

Nomenclature of the Forms of Crystalline and Non-Crystalline Silica

Deane K. Smith
Emeritus Professor of Mineralogy
The Pennsylvania State University

The term “silica” implies the chemical composition SiO_2 whether or not the material is crystalline or glass, but historically, it is also used to include the hydrous phases $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ as well. Pure SiO_2 forms three-dimensional networks of corner linked SiO_4 tetrahedra in all its physical states except for stishovite and silica W. The large number of different ways that the linkages may take leads to many different forms of SiO_2 . This network linkage also occurs in the glassy state which accounts for its very high viscosity.

The term “crystalline” is applied when the arrangement of atoms in the material is highly ordered in both short- and long-range in three-dimensions, and a distinct sharp X-ray powder diffraction pattern is obtained. The term “non-crystalline” applies to materials that may contain some short-range order but lack long-range order in three-dimensions and produce X-ray powder diffraction patterns composed of broad maxima, which may or may not be mixed with sharper maxima. Sometimes the term “X-ray amorphous” is used, but this term should be applied only when the diffraction pattern consists of one or two broad bands of intensity as is obtained from the glassy state. “2-D crystalline” is sometimes applied when there is long-range order in two-dimensions and short-range order in the third-dimension, *i.e.* the clay minerals.

Two terms commonly applied to silica are “micro-crystalline” and “crypto-crystalline”. Both these terms should apply to essentially 100% crystallinity. Micro-crystalline should be used when the crystallites are resolvable in the standard optical petrographic microscope. Crypto-crystalline applies to crystallites whose dimensions are so small that they are not resolvable in the petrographic microscope yet the diffraction pattern still contains sharp peaks. The break between these two terms is around 0.2 - 0.5 μm (200 - 500 nm). Unfortunately, micro-crystalline has also been used to imply a mixture of domains of short-range ordered structure in a matrix of disordered material.

Mineral names are assigned by the discoverer and approved by the International Mineralogical Association. Archaic minerals have names whose origins are lost in antiquity, and sometimes a single mineral may have more than one name because the discoverers did not know of the previous designation. There also may have been different names in different languages. Quartz for, example, was called Crystallos in Greek and Crystallus in Latin. In addition to mineral names, there are varietal names which are often used for specific colors, habits or microstructures. Quartz has many varieties including smoky, amethyst, citrine, etc. In the following list, mineral names are in bold type and varietal names are in italics. All other names are incidental and related to some physical property, texture, or locality

The Phases of Crystalline Silica

Quartz

This mineral is abundant in the Earth's crust and ubiquitous around us. It is usually very crystalline and gives a very sharp powder diffraction pattern whether it occurs in large crystals or as micro-crystalline or crypto-crystalline masses. Micro-crystalline or crypto-crystalline quartz sometimes is termed "*chalcedony*" or "*chert*" where chalcedony is a mineralogical term and chert is a rock term. Additional terms are used such as "*quartzine*" depending on the micro-structure, *i.e.* the fibrous nature and orientation of the fiber growth. There are also many varietal terms based on color used for quartz, such as "*rock crystal*", "*smoky*", "*amethyst*", "*cairngorm*" and "*citrine*", and several rock terms such as "*agate*", "*chert*", and "*jaspar*" that are used in popular as well as scientific literature. Agates and jaspers also have many local names such as Montana, Faribairn, crazy-lace, Paisley, Owyhee, Succor Creek, that depend on locality or pattern.

IARC has classified quartz as a carcinogen under some industrial exposures. The relation of biological activity and the physical nature of the particles is still under study.

Cristobalite

Cristobalite is a common product in volcanic rocks and in industry where high firing temperatures are involved and the environment is essentially dry. It is easily formed by firing pure silica gels and fine-grained quartz at temperatures above 1450°C. It may also form at lower temperatures if appropriate fluxing and stabilizing agents are present such as the alkaline-earth elements. Almost all synthetic cristobalite and most natural cristobalite contains significant concentrations of stacking faults giving it a partial tridymite character.

The terms "*lussatite*" and "*lussatine*" are to cristobalite as chalcedony and quartzine are to quartz. They are microcrystalline or cryptocrystalline varieties which show different textures depending on the fibrous habit. Modern literature tends to equate these terms to opal-CT and opal-C, but these opal forms are optically isotropic, whereas cristobalite is optically anisotropic. The use of these terms should not be applied loosely to the opals.

IARC has classified cristobalite as a carcinogen under some industrial exposures. Its activity should be somewhat greater than quartz because it is metastable at ambient conditions whereas quartz is the stable form.

Tridymite

This mineral is an enigma. There has long been a debate whether it is a true form of pure crystalline silica. The presence of alkalis promotes its formation in synthesis and may also be required to form a true tridymite in nature. It is a very rare mineral both in nature, where it is restricted to volcanic environments, and in the industrial environment.

