# Silica, Crystalline (Respirable Size)

CAS No.: none assigned

Known to be a human carcinogen

First listed in the *Sixth Annual Report on Carcinogens* (1991)

Also known as crystalline silicon dioxide

## Carcinogenicity

Respirable crystalline silica, primarily quartz dusts occurring in industrial and occupational settings, is *known to be a human carcinogen* based on sufficient evidence of carcinogenicity from studies in humans. Respirable crystalline silica was first listed in the *Sixth Annual Report on Carcinogens* in 1991 as *reasonably anticipated to be a human carcinogen* based on sufficient evidence of carcinogenicity from studies in experimental animals; the listing was revised to *known to be a human carcinogen* in the *Ninth Report on Carcinogens* in 2000.

### *Cancer Studies in Humans*

Exposure of workers to respirable crystalline silica is associated with elevated rates of lung cancer. The link between human lung cancer and exposure to respirable crystalline silica was strongest in studies of quarry and granite workers and workers involved in ceramic, pottery, refractory brick, and diatomaceous earth industries. Human cancer risks are associated with exposure to respirable quartz and cristobalite but not to amorphous silica. The overall relative risk is approximately 1.3 to 1.5, with higher risks found in groups with greater exposure or longer time since first exposure. Silicosis, a marker for exposure to silica dust, is associated with elevated lung cancer rates, with relative risks of 2.0 to 4.0. Elevated risks have been seen in studies that accounted for smoking or asbestos exposure, and confounding by co-exposure is unlikely to explain these results (IARC 1997).

### *Cancer Studies in Experimental Animals*

In rats, exposure to various forms of respirable crystalline silica by inhalation or intratracheal instillation consistently caused lung cancer (adenocarcinoma or squamous-cell carcinoma). Single intrapleural or intraperitoneal injections of various forms of respirable crystalline silica also caused lymphoma in rats (IARC 1997).

### *Studies on Mechanisms of Carcinogenesis*

Respirable crystalline silica deposited in the lungs causes epithelial injury and macrophage activation, leading to inflammatory responses and proliferation of the epithelial and interstitial cells. In humans, respirable crystalline silica persists in the lungs, culminating in the development of chronic silicosis, emphysema, obstructive airway disease, and lymph-node fibrosis. Respirable crystalline silica stimulates (1) release of cytokines and growth factors from macrophages and epithelial cells, (2) release of reactive oxygen and nitrogen intermediates, and (3) oxidative stress in the lungs. All of these pathways contribute to lung disease. Marked and persistent inflammation, specifically inflammatory-cell-derived oxidants, may provide a mechanism by which respirable crystalline silica exposure can result in genetic damage in the lung parenchyma. In one study, human subjects exposed to respirable crystalline silica showed increases in sister chromatid exchange and chromosomal aberrations in peripheral blood lymphocytes. Most cellular genotoxicity studies with quartz gave negative results; however, *in vitro* exposure to some quartz samples caused micronucleus formation or cell transformation in several cell types, including Syrian hamster embryo cells, Chinese hamster lung cells, and human embryonic lung cells (IARC 1997).

## Properties

Silica ($SiO_2$) is a group IV metal oxide that exists as colorless or white trigonal crystals and has a molecular weight of 60.1. It occurs naturally in crystalline and amorphous forms, and the specific gravity and melting point both depend on the crystalline form. The basic structural units of the silica mineral are silicon tetrahedra ($SiO_4$). Slight variations in the orientation of the tetrahedra result in the different polymorphs of silica; crystalline silica has seven polymorphs. In crystalline silica, silicon and oxygen atoms are arranged in definite regular patterns throughout (Parmeggiani 1983).

