Special Publication

CRYSTALLINE SILICA PRIMER

Staff, Branch of Industrial Minerals

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[Illustrations are not available in the PDF version of the Crystalline Silica Primer. Contact Robert Virta at the U.S. Geological Survey for a copy of the complete report with illustrations.]

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ABSTRACT

Crystalline silica is the scientific name for a group of minerals composed of silicon and oxygen. The term crystalline refers to the fact that the oxygen and silicon atoms are arranged in a threedimensional repeating pattern. This group of minerals has shaped human history since the beginning of civilization. From the sand used for making glass to the piezoelectric quartz crystals used in advanced communication systems, crystalline silica has been a part of our technological development. Crystalline silica's pervasiveness in our technology is matched only by its abundance in nature. It's found in samples from every geologic era and from every location around the globe.

Scientists have known for decades that prolonged and excessive exposure to crystalline silica dust in mining environments can cause silicosis, a noncancerous lung disease. During the 1980's, studies were conducted that suggested that crystalline silica also was a carcinogen. As a result of these findings, crystalline silica has been regulated under the Occupational Safety and Health Administration's (OSHA) Hazard Communication Standard (HCS). Under HCS, OSHA-regulated businesses that use materials containing 0.1% or more crystalline silica must follow Federal guidelines concerning hazard communication and worker training. Although the HCS does not require that samples be analyzed for crystalline silica, mineral suppliers or OSHA-regulated businesses may choose to do so if they wish to show that they are exempt from the requirements of HCS.

Because crystalline silica is an extremely common mineral and the HCS will affect many mineral commodities, it is important then, that there be as clear an understanding as possible of what is and what is not crystalline silica, and where it is found and used, and how it is qualitatively and quantitatively identified. This primer is an attempt to accomplish this in as nontechnical a manner as possible. This primer will examine crystalline silica. Part I will describe, in nonscientific terms, what crystalline silica is and how we come in contact with it. Part II will discuss the regulatory decisions that have created new interest in this ancient and widespread substance and will present a nontechnical overview of the techniques used to measure crystalline silica. Because this primer is meant to be a starting point for anyone interested in learning more about crystalline silica, a list of selected readings and other resources is included. The detailed glossary, which defines many terms that are beyond the scope of this publication, is designed to help the reader move from this presentation to a more technical one, the inevitable next step.

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PART I.

UNDERSTANDING CRYSTALLINE SILICA

Crystalline silica is an indispensable part of both the natural and the technological worlds. We all come in contact with it daily and have all our lives. It has been called one of the building blocks of our planet. Although it is a mainstay of modern technology, it is neither modern nor manufactured. It was known to the ancients, and its uses are still being expanded today.

What Is Silica?

Other substances whose names sound similar—silicon, silicone, and silicates—are sometimes confused with silica. The terms may sound alike, but each means something quite distinct. Knowing the differences among these four substances is crucial to understanding what crystalline silica is and, perhaps just as important, what it is not.

Silicon Is an Element

All matter in the universe is formed from the 107 or so chemical elements known to exist. A chemical element is the simplest form of matter, a fundamental substance that consists of only one kind of atom. Silicon is the second most common element in the Earth's crust, second only to oxygen, and together silicon and oxygen make up approximately 75% of the Earth on which we live and from which we get all that we use in our daily lives.

Strictly speaking, silicon (whose chemical symbol is Si) is classified as a nonmetal, but it possesses some of the properties associated with metals. There are eight elements, in fact, that fall on the borderline between metals and nonmetals. Some scientists refer to these as *metalloids*. One property associated with metals, for example, is their ability to conduct electricity. Silicon's electronic capabilities are unusual: At high temperatures, it acts like a metal and conducts electricity, but at low temperatures, it acts like an insulator and does not. It is said to be a *semiconductor*. This unusual property made silicon the perfect element to move technology first into the world of transistors, then into the world of integrated circuits, and finally into the world of today's computer chip.

Silicon is the backbone of the computer chip. The pure silicon needed for this use, however, does not exist in nature; it is formed from silica sand. Thin slices of pure silicon are then etched with the intricate electronic circuits needed to run the computer.

Silica Is Chemical Compound

The compound silica (SiO_2) is formed from silicon and oxygen atoms. A chemical compound is defined as a distinct and pure substance formed by the union of two or more elements. Because oxygen is the most abundant element in the Earth's crust and silicon is the second most abundant, the formation of silica is quite common in nature. The silica sand, just mentioned as the substance used to derive pure silicon, is made of quartz, which is the most common form of silica found in nature.

Silica can also be biological in origin, produced by tiny organisms. The most significant of these are *diatoms* (plants) and *radiolarians* (animals), both of which extract silica from the water around them to form their structures or shells. For both organisms, silica is a nutrient they must have to survive. In nature, they use the dissolved silica that originates from sedimentary rocks at the bottom of a lake, river, or ocean. When diatoms grown in the laboratory extract all the available silica from the aquarium water, they attach themselves to the walls of the aquarium and use the small amounts of dissolved silica etched from the glass itself. In nature, when diatoms and radiolarians die, they sink to the bottom of the water and accumulate into sediment, which can become hardened into diatomite and radiolarite. Diatomite is a commercially useful rock. It's highly porous and, thus, is effective for filtering as well as for use as filler and as a mild abrasive.

Thus, silica can be found in more than one state—*amorphous* as in the remains from a diatom and crystalline as in a quartz crystal, as we shall explain later. Both are SiO_2 , but they are quite different physically. What's more, silica in its *crystalline state* is found in more than one form. This phenomenon is *called polymorphism* (literally "many forms").

Silicates Are Compounds Of Silicon and Oxygen Plus Other Elements

When silicon and oxygen bond with other elements, they do so in a paired formation. Scientists call this pairing the *silicon-oxygen* (SiO_4) *tetrahedron* because it is made of four oxygen atoms and one silicon atom. *Tetrahedron* means "four surfaces" and refers to the shape of the SiO_4 compound. The silicon-oxygen tetrahedron bonds most frequently with sodium, potassium, calcium, magnesium, iron, and aluminum to form silicates.

Silicates constitute the most abundant class of minerals. Geologists regard silicate minerals as the basic materials out of which most rocks are created.

Silicones Are Synthetic Compounds

Silicones are *polymers*, a type of synthetic compound. Developed commercially during World War II, silicones are formed from two or more silicon atoms linked with carbon compounds (referred to as *organic compounds*). Most silicones contain oxygen as well. Unlike what happens when silica and silicates form, in silicone, the silicon and oxygen do not take the tetrahedral shape but instead form chain-like structures called *silicon polymers*. Polymerization is a chemical reaction in which small organic molecules combine to form larger molecules that contain repeating structural units of the original molecules.

Silicones can range from liquids (used as water repellents and defoamers) to greases and waxes (used as water- and heat-resistant lubricants) to resins and solids (used to make special heat- and chemical-resistant products including paints, rubbers, and plastic parts). Probably silicone's most highly publicized use is in the manufacture of breast implants.

What Is Meant by Crystalline?

We mentioned that the compound silica, which is formed by the chemical reaction of silicon

and oxygen, can be either crystalline or noncrystalline. Depending upon the extremes of temperature and pressure it has been subjected to or, in some cases, the speed at which it cooled, a solid can take on different forms. Diatomite, described earlier, and quartz are identical chemically (*both* SiO_2) and both are solids at room temperature, but their physical forms-and their internal structures-are very different.

