PB92-200997

IC 9317

BUREAU OF MINES
INFORMATION CIRCULAR/1992

Crystalline Silica Overview: Occurrence and Analysis

By Sarkis G. Ampian and Robert L. Virta

UNITED STATES DEPARTMENT OF THE INTERIOR

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA 22161

Mission: As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for the public lands and promoting citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.

i.C

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. BuMines-IC 9317	2.	3. PB92-200997

4. Title and Subtitle

CRYSTALLINE SILICA OVERVIEW: OCCURRENCE AND ANALYSIS

5. Report Date

6.

7. Author(s)

Sarkis G. Ampian and Robert L. Virta

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Division of Mineral Commodities
Bureau of Mines
810 7th Street, NW
Washington, DC 20241

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.
(C)
(G)

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words)

The Occupational Safety and Health Administration (OSHA) has regulated crystalline silica under its Hazard Communication Standard (HCS) since 1987 because crystalline silica was found to be a probable human carcinogen by the International Agency for Research Against Cancer (IARC). The standard requires that all materials handled by OSHA-regulated facilities be labeled according to the requirements of HCS and that workers receive proper training on the handling of the material if the crystalline silica content equals or exceeds 0.1 weight percent (0.1%).

Two major concerns with the HCS are the widespread occurrence of crystalline silica in nature and the suitability of current technology for routinely determining crystalline silica concentrations at the 0.1% HCS level. Crystalline silica can be quantified at the 0.1% level by X-ray diffractometry if (1) none of the accessory minerals has X-ray diffraction reflections that overlap with those of crystalline silica and (2) the standard has a particle size distribution and crystallinity similar to those of the sample. In some instances, it may not be possible to determine the crystalline silica content with any degree of certainty. Other concerns include the classification of some silica polymorphs as crystalline or noncrystalline and the suitability of metastable high-temperature standards, such as cristobalite and tridymite, for regulatory analysis.

17. Document Analysis a. Descriptors

Crystalline silica
Occupational Safety and Health Administration
World Health Organization
Regulation
Quartz
Tridymite
Silica
Spectral overlap
Silica tetrahedron
Diatomite
Hazard Communication Standard
Mine Safety and Health Administration
International Agency for Research Against Cancer
X-ray diffractometry
Cristobalite
Carcinogen
NIST standard
Polymorphs
Amorphous silica
Respirable silica

c. COSATI Field/Group

18. Availability Statement:	19. Security Class (This Report)	21. No. of Pages 35
	20. Security Class (This Page)	22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce

i.a

Information Circular 9317

Crystalline Silica Overview: Occurrence and Analysis

By Sarkis G. Ampian and Robert L. Virta

UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary

BUREAU OF MINES
T S Ary, Director

Library of Congress Cataloging in Publication Data:

Ampian, Sarkis G.

Crystalline silica overview : occurrence and analysis / by Sarkis G. Ampian ; with an introductory section on geological and commerical occurrences by Robert L. Virta.

p. cm. — (Information circular; 9317)

Includes bibliographical references (p. 26).

Supt. of Docs. no.: I 28.27:9317.

1. Silica. 2. Silica—Toxicology. 3. X-rays—Diffraction. I. Virta, Robert L. II. Title. III. Series: Information circular (United States. Bureau of Mines); 9317.

TN295.U4 [TN948.S6] 622 s—dc20 [549'.6'0287] 92-700 CIP

1.0

i.d

CONTENTS

ILLUSTRATIONS

TABLES

CONTENTS—Continued

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom	μm	micrometer
°C	degree Celsius	mg	milligram
hr	hour	min	minute
kg	kilogram	mm	millimeter
μg	microgram	s	second

CRYSTALLINE SILICA OVERVIEW: OCCURRENCE AND ANALYSIS

By Sarkis G. Ampian[1] and Robert L. Virta[2]

ABSTRACT

Crystalline silica (quartz, cristobalite, and tridymite) is regulated by the Mine Safety and Health Administration (MSHA) and Occupational Safety and Health Administration (OSHA) because of its potential for causing debilitating but nonmalignant lung diseases. In 1987, the International Agency for Research Against Cancer (IARC) conducted a review of the health literature and concluded that crystalline silica was a probable human carcinogen. As a result of this finding, OSHA was required to regulate crystalline silica under its Hazard Communication Standard (HCS). The standard requires that all materials handled by OSHA-regulated facilities be labeled according to the requirements of HCS and that workers receive proper training on the handling of the material if the crystalline silica content equals or exceeds 0.1 weight percent (0.1%).

MSHA currently is considering enacting its own HCS. This will be similar to OSHA's HCS. If the standard is enacted, most mineral producers will have to determine the respirable monitor filter and bulk crystalline silica contents of their ores and products so that workers and/or customers will know whether they are in compliance with the 0.1% HCS and/or the OSHA permissible exposure level (PEL) of 50 μg for an 8-hour workday for respirable crystalline silica as determined from monitor samples.

