Supplementary Material for *"Iron speciation of natural and anthropogenic dust by spectroscopic and chemical methods"*

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1) Sampling sites maps

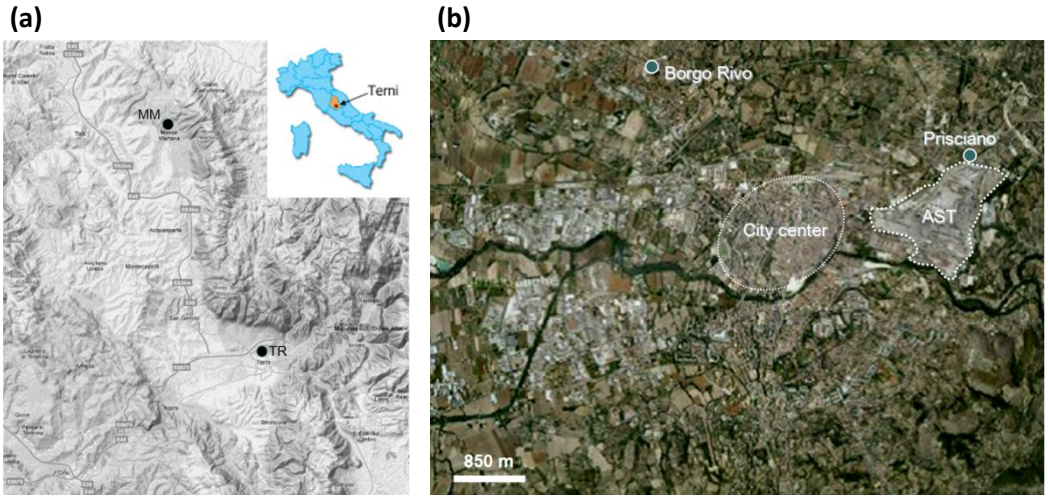

Figure S1 – (a) Geographical terrain map of the two sampling sites: Monte Martano (MM) and Terni (TR). (b) Map of the Terni city, the AST factory area and the two urban monitoring sites are marked.

2) Saharan dust advection: December 2014

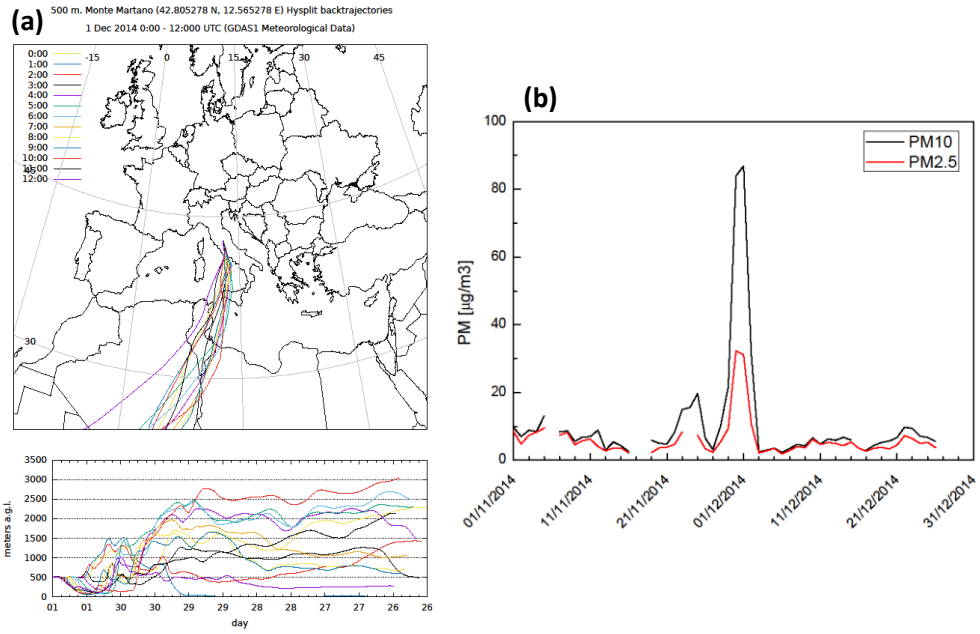

Figure S2 – (a) HYSPLIT hourly back-trajectories finishing over Monte Martano on December 1st 2014. Clear provenance of air masses from Algeria and Tunisia during the whole advection. (b) Mass concentration (PM_{10} and $PM_{2.5}$) trends recorded at Monte Martano in November and December 2014

