

## **Long-term monitoring of atmospheric pollution in Maritime Antarctic with lichen**

### ***Usnea aurantiaco-atra* (Jacq.) Bory : a magnetic and elemental study.**

Supplemental Information

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### **Details on analytical techniques and methods**

#### *Magnetic measurements*

The following measurements were performed using a Vibrating Sample Magnetometer (VSM) from Lakeshore, which is part of the Mineral Magnetism Analysis Platform situated at IPGP-IMPIC. Acquisition of Saturated Isothermal Remanent Magnetization (SIRM) with increasing laboratory field were measured up to 1 T. These curves are useful to determine the saturating field of SIRM which can help identifying the magnetic minerals that carry the magnetization (Fig. SI-1a). Hysteresis curves, i.e., the variation of the magnetization with an applied field, were measured in a maximum field of 0.5 T and enabled us to obtain the values of coercive field  $H_c$ , saturation magnetization  $M_s$  and remanent magnetization  $M_r$  (Fig. SI-1b). Coercivities of remanence  $H_{cr}$  were obtained with the backfield curves, which measure the decrease of the remanent magnetization after saturation with an increasingly negative laboratory field (Fig. SI-1c). These four values were then combined as the usual hysteresis parameters  $M_r/M_s$  and  $H_{cr}/H_c$  and plotted on a Day-diagram (Day et al. 1977) superimposed with the mixing curves of Dunlop (2002) to obtain an indication of magnetic domain state.  $M_r$ ,  $M_s$  and susceptibility values were all normalized by the mass of the powder contained in each gelcap.

First-Order Reversal Curve (FORC) diagrams, calculated from multiple minor hysteresis curves, can provide, in first approximation, information such as a measure of the distribution of microcoercivities (along the horizontal axis) and interaction fields (along the vertical axis) in a sample. Magnetic grains with different domain state plot in different areas of the FORC diagram (Roberts et al. 2000); it is therefore a powerful tool to characterize magnetic grain sizes even for samples containing a mixed grain-size assemblage. FORC diagrams were analyzed using the FORCinel software (Harrison & Feinberg 2008; Egli 2013).

#### *Instrumental Neutron Activation Analysis*

The finest fraction of the substrate (<75  $\mu\text{m}$ ) were placed in polystyrene capsules. The concentrations of the elements Na, Sc, Cr, Fe, Co, As, La, Ce, Sm, Eu, Yb, Hf were determined using neutrons from a reactor type pool of 5 MW of nominal power, enriched at 19.75% by  $^{235}\text{U}$  belonging to the Chilean Nuclear Energy Commission. An irradiation position with a thermal neutron flux ( $\phi_{\text{th}}$ ) of  $1.5 (4) \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$ , 6 hour of irradiation time and a Ge (Li) Hyperpure as detector were used. Quantification was performed by the standard or comparator method using four certified reference materials NIST2711a, NIST2710a, NIST1648a and GBW7312.

#### *Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES and AAS)*

Three hundred mg of substrates were treated with an acid mixture (3 mL of 65%  $\text{HNO}_3$  and 3 mL of 40% HF, both reagents from Merck) following the "Application Notes for Microwave Digestion" guide (1996) of the Milestone MLS 1200 MEGA microwave oven, according to USEPA method 3052 (1996); duplicates and blanks were also made. The reference material Quality Control Standard 26, High Purity Standards of NIST were used for the control of solids digestion.

Vanadium, Cr, Mn, Co, Ni, Cu, Zn, Cd, Ba, and Pb were simultaneously quantified by inductive coupled plasma-mass spectrophotometer (ICP-OES) MAT VG Plasma Quad, Fisons Instruments). Magnesium, Al, and Fe were quantified by atomic absorption spectrophotometry (AAS, Perkin-Elmer model 110-B).

Calibration curves and range and sensitivity determination curves were constructed.

Experimental quantification limits for analyses were established considering a 10% deviation from blank readings. *Pseudevernia furfuracea*, Standard No. 482, Community Bureau of Reference, BCR, Commission of the European Community was used as a reference material.

## References

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- ROBERTS, A.P., PIKE, C.R. & VEROSUB, K.L. 2000. First-order reversal curve diagrams: A new tool for characterizing the magnetic properties of natural samples. *Journal of Geophysical Research: Solid Earth*, **105**, 10.1029/2000JB900326.

## Supplemental figures

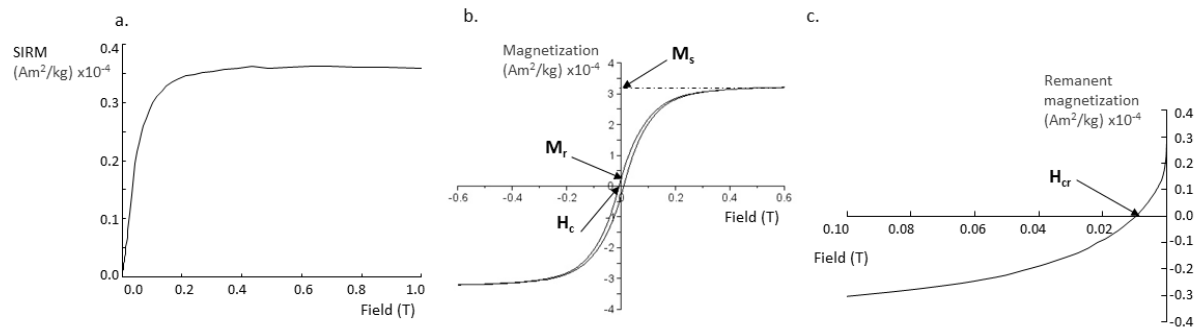


Figure SI-1. Definition of the various magnetic measurements carried out in this study. a: Measurement of Saturation Isothermal Remanent Magnetization (SIRM); b: Hysteresis loop and definition of hysteresis parameters; c: Backfield magnetization curve and definition of coercivity of remanence.