Any carcinogenicity of tridymite has not been directly studied, but it should be similar to cristobalite. It is not sure what affect the presence of the alkalis have on its reactivity. Although “ideal” tridymite has a distinctive X-ray powder diffraction pattern, most specimens, both natural and synthetic, produce a pattern with considerable cristobalite character due interstacking disorder.

Coesite

Coesite is a mineral that requires high pressure for its formation. It is rare in nature and non-existent in most industrial operations. Its carcinogenicity has not been studied.

Stishovite

Stishovite is the only form of crystalline silica that has the Si in 6-coordination. Compared to coesite, it requires considerably higher pressure for its formation. It is very rare in nature and non-existent in industrial operations except where it is being deliberately synthesized. Its carconogenicity has not been studied.

Melanophlogite

This mineral is a form of silica that has a clatharate-like open structure and appears to always be associated with organic material that may be responsible for its existence. It is rare in nature and has not been reported from any industrial operation. No studies have been done in its carcogenicity.

Moganite

This mineral is a newly recognized species that may be quite abundant in nature, particularly asociated with microcrystalline or cryptocrystalline quartz. It has a crystal structure closely related to that of quartz; essentially that of quartz twinned periodically on the atomic scale.

Any carcinogenicity has not been determined, but its similarity to quartz would imply similar reactivity. Its similarity to quartz results in a X-ray powder diffraction pattern that is also similar to quartz, and if it does exist in industrial operations, it would be included as quartz in quantitative analyses.

“Keatite”

This phase of silica has never been recognized in nature, and hence, it is not a true mineral, but it is a true form of pure silica. This phase is not important in industrial processing because of its very restrictive conditions of formation. It has a distinctive X-ray powder pattern, so it can be detected if it were to be present in a sample.

“Silica W”

This phase is different from all the other forms of silica in that the crystal structure is not a framework composed of corner-shared tetrahedra but rather a chain of edge-shared tetrahedra forming a fibrous structure. It is not known to form in nature, and its occurrence in industrial products has never been confirmed either.

Silhydrite, $3\text{SiO}_2 \cdot \text{H}_2\text{O}$

Silhydrite is a rare mineral found in nature as a reaction rind on nodules of chalcedony. Its carcinogenicity has never been studied, and it probably is not significant in industrial products because of its rarity. It is the only crystalline silica hydrate.

Magadiite, $\text{NaSi}_7\text{O}_{13}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, and mountainite, $\text{Ca}_2\text{Si}_4\text{O}_{10} \cdot 3\text{H}_2\text{O}$, are closely related minerals to silhydrite, but they contain alkali and alkaline earth elements as essential components

The phases of Non-Crystalline Silica

Opal as a mineral has been known from antiquity dating to at least Roman times. The earliest mines that produced gem grade opal are in what is now Hungary in the Carpathian Mountains. Trade routes brought the gem materials to the Roman Empire around 200-100 BC from working near Czerwenitzna according to Bauer (1904). Modern gem opal comes from several sources but primarily Australia where it occurs at many localities. This opal, known as “precious” or “noble” opal is highly valued. Opal worthless for its gem applications is termed “potch” or “common” opal.

The origin of the play of colors that define precious opal was not understood until the studies of Jones, et al. (1964) and Darraugh, et al. (1965) where it was shown that such opal was composed of ordered arrays of uniform spherical clusters of gel-like silica. The ordered arrangement created an optical diffraction grating that diffracted visible light into the spectral array of colors. Potch opal was shown to contain similar spherical clusters but of non-uniform size and without orderly packing. Opal was further classified by Jones and Segnit (1971) into opal-A, opal-CT and opal-C based on the X-ray powder diffraction pattern. This classification with some modification is still in use today primarily by Floerke (1991).

Although mineralogists only recognize “opal” as a mineral name, there are many varieties that are now recognized by mineralogists and other scientists. The composition of opal is $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ where n is usually 0.5 to 2. Opal is characterized by the existence of spherical clusters of clathrate-like spheres of hydrated silica arranged either homogeneously or heterogeneously. The water, which may exist as internal or surface silane ($-\text{Si}-\text{OH}$) groups, attached or adsorbed water, is considered essential to definition of opal. It is the nature of this water that strongly influences the type of opal that is formed.

There have been no studies on the carcinogenicity of opal. Its non-crystalline character and the presence of water in several forms will certainly modify its reactivity compared with crystalline forms of silica. The presence of abundant silane groups on the surface of quartz particles reduces the reactivity of the surface, and the abundance of water in opal should have an even more pronounced effect.

All the phases of opal are encountered in mining operations where the rocks containing the mineral are exploited for commercial products. Opal also occurs as a minor phase in bentonite deposits and in other rocks that form from the alteration of volcanic ash by surface and subsurface waters. In fact, much of the precious opal is believed to form when ground water leaches the silica from the near surface volcanic ash and deposits it in open fissures deeper in the ground.

