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Supplementary Materials

Mineralogy and Zn Chemical Speciation in a Soil-Plant System from a Metal-Extreme Environment: A Study on *Helichrysum microphyllum* subsp. *tyrrhenicum* (Campo Pisano Mine, SW Sardinia, Italy)

Maria Enrica Boi [1,2,3], Daniela Medas [1,*], Giuliana Aquilanti [4], Gianluigi Bacchetta [2,3], Giovanni Birarda [4], Giovanna Cappai [5], Ilaria Carlomagno [4], Maria Antonietta Casu [6], Alessandra Gianoncelli [4], Carlo Meneghini [7], Martina Piredda [5], Francesca Podda [1], Marco Porceddu [2,3], Valentina Rimondi [8,9], Lisa Vaccari [4] and Giovanni De Giudici [1]

1 Department of Chemical and Geological Sciences, University of Cagliari, Cittadella Universitaria di Monserrato-Blocco A S.S. 554 bivio per Sestu, 09042 Monserrato (CA), Italy; menricaboi@gmail.com (M.E.B.); fpodda@unica.it (F.P.); gbgiudic@unica.it (G.D.G.)

2 Department of Life and Environmental Sciences, Centre for the Conservation of Biodiversity (CCB), University of Cagliari, Viale Sant'Ignazio da Laconi 11-13, 09123 Cagliari, Italy; bacchet@unica.it (G.B.); porceddu.marco@unica.it (M.P.)

3 Sardinian Germplasm Bank-Hortus Botanicus Karalitanus, University of Cagliari, Viale Sant'Ignazio da Laconi 9-11, 09123 Cagliari, Italy

4 Elettra-Sincrotrone Trieste, Strada Statale 14-km 163,5 in AREA Science Park, 34149 Basovizza, Trieste, Italy; giuliana.aquilanti@elettra.eu (G.A.); giovanni.birarda@elettra.eu (G.B.); ilaria.carlomagno@gmail.com (I.C.); alessandra.gianoncelli@elettra.eu (A.G.); lisa.vaccari@elettra.eu (L.V.)

5 Department of Civil and Environmental Engineering and Architecture, University of Cagliari, Piazza d'Armi 1, 09123 Cagliari, Italy; gcappai@unica.it (G.C.); piredda@unica.it (M.P.)

6 Unità Operativa di Supporto (UOS) of Cagliari, National Research Council, Institute of Translational Pharmacology, Scientific and Technological Park of Sardinia POLARIS, 09010 Pula, Italy; mariaantonietta.casu@ift.cnr.it

7 Department of Sciences, University of Roma Tre, Via della Vasca Navale 84, 00146 Rome, Italy; carlo.meneghini@uniroma3.it

8 Department of Earth Sciences, University of Florence, Via G. La Pira 4, 50121 Florence, Italy; valentina.rimondi@unifi.it

9 CNR-Institute of Geosciences and Earth Resources, Via G. La Pira, 4, 50121 Florence, Italy

* Correspondence: dmedas@unica.it

Table S1. Coordinates (WGS84) and characteristics of the sampling sites.

Sampling site	Coordinates	Characters	Substrate
Campo Pisano mine dump (CP) - Iglesias (SW Sardinia)	CP1 39°29'56.19"N, 8°53'77.92"E CP2 39°29'60.08"N 8°53'71.84"E CP3 39°29'58.94"N	Geochemical anomaly in Zn + mining activity	Pyrite rich mine waste, carbonate rich material covering the mine waste surface

	8°53'55.51"E		
Outside the mine dump (OCP) - Iglesias (SW Sardinia)	OCP1 39°29'23.0"N, 8°54'38.50" E OCP2 39°29'23.58"N, 8°54'39.1" E OCP3 39°29'23.19"N, 8°54'38.19" E	Geochemical anomaly in Zn	Carbonates rocks, close to ore outcrop

1. Chemical Analysis

Soils and rhizospheres were digested using a concentrate acid mixture of 9 ml of HNO_3 (65,7% Carlo Erba reagents, Cornaredo, Milano, Italy) and 4 ml of HF (40%, Carlo Erba reagents, Cornaredo, Milano, Italy); plant tissues were acid digested with 9 ml of HNO_3 and 0.5 ml of HF. In order to evaluate accuracy of the procedures, reference materials (respectively, GSS-4 - Institute of Geophysical and Geochemical Exploration, China, limy-yellow soil for rhizosphere, GSV-2 - Institute of Geophysical and Geochemical Exploration, China, bush twigs and leaves, and INCT-PVLT-6 - Institute of Nuclear chemistry and technology, Warszawa, Poland, Polish Virginia Tobacco leaves, for plant tissues) and blanks were processed by applying the previous two methods. After digestion, standards and samples were almost dried on hot plate, and then filtered at 3-5 μm. Finally, the samples were diluted to 50 ml (1% HNO_3) and metals were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) at the following wavelengths: Zn 213.857 nm; Pb 220.353 nm; Cd 228.802 nm.

2. TwinMic Microscope

The TwinMic microscope was operated in Scanning Transmission mode (STXM), where the monochromatised X-rays are focused on the sample through a suitable zone plate diffractive optics. While the sample is raster-scanned across the microprobe, a fast readout CCD camera (iXon DV860-BV Andor Technology, 2003, Belfast, Ireland)) collects the transmitted X-rays [1,2] through an X-ray-visible light converting system, 8 SDDs [3,4] (pndetector, Munich, Germany) acquire the XRF photons emitted by the specimen (processing electronics from XGlab, Milano, Italy). This set-up allows the simultaneous collection of X-ray absorption and phase contrast images together with elemental maps, providing morphological and chemical information respectively.