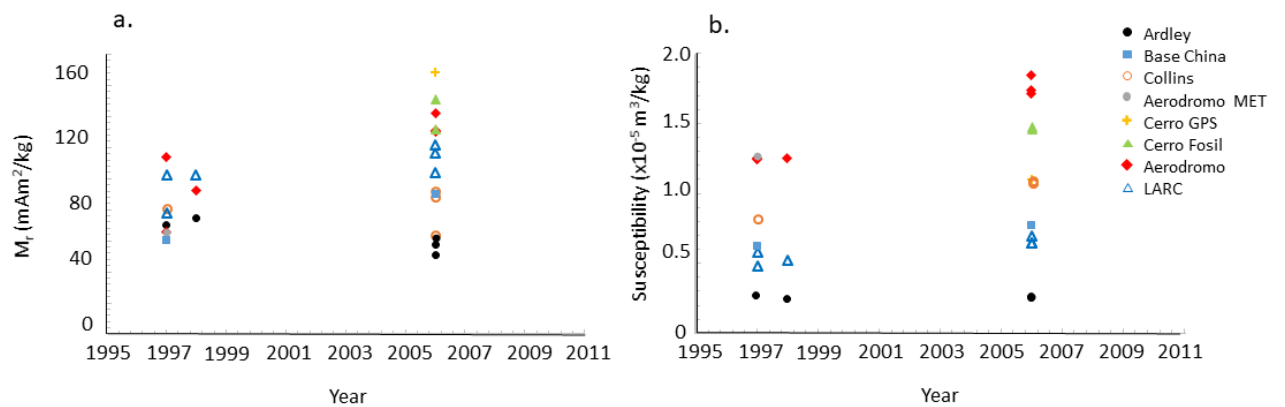


Figure SI-2. Variation of a: SIRM and b: magnetic susceptibility with time for substrate samples of 1997, 1998 and 2006 from the different sites.

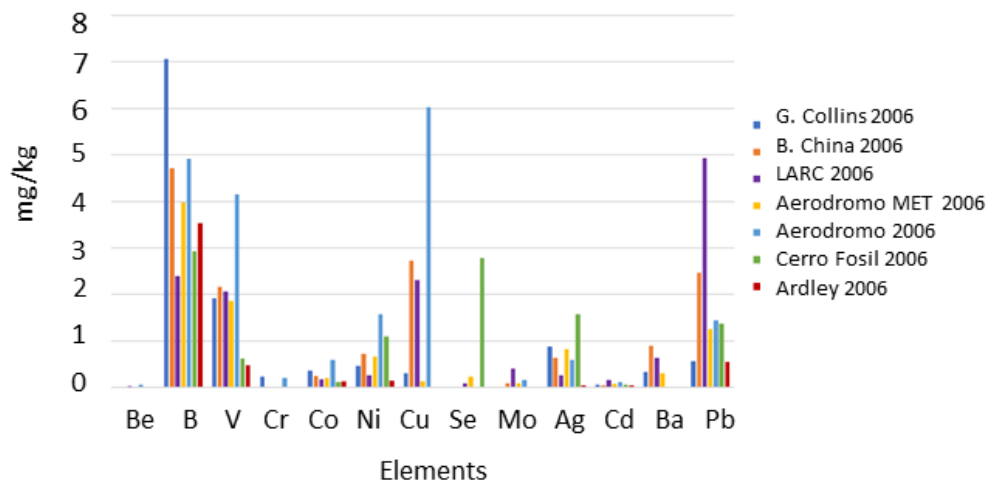


Figure SI-3. Concentrations of 13 minor elements determined by ICP-OES of *Usnea aurantiaco-atra* (Jacq.) Bory from the sites sampled in the year 2006.

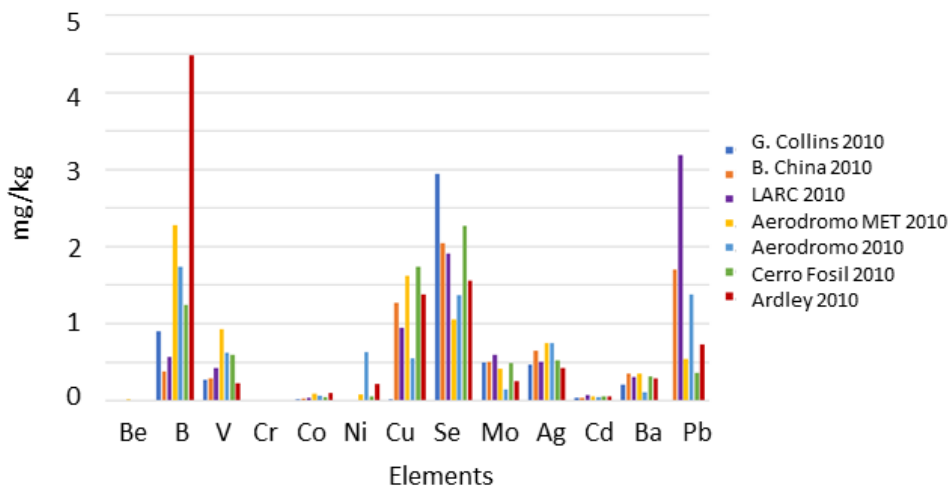


Figure SI-4. Concentrations of 13 minor elements determined by ICP-OES of *Usnea aurantiaco-atra* (Jacq.) Bory from the sites sampled in the year 2010.