Two major concerns with the HCS are the widespread occurrence of crystalline silica in nature and the suitability of current technology for routinely determining crystalline silica concentrations at the 0.1% HCS level. Most ores are extracted from silica-bearing deposits and it is a common constituent of rocks and soils. OSHA's HCS will have the greatest impact on the producers of crushed stone, diatomite, dimension stone, gravel, industrial sand, perlite, pumice, pyrophyllite, sand, and talc because these materials frequently are shipped directly from the mill to the customer. MSHA's HCS would affect nearly all mineral producers.

Those producers that have crystalline silica present in concentrations near the 0.1% cutoff point will have the most difficulty with the analysis. Crystalline silica can be quantified at the 0.1% level by X-ray diffractometry in simple systems containing one, two, and possibly three minerals if (1) none of the accessory minerals has X-ray diffraction reflections that coincide or overlap with those of crystalline silica and (2) the standard has a particle size distribution and crystallinity similar to those of the sample. In some instances, it may not be possible to determine the crystalline silica content of a sample with any degree of certainty using the recommended regulatory protocol. In all cases, it is recommended that a qualified mineralogist identify the minerals in a sample prior to any regulatory analysis. Additionally, the uncertainty as to whether some silica polymorphs should be classified as crystalline or noncrystalline and the suitability of metastable high-temperature standards, such as cristobalite and tridymite, for regulatory analysis at ambient temperatures should be addressed further.

This overview is written both to highlight these problems and to serve as a guide for analysts, regulators, and industry personnel who are involved in the crystalline silica issue. It also covers some of the difficulties and/or shortcomings in quantifying crystalline silica, such as the ubiquitous mineral quartz, in the workplace.

---

[1] Physical scientist, formerly with Branch of Industrial Minerals, U.S. Bureau of Mines, Washington, DC. Prepared the section on X-ray Diffraction Analysis and Problems.

[2] Physical scientist, Branch of Industrial Minerals, U.S. Bureau of Mines, Washington, DC. Prepared the section on Geological and Commercial Occurrences.

INTRODUCTION

Crystalline silica (quartz, cristobalite, and tridymite) is regulated by the Mine Safety and Health Administration (MSHA) and Occupational Safety and Health Administration (OSHA) because of their potential for causing debilitating but nonmalignant lung diseases (*33*).[3] In 1987, the International Agency for Research Against Cancer (IARC) conducted a review of the health literature and concluded that crystalline silica was a probable human carcinogen (*43*). As a result of this finding, OSHA was required to regulate crystalline silica under its Hazard Communication Standard (HCS). The standard requires that all materials handled by OSHA-regulated facilities be labeled according to the requirements of HCS if the crystalline silica content equals or exceeds 0.1 weight percent (0.1%). Additionally, workers must receive proper training on the handling of the material through written communication (e.g., Material Safety Data Sheets, container labeling) and worker training (29 CFR 1900). Although OSHA's HCS is concerned with respirable crystalline silica, no size restriction is given in the regulation.

While OSHA is responsible for ensuring worker safety in the occupational setting, not at the mine site, its regulation of crystalline silica does affect the minerals. Many mineral producers sell products directly to OSHA-regulated sites and would have to provide information on the concentration of crystalline silica in these products. The Bureau of Mines has received many inquiries from mineral producers, consumers, and analysts concerning the impact of the HCS because of the widespread occurrence of crystalline silica, ambiguities in the mineralogical definition of crystalline silica and how crystalline silica is identified using X-ray diffraction analysis, the quality of analyses performed by various laboratories, and the difficulty in performing quantitative analysis at the 0.1% level.

This paper will discuss the definition of crystalline silica, its occurrences, and the types of mining operations that may be affected by the regulation of crystalline silica. It also will highlight some of the difficulties associated with the present methods for determining the crystalline silica content in samples and provide recommendations that may avoid some of these shortcomings. The problems with the availability of quartz and cristobalite standards and the use of one standard for materials possessing a wide range of crystallinities and particle sizes are discussed. Other problems covered include positive mineral identifications, overlapping and interfering diffraction peaks with the principal quartz and cristobalite lines, the controversy over the crystallinity of some forms of silica, and the sensitivity of the methods. In addition, recommendations are made to help avoid many of these problems.

ACKNOWLEDGMENTS

The authors are grateful to the many Bureau of Mines commodity specialists; John W. Thatcher and Jerry W. Gregory, Mine Safety and Health Administration, Denver, CO; Dr. S. J. Dapkunas and Dr. W.P. Reed, National Institute of Science and Technology (NIST), Gaithersburg, MD; Dr. William J. Miles[4] and Dr. Robert D. Hamilton, Manville Corp., Denver, CO.; Dr. I. Edgar Odom, American Colloid Co., Arlington Heights, Il.; Dr. C.S. Thompson, R.T. Vanderbilt Co., Inc., Norwalk, CT; Dr. Warren C. Lynn, U.S. Department of Agriculture, National Soil Survey, Lincoln, NE; Dr. Malcolm Ross and Dr. John W. Hosterman, U.S. Geological Survey (USGS), Reston, VA.; Robert C. Freas, Franklin Limestone Co., Nashville, TN; Bill E. Leach, Kentucky-Tennessee Clay Co., Mayfield, KY; Carroll B. Kay, Kyanite Mining Corp., Dillwyn, VA.; Jeff R. Kinblom, NYCO, Wellsboro, NY; and W. Frank McClune, Powder Diffraction File, Swarthmore, PA.

