The surface of quartz catalyses the formation of radical species from aminoacids and peptides: a possible implication in silica - related health effects

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The inhalation of quartz dusts causes silicosis, lung cancer and several autoimmune diseases while no adverse effects, so far, have been associated to the inhalation of artificial amorphous silica forms(1). Quartz dusts may elicit different pathogenic responses depending upon their chemical, mechanical and thermal history. This variability is strictly linked to the physicochemical properties and the reactivity of the surface of the quartz particles. The mechanism of action of quartz dusts at the molecular level is still partially obscure, however it is widely accepted that Reactive Oxygen Species (ROS), originated both from phagocytic cells (macrophages and PMN) and directly from the surface of the silica particles, may play a crucial role in the development of inflammation and cell damage (2). The generation of radicals species, particularly $OH^{\bullet}$ radicals, at the surface of quartz is due to the presence of both poorly uncoordinate iron ions, present as trace impurities, and defects on the silica framework which are formed during the grinding processes. The ability of quartz particles to cause DNA damage and lipid peroxidation is well documented (3). Conversely, little is known about the ability of silica to damage proteins and enzymes. In this communication the spin trapping technique (DMPO), applied to suspensions of variously modified quartz dusts, has been employed to investigate the mechanisms of generation of free radicals and the reactivity toward aminoacids and peptides. The reactivity toward glycine, proline and cysteine of several quartz dusts with different reactivity at the surface (aged, freshly ground and heated quartz dusts) has been studied. Quartz dusts reacts with glycine and proline by causing the abstraction of an hydrogen atom. Glycine undergo b-fragmentation by producing $CO_2^{\bullet-}$ radicals following a mechanism previously described by other authors (4). Cysteine, both in the free form or inside the glutathione molecule, is rapidly oxidised at the surface of quartz. Conversely, amorphous silica appear inactive. Ground quartz dusts appear to be more reactive than amorphous silica toward all the aminoacids tested. The reactivity of quartz toward glycine, cysteine and proline may have important implications in the mechanisms of toxicity of silica.

[1] IARC Monographs on the Evaluation of the carcinogenic risk of chemicals to humans, Silica, some silicates, coal dusts para-aramid fibrils, 1997, 68, Lyon, France.
[2] B. Fubini and C. Otero-Arean, Chem. Soc. Rev. 1999, 28, 373-381.
[3] B. Fubini The surface properties of silicas (Legrand J.P. ed) 1998, 5, 415-464, J. Wiley and Sons, Chichesterl, U.K.
[4] M. J. Davies, S. Fu, R. T. Dean Biochem. J. 1995, 305, 643-649.