

Fe speciation in industrial quartz reagents: insights from XAS spectroscopy on bulk materials and suspended dusts

Francesco Di Benedetto¹, Fabio Capacci², Francesco D'Acapito³, Gabriele Fornaciai¹, Massimo Innocenti¹, Giordano Montegrossi⁴ and Maurizio Romanelli¹

¹University of Florence, Department of Chemistry, Sesto Fiorentino, Italy

²Health Agency of Florence, Firenze, Italy

³CNR-IOM-OGG, c/o European Synchrotron Radiation Facility, Grenoble, France

⁴IGG-CNR, Firenze, Italy

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.

The present study is aimed to exploit the knowledge about the presence and speciation of Fe in selected industrial samples, and the fate of Fe species in the dusts suspended in air during the industrial processing. Micrometer scale quartz particles can substantially differ from larger size dusts mainly for two reasons: 1) intrinsically, Fe- content and crystal chemistry can be different because at least a mechanical treatment has occurred; and b) extrinsically, chaotic mechanisms of powder transport in air modify mineralogical associations and select specific shapes.

The Fe speciation in the sampled materials has been carried out through X-Ray Absorption Spectroscopy (XAS), which represents probably the unique experimental technique able to provide a definite picture of breathable Fe species, in terms of valence state, chemical neighbourhood (geometry and nature of ligands) and relationships with the host silica crystal.

The EXAFS experimental results point to some specific evidences. Most industrial and reference samples present an occasional and heterogeneous contamination by traces of elemental Fe, which cannot be ascribed to manipulation during the analytical investigation. Trivalent Fe is found mostly partitioned between two types of structures: a more organised one, similar to the crystal structure of hematite, and an amorphous like phase, where cation ordering beyond the first anionic coordination shell is not experimentally observed.

Evolution of the Fe speciation in industrial samples during their processing is also well traced by the information contained in the pre-edge regions, where changes in the most relevant valence state and coordination are experimentally observed. Interestingly, the presence of Fe(II) species is not observed in the studied samples. The experimental changes observed among the bulk samples, and between bulk and suspended dusts are discussed in terms of the differences among the considered production lines (i.e. ceramic production, microcasting of noble metal alloys, casting of iron alloys).