The Crystalline State

In a crystalline substance (such as quartz), the atoms and molecules make up a threedimensional repeating pattern. The pattern unit is repeated indefinitely in three directions, forming the crystalline structure. This is similar to floor tiles, in which a two-dimensional pattern unit, say one made of two black tiles and four white tiles, is repeated indefinitely in two directions. This repeating pattern can be altered. It would be possible to change the positions of the two black tiles and four white tiles in relationship to one another and still have a pattern that could be repeated indefinitely in two directions, but the resulting design would be different. Likewise, the internal structure of the crystal can be changed and the resulting crystalline substance would be changed.

The Noncrystalline State

Now, picture the black tiles and white tiles, still in the same relative proportions of two to four, randomly placed on the floor, forming no pattern whatsoever. Such is the structure of a noncrystalline, or amorphous, substance. A diatom is an example of silica in a noncrystalline state.

Some amorphous materials exhibit short-range ordering of their atoms. Using the analogy of the floor tiles one last time, suppose the two black tiles and four white tiles formed a pattern, and it was a pattern governed by some sort of rule, but it was not a *repeating* pattern. The distinguishing feature of a crystalline substance is that you can take any portion of it and see the whole. With a nonrepeating pattern, you can't do that. Some short-range orderliness may exist, but no predictable order extends over a long distance.

Scientists call this state glassy. Not surprisingly, window glass, which forms when molten glass is quenched, is an example of silica in a glassy state. It is not crystalline because it cooled too rapidly for the atoms to arrange themselves into a long-range periodic structure, but it contains short-range ordering that many amorphous materials do not possess. Glassy and amorphous materials are considered to be synonymous by many scientists because both are noncrystalline.

Focusing on Crystalline Silica

We have discussed four terms that are often confused—silicon, silica, silicates, and silicone, and we have narrowed our discussion to silica, the compound formed from the elements of silicon and oxygen.

We have seen how silica can be crystalline or noncrystalline This primer's focus is on silica in

its crystalline state only.

Crystalline Silica's Forms

Crystalline silica exists in seven different forms or polymorphs, four of which are extremely rare. The three major forms, quartz, cristobalite, and tridymite, are stable at different temperatures. Within the three major forms, there are subdivisions. Geologists distinguish, for example, between alpha and beta quartz, noting that at 573 °C, quartz changes from one form to the other. Each of these subdivisions is stable under different thermal conditions. Foundry processes, the burning of waste materials, and other manufacturing procedures can create the kinds of conditions necessary for quartz to change form. In nature, quartz in its alpha, or low, form is most common, although both lightning strikes and meteorite impacts can change alpha quartz into keatite or coesite. Alpha quartz is abundant, found on every continent in large quantities. In fact, alpha quartz is so abundant and the other polymorphs of crystalline silica are so rare, some writers use the specific term quartz in place of the more general term *crystalline silica*.

Where Crystalline Silica Is Found

Crystalline silica, usually in the form of alpha quartz, is everywhere. It is in every part of every continent. It occurs plentifully in nature and is used commonly in industry.

The Natural Occurrence of Crystalline Silica

All soils contain at least trace amounts of crystalline silica in the form of quartz. It may have been part of the rock that weathered to form the soil, it may have been transported, or it may have crystallized from an amorphous (*that is, a noncrystalline*) silica that formed during the weathering process. Quartz is also the major component of sand and of dust in the air. Quartz is present in igneous rocks-but only those that contain excess silica. As magma cools, olivine, pyroxenes, amphiboles, feldspars, and micas form first. These minerals (*all silicates*) need silica to form, because silicates are made from silicon, oxygen, and a metal, usually one of the six most common metals. Quartz forms only if sufficient silicon and oxygen are left over after these silicates have formed. Nature's odds are stacked in quartz's favor, however. The fact that quartz is the second most common mineral in the world (*feldspar is most common*) indicates that plenty of silicon and oxygen were left over during the cooling process to allow ample quantities of quartz to form. In fact, the average quartz content of igneous rocks is 12%.

In geologic history, igneous rocks originated from magma, the material carried to the surface from the Earth's molten core. The other two types of rocks are sedimentary and metamorphic. Quartz is abundant in all three types of rock. It is one of Earth's primary building blocks.

The *rock cycle* describes the relationship between the three types of rock. Igneous rocks reflect activity (*heat and pressure*) beneath Earth's crust; metamorphic rocks reflect activity both beneath the crust and within and at the surface; and sedimentary rocks reflect conditions (*wind, water, and ice*) at the Earth's surface. Over geologic time, sedimentary rocks maybe altered by

heat and/or pressure to create metamorphic or igneous rocks. All rocks may be eroded to make sediments that, in turn, harden (*lithify*) into sedimentary rocks. Thus, the history of the Earth's crust, the lithosphere, is one of continuous change. During these changes, quartz endures. It is one of Earth's harder minerals, so it resists erosion, and it is soluble in very few chemicals, so it is seldom dissolved.

In Igneous Rocks. Crystalline silica is present in igneous rocks that contain excess silica. It is a common component of granite, rhyolite, quartz diorite, quartz monzonite, and andesite, to name a few. Crystalline silica as quartz also may be present in deposits of hardened, or *consolidated*, volcanic ash, known as *volcanic tuffs.* When magma spews from a volcano, it drops in temperature so rapidly that the ash is usually glassy, a noncrystalline state. The 1980 eruption of Mount St. Helens is a perfect example of this process. If the silica crystallizes before the molten rock leaves the volcano then the quartz is imbedded in a glassy matrix.

Volcanic glasses do crystallize over time, so a complex mixture of finely crystalline quartz and silicates eventually replaces the volcanic glass. Cristobalite and tridymite, the rarer forms of cystalline silica, may also be present in *volcanic tuffs*.

In Sedimentary Rocks. Crystalline silica in the form of quartz is an extremely common component of sedimentary rocks. Sedimentary rocks form when minerals released during weathering or by chemical precipitation accumulate in a basin and are consolidated. Quartz, which is extremely resistant to physical and chemical breakdown by the weathering process, stays intact chemically even when fragmented and dispersed by erosion, wind, or other weathering processes. Quartz is present in a variety of sedimentary rock types, ranging from sandstones to conglomerates, in trace to major amounts.

In Metamorphic Rocks. Metamorphic rocks, which form through heat or pressure, also contain crystalline silica as quartz. New textures may be created in the rock (for example, lineations or increased crystal sizes), and new minerals may be formed during metamorphism. Quartz may be present in the original rock, it may crystallize from silica-bearing fluids that entered the rock during metamorphism, or it may form as part of the metamorphic transformation.

Crystalline Silica in the Industrial Setting

Because of its abundance in the earth, silica, in both its crystalline and noncrystalline states, is present in nearly all mining operations. It is in the host rock, in the ore being mined, as well as in what geologists call the overburden, the soil and surface material above the bedrock. Most ores are mined from deposits containing crystalline silica. The mineralogy of the deposit and, to some extent, the processing of the ore determine the quartz content of the final product. Sand and gravel consist mostly of quartz, where as the quartz content of crushed stone will vary from region to region. Table 1 lists some common commodities, the form of silica they contain, and their commercial uses.

