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Report:

Health effects due to crystalline silica (commonly found in two polymorphs, quartz and cristobalite) have been proposed to be mediated through radical species formed and/or modified at the mineral surface. Nevertheless, the rise of carcinogenic activity was also experimentally studied in relation to the presence, crystal chemistry and bioavailability of hetero-species (as e.g. Al, Fe) at the surface of quartz: these, in fact, can modulate the concentration of radicals in vivo, due to catalytic processes. (**Fubini et al, 1995; Fenoglio et al., 2003; Goldsmith et al., 1986; Amandus et al., 1997; ACGIH, 2006; Di Benedetto et al., 2010, 2013)**.

Within this context, our research group succesfully applied X-ray Absorption Spectroscopy (XAS) to study and classify the speciation of Fe associated to crystalline silica dust, from occupational and environmental sources. Among several results, we want to stress that our experimental protocal was able to sort out that under specific circumstances, depending on the source apportionment of the dusts, the Fe coordination is undersaturated (i.e. < six coordinating oxygen anions) and that this species is not associated to a crystalline phase. The attribution of this species is likely to consist of the non saturated Fe complexes at quartz surface, imputed to play a prominent role in modulating health effects.

The present experiment was dedicated to investigate the Fe speciation associated to the so-called “natural ground”, i.e. the silica usually suspended in urban dusts (airborne particulate). It is largely accepted that silica is one of the main constituents of urban particulate, especially in its coarse fraction (PM_{10}). The knowledge of the features of Fe speciation in these materials is fundamental to define a “zero-level” for workers and people exposure to silica.

During the experiment we analysed ten urban aerosol samples collected in the metropolitan Firenze-Prato-Pistoia district (Tuscany, Italy), one of the most populated district of central Italy (presently summing up to more than one million inhabitants). Aerosol samples have been collected through environmental samplers on

vinylacrylic filters. 8 hours exposures were chosen in order to improve the total amount of dust collected. Powders granulometry was cut to respirable dusts (<4 μm, i.e. PM_4), which is an intermediate level between coarse and fine particulate. The choice of this cut-off for dust granulometry is dictated by the international standards of sampling for health effects. Ten additional samples, consisting of filters of previous sampling campaigns promoted and performed by the Local Environmental Agency of Florence were also analysed.

Conventional XAS spectra have been collected at the Fe K-edge (7.112 keV) in Fluorescence mode. All measurements were carried out at room temperature, in order to preserve the filters for further characterisations. The energy calibration, which is a peculiar and critical issue for this experiment, was accomplished by co-analysing a metal Fe foil in chambers before and after the experimental chamber.

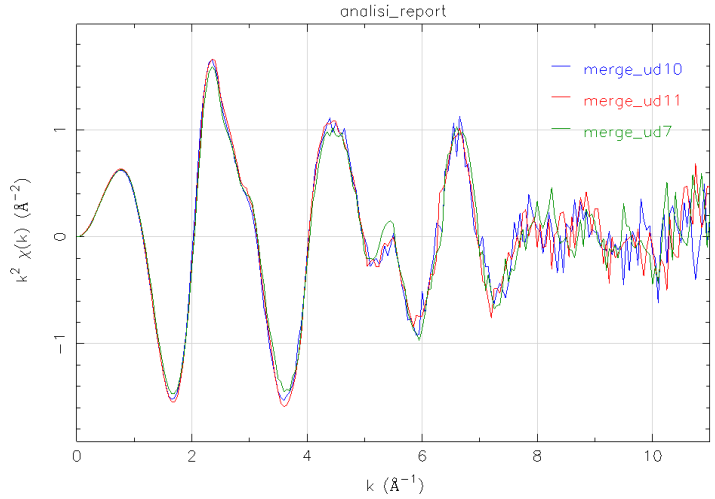
Owing to the limited amount of dusts collected (the total amount of dusts over each filter usually ranges in amounts < 2 mg) and of the even lower amount of total Fe contained in each sample, we performed repeated spectral acquisitions for each sample

Preliminary results

During the assigned beamtime, we were able to successfully investigate all the previously cited samples (20 airborne dust filters). Indeed, we acquired 2-3 scans for each filter. From a preliminary consideration of all the acquired spectra, samples can be divided on two categories:

1) samples with a close similarity in the repeated spectra, generally (but not sistematically) associated to a higher Fe content (estimated from the jump of the Fe K edge in the Fluorescence mode acquisition);
2) samples with a large heterogeneity, where repeated spectra generally show significant differences: this occurs in samples with both diluted and concentrated Fe.

An example of the experimental EXAFS of three samples of the group 1) is shown in the Figure below. An apparent contribution due to multiple coordination shells is present. As already observed for samples coming from occupational sources (**Di Benedetto et al., 2013**), a complex Fe speciation is a usual characteristic of these samples. Further modeling is, of cours, in progress. Samples belonging to group 2) show also spectra were the contribution arising from successive coordination shells is largely depleted if not negligible, thus suggesting a relevant role played by non-crystalline Fe compounds in the airborne dusts.



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