The authors also thank JCPDS (Joint Committee on Powder Diffraction Standards) and the International Centre for Diffraction Data (ICDD), publishers of the Powder Diffraction File (PDF), 1601 Park Lane, Swarthmore, PA 19081-2389, for permission to publish PDF data.

GEOLOGICAL AND COMMERCIAL OCCURRENCES

GEOLOGY AND MINERALOGY

Silicon is one of the most abundant elements in the Earth's crust, second only to oxygen. It accounts for 28% of the weight of the lithosphere but never occurs in nature in an uncombined state (*3*). Silicon combines with oxygen to form a silica tetrahedron. The silica tetrahedron is "the fundamental unit on which the structure of all silicates is based" (*12*). It consists of a shared oxygen atom at each of the four corners of a tetrahedron and one silicon atom in the center of the tetrahedron (fig. 1). The oxygen atoms are equidistant from each other, and the silicon atom is equidistant from each of the oxygen atoms. These silica tetrahedra along with modifying oxides of the

---

[3] Italic numbers in parentheses refer to items in the list of references at the end of this report.

[4] Present address: Miles Industrial Mineral Research, Golden, CO.

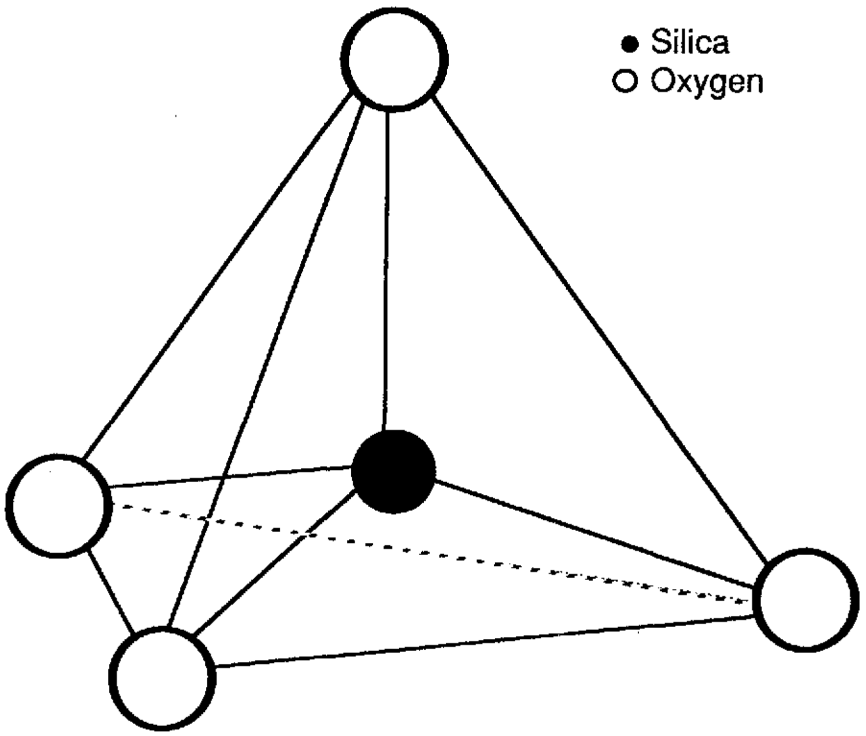


Figure 1.—Silica tetrahedron.

alkaline and alkaline-earth metals and/or transition metals form all silicate minerals.

Silicates are the largest group of minerals, accounting for 25% of all known minerals and almost 40% of the common minerals. They form over 90% of the Earth's crust (*12*). Silicates are essential constituents of most common rocks with the exception of chemical precipitates and biogenic deposits. The most common of the rock-forming silicates are feldspars, quartz, pyroxenes, amphiboles, clay minerals, and micas. Quartz, the most common form of silica, accounts for approximately 12% of the Earth's lithosphere, second only to the feldspars (*3*).

Silica

Silica, the oxide form of silicon, can be crystalline or amorphous. Crystalline silica is composed of silicon and oxygen atoms that are tetrahedrally arranged in a three-dimensional network (fig. 2). This regular arrangement of the atoms imparts a periodic structure to the crystal. This contrasts sharply with amorphous silica, which is composed of randomly distributed silicon and oxygen atoms that exhibit no periodicity in their arrangement (*12*, *23*, *40*).

Quartz, tridymite, cristobalite, coesite, keatite, and stishovite are the polymorphic forms of silica. The spacings and lattice planes formed by rows of atoms and the angular relationship between atoms establish the crystal structure, crystal symmetry, and properties for each polymorph (table 1) (*12*, *29*).