Quartz, cristobalite, and tridymite are the three most common crystalline forms of free silica (USBM 1992). Quartz is by far the most common; it is found abundantly in most rock types, including granites and quartzites, and in sands and soils. Cristobalite and tridymite are found in volcanic rocks. All three forms are interrelated and may change their form under different temperature and pressure conditions. The structure of quartz is more compact than that of tridymite or cristobalite (IARC 1987, 1997). Quartz melts to a glass, and its coefficient of expansion by heat is the lowest of any known substance. Silica is practically insoluble in water at 20°C and in most acids; but its solubility increases with temperature and pH and is affected by the presence of trace metals. The rate of solubility also is affected by particle size, and the external amorphous layer in quartz is more soluble than the crystalline underlying core. Silica dissolves readily in hydrofluoric acid, producing silicon tetrafluoride gas (Merck 1989, IARC 1997).

## Use

Because of its unique physical and chemical properties, crystalline silica has many uses. Commercially produced silica products include quartzite, tripoli, ganister, chert, and novaculite. Crystalline silica also occurs in nature as agate, amethyst, chalcedony, cristobalite, flint, quartz, tridymite, and, in its most common form, sand (IARC 1997). Naturally occurring silica materials are classified by end use or industry. Sand and gravel are produced almost exclusively for road building and concrete construction, depending on particle size and shape, surface texture, and porosity (IARC 1987).

Silica sand deposits, commonly quartz or derived from quartz, typically have a silica content of 95%; however, impurities may be present at up to 25%. Silica sand has been used for many different purposes over many years. In some instances, grinding of sand or gravel is required, increasing the levels of dust containing respirable crystalline silica. Sand with low iron content and more than 98% silica is used in the manufacture of glass and ceramics. Silica sand also is used in foundry castings, in abrasives (such as sandpaper and grinding and polishing agents), in sandblasting materials, in hydraulic fracturing to increase rock permeability to increase oil and gas recovery, as a raw material for the production of silicon and ferrosilicon metals, and as a filter for large volumes of water, such as in municipal water and sewage treatment plants (IARC 1997).

Extremely fine grades of silica sand products are known as flours. Silica flour, not always labeled as containing crystalline silica and often mislabeled as amorphous silica, is used industrially as abrasive cleaners and inert fillers. Silica flour may be used in toothpaste, scouring powders, metal polishes, paints, rubber, paper, plastics, wood fillers, cements, road surfacing materials, and foundry applications (NIOSH 1981). Cristobalite is a major component of refractory silica bricks; the high temperatures at which the bricks are fired convert the quartz mainly to cristobalite (IARC 1997).

## Production

Silica used in commercial products is obtained mainly from natural sources (IARC 1997). U.S. production of silica sand (industrial sand and gravel combined) was estimated at 28.5 million metric tons (62.7 billion pounds) in 1997 and 27.9 million metric tons (61.4 billion pounds) in 2001 (Dolley 2008). U.S. production of high-purity quartz was 800,000 lb in 1983 (IARC 1987). Natural quartz crystals are no longer mined in the United States. Synthetic quartz crystals (hypothermally cultured quartz crystals) now are used as the raw material for quartz production (Dolley 2009). The precursor material for synthetic quartz crystals is lasca (high-purity quartz dust), which was mined in the United States for many years; however, U.S. mining and processing of lasca ended in 1997. Lasca mining production was estimated at 1 million pounds in 1985 and 600,000 lb in 1988. In 2009, three U.S. firms produced cultured quartz crystals from imported and stockpiled lasca. No data on U.S. imports or exports of quartz crystal (industrial) were reported in 2009, but in 2017, imports of silica sands and quartz sands totalled 1.5 billion pounds, and exports of 10.1 billion pounds indicated that large-scale U.S. production of silica continued (USITC 2018).

## Exposure

Crystalline silica is an abundant and commonly found natural material. Human exposure to respirable crystalline silica, primarily quartz dust, occurs mainly in industrial and occupational settings. Non-occupational exposure to respirable crystalline silica results from natural processes and anthropogenic sources; silica is a common air contaminant. Residents near quarries and sand and gravel operations potentially are exposed to respirable crystalline silica. A major source of cristobalite and tridymite in the United States is volcanic rock in California and Colorado (NIOSH 1986). Local conditions, especially in deserts and areas around recent volcanic eruptions and mine dumps, can give rise to silica-containing dust (IARC 1987).