The Many Uses of Crystalline Silica

Crystalline silica, again primarily in the form of quartz, has been mined for thousands of years. in the first century A.D., the Roman scholar Pliny described in some detail, although his

understanding was limited by the technology of his time. The ancients believed quartz to be very deep-frozen ice, which could no longer be remelted. In fact, to prove this hypothesis, Pliny pointed out that quartz seemed to be found most frequently in the vicinity of glaciers. Although they may not have understood its true nature, early civilizations did understand its value as a gemstone. Today, quartz is used for a whole spectrum of products (Table 2) from high-technology applications in the electronics and optical fields to everyday uses in building and construction.

In Glass, Ceramic, and Fine China Manufacturing

One of the major uses of crystalline silica is as a raw material for glass manufacture. The first glass was probably made in Egypt more than 5,000 years ago. Today, the process has become highly refined. To ensure a very pure product, the specifications for glass are exceptionally stringent. A pure crystalline silica is used; the iron content must be less than 0.03%, and there are strict limits on the amounts of other impurities. Even the grain size of the crystals is specified. In the finished glass, the silica content must be at least 98.5%. Ceramics, porcelain, and fine china are made from finely ground crystalline silica, called *silica flour*.

In Construction

Building materials, such as concrete and dimension stone (sandstone, granite, and limestone are examples) contain crystalline silica in the form of quartz. Dimension stone is commonly used to build churches, government buildings, and monuments. In the Nation's capital, for example, the White House is built of sandstone, the Smithsonian Institution's original building of sandstone, the exterior of the Museum of Natural History of granite, and the Treasury building of granite and sandstone. Quartz is a component of cement, another technological development dating from ancient times. In the past, sandpaper and grinding wheels were made from quartz, and it was the primary abrasive used in sandblasting operations.

Quartz is also used as functional filler in plastics, rubber, and paint. In George Washington's time, it was the fashion to add sand to paint. Thus, the wooden exterior of Mount Vernon, Washington's home in Virginia, was painted with a sand-paint mixture to give it the look of stone.

Commodity	Form of Silica in the Deposit	Major Commercial Applications
Antimony	Quartz	Flame retardants, batteries, ceramics, glass, alloys
Bauxite	Quartz	Aluminum production, refractories, abrasives
Beryllium	Quartz	Electronic applications
Cadmium	Quartz, jasper, opal, agate, chalcedony	Batteries, coatings and platings, pigments, plastics, alloys
Cement	None	Concrete (quartz in concrete mix)
Clay	Quartz, cristobalite	Paper, ceramics, paint, refractories
Copper	Quartz	Electrical conduction, plumbing, machinery
Crushed stone	Quartz	Construction
Diatomite	Quartz, amorphous silica	Filtration aids
Dimension stone	Quartz	Building facings
Feldspar	Ouartz	Glass, ceramics, filler material
Fluorspar	Quartz	Acids, steel making flux, glass, enamel, weld rod coatings
Garnet	Quartz	Abrasives, filtration, gem stone
Germanium	Quartz, jasper, opal, agate. chalcedony	Infrared optics, fiber optics, semiconductors
Gold	Quartz, chert	Jewelry, dental, industrial, monetary
Gypsum	Quartz	Gypsum board (prefabricated building product), industrial and building plaster
Industrial sand	Quartz	Glass, foundry sand
Iron ore	Chert, quartz	Iron and steel industry
Iron oxide pigment	Chert, quartz, amorphous	Construction materials, paint, coatings
(natural)	silica	
Lithium	Quartz	Ceramics, glass, aluminum production

Table 1.—Silica In Commodities And End-Product Applications

Magnesite Mercury Mica Perlite Phosphate rock	Quartz Quartz Quartz Amorphous silica, quartz Quartz, chert	Refractories Chlorine and caustic soda manufacture, batteries Joint cement, paint, roofing Building construction products Fertilizers	
Pumice	Volcanic glass, quartz	Concrete aggregate, building block	
Pyrophyllite	Quartz	Ceramics, refractories	
Sand and gravel	Quartz	Construction	
Selenium	Quartz	Photocopiers, glass manufacturing, pigments	
Silicon	Quartz	Silicon and ferrosilicon for ferrous foundry and steel industry; computers; photoelectric cells	
Silver	Quartz, chert	Photographic material, electrical and electronic products	
Talc	Quartz	Ceramics, paint, plastics, paper	
Tellerium	Quartz	Steel and copper alloys, rubber compounding, electronics	
Thallium	Quartz, jasper, opal, agate, chalcedony	Electronics, superconductors, glass alloys	
Titanium	Quartz	Pigments for paint, paper, plastics, metal for aircraft, chemical processing equipment	
Tungsten	Quartz	Cemented carbides for metal machining and wear-resistant components	
Vanadium	Quartz, amorphous silica	Alloying element in iron, steel, and titanium	
Zinc	Quartz, jasper, opal,	Galvanizing, zinc-based alloys, chemicals, agriculture agate, chalcedony	
Zircon	Quartz	Ceramics, refractories, zirconia production	

Table 1.—Silica In Commodities And End-Product Applications (cont'd.)

Table 2.—Common products containing 0.1% or more crystalline silica			
At Work	At Home	Everywhere	
(in the process of manufacturing or using the following items)	(as a consumer of the following items)	(exposure could be on the job or at home)	
Asphalt filler-is usually composed of quartz and stone aggregate.	Art clays and glazes-contain clay, and sometimes crystalline silica.	Caulk and putty-contain clay, which can have a low to moderate crystalline silica content, as a filler.	
Bricks-have a high concentration of sand. Contains quartz and possibly cristobalite.	Cleansers-contain pumice and feldspar as abrasives.	Dust-(whether household or industrial) contains crystalline silica.	
Concrete-like asphalt filler, contains stone aggregate.	Pet litter-is composed priarily of clay.	Fill dirt and topsoil-contain sand. Because the crystalline silica content of common soil is so high,	
Jeweler's rouge-contains cryptocrystalline silica.	Talcum powder-contains talc.	group most at risk for exposure to respirable crystalline silica.	
Jewelry and crystals-amethyst and quartz are crystalline silica.	Unwashed root vegetables-(such as potatoes and carrots) are coated with soil, which has a high crystalline silica content.	Foam in furniture and on rug backings-contain talc and silica.	
Mortar-contains sand.	Pharmaceuticals_contain clavs and tale as filler	Paint-contains clay, tale, sand, and diatomite	
Municipal water filter beds-are constructed from	Often the dosage of active ingredient in a medication	i ant contains enty, tale, said, and diatonne.	
both sand (crystalline silica) and diatomite (amorphous silica).	is so minute that filler (listed as an inert ingredient) must be added to make the substance manageable to take.		
Plaster-is made from gypsum but sometimes			
contains silica.	Sand-is crystalline silica. Beach sand, play sand for sandboxes, and the sand used on golf courses are no		
Plastic in appliaces-can contain clay, talc, crushed limestone, and silica as fillers.	different than industrial sand used for construction, in sandblasting, or on icy roads. All are largely crystalline silica.		
Rofing granules-are made from sand and aggregate.			
Wallboard-is made from gypsum.			

In Heavy Industry

Foundry molds and cores for the production of metal castings are made from quartz sand. The manufacture of high-temperature silica brick for use in the linings of glass- and steel-melting furnaces represents another common use of crystalline silica in industry. The oil and gas industry uses crystalline silica to break up rock in wells. The operator pumps a water-sand mixture, under pressure, into the rock formations to fracture them so that oil and gas may be easily brought to the surface. More than 1 million tons of quartz sand were used annually for this purpose during the 1970's and early 1980's when oil-well drilling was at its peak.