Table 1.—Properties of selected crystalline silica polymorphs

	Quartz	Tridymite	Cristobalite
Crystal system . . .	Hexagonal	Orthorhombic	Tetragonal.
Refractive index . .	ω 1.544 ϵ 1.553	α 1.471-1.479 β 1.472-1.480 γ 1.474-1.483	ϵ 1.484. ω 1.487.
2V (all varieties) . .	66° to 90°	66° to 90°	66° to 90°.
Density (g/cm^3) . .	2.65	2.27	2.33.
Hardness	7	7	7.
Cleavage	Conchoidal	Poor prismatic	Conchoidal.
Color	Colorless, black, purple	Colorless	Colorless, white, yellowish.
Unit cell, Å:			
a	4.913	9.88	4.97.
b	NAp	17.1	NAp.
c	5.405	16.3	6.92.
Space group	$P3_121$ or $P3_221$	F222	$P4_12_1$ or $P4_32_1$.

NAp Not applicable.

Source: Adapted from Deer (*4*).

The crystal structures of the different forms of crystalline silica are stable over specific temperature ranges. As the temperature changes, the crystal structure becomes unstable and atoms within the crystal migrate to create a more stable configuration for that temperature (table 2). Alpha and beta forms (i.e., α-quartz and β-quartz) are variations of the same crystal structure. In the α-quartz to β-quartz transformation, there is bond rotation but bonds

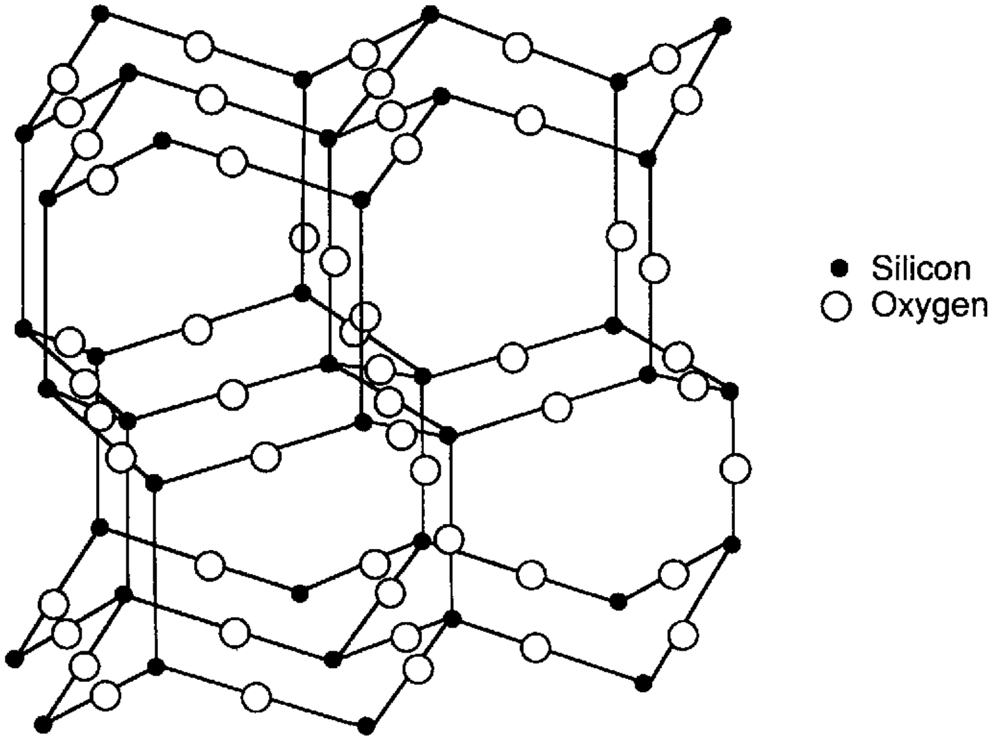


Figure 2.—Structure of β **tridymite.**

between oxygen and silicon are not broken. Bonds between oxygen and silicon for the different forms (quartz, cristobalite, tridymite, etc.) must be broken and reoriented, and oxygen and silicon must migrate to form a new crystal lattice. The transformation from one crystal structure to another takes place gradually except for the α- to β-quartz transition. Consequently, silica polymorphs may exist metastably at temperatures that are not within their normal stability range (table 2) (*4,12*). Given adequate time, a metastable phase generally will transform to a more stable crystalline phase. That is one reason why cristobalite, amorphous silica, and glass generally are not observed in geologically ancient deposits (*23*).

Table 2.—Stability fields for crystalline silica minerals

Polymorph	Stability field
α-quartz	Stable up to 573 °C.
β-quartz	Stable between 573° and 870 °C.
α-tridymite	Metastable below 117 °C.
β_1-tridymite	Metastable between 117° and 163 °C.
β_2-tridymite	Stable between 870° and 1,470 °C.
α-cristobalite	Metastable between 200° and 275 °C.
β-cristobalite	Stable between 1,470° and 1,713 °C; metastable between 200° and 1,470 °C.
Coesite	Stable between 450° and 800 °C and above 38,000 atmospheres.
Keatite	Unknown.
Stishovite	Stable above 1,200 °C and 130,000 atmospheres.
Silica glass	Metastable below 1,713 °C.