3) Self-absorption

No amplitude distortion between fluorescence and transmission k-space spectra has been observed for the sample with the highest iron concentration, namely AST_E45 (see Figure S1). Consequently, self-absorption effects can be safely ruled out also for the other (more diluted) samples.

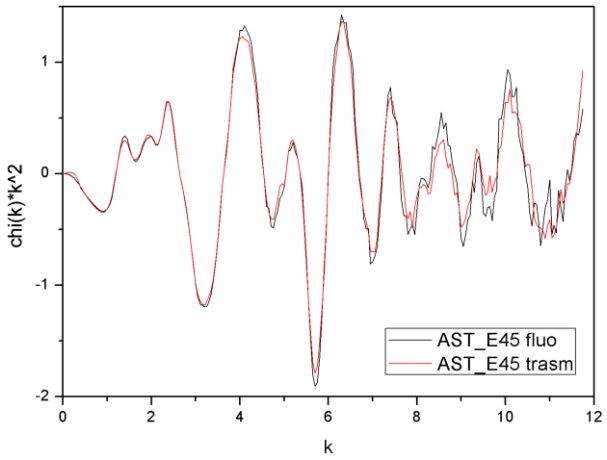

Figure S3 - Comparison between fluorescence and transmission k-space spectra for the AST_E45 sample.

4) XANES comparison with standard compounds

The XANES spectrum of the AST_E45 sample result more similar to that of the maghemite standard than to the magnetite one. This observation suggest the spinel structure observed in the sample to be defective.

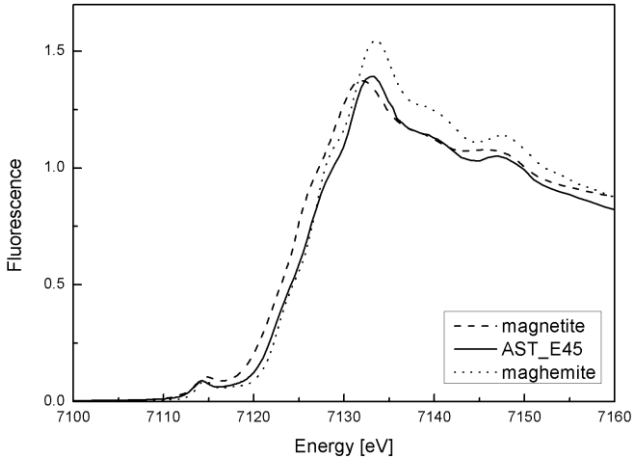

Figure S4 - Comparison between the AST_E45 sample and magnetite and maghemite standards in the XANES region

5) Bond Valence Method calculations

The interatomic distances calculated in Table S1 are taken from the Bond Valence Method (BVM) that is a phenomenological theory based on (X-ray or neutron) diffraction data from a wide set of materials. Diffraction gives the position of the atoms averaged over thermal vibrations so the data calculated from BVM are exactly the same quantities obtained by XAS. It has to be kept in mind that there is a fundamental

difference between the error on the bond distance (R) and the value of the standard deviation (σ). The former is the uncertainty on the position of the peak of the interatomic distance distribution function, the latter is its width. This means that (in a thermal vibration perspective) the distance oscillates with a certain amplitude σ around a value R, where R is known with his proper error value.