The phases of opal

Opal-A_G

The best known form of opal is “precious opal” which implies that it shows a play of colors in white light that is due to diffraction from the regular packing of the clathrate-like silica gel spheres. Although the packing of the spheres may be regular, there is neither short-range nor long-range order in this material, and the X-ray powder diffraction pattern is characterized by a distinct broad hump and a possible weak second hump indicative of material that is “X-ray amorphous”. The subscript G has been added to indicate that the structure of the silica network is gel-like in that it is composed of large cages with included water essential to the stability of the structure. Most but not all precious opal is opal-A_G.

Opal that shows no play of colors is also composed of the same spherical clusters, but they are non-uniform in size and do not pack in an orderly manner thus destroying any possible diffraction of the light. This type of opal is termed collectively “potch opal” and includes the massive varieties. Porous varieties of inorganic origin such as *geyserite* and materials composed of tests of micro-organisms such as *diatomite* and *radiolarite* are also recognized. The X-ray powder diffraction pattern is essentially identical for all these types of opal regardless of their origin.

Opal-CT

In opal-CT there is the beginning of the formation of domains of short-range ordering which have arrangements of silica and water that is similar to the arrangement of atoms in cristobalite and tridymite. The X-ray diffraction pattern is distinguished by the presence of a well-defined broad hump with a satellite peak on the low-angle side and a possible shoulder on the high-angle side. A second weaker peak at a higher angle is also present. The ordered regions occur in a matrix of disordered opal, but it is difficult at this time to suggest that the system is two-phase. There is no evidence yet to show that the ordered domains have lost their water and are anhydrous. The fraction of the material which is composed of ordered domains is very small. The term micro-crystalline should not be applied to this material.

Opal-C

Opal-C shows considerably more short-range order than opal-CT in that the diffraction pattern does not have as broad a hump and the satellite characteristics are weak or generally absent. In addition, there may be as many as 8 recognizable peaks in the diffraction pattern. Although the peaks are very similar to the pattern for crystalline cristobalite, true long-range order has not yet been attained, and the role of the water is still critical to the structure. The fraction of material in ordered domains is higher than for opal-CT, but it is probably less than 50%. Tests other than X-ray diffraction may be necessary to distinguish opal-C from cristobalite. Terms such as “cristobalite-like” and “tridymite-like” are often applied to opal-C and opal-CT may be misleading because they are interpreted by readers to imply a true two-phase crystalline–non-crystalline system

which is probably not true. This terminology is not to be recommended. Also the term micro-crystalline should not be applied to this material until evidence is found to show that the ordered domains are free of water in any form.

Opal-A_N (*Hyalite*)

This form of opal occurs in volcanic environments where the silica deposits at elevated temperatures. The subscript “N” is to imply its structure is network-like similar to silica glass rather than composed of separate gel spheres; however, it still contains significant water.

Natural silica glasses

Although silica as a true glass structure is known from nature, the varieties are not recognized as minerals. It differs from opal in that all varieties are essentially anhydrous. The physical structure is a network essentially identical to that for man-made silica glass. The silica glasses have not been shown to be carcinogenic either in bulk or fibrous form. The general mineralogical term for the natural glasses is *lechatelierite*. Two types of natural modes of formation are recognized. The first occurs when fusion of sand results from lightning strikes which melts the local quartz grains and quenches the result as a glass. This type of material is termed *fulgurite*. The second type includes glass buttons found in the Lybian desert and Australia which are believed to have a meteoritic origin. They are called *tectites* or more commonly *Lybian desert glass* or *oldavite*.

Silica glass is not recognized as a carcinogen. It is an industrially important product in many applications both as bulk materials and in fibrous form.

Summary

Silica as a crystalline material takes many different forms. Of the many forms, quartz and cristobalite are the forms found in the industrial environment where some evidence points to carcinogenic character. Tridymite and moganite are probably also carcinogenic under some conditions, but they are rare in industrial environments based on reported analyses to date. Moganite may be abundant, but it is easily confused with quartz reported as quartz in analyses. These phases are distinguished by their X-ray powder diffraction patterns, so when it is necessary to confirm the specific phase, it is necessary to employ X-ray diffraction in the analysis.

There are several non-crystalline forms of silica including the opals and silica glasses. Any carcinogenicity of these forms has not been established. Confusion arises from the similarity of the non-crystalline opal-C and the crystalline cristobalite both in the X-ray powder diffraction pattern and when examined by infra-red methods. Proper identification of the true phase requires an understanding of the differences of opal and cristobalite and the application of additional tests primarily for the role of the water present.

X-ray powder diffraction patterns for the several forms of opal are attached to show how distinct the varieties actually are. In addition, theoretical patterns of quartz and moganite are attached to show that the moganite would be quantified as quartz by current analytical methods.

Figures

Figure 1. Opal-A Cooper Pedy, Australia

Figure 2. Opal-CT Queretaro, Mexico

Figure 3. Opal-C, Adrian, Oregon

Figure 4. Cristobalite, theoretical

Figure 5. Tridymite, theoretical

Figure 6. Quartz, theoretical

Figure 7. Moganite, theoretical

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