Quartz, the stable form of crystalline silica at ambient temperatures and pressures, is the most abundant of the crystalline silica minerals (*23*). Cristobalite and tridymite, while relatively rare, are the next most abundant forms of crystalline silica. Stishovite and coesite are rarely observed in nature. Keatite is a synthetic form that has not been found in nature (*4, 23*).

Substitution is greatest in cristobalite and tridymite because they have open crystal structures that permit replacement of silicon by aluminum and the inclusion of modifying oxides of the alkaline and alkali-earth metals within the structure. Little substitution occurs in quartz, and deviations in its composition often are attributed to mineral inclusions rather than to substitution (*4*).

Silica in Rocks and Soils

Quartz is present in igneous rocks such as granite and rhyolite. As magma cools, silica first is consumed in the crystallization of olivine, pyroxenes, amphiboles, feldspars, and micas. Quartz crystallizes only if all of the silica has not been used in the formation of these silicates. It is common in granite, quartz syenite, quartz monzonite, granodiorite, quartz diorite, quartz gabbro, rhyolite, quartz latite, dacite, quartz basalt, and pumice. Quartz also is present in trace to minor amounts in monzonite, latite, diorite, and andesite, and it is rare in gabbros, basalts, pyroxenites, and peridotites. It is common in hydrothermal veins associated with igneous formations. The average quartz content of igneous rocks is 12% (*3*). Cristobalite and tridymite occur in rhyolite, trachyte, andesite, dacite, basalts, and obsidian, although they represent a very small fraction of the crystalline silica present in igneous rocks (*3, 4, 12, 23, 37*).

Quartz is present in volcanic tuffs, which are deposits of consolidated volcanic ash (*7*). Because the ash cools rapidly, it is glassy (noncrystalline) rather than crystalline. However, quartz may crystallize before the magma is blown from the volcano as an ash and be present as crystals or phenocrysts in a glassy matrix. Volcanic glasses devitrify (crystallize) over time, so a complex mixture of finely crystalline quartz and other silicates eventually replaces the volcanic glass through the alteration process. Cristobalite and tridymite are rare but may be present in some volcanic tuffs.

Quartz is an extremely common constituent of sedimentary rocks. Sedimentary rocks are formed when minerals released during the weathering of rocks accumulate in a depositional basin and are consolidated (*29*). Quartz is extremely resistant to chemical weathering and is very hard (7 on the Mohs' scale), so that it becomes a common detrital mineral. It is present in trace to major amounts in a wide variety of sedimentary rock types, ranging from shales to siltstones to sandstones and conglomerates (*4, 37*). Chemically precipitated rocks such as limestones or dolostones may contain quartz if it was present in the depositional basin during the precipitation of the carbonate.

Quartz is present in metamorphic rocks, which are rocks that form through the application of heat, pressure, and/or introduced hydrothermal fluids. New textures may be developed (e.g., crystal reorientation, new crystal growth) and new minerals may be formed during metamorphism (*29*). Quartz may be present in the rock that is metamorphosed, it may crystallize from silica-bearing fluids introduced into the rock during metamorphism, or it may form as part of the metamorphic process. Quartz is found in quartzites, phyllites, schists, gneisses, and some slates, which are the metamorphic equivalents of quartz-bearing sedimentary and igneous rocks (*4, 37*). Tridymite occurs in some highly metamorphosed impure limestones and arkoses (*4*). Coesite and stishovite occur in rocks associated with meteor impacts (*4*).

Quartz is one of the most common nonclay minerals in soils along with feldspars, micas, amphiboles, and carbonates (*20*). Most soils contain at least trace amounts of quartz, which can occur either as a residual component of a rock that has weathered to form the soil or crystallized from amorphous silica that formed during the weathering process (*20, 42*). Quartz is the dominant form, although cristobalite also may be present in the soil in trace amounts.

Cryptocrystalline and Amorphous Silica

Cryptocrystalline silica is called chert or chalcedony depending on the color and texture of the rock (*4, 12*). Chert and chalcedony are composed of quartz crystals that are too small to be observed under the microscope. They form from colloidal silica that was deposited as a hydrated gel. As the gel loses water over time, extremely fine quartz crystals grow, forming the minerals. Chalcedony and chert are found as fillings or linings of cavities in rocks, as bands and nodules in the host rock, and in soils (*12, 35, 42*). Tripoli is a rock composed of finely disintegrated chert (*40*). Rottenstone is a rock composed of fine grains of silica and silicates that results from the decomposition of siliceous limestone and shales (*40*).

