

tathione with several silica dusts (crystalline and amorphous and variously modified by heating or grinding). The dust have been incubated for different periods of time with controlled solutions of the two antioxidants. The concentrations were kept either close to the physiological ones, in order to mimic what happens *in vivo* or much higher to enhance the chemical effects to be detected. In order to evidence the effect of silica on ascorbic acid and glutathione the concentration of the antioxidants in the solution has been monitored by means of UV-Vis spectroscopy and the adsorption of the solute molecules at the particle surface has been detected by means of UV-Vis diffuse reflectance spectroscopy. Various surface properties taking place as a consequences of contact with antioxidants, have been studied: surface radicals and dangling bonds (Electron Paramagnetic Resonance spectroscopy), potential to release free radicals in solution ("spin trapping" technique), distribution of silanols (SiOH) at the surface and degree of surface hydrophilicity (Infra Red spectroscopy and adsorption calorimetry).

In all cases crystalline dusts were far more reactive than amorphous silicas, each polymorph reacting with antioxidants to a different extent. Freshly ground quartz was the most reactive with both ascorbic acid and glutathione. While ascorbic acid reacts with the quartz surface via different mechanisms (adsorption, partial silica dissolution, ready consumption of surface radicals), glutathione appears to be simply oxidized by contact with freshly ground surfaces.

In both cases however there is evidence that contact with quartz particles and not with amorphous silica may cause depletion in the antioxidant levels of the biological fluids in contact with the particle, hence contributing to the overall oxidative stress.



17 Respirable silica particle occlusion by aluminosilicate: surface properties of dusts with disease risk anomalies

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The respirable quartz component of dusts is being surface-analyzed for sub-micrometer thick aluminosilicate occlusion or coating. This respirable component is being surface-analyzed for dusts with some observed anomaly in disease risk, that is, for silica and silicate dusts whose activity for fibrotic lung disease is not fully predicted by the respirable quartz component. This is to determine whether biological availability of the surfaces of silica particles is a parameter in defining the risk of fibrosis from silica dust exposures. Scanning electron microscopy (SEM)-energy dispersive X-ray analysis is modified by collecting Si and Al X-ray spectra from a particle at high and at low electron beam energies, e.g., 20 keV and 5 keV. Both an analytical mathematical model, using a Beer's law expression for electron beam and X-ray attenuation in the particle, and a more general model using Monte Carlo numerical solution techniques, provide a basis for comparison of the two spectra. This is to infer whether the particle aluminum con-

tent is structured as an aluminosilicate coating on a silica core particle or whether the aluminum is distributed throughout the particle. Fields of particles from a sample are subjected to automated analysis at each of the two electron beam voltages, and the ratio of measured Si and Al X-ray line intensities determined for each particle to infer its surface structure. Respirable dust samples have been analyzed from a clay mine and preparation facility, from low temperature ashed samples of MSHA-sampled respirable coal mine dusts, and from a group of metal mines and pottery works in China. MSHA samples were from mines of differing coal rank from US regions exhibiting the anomalous "coal rank effect" in coal workers pneumoconiosis prevalence. The Chinese dust samples were from metal mines and pottery works in China for which a recent epidemiological study found differences in silicosis risk when normalized for total dust exposure and to calculated respirable silica exposure. Fractions of respirable silica particles evidenced surface occlusion by aluminosilicate sub-micrometer coatings. These were observed by SEM not to be particle aggregates. The fraction of particles with such occlusion generally decreased with coal mine dusts of increasing coal rank, and generally increased for the Chinese pottery dusts versus metal mine dusts. Results suggest that a decreased fraction of aluminosilicate surface-occluded silica particles is associated with increased fibrotic lung disease risk. The surface analysis method employed did not detect trace contamination of particle surfaces such as can be seen by Auger spectroscopy or X-ray photo-electron spectroscopy. The occlusion observed was on the order of 0.01 to 0.1 micrometer thickness. This may represent surface coatings which would persist for extended times for respired particles *in vivo*, suppressing or significantly delaying biological contact with the underlying quartz surface and the consequent onset of fibrogenic processes.

18 Cytotoxic activity of yellow sand (Asian dust storm) with the reference to SiO₂ and TiO₂

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Background: The global effect of the diffusion of Asian dust storm (so called "yellow sand") particles in the atmospheric environment is of large concern in Asia-Pacific region. In spring, the dust-laden air masses are transported across the Asian continent and most people, especially in young and old are concerned about the respiratory health because of the dusty air. Recently, such an atmospheric phenomenon is known to be the cause of the massive damage affecting public health of personnel and facilities. And it becomes a very critical issue to evaluate the hazardous constituents in yellow sand by sampling and analysis of ion concentrations annually.

Objectives: The present study was done to compare the cytotoxicity of dust focusing on yellow sand with the referent toxicity of silica and titanium dioxide.

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