Quartz sand is also used for filtering sediment and bacteria from water supplies and in sewage treat ment. Although this use of crystalline silica has increased in recent years, it still represents a small proportion of the total use.

High-Tech Applications

Historically, crystalline silica, as quartz, has been a material of strategic importance. During World War II, communications components in telephones and mobile military radios were made from quartz. With today's emphasis on military command, control, and communications surveillance and with modern advances in sophisticated electronic systems, quartz-crystal devices are in even greater demand.

In the field of optics, quartz meets many needs. It has certain optical properties that permit its use in polarized laser beams. The field of laser optics uses quartz as windows, prisms, optical filters, and timing devices. Smaller portions of high-quality quartz crystals are used for prisms and lenses in optical instruments. Scientists are experimenting with quartz bars to focus sunlight in solar-power applications.

Quartz crystals possess a unique property called *piezoelectricity*. A piezoelectric crystal converts mechanical pressure into electricity and vice versa. When a quartz crystal is cut at an exact angle to its axis, pressure on it generates a minute electrical charge, and likewise, an electrical charge applied to quartz causes it to vibrate more than 30,000 times per second in some applications.

Piezoelectric quartz crystals are used to make electronic oscillators, which provide accurate frequency control for radio transmitters and radio-frequency telephone circuits. Incoming signals of interfering frequencies can be filtered out by piezoelectric crystals. Piezoelectric crystals are also used for quartz watches and other time-keeping devices.

Synthetic Crystalline Silica

Today, industry does not depend entirely on natural quartz for strategic applications. Since the 1940's, well-established techniques for synthetically growing quartz have been used and refined. Synthetic quartz crystals are grown in heavy-duty pressure cookers called *autoclaves* under pressures ranging from 1,500 to 20,000 pounds per square inch and at temperatures of 250° to 450° C.

Natural crystalline silica may contain impurities or be flawed in some way, but synthetic crystals can be flawless. They can also be made to grow in a particular shape and size for specific needs.

Part II.

THE REGULATION OF CRYSTALLINE SILICA

It has been estimated that over 3 million workers in the United States are exposed to silica dust in their occupations. Because of this contact there has been much interest in how exposure to crystalline silica affects one's health.

Scientists have known for decades that prolonged and excessive exposure to crystalline silica dust causes silicosis, a noncancerous lung disease. This was most dramatically demonstrated by the significant increase in reported silicosis cases following the invention of the pneumatic hammer drill in 1897, the introduction of sand blasting in 1904, and the undertaking of a major tunneling project in the mid 1930s through a ridge of nearly pure quartz. These events helped spawn dust-control standards which have continued to evolve through the years.

During the 1980's, studies were conducted that suggested that crystalline silica also was a carcinogen. In 1987, the International Agency for Research on Cancer (IARC), an agency of the World Health Organization, evaluated the available medical literature on silica. Based on this evidence, IARC concluded that crystalline silica (but not noncrystalline, or amorphous, silica) was a *2A substance*, a probable carcinogen for humans.

These findings have attracted attention for several reasons. With the publication of the first study suggesting that crystalline silica was a carcinogen, crystalline silica became regulated under HCS as a carcinogen. Under HCS, OSHA-regulated businesses that use materials containing 0.1% or more crystalline silica must follow Federal guidelines concerning hazard communication and worker training under HCS. While the IARC finding did not trigger any Federal regulations, the work of that organization is important because it has captured the attention of the mining industry.

The following sections discuss OSHA's HCS and the IARC evaluation process.

OSHA's Hazard Communication Standard

In the development of the HCS, OSHA realized that the task before it was herculean: to evaluate all the substances to which workers are exposed, as many as 650,000 of which were potentially hazardous. In addition, OSHA's rule-making process, once a substance had been determined to be hazardous, was time-consuming. OSHA decided that little information about hazards and protective measures would be made available to employees if the substance-by-substance approach to analysis and regulation were the only one pursued. The Agency decided to adopt a generic approach, and promulgated the HCS, which requires container labeling, material safety data sheets, and training. Specifically, HCS has the following requirements:

Chemical manufacturers and importers—must determine the hazards of the product. The regulation states that "if a mixture has been tested as a whole to determine its hazards, the results of such testing shall be used to determine whether the mixture is hazardous. If a mixture has not been tested as a whole to determine whether the mixture is a health hazard, the mixture shall be assumed to present the same health hazards as do the components that comprise 1% (by weight or volume) or greater of the mixture, except that the mixture shall be

assumed to present a carcinogenic hazard if it contains a component in concentrations of 0.1% or greater which is considered to be a carcinogen under paragraph (d)(4) of this section."

Chemical manufacturers, importers, and distributors—must communicate the hazard information and associated protective measures to customers through the use of labels and "material safety data sheets."

Employers—must (1) identify and list hazardous chemicals in their workplaces; (2) obtain material safety data sheets and labels for each hazardous chemical; (3) develop and implement a written hazard communication program, including labels, material safety data sheets, and employee training; and (4) communicate hazard information to their employees through labels, material safety data sheets, and formal training programs.

Coverage of mixtures is based on the amount of the hazardous or carcinogenic material present. A mixture is considered to represent the same health hazard as any hazardous component present in concentrations of 1% or greater (by weight or volume) or any carcinogenic component present in concentrations of 0.1% or greater. Suppliers are held responsible for determining whether a substance is covered, including whether the quantity of the hazardous chemical in a mixture exceeds these cut-offs. Testing is not required; the employer may assume that if the hazardous chemical is present, the mixture is covered. The employer must label all hazardous chemicals, in accordance with the HCS, provide material safety data sheets, and train exposed workers.

To help ensure that hazard evaluations by different suppliers would be consistent, OSHA refers to a number of existing documents as providing definitive findings of hazard. These include IARC and the National Toxicology Program carcinogenicity reviews. In addition, hazardous and carcinogenic chemicals listed in the Code of Federal Regulations (29 CFR 191 0, Subpart Z, *Toxic and Hazardous Substances*, OSHA) and in *Threshold Limit Values for Chemical Substances and Physical Agents in Work Environment* (American Conference of Governmental Industrial Hygienists) are covered under HCS. However, one properly conducted scientific study in the literature establishes a hazard for purposes of the HCS.

The IARC Evaluation Process

The International Agency for Research on Cancer, headquartered in Lyon, France, began its program to evaluate chemicals and cancer risks in 1967. It holds working group meetings in Lyon, usually 1 week long each, about three times a year. Each group focuses on a chemical or group of chemicals. Recently,other areas of study, such as radiation and viruses, have been included in addition to chemicals. Topics for study are selected on the basis of two criteria: there is both evidence of human exposure and some evidence or suspicion of carcinogenicity.

IARC assigns an expert on the chemical to survey the scientific literature, review toxicology studies, and summarize the results. Assignments to subject-matter experts are usually made 1 year in advance of the working group meetings. During the week-long meeting, the working group breaks into two subgroups: chemistry and toxicology. These subgroups examine the validity of the materials supplied by the assigned experts. The two subgroups also agree on terminology and any special definitions required. At the end of the week, the two subgroups

come together for a plenary session; the monographs are issued from the plenary session. If significant new data become available after a monograph has been published, the chemical will be reevaluated at a subsequent meeting, and a revised monograph may be published.

IARC does not commission any health studies or replicate any studies it uses nor does it control the literature reviewed by the experts for its monograph assignments although research may be sponsored by other IARC groups. The choice of studies to be included in the monograph is at the descretion of the expert panel.