Opal is a hydrated amorphous form of silica (*12, 40*). There is no periodicity to the arrangement of the silica tetrahedra, so a crystal lattice is not developed (*23*). Cristobalite and tridymite ordering may be present in minor amounts in the amorphous opal matrix (*23*). Opal, like cryptocrystalline quartz, is formed from a colloidal suspension of silica. Unlike chalcedony and chert, opal may contain up to 20% water (*12, 35*). Opal is observed only in geologically young deposits because it recrystallizes into chalcedony over time (*23, 30*).

Biogenic silica is formed when microscopic planktonic organisms such as diatoms secrete shells composed of amorphous silica. When the microscopic organisms die, the silica shells sink to the bottom of the seafloor or lakebed and accumulate (*13, 17*). Eventually, the sediment is consolidated to form a silica-rich rock called diatomite (diatomaceous earth). Biogenic silica is a hydrated amorphous silica (*17*); it also is found in the structure of certain grasses such as rice and sugarcane.

Glass

Glass is a silica-rich material that is formed naturally. It also can be prepared synthetically. Natural glasses form when lava is quenched. Minerals are not present because there is insufficient time for the atoms to arrange themselves into a periodic crystalline structure (*40*). Obsidian is a typical glass. It forms when lava flowing from a volcano is quenched by contact with air or water (*40*). Perlite is a volcanic glass that is similar to obsidian but contains water in its structure (*29*). Glasses may devitrify over time.

MINING AND THE REGULATION OF CRYSTALLINE SILICA

Silica is present in nearly all mining operations. It may be present in the ore, the host rock, and/or the overburden. Many metallic and nonmetallic mineral commodities are extracted from deposits containing crystalline silica (table 3). A few examples are clay for bricks and ceramics, iron for steel, copper for wire, sand for concrete and glassware, and dimension stone for decorative building facings.

Table 3.—Silica: Mineral deposits and commodities

Commodity[1]	Form of silica in deposit[2]	Major commercial applications
Antimony	Quartz	Flame retardants, batteries, ceramics, glass, alloys.
Bauxite	do.	Aluminum production, refractories, abrasives.
Beryllium	do.	Electronic applications.
Cadmium	Quartz, jasper, opal, agate, chalcedony	Batteries, coatings and platings, pigments, plastics, alloys.
Cement	None	Concrete (sand, clay, and shale used in concrete mix).
Clay	Quartz, cristobalite	Paper, ceramics, paint, refractories, bricks.
Copper	Quartz	Electrical conduction, plumbing, machinery.
Crushed stone	do.	Construction.
Diatomite	Quartz, amorphous silica	Filtration aids.
Dimension stone	Quartz	Building facings.
Feldspar	do.	Glass, ceramics, filler materials.
Fluorspar	do.	Acids, steelmaking flux, glass, enamel, weld rod coatings.
Garnet	do.	Abrasives, filtration, gem stone.
Germanium	Quartz, jasper, opal, agate, chalcedony	Infrared optics, fiber optics, semiconductors.
Gold	Quartz, chert	Jewelry, dental, industrial, monetary.
Gypum	Quartz	Prefabricated product (gypsumboard), industrial and building plaster.
Industrial sand	do.	Glass, foundry sand.
Iron ore	Chert, quartz	Iron and steel industry.
Iron oxide pigment (natural)	Chert, quartz, amorphous silica	Construction materials, paint, coatings.
Lithium	Quartz	Ceramics, glass, aluminum production.
Magnesite	do.	Refractories.
Mercury	Quartz, chert	Chlorine and caustic soda manufacture, batteries.
Mica	Quartz	Joint cement, paint, roofing.
Perlite	Amorphous silica, quartz	Building construction products.
Phosphate rock	Quartz, chert	Fertilizers.
Pumice	Volcanic glass, quartz	Concrete aggregate, building block.
Pyrophyllite	Quartz	Ceramics, refractories.
Sand and gravel	do.	Construction materials.
Selenium	do.	Photocopiers, glass manufacturing, pigments.
Silicon	do.	Silicon and ferrosilicon for ferrous foundry and steel industry.
Silver	Quartz, chert	Photographic material, electrical and electronic products.
Talc	Quartz	Ceramics, paint, plastics, paper.
Tellerium	do.	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.
Tungsten	do.	Cemented carbides for metal machining and wear-resistant compounds.
Vanadium	Quartz, amorphous silica	Alloying element in iron, steel, titanium.
Zinc	Quartz, jasper, opal, agate, chalcedony	Galvanizing, zinc-based alloys, chemicals, agriculture.
Zircon	Quartz	Ceramics, refractories, zirconia production.

[1] Underlined commodities have direct sales to OSHA-regulated sites, crystalline silica may be present in the final product.

[2] Deposit may contain trace to major amounts of silica. Silica may not be present in all deposits for a given commodity. For chemicals and metals, the column refers to the ore source.

Since the concern of OSHA's HCS is crystalline silica in materials handled by operations under OSHA jurisdiction, not all mineral industries are directly affected. Mining operations that are regulated by MSHA will not be directly affected but may be required to supply information to fabricators and manufacturers that are regulated by OSHA. Operations that do not have crystalline silica in their final product will not be affected. These include the ferrous and nonferrous metals industries and several of the industrial minerals industries.