Consumers may be exposed to respirable crystalline silica from abrasives, sand paper, detergent, grouts, and concrete (IARC 1997). Crystalline silica may also be an unintentional contaminant; for example, diatomaceous earth, used as a filler in reconstituted tobacco sheets, may be converted to cristobalite as it passes through the burning tip of tobacco products (IARC 1987).

Respirable quartz levels exceeding 0.1 mg/m$^3$ are most frequently found in metal, nonmetal, and coal mines and mills, granite quarrying and processing, crushed-stone and related industries, foundries, the ceramics industry, construction, and sandblasting operations (IARC 1997). The National Occupational Hazard Survey (conducted from 1972 to 1974) estimated that 81,221 workers potentially were exposed to quartz (NIOSH 1976). The National Occupational Exposure Survey (conducted from 1981 to 1983) estimated that 944,731 workers, including 112,888 women, potentially were exposed to quartz and that 31,369 workers, including 2,228 women, potentially were exposed to cristobalite (NIOSH 1990). The National Institute for Occupational Safety and Health (NIOSH 2002) estimated that 522,748 workers in nonmining industries and 722,708 workers in mining industries potentially were exposed to respirable crystalline silica in 1986.

Potential exposure to respirable crystalline silica has been studied in metal and nonmetal mining and milling operations. Workers in sandstone, clay, shale, and miscellaneous nonmetallic mineral mills had the highest exposure to silica dust. Within the mills, the workers with the highest exposure were baggers, general laborers, and personnel involved in the crushing, grinding, and sizing operations. Workers in the granite and stone industry and in construction also are potentially exposed to respirable crystalline silica. Potential exposure was highest for sculptors and carvers, stencil cutters, polishers, and sandblasters; for these occupations, the silica content of respirable dust ranged from 4.8% to 12.2%. Concentrations of respirable crystalline silica ranged from 0.01 to 0.20 mg/m$^3$ in clay-pipe factories and from 0 to 0.18 mg/m$^3$ in a plant producing ceramic electronic equipment parts. Silica concentrations of at least twice the permissible exposure limit were found in 10% of 348 air samples collected from glass-manufacturing industries and 23% to 26% of samples from clay-products and pottery industries. One third of samples from fibrous-glass plants had concentrations of respirable crystalline silica in excess of 0.10 mg/m$^3$, and 23% of samples collected in iron and steel foundries had concentrations in excess of 0.20 mg/m$^3$ (IARC 1987). Occupational exposure to cristobalite may occur in industries where silica products are heated, including refractory brick and diatomaceous earth plants and ceramic and pottery manufacturing plants (IARC 1997).

## Regulations

***Mine Safety and Health Administration (MSHA, Dept. of Labor)***

Silica sand or other materials containing more than 1% free silica shall not be used as an abrasive substance in abrasive blasting in underground areas and underground mines.

***Occupational Safety and Health Administration (OSHA, Dept. of Labor))***

While this section accurately identifies OSHA's legally enforceable PELs for this substance in 2018, specific PELs may not reflect the more current studies and may not adequately protect workers.

Permissible exposure limit (PEL) = 50 μg/m$^3$ for respirable crystalline silica (quartz, cristobalite, and tridymite).

Action level = 25 μg/m$^3$ for respirable crystalline silica (quartz, cristobalite, and tridymite).

## Guidelines

***American Conference of Governmental Industrial Hygienists (ACGIH)***

Threshold limit value – time-weighted average (TLV-TWA) = 0.025 mg/m$^3$ (respirable fraction).

***National Institute for Occupational Safety and Health (NIOSH, CDC, HHS)***

Recommended exposure limit (REL) = 0.05 mg/m$^3$.

Immediately dangerous to life and health (IDLH) limit = 25 mg/m$^3$ for cristobalite, tridymite; = 50 mg/m$^3$ for quartz, tripoli.

Listed as a potential occupational carcinogen.

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