	N=4	N=5	N=6
Fe^{2+}	1.990	2.073	2.140
Fe^{3+}	1.865	1.948	2.015

Table S1 - Fe-O bond distances in Å, calculated using the Bond Valence Method parameter 2013 version (Newville 2005 *"Using bond valence sums as restrains in xafs analysis"* Physica Scripta, T115:159-161)

6) <u>SEM analysis aerosol particles in the Saharan dust sample</u>

The particle assemblage of the Saharan dust advection mostly consists of silicates (clay minerals, quartz and feldspar in this order of abundance) and carbonates (calcite and minor dolomite) with minor sulfate (lamellar gypsum) and Fe oxides/hydroxides amounts (Fig. S5a). Most iron particles are present as micro-nanoparticles included in the clay minerals (see the detail of the chlorite grain in Fig. S5b with corresponding EDS microanalysis, Fig. S5c), while isolated crystals are very rare (Fig. S5d).

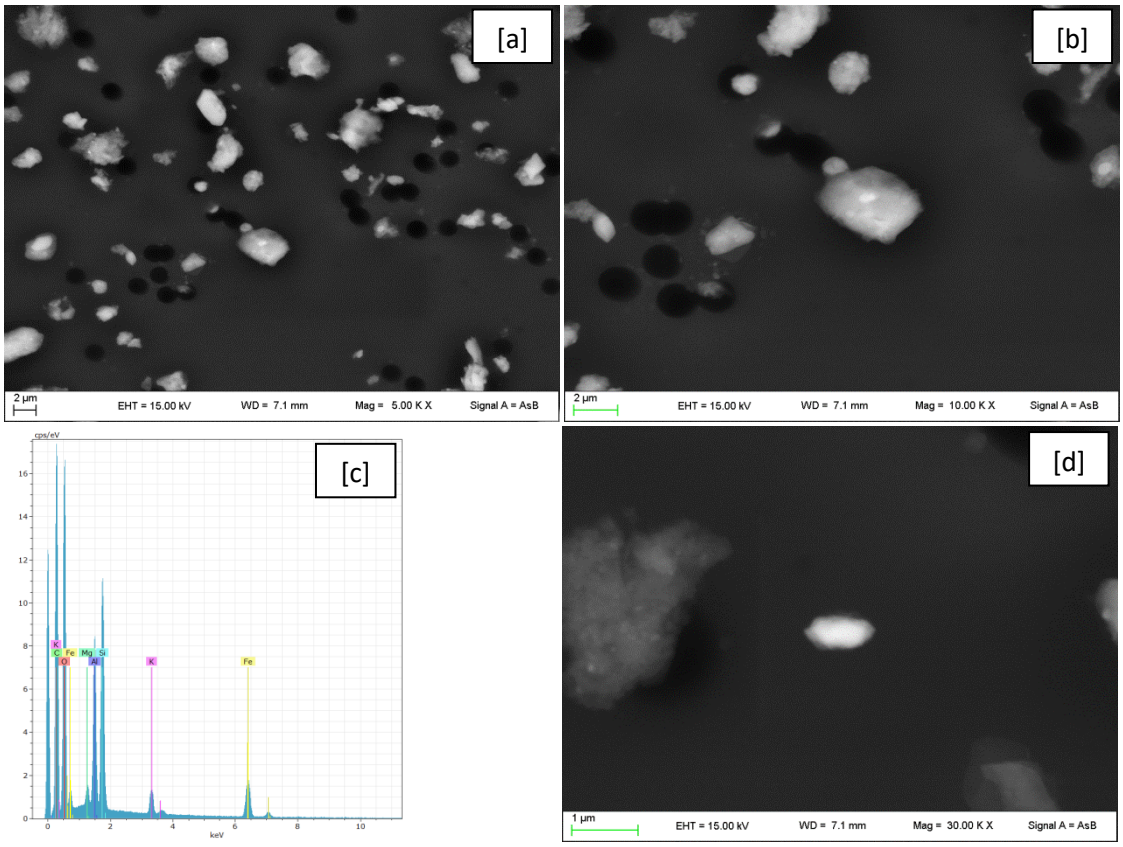

Figure S5 – SEM-EDX analysis of the Saharan dust sample.