OSHA's HCS will have the greatest effect on the clay, crushed stone, sand and gravel, pyrophyllite, talc, calcined and uncalcined diatomite, perlite, and pumice industries. This is because these industries sell mineral products that may contain trace to major amounts of crystalline silica directly to OSHA-regulated facilities. Some clay, pyrophyllite, and talc products do not contain quartz, while others may contain trace to minor amounts. The content is determined by the mineralogy of the deposit and, to some extent, by the processing of the crude ore. Sand and gravel always contain crystalline silica as the major constituent. The crystalline silica content of crushed stone will vary greatly from deposit to deposit. A crushed quartzite is composed entirely of quartz, while a crushed diabase may contain only trace amounts. Most diatomite, perlite, and pumice products will contain trace to minor amounts of crystalline silica. Diatomite that is agglomerated by sintering to the softening point of the silica glass may contain greater amounts of crystalline silica (cristobalite) than unsintered diatomite since crystallization of silica minerals may occur during the sintering process.

The commodities affected by HCS are used by a wide variety of industries. Clay and talc are used by the paper, ceramics, paint, refractories, plastics, rubber, and chemical industries. Pyrophyllite is used by the refractories and ceramics industries. Perlite is used by the construction and gardening industries, and crushed stone, sand, and gravel are used by the construction and chemical industries. For commodities such as clay, sand, and gravel, there are few economically viable or technologically sound substitutes that contain no crystalline silica (e.g., sand and gravel in concrete). For clays, sand, and gravel, there are more than 4,500 companies that could be affected (*41*).

MSHA has proposed a Hazard Communication Standard, which is under review. This ruling would affect almost all mining operations because quartz is present in most overburdens and host rocks. The cost of labeling for OSHA's HCS and MSHA proposed regulation is minimal relative to the overall costs of operating a mine and mill. However, additional costs will be incurred for sampling, analysis, loss of sales in some markets due to silica content, and litigation that is associated with almost any material that is categorized as a carcinogen. The cost of analysis can range from $25 per sample to several hundred dollars per sample depending on the instrument used and the complexity of the analysis. Sales losses and litigation costs are more difficult to assess because they are dependent on society's <u>perception</u> of the risks imposed by the use of materials that contain crystalline silica.

X-RAY DIFFRACTION ANALYSIS AND PROBLEMS

Most mineral producers will, therefore, have to determine the respirable monitor filter and bulk crystalline silica contents of their ores and products so that workers and/or customers, who are regulated by either MSHA or OSHA, will know whether they are in compliance with the 0.1% HCS and/or the OSHA permissible exposure level (PEL) of 50 μg for an 8-hour workday for respirable crystalline silica as determined from monitor samples. This section addresses the public inquiries and the pertinent literature and highlights some of the difficulties associated with the present regulatory determination methods for crystalline silica in mineral and material samples in general, and the 0.1% HCS level in particular, in an attempt to arrive at a set of recommendations capable of mitigating many of these shortcomings. The limitations of the present quartz and cristobalite standards in the areas of reproducible availability of equivalent standard materials are stressed, as is the advisability of one standard each for the wide range of crystallinity (both stable and metastable) and range of particle sizes (both respirable and bulk) of the material analyzed. Other major problems discussed include positive mineral and phase identifications, common overlapping and interfering diffraction peaks with the principal quartz and cristobalite lines, whether the silica variety is crystalline or not (the basis for the opal-CT (cristobalite and tridymite) controversy), matrix effects versus lighter loadings, and intensity-sensitivity-background noise relationships, all impacting significantly on the quantification methods at the 0.1% HCS level. These discussions are augmented with additional discussions of figures prepared from typical X-ray diffraction patterns of common rocks and minerals, and respirable monitor samples usually encountered in quantitative crystalline silica determinations. Specially prepared marble samples at the 0.1% HCS level are employed to both help clarify and illustrate some of the outstanding problems with examples. In addition, recommendations are advanced to help avoid many of these dilemmas and to reduce the potential inability to make either a positive identification or a meaningful quantification of a sample's crystalline silica content.

SAMPLE PREPARATION

The ores, minerals, and materials investigated are listed in table 4. The localities of the geological samples are listed only by State because of industry concern about a more specific identification of its ores and products. This reservation diminished neither the mineral industry's support nor its enthusiasm for this effort.

Table 4.—Materials and origin

Material	Origin
Quartz[1]	Unknown.
Cristobalite[2]	Unknown.
Chert	Colorado.
Tripoli[3]	Oklahoma.
Glass[4]	Nevada.
Perlite[3]	Armenia.
Gem opal	Australia.
Opalized diatomite[3]	California.
Diatomite[3]	California.
Soil	Florida.
Soil	Illinois.
Soil	Kansas.
Soil	Montana.
Ball clay[3]	Kenucky-Tennessee.
Mica schist	New York.
Graphitic schist.	South Dakota.
Barite[3]	China.
Bentonite[3]	Wyoming.
Tertiary claystone[3]	Southern States.
Muscovite mica[3]	New England.
Kaolin[3]	Georgia.
Kyanite[3]	Virginia.
Wollastonite[3]	New York.
Graphite	Alabama.
Marble/calcite[3]	New York.
Respirable dust[6]	California.