Chemicals Studied are Classified into Four Categories

Group 1.—The agent is carcinogenic to humans. This classification is reserved for those substances for which sufficient evidence of carcinogenity in humans has been found. *Sufficient evidence in humans* is defined by IARC to mean a causal relationship between exposure to the agent and the development of human cancer.

Group 2.—This group is divided into two subgroups: probably carcinogenic and possibly carcinogenic.

Group 2A.—The agent is probably carcinogenic to humans. This classification is applied when studies demonstrate that there is limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals. *Limited evidence in humans* is defined by IARC as evidence that shows some association between exposure to the agent and the development of cancer. The evidence is considered limited, however, because even though the two positives may be credible, chance, bias, or confounding factors cannot be ruled out. IARC defines *sufficient evidence in experimental animals* as documentation of a causal relationship based on the results from studies involving two or more species of animals or from two or more independent studies in one species carried out at different times or in different laboratories. In its Supplement 7 to *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, IARC states, "in the absence of adequate data on humans, it is biologically plausible and prudent to regard agents for which there is *sufficient evidence of* carcinogenicity in experimental animals as if they presented a carcinogenic risk to humans" (p. 30).

Group 2B.—The agent is possibly carcinogenic to humans. When there is limited evidence in humans, but an absence of sufficient evidence in experimental animals, the chemical is classified as 2B.

Group 3.—The agent is not classifiable as to its carcinogenicity to humans. When studies do not provide sufficient data to classify a chemical into any of the other categories, IARC assigns it to group 3.

Group 4.—The agent is probably not carcinogenic to humans. IARC reserves this category for chemicals for which evidence from both human and experimental animal studies suggests a lack of carcinogenicity.

IARC Classification of Silica

IARC Monograph 42 (1987) evaluates silica as follows:

There is sufficient evidence for the carcinogenicity of crystalline silica to experimental animals. There is *inadequate evidence* for the carcinogenicity of amorphous silica to experimental animals. There is *limited evidence* for the carcinogenicity of crystalline silica to humans. There is *inadequate evidence* for the carcinogenicity of amorphous silica to humans (p.11). Thus, when the working group reviewed the medical and scientific literature submitted to it for study, it found that there was evidence of an increased incidence of malignant tumors in animals exposed to crystalline silica. The working group also found a causal relationship in humans, although other confounding factors could not be excluded. These are the criteria required by IARC to classifying crystalline silica as a 2A substance.

It is important to note that not all the studies IARC examined show a link between exposure to silica and cancer. One important group of studies, cited in IARC's list of references, is compiled in *Silica, Silicosis, and Cancer: Controversy in Occupational Medicine* (1986), edited by David F. Goldsmith, Deborah M. Winn, and Carl M. Shy. Conclusions from several of the studies point to the controversy referred to in the volume's title:

"Regulation of silica on the basis of potential carcinogenicity is premature" (p. 477). I.T.T. Higgins, "Is the Current Silica Standard Adequate?"

"The present epidemiological and experimental data do not permit the conclusion that exposure to crystalline or amorphous SiO_2 is associated with increased risk of lung cancer": (p. 491). E. Mastromatteo, "Silica, Silicosis, and Cancer: A Viewpoint from a Physician Employed in Industry"

"In reviewing the information we have on the health hazards of silica exposure, we find we have received positive and negative findings on the issue of silica and cancer, and our staff have told us a lot about interactions. They have told us that they are not certain it is silica alone that may be causing cancer" (p. 529). M. Schneiderman and D. M. Winn, "Where Are We with the SiO_2 and Cancer Issue?"

This section provides an update on IARC activities concerning crystalline silica since the 1992 publication of the Crystalline Silica Primer.

Amended IARC evaluation of crystalline silica as a carcinogen (1996)

In October 1996, an IARC panel met to evaluate the carcinogenicity to humans from exposure to crystalline silica. The panel concluded that crystalline silica inhaled in the form of quartz or cristobalite from occupational sources should be classified as carcinogenic to humans (Group 1). The change in classification was based on "a relatively large number of epidemiological studies that together provided sufficient evidence in humans for the carcinogenicity of inhaled crystalline silica under the conditions specified." The panel found many cases of elevated lung cancer risk not explained by confounding factors. Rodent carcinogenicity studies supported the human evidence. The panel also found that "evidence that amorphous silica is a carcinogenic risk factor was considered to be inadequate upon grounds of both epidemiology and experimental studies. Amorphous silica was not classifiable as to its carcinogenicity to humans (Group 3)." The results of the IARC study are published in *Silica, Some Silicates, Coal dust and para-Aramid Fibrils* in *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans,(Vol. 68).*

Regulatory Activities of Other Agencies

MSHA and State legislators also are becoming involved in the silica controversy. MSHA has proposed an HCS similar to OSHA'S. The proposal is still under review following a public comment period. MSHA's proposal also would use the results of IARC, NTP, and OSHA studies to determine which materials were carcinogenic. The enactment of such a regulation would affect nearly all mines because most ores are extracted from silica-bearing rock types. California passed the Safe Drinking Water and Toxic Enforcement Act of 1986 that includes crystalline silicaof respirable size on its list of carcinogens. California's Air Toxic Hot Spots Act and Air Quality Act have the potential to restrict the emissions of crystalline silica. There is concern that burning of rice hulls and straw after harvesting generates an ash that usually contains residual biogenic silica. These regulations would have an adverse effect of the economics of these crops.

The Complexities of Measurement

Crystalline silica is a very common material. It is present in a most mineral operations, many of which sell crude or processed materials to OSHA-regulated sites. Sampling at factories, construction sites, or even the mine site will be greatly increased if a mineral supplier or OSHA-regulated employer wishes to prove that the concentration of crystalline silica is less than 0.1% for carcinogens, thereby exempting the company from the requirements of HCS.

Because crystalline silica is a common mineral, it is assumed that it is easy to measure. Unfortunately that isn't always the case. Determining whether a particular *state* of silica is present and how much of that state a sample contains, however, can be a much more complicated problem. Under certain conditions, current techniques and equipment can't distinguish very well between its physical states at the low concentration level specified by HCS. Analysis can be difficult or even impossible for some samples. From an analyst's point of view, the problem is mainly one of equipment sensitivity.

In short, these are the problems analysts face when trying to pinpoint, so precisely, the crystalline silica content of a sample:

Variability.—The crystallinity of silica from different deposits, even from slightly different locations within the same deposits is not necessarily the same. This raises two problems. First, a single standard (that is, the reference material to which the silica in the sample is compared) may not be appropriate. Using a standard that matches the particle size and crystallinity of the silica in the sample is essential for an accurate analysis. Second, obtaining a representative sample, when the sample size is so small and the deposit is so large, is nearly impossible.

Presence of other minerals.—Nearly all samples contain more than just silica. Some of these minerals interfere with the data interpretation, making the accurate determination of silica content difficult or impossible.

Presence of other states.—Some samples contain silica in more than one state. Because of the way it forms, silica may exhibit different degrees of crystallinity. Quartz present can be intermingled with noncrystalline silica since natural quartz may have a noncrystalline coating. Silica cementing quartz grains together in a sandstone may have a different crystallinity than the quartz grains. Even X-ray diffraction, the most effective measurement technique, can

distinguish between crystalline and noncrystalline silica only when rigid sampling protocol is followed and only when the sample has few other minerals.

