-saturated solution and then Pb-EDTA solution, both at 0.3 mL/min. In situ synchrotron XR measurements revealed evidence for incorporation of Pb into the calcite lattice as well as the formation of cerrusite ($PbCO_3$) with its (021) plane oriented parallel to calcite (104). The reacted calcite was further studied ex situ by atomic force microscopy (AFM) and optical microscopy. AFM imaging of the reacted surface outside the X-ray beam footprint showed narrow overgrowths atop steps and sparse precipitates on terraces (Fig. 1a). Different behavior was seen within the X-ray beam footprint; it contained abundant trapezoidal-and hexagonal-shaped precipitates oriented mainly along a single crystallographic direction, which is consistent with heteroepitaxial cerussite (021) overgrowths (Figs. 1b and 2). X-ray microfluorescence spectroscopy showed that the trapezoidal growth islands are Pb-rich. Features similar to those in Fig. 1a were observed by AFM in separate ex situ experiments without exposure to X-rays. These observations suggest that the X-ray beam enhanced precipitation even at bulk-undersaturated conditions with respect to cerussite (log SI = -2.3), possibly by photolytic destabilization of the Pb-EDTA$^{2-}$ solution complex.

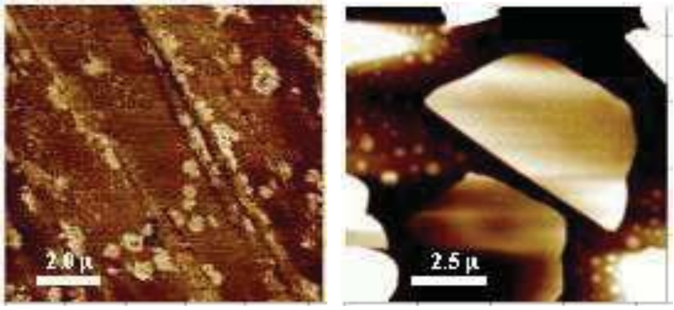

**Figure 1:** AFM images of the reacted calcite surface. (a) phase contrast image outside the X-ray beam footprint; (b) height image of an area within the X-ray beam footprint (*z*-scale: 100 nm).

**Figure 2:** The reacted calcite surface imaged within the X-ray beam footprint, observed under reflected light microscopy. Cerussite occurs as trapezoidal precipitates showing euhedral (021) growth face.