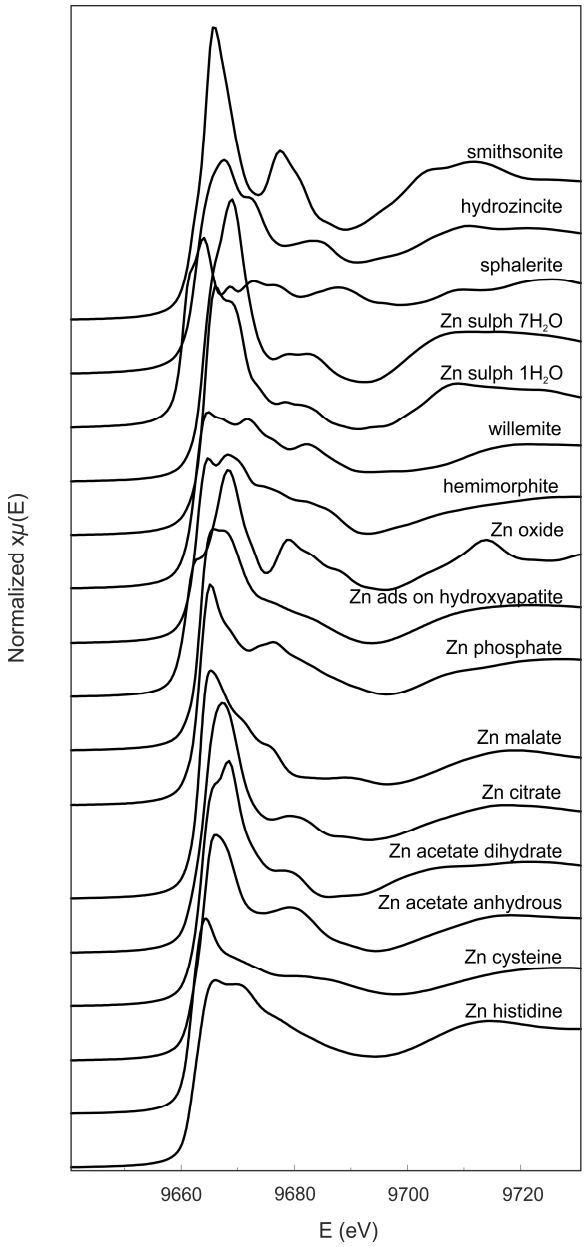

Figure S1. Zn K-edge X-ray absorption near edge structure (XANES) spectra of the reference compounds.

3. Infrared Microspectroscopy

After the acquisition, FTIR data were corrected for water vapor and atmospheric carbon dioxide and a rubberband baseline was applied; in addition, pixels of the FPA images were binned 2×2 in order to increase the signal to noise ratio. A hierarchical cluster analysis (HCA) with Euclidian distances and ward clustering algorithm was used to remove the empty areas and those at the edges heavily affected by scattering, calculating the Euclidian distances and the k segments. Then, for selected spectra bands, band intensity was calculated as area integral or peak intensity relative to a local baseline.

A dataset comprising a root section and a stem section were grouped together and then analyzed using principal component analysis (PCA), in order to identify the spectral components that better differentiate roots from stems. HCA filtered, baseline corrected and normalized spectra from stem and root were used as the input of the PCA, and the results are presented as scatterplot of the transformed data along two axes that represent two eigenvectors of the PCA [5]. Data were

analyzed with Quasar [6,7] and plotted with OriginPro 2019 (Originlabs Corporation, Maryland, US).

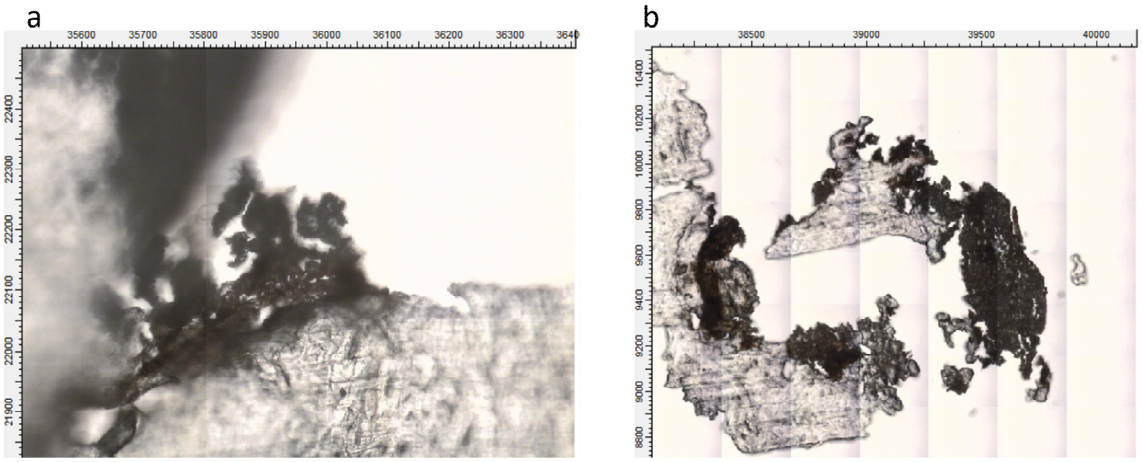

Figure S2. Optical images of a stem (a) and a root (b) section of H. tyrrhenicum from the Campo Pisano mine dump.

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