Effect of human interference.—The very act of taking a sample can change the sample. The grinding and pulverizing required to get a small enough portion to analyze subjects the silica to heat and pressure, the very forces that, in nature, change crystalline surfaces to disordered amorphous surfaces. The analyst can't measure how much of it transforms from noncrystalline to crystalline during sample preparation.

The seven techniques that scientists use to measure how much crystalline silica are given substance contains are summarized in table 3.

Table 3.—Methods used to detect quartz in a sample			
Name	Description of Technique	Accuracy	Remarks
Optical microscopy	Samples are visually examined and the mineralogy is determined.	Accurate to within a few percent.	Requires considerable skill by analyst to identify the minerals present. Uses small samples.
Electron microscopy	Particle composition and morphology are determined. Crystal structure is determined with transmission electon microscopy. Resolves very small particles.	Accuracy limited due to the nature of the analysis.	Cannot differentiate crystalline and amorphous silica except when transmission electron microscopy is used. Methods are slow, expensive, and samples are very small.
Thermal analysis	Measures a mineral's response to temperature changes.	Accurate only for quantities over 1%.	Can be used only on very small samples.
Selective dissolution	Minerals are dissolved selectively using acids. Quartz generally is less soluble than other minerals so it remains in the residue. The residue is analyzed to determine the content of crystalline silica.	Not very accurate.	Particle size and sample composition affect the accuracy of this method. Fine-grained quartz, cristobalite, and tridymite may dissolve; other minerals may not dissolve.
Separation based on density	A finely ground sample is suspended in a heavy liquid. The denser minerals settle faster than less dense minerals. By varying the density of the liquid, minerals with different densities can be separated from one another.	Not satisfactory for rountine analysis.	Particle size, shape, and surface charge affect settling rates. The technique is slow and difficult to perform. Many of the heavy liquids used are highly toxic.
Infrared spectroscopy	Minerals absorb infrared light at specific wavelengths. By examining how the light is absorbed by the sample, the analyst can identify the minerals in the samples.	Accurate to about 1%.	Requires very small samples, the analyst must be sure that samples are representative of the deposit.
X-ray diffraction	X-rays are diffracted by the lattice planes of the minerals in the sample. By observing the intensity of the diffracted X-rays at different angles of incidence, the analyst can determine the identity and concentrations of minerals in sample.	Most accurate; typically, the limit is about 1%	The degree of crystallinity (from amorphous to highly crystalline) and the presence of silicates can affect the accuracy of the quantitive analysis.

Conclusions

Crystalline silica is the scientific name for a group of minerals composed of silicon and oxygen atoms that are arranged in a three-dimensional repeating pattern. There are several forms of crystalline silica, the most common of which are quartz, cristobalite, and tridymite. Crystalline silica is ubiquitous, being in rocks from every geologic era and from every location around the globe.

Crystalline silica's abundance in nature is matched by its pervasiveness in our technology. From the sand used for making glass to the piezoelectric quartz crystals used in advanced communication systems, crystalline silica has been a part of our technological development.

Scientists have known for decades that prolonged and excessive exposure to crystalline silica dust in mining environments can cause silicosis, a noncancerous lung disease. During the 1980's, studies suggested that crystalline silica was a carcinogen. In 1987, IARC labeled crystalline silica as a "2A substance," a probable human carcinogen following a review of the available medical literature on silica. *[Subsequently, upgraded to a 1A substance following a review of the health literature in 1996]*. With the publication of the first study, crystalline silica was regulated under OSHA's HCS as a carcinogen. To demonstrate that they are exempt from the requirements of HCS, suppliers must now analyze the crystalline silica content at the 0.1% level and must now more carefully consider whether the silica is crystalline or noncrystalline; whether it is a regulated form of crystalline silica; or whether it is a mixture of several silica types.

Because this action has implications which go beyond the mine and mineral processing industries, it is important that there be as clear an understanding as possible about crystalline silica. This primer is meant to be a starting point for which to learn about its mineralogy, occurrences, uses in society, and regulations affecting its use. A detailed glossary and a list of selected readings and other resources are included to help the reader move from this presentation to a more technical one, the inevitable next step.

LIST OF RESOURCES AND SELECTED READINGS

Recommended Readings

Basic Information

Boegel, Hellmuth. The Studio Handbook of Minerals. John Sinkankas (ed.). New York: The Viking Press, 1968.

Miles, W.J. The Mining Industry Responds to Crystalline Silica Regulations. Mining Engineering, 19, 1990, pp. 345-348.

Symes, R. F., and R. R. Harding. Crystal and Gem. New York: Alfred A. Knopf, 1991. Zim, Herbert S., and Paul R. Shaffer. Rocks and Minerals. New York: Western, 1957.

Technical Data

Ampian, Sarkis G., and Robert L. Virta. Crystalline Silica Overview: Occurrence and Analysis. BuMines IC 9317/ 1992.

Craighead, John E., and the Silicosis and Silicate Disease Committee. Diseases associated with exposure to silica and nonfibrous silicate minerals. Archives of Pathology and Laboratory Medicine, 1 1 2, 1988, pp. 673-720.

Hamilton, R. D., N. G. Peletis, and W. J. Miles. Detection and Measurement of Crystalline Silica in Minerals and Chemicals. In Regulation of Crystalline Silica. Littleton, Colorado: Manville Corporation, 1990.

- Murray, H. H. Occurrence and Uses of Silica and Siliceous Materials. Preprint from the Society for Mining, Metallurgy, and Exploration, Inc. Littleton, Colorado, 1990.
- World Health Organization, International Agencyfor Research on Cancer. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, silica and some silicates. (Vol. 42), 1987.

Other Resources

Chemical Manufacturers' Association, Chemstar Crystalline Silica Panel 2501 M Street, NW, Washington, DC 20037

International Diatomite Producers Association

26 Wind Jammer Court, Long Beach, CA 90803

Refractories Institute

500 Wood Street, Suite 326, Pittsburgh, PA 15222

U. S. Geological Survey, Department of the Interior 12201 Sunrise Valley Drive, Reston, Virginia 20192

GLOSSARY

This glossary contains terms used in this primer as well as terms the reader might encounter when consulting other sources for more information about crystalline silica.

2A SUBSTANCE—Ranked by IARC as probably carcinogenic to humans, that is, there is limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experiments with animals. (See *IARC Monographs on the Evaluations of Carcinogenic Risks to Humans.*) Crystalline silica is currently ranked as a 2A substance.

AGATE—Cryptocrystalline form of silica. Composed of extremely fine (*submicroscopic*) crystals of silica.

AGGREGATE—Can mean either a group of materials or any of several hard, inert substances (such *as sand, gravel, or crushed stone*) used for mixing with cement.

AMORPHOUS see NONCRYSTALLINE.

ATOM—A minute particle of matter. The smallest particle of an element that can enter into chemical reactions.

BEDROCK—The rock underlying the soil or other surface material.

CARCINOGEN—Causing cancer. In scientific literature, the terms *tumorigen, oncogen*, and *blastomogenal* all have been used synonymously with carcinogen although occasionally,

tumorigen has been used specifically to connote a substance that induces benign tumors. The *Federal Register* (Vol. 52, No. 163, p. 31884) reports the following definition of *carcinogen* under Federal regulation 29CFRl201: 'A chemical is considered to be a carcinogen if: (a) It has been evaluated by the International Agency for Research on Cancer (IARC), and found to be a

carcinogen or potential carcinogen; or (b) It is listed as a carcinogen or potential carcinogen in the *Annual Report on Carcinogens* published by the National Toxicology Program (NTP) (latest edition); or (c) It is regulated by OSHA as a carcinogen.'

