

## Experiment title (EV-40): Understanding the Zn biomineralization processes within native plant roots

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### Report

During an EU funded project (UMBRELLA, grant N. 226870 <http://www.umbrella.uni-jena.de>), plant growth assisted by microbes and fungi was investigated in six European mine sites, including the abandoned Naracauli mine (Sardinia). An issue of the research is that some typical plants (*Pistacia lentiscus*; *Euphorbia pityusa*) are able to grow in mine tailings rich in heavy metals. The aim of this work is to understand the processes that can be involved in phytoremediation and predict metal stability over a long time. To do this, EXAFS analysis is essential to define the chemical speciation of metals in the plant root-soil system.

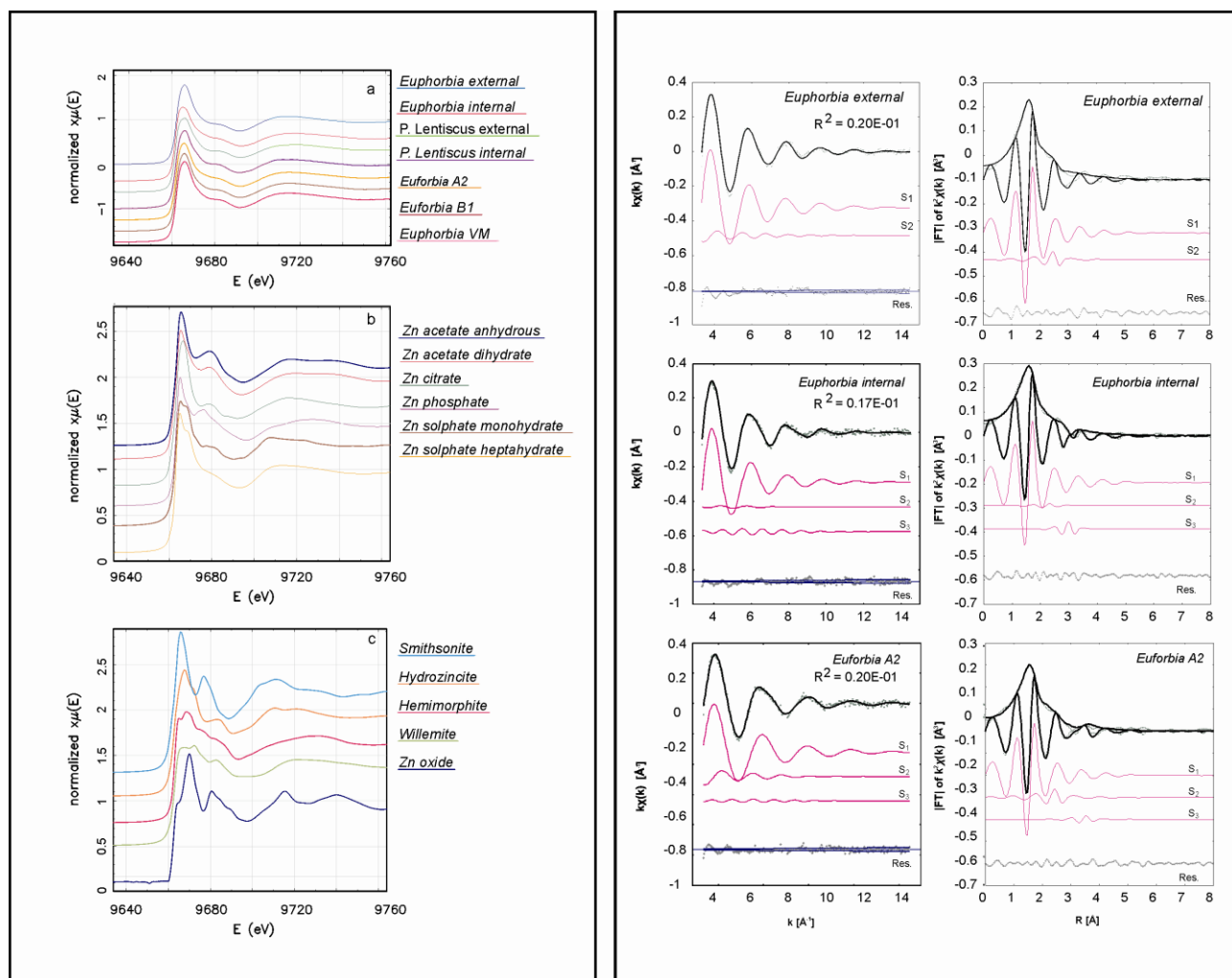
Plants were harvested as close as possible to the synchrotron measurements according to the established protocols (see Mc Near et al., 2010). Different portions of the roots have been selected: 1) external cortex, 2) inner cortex, 3) root bodies. Dry samples were directly pressed to have manageable pellets suitable for XAS experiments. XAS measurements were carried out at the Zn K-edge (9,659 eV) and spectra were measured in transmission and fluorescence geometry. Standard procedures were used for data normalization and to extract the structural EXAFS (extended X-ray absorption fine structure) signal  $\chi(k)$ . The EXAFS data refinement was performed using the FITEXA code (Meneghini et al., 2012). In addition to the root samples, a set of standard compounds was selected and Zn K edge spectra were measured during the same proposal experiment EV-40 at the BM23- XAS beamline: comparison of Zn XANES collected on roots and reference compounds, represents an easy method to understand chemical speciation of Zn in roots.

Figures 1a, b and c (left panel) report the near edge region of the normalized spectra of reference compounds and selected samples. All root body samples are characterized by similar Zn K-edge XANES spectra, then they have similar Zn local environment. On the other hand, external cortex and inner cortex samples show some differences. It has been observed that all the natural XANES spectra are significantly different from those collected on reference compounds, suggesting definitive local structure differences.

Figure 1 (right panel) reports the Zn EXAFS spectra of selected root samples with the best fit curves, and the Fourier transforms (FT). Analysis of root samples spectra indicates weakly structured EXAFS signal and nearly absent next neighbor shells (FT). This points out lack of long range order for Zn positions in these samples. Quantitative analysis of the root body samples demonstrates that Zn coordinates 5 O atoms (around  $R_{ZnO} \sim 2 \text{ \AA}$ ) in all the natural samples, and a weak next neighbor Zn-Si shell is found around  $R_{ZnSi} \sim 3 \text{ \AA}$  with coordination number around 1, demonstrating that ZnO<sub>5</sub> polyhedra belong to a short range ordered structure linked to Si atoms. In some cases, a third shell Zn-Zn was recognized around 3.6  $\text{\AA}$  suggesting some degree

of medium range order of Zn containing phase. Noticeably the Zn-Si shell is observed only analyzing the Zn EXAFS spectra of external cortex.

These results are in agreement with soft X-ray scanning transmission microscopy measurements (made at Elettra, TwinMic beamline). In fact, it was observed that Zn is adsorbed from the soil minerals and migrates towards the inner part of the plant root. On the other hand, Si is concentrated in the external part (the rim of the root).



**Figure 1.** On the left panel, the Zn K near-edge region of the XAS spectra collected on the measured samples. a) root samples b) and c) reference compounds. On the right panel, the best fits of experimental EXAFS spectra for selected root samples, and Fourier transforms of EXAFS spectra.

## References

- McNear Jr. et al. (2010) Phytochemistry 71, 188-200.
- Menehuni et al. (2012). Nuclear Instrum and meth.B. 285: 153-157.