CHALCEDONY—Cryptocrystalline silica. Composed of extremely fine (*submicroscopic*) silica crystals.

CHEMICAL CARCINOGENESIS—An IARC term, although one that is widely used elsewhere. It refers to the "induction by chemicals (or complex mixtures of chemicals) of neoplasms that are usually observed, the earlier induction of neoplasms that are commonly observed, and/or the induction of more neoplasms than are usually found" (IARC Monograph 42). *Neoplasms* are tumors.

CHEMICAL COMPOUND—A distinct and pure substance formed by the union of two or more elements in definite proportion by weight.

CHEMICAL ELEMENT—A fundamental substance that consists of only one kind of atom and is the simplest form of matter.

CHERT—Cryptocrystalline silica. Composed of extremely fine (*submicroscopic*) silica crystals. **COESITE**—A rare form of crystalline silica. Believed at first to exist only as a synthetic form of crystalline silica, it was formed in the laboratory using two different methods. Subsequently, it has been found in nature in the Meteor Crater in Arizona. It was also found to occur as a result of shock-wave experiments and nuclear explosions.

COLLOIDAL SILICA—Extremely fine amorphous silica particles dispersed in water. Colloids do not settle out of suspension over time. Colloidal silica is used commercially as binders and stiffeners and as polishing agents.

COMPOUND see CHEMICAL COMPOUND.

CONSOLIDATION—in geological terms, any process by which loose, soft, or liquid earth materials harden into rock.

CRISTOBALITE—The form of crystalline silica that is stable at the highest temperature. It occurs naturally in volcanic rock.

CRYPTOCRYSTALLINE SILICA—Silica with submicrometer crystals formed from amorphous, often biogenic, silica that undergoes compaction over geologic time. Examples are flint and chert. Also called *microcrystalline silica*.

CRYSTALLINE—Having a highly structured molecular arrangement. The atoms and molecules form a three-dimensional, repeating pattern, or lattice.

DERIVED—A substance formed from the products that result when a more complex substance is destroyed. Pure silicon is said to be derived from quartz sand.

DEVITRIFY —To change from glassy form to the crystalline state.

DIATOMACEOUS EARTH see DIATOMITE.

DIATOMITE—A rock high in amorphous silica content, formed from the structures of tiny fresh- and salt-water organisms called diatoms. Diatomite has several commercial uses.

DIMENSION STONE—Building stone quarried and prepared in regularly shaped blocks to fit a particular design.

DISPLACIVE TRANSFORMATION—A high-to-low crystal transformation that does not involve the breaking of molecular bonds. For example, the transformation of low quartz to high quartz involves only the rotation of the silicon-oxygen tetrahedra. Displacive transformations are usually rapid.

ELEMENT see CHEMICAL ELEMENT.

EPIDEMIOLOGICAL STUDIES —Studies of illness involving human subjects over the long term. They generally involve analyses of real-world incidence of the illness with little or no attempt to control factors that potentially could contribute to the onset or severity of the illness. This contrasts with laboratory studies, which are generally performed on animals, are short term, and have variables that are controllable.

ETHYL SILICATE, $Si(OC_2H_5)_4$ —A colorless, flammable liquid with a faint odor. It is an OSHA-regulated substance.

FREE SILICA—informal name for a pure crystalline silica, which is chemically uncombined. **FUSED QUARTZ**—The material formed by the rapid melting of quartz crystals. A meteor strike or a lightning bolt striking sand can form fused quartz. The term quartz glass is often erroneously used to mean fused quartz, but quartz glass is a misnomer because quartz is crystalline and glass is noncrystalline.

FUSED SILICA—The material formed by heating cristobalite to the melting point (1710 $^{\circ}$ C) and cooling it rapidly.

GLASSY—Having a semistructural molecular arrangement. Atoms and molecules may form a pattern but it has only short-term or partial order and does not repeat predictably in three dimensions.

GRAVIMETRIC SAMPLING—Quantitative chemical sampling in which the substances in a compound are measured by weight.

HOST ROCK—A rock that contains ores or minerals of value.

IARC—The International Agency for Research on Cancer, an agency of the United Nations' World Health Organization.

IGNEOUS ROCK—A rock that has solidified from a molten state.

JASPER—Cryptocrystalline silica. Composed of extremely fine (submicroscopic) silica crystals. **KEATITE** —A synthetic and rare form of crystalline silica, formed by the crystallization of amorphous silica. It is transformed to cristobalite at a temperature of 1620 °C.

LITHIFY—To harden into rock.

MACROPHAGE—A large phagocyte, a type of cell in the body that engulfs foreign materials and consumes debris and foreign bodies.

MAGMA—A natural hot melt of rock-forming materials (primarily silicates) and steam. Magma is in motion. Geologists speculate that it originates just below the earth's crust and is fed by new material from greater depths.

MATERIAL IMPAIRMENT—Cited in the *Federal Register* (1/19/89), regulation 29 CFR 1910, as "…life threatening effects; disabling effects; various diseases; irritation to different organs or tissues; and changes in organ functions indicative of future health decrements" (p. 2361).

METAL—A type of element. Metals are usually hard and lustrous, malleable (they can be pounded into sheets), ductile (they can be drawn into wires), and can conduct electricity and heat. **METALLOID**—A group of elements, eight in all, that form the boundary (on the periodic table)

between the metal elements (such as copper, iron, tin, gold) and the nonmetal elements (such as carbon, nitrogen, hydrogen). Metalloids possess some of the properties of the metals and some of the properties of the nonmetals.

METAMORPHIC ROCK—Rocks that have undergone changes from the pressure and temperatures in the Earth's interior.

METASTABLE—Possessing an energy state that is not stable, yet will not change spontaneously. An outside force is required to change.

METHYLSILICATE—AN OSHA-regulated substance, $(CH_3O)_4Si$; it exists in the form of colorless needles.

MICROCRYSTALLINE SILICA see CRYPTOCRYSTALLINE SILICA.

MINERAL—Naturally occurring crystalline solids, most of which are made from oxygen, silicon, sulfur, and any of six common metals or metal compounds.

MOLECULE—The smallest particle of a substance that retains the qualities of the substance and is composed of one or more atoms.

NEOPLASM—A tumor.

NONCRYSTALLINE—Having an unstructured molecular arrangement. The atoms and molecules are randomly linked, forming no pattern.

NONMETAL—Elements that do not exhibit the properties of metals. Usually poor conductors of electricity and heat.

OPAL—An amorphous form of silica.

ORGANIC COMPOUND—A chemical compound containing carbon.

OSHA—The Occupational Safety and Health Administration, an agency of the U.S. Department of Labor.

OVERBURDEN —Material overlying the ore in a deposit.

PERMISSIBLE EXPOSURE LIMIT (PEL)—An OSHA term. It refers to the concentration of a substance to which a worker is allowed to be exposed as a time-weighted average.

PHAGOCYTIZED—To be removed from the body by the action of phagocytes, cells in the body that engulf foreign materials and consume debris and foreign bodies. It is believed that upon exposure to airborne crystalline silica particles, 80% of the particles are phagocytized and eliminated within a short time.

PIEZOELECTRICITY—The ability of some crystals to convert mechanical pressure to electricity and to convert electricity to vibration. A quartz crystal in a watch is an example of applied *piezoelectricity*.

POLYMERIZATION—A chemical reaction in which small organic molecules combine to form larger molecules that contain repeating structural units of the original molecules. The product of polymerization is called a *polymer*.

POLYMORPH—Literally "many forms." To be polymorphic means to have or assume several forms. In reference to crystals, it is the characteristic of crystallizing in more than one form. For example, crystalline silica can be in the form of quartz, cristobalite, tridymite, or others.

PRECIPITATED SILICA—Amorphous silica that is precipitated from either a vapor or solution.

QUARTZ—The most common type of crystalline silica. Some publications will use quartz and crystalline silica interchangeably, but the term *crystalline silica* actually encompasses several forms: quartz, cristobalite, tridymite, and several rarer forms.

RADIOLARIAN EARTH—Soil, high in amorphous silica content, composed predominantly from the remains of radiolaria. Radiolarian earth that has been consolidated (hardened) into rock is called radiolarite.

RADIOLARITE—A rock, high in amorphous silica content, formed from the shells of tiny freshand salt-water organisms called radiolaria.

RECONSTRUCTIVE TRANSFORMATION—A crystal transformation that involves the breaking of molecular bonds. For example, the transformation of quartz to tridymite involves the restructuring of the molecules. It is generally a slow transformation.

RESPIRABLE CRYSTALLINE SILICA (RESPIRABLE DUST)—May be defined as dust that contains particles small enough to enter the gas-exchange region of the human lung (about 3.5 microns). One of the studies to which IARC refers in its monograph (Vol. 42, 1987) found that particle size for crystalline silica (in the form of an alpha quartz sandstone with the trademark Min-U-Sil 15) was distributed as follows: particles larger than 5 microns constituted about 0.1% of the sample, particles between 2 and 4.9 microns, about 7%; and particles less than 1.9 micron, 92.8%. The Silicosis and Silicate Disease Committee (National Institute for Occupational Safety and Health) states that particles less than 1 micron in size are the most troublesome and that particles in the range of 0.5 to 0.7 microns are retained in the lung. (See *Archives of Pathology and Laboratory Medicine*, Vol. 112, July 1988). As early as 1943, however, the Department of Labor established a limit of no more than 5 million particles of free silica under 10 microns in size per cubic foot of air. (See *Silicosis*, Industrial Health Series No. 9, U.S. Department of Labor, Division of Labor Standards, 1943.)

ROCK CYCLE—A cycle taking place over geologic time in which the three types of rock are related. Sedimentary rocks are changed into metamorphic rocks or melted to create igneous rocks. Sedimentary, metamorphic, and igneous rock may be eroded to make sediments that then harden into sedimentary rock.

SEDIMENTARY ROCK—A rock formed by the accumulation and consolidation of minerals that have been either transported to a particular site by wind, water, or ice or precipitated by a chemical reaction at the site.

SEMICONDUCTOR—Materials that act as conductors within certain temperature ranges; at other temperatures they act as insulators. The elements silicon and germanium are examples of semiconductors of electricity. This unusual electrical capability has led to silicon's use in transistors, integrated circuits, and computer chips.

SILICA—A compound formed from silicon and oxygen. Silica is a polymorph, that is, it exists in more than one state. The states of silica are crystalline and noncrystalline (also called amorphous). Crystalline silica can take several forms: quartz (most common), cristobalite, tridymite, and four more rare forms.

SILICA BRICK—Brick composed of silica that is used as a lining in furnaces.

SILICA GEL—Amorphous silica, prepared in formation with water. Removal of the liquid creates xerogels and further treatment with alcohol creates aerogels. Silica gels are used as drying agents and to alter viscosity of liquids.

SILICA FLOUR—Finely ground quartz, typically 98% of the particles are below 5 microns in diameter.

SILICA SAND—A common term in industry. It generally is used to mean a sand that has a very high percentage of silica, usually in the form of quartz. Silica sand is used as a source of pure silicon and as a raw material for glass and other products. Also called *quartz sand*.

SILICATES—Compounds formed from silicon, oxygen, and other elements. See SILICATE MINERALS AND SILICON-OXYGEN TETRAHEDRON.

SILICATE MINERALS—Minerals containing silicon, oxygen, and a metal or metal compound. Silica tetrahedra form the framework of silicate minerals. Examples are olivine, pyroxene, amphibole, feldspar, and mica.

SILICA W—A synthetic form of crystalline silica. It reacts rapidly with water transforming into amorphous silica.

SILICEOUS—A term used to describe a rock with a high silica content, especially one

containing free silica rather than silicates.

SILICIC ROCK—An igneous rock containing more than two-thirds SiO_4 , by weight, usually as quartz or feldspar. Granite is an example of silicic rock.

SILICON—The second most common element in the Earth's crust. (Oxygen is the most common.) Silicon's chemical symbol is *Si*. Silicon is a metalloid, possessing some of the properties of a metal and some of the properties of a nonmetal. Pure silicon does not exist in nature. Silicon derived in the laboratory exists as black to gray, lustrous, needlelike crystals, and is an OSHA-regulated substance.

SILICON CARBIDE (*SiC*) —A green to blue black iridescent crystal. It is an OSHA-regulated substance.

SILICON DIOXIDE—Silica (*SiO*₂).

SILICONES—Synthetic compounds formed from two or more silicon atoms linked with carbon compounds. Most silicones contain oxygen as well. Silicones are formed by a process called polymerization; the molecular structure is a chain, not the tetrahedral shape of the molecules of silica or the silicates. *See also* POLYMERIZATION.

SILICON-OXYGEN TETRAHEDRON—Silicon and oxygen bond in a paired formation with four oxygen atoms and one silicon atom. Its chemical symbol is SiO_4 . *Tetrahedron* literally means "four surfaces" and refers to the way the molecule looks internally. Picture four spheres (the oxygen atoms) touching a smaller sphere (the silicon atom) held in the pocket in the middle of the spheres. Lines drawn between the centers of the spheres would form a regular, four-sided prism, a tetrahedron. Although many structures are possible in nature, geologists seldom encounter more than a relatively small number, primarily because most rocks are made up of silicate minerals, which combine in the silicon-oxygen tetrahedron. The silicon-oxygen tetrahedron bonds most frequently with sodium, potassium, calcium, magnesium, iron, and aluminum.

SILICON TETRAHYDRIDE (SiH_4)—A colorless gas used in the manufacture of semiconductors. Also called silane. It is an OSHA-regulated substance.

SILICOSIS—A pneumoconiosis characterized by scarring of lung tissue, which is contracted by prolonged exposure to high levels of respirable silica dust or acute levels of respirable silica dust. **STABLE**—Possessing an energy state that is balanced and will not change spontaneously, resistant to energy change.

STATES OF MATTER—A substance can be in a solid, liquid, or gas state. These three are called *states of matter*.

STISHOVITE—The most dense form of crystalline silica. It is rare and at first was believed to exist only as a synthetic. It was initially found to occur as a result of shock-wave experiments and of nuclear explosions. Subsequently, it was found in nature in the Meteor Crater in Arizona.

TETRAHEDRON—A solid geometric shape with four surfaces. See SILICON-OXYGEN TETRAHEDRON.

TRIDYMITE—A form of crystalline silica. It is found in nature in volcanic rocks and stony meteorites. It is also found in fired silica bricks.

VITREOUS SILICA—Glassy silica. The term is sometimes use to refer to any noncrystalline substance.

VITRIFY—To form as a glass.

VOLCANIC TUFFS—Deposits of volcanic ash that have hardened into rock.