[1] NIST Standard - quartz.
[2] NIST Standard - cristobalite.
[3] Commercially available.
[4] Powdered microscope slide.
[5] Drilling mud grade.
[6] Monitor sample.

The ores examined are generally mined from either open pit or underground mines. The blasted ores or excavated ores are then primary-crushed in jaw or gyratory crushers (for hard rock) and roller-shredders (clay). The primary material is then further reduced in a secondary grinding system, beneficiated if required, and conveyed to a Raymond, ball, or equivalent milling system for product manufacturing. These commercial products and standard materials were used in the Bureau's X-ray diffraction studies. The study materials were either mechanically or hand ground with a mullite mortar and pestle to minus 325 mesh. The samples analyzed were hand-loaded and compressed at 30 psig in circular plastic X-ray sample holders to maximize random orientation of particles.

The specially prepared marble samples with total 1.0% addition of either quartz, graphite, or muscovite mica were prepared from previously ground material and mixed in a Spex-Mill[5] with plastic balls for 20 min prior to pressing and X-ray diffraction examination.

EXPERIMENTAL PROCEDURES AND DISCUSSION

Instrumentation

X-ray diffraction data at room temperature were obtained on a Seimans D500/Siemac V computer controlled diffractometer operated under the following conditions: Beta-filtered $CuK\alpha$ radiation; 30 ma; step scanning mode; scan angle, 4°-76° 2θ; step size, 0.05° 2θ; count time, 1.0 s per step; diffracted beams monochromatized with a curved graphite crystal monochromator; and a scintillation counter detector.

Standard Materials

The NIST quartz and cristobalite standards shown in figures 3 and 4 (to be discussed later) were prepared from a commercially available ground quartz marketed only on performance characteristics. The precursor raw materials for these two standards, the ground quartz or crystalline silica product, are presently mined, beneficiated, prepared, and manufactured at three locations using distinct processing schemes. It is unclear which operation supplied the standard raw material or if it was obtained from a single location. Geologically the deposits from which these raw materials were recovered range from quartz-cemented sandstones to metamorphosed quartzites. The quartz and/or sand grains in these types of deposits are usually relatively free from contaminants, while the cements usually host diverse trace elements and mineral contaminants. The principal accessory minerals in these deposits range from clays to micas, feldspars, and iron oxides through heavy mineral suites such as zircon, tourmaline, apatite, magnetite, rutile, ilmenite, kyanite, and monazite. The accessory minerals and cementitious materials could be further altered by heat-related metamorphic processes.

In addition, modernizations at these three plants have significantly altered their comminution circuits. Grinding circuits can no longer be duplicated and/or reproduced since mills may now include both silica and ceramic balls and liners. These changes alone would affect both the chemistry, notably alumina contamination, and the particle size distribution of the finished product. Another problem to be considered is the source of quartz material: either cemented sandstone or quartzite. During the grinding step

---

[5] Reference to specific products is made to facilitate descriptions and does not imply endorsement by the Bureau of Mines.

of the sandstones, there is a tendency for the poorly crystallized impure and softer silica cement to report in the fines and ultimately be preferentially concentrated in these fine-grained crystalline standards. A similar bias undoubtedly exists for the metamorphosed quartzitic material. The percentage content of the better crystallized, larger, harder, and usually purer sand and/or quartz grains reporting in fines products is unfortunately unknown.

The NIST quartz (*24*) and cristobalite (*25*) standards were intended to be respirable standard reference materials (SRM) for respirable silica dusts. These candidate materials are both crystalline and have a particle size distribution in the inhalable-respirable size range of 0.5 to 5 μm. This particle size distribution will severely limit their usefulness in quantifying coarser bulk materials at the 0.1% HCS level. The particle size distribution of bulk materials is typically larger, thereby exhibiting dissimilar line intensity shapes on which positive identification and quantitative analysis are calculated. It will be shown later how mismatched standards in some instances may cause 20% errors in crystalline silica determination.

The impure natural quartzose materials were prepared by numerous hot acid leaches and washes prior to drying, and subsequent crystallographic and particle size distribution determinations were made prior to final characterization and certification as SRM for quantification by X-ray diffraction techniques. This preparation scheme, with its repetitious leachings, washings, and decantations, followed by overnight drying in shallow pans, probably altered the original particle size distribution, chemistry, and character of the natural material (*31*). The difficulty in redispersing the dried agglomerated cakes, coupled with the solubility of contaminants and finely divided quartz (both cementitious and grain) in mineral acids, was largely responsible for this divergence in particle size distribution from the original starting material. Goldberg and Jacobson (*8*) report significant attack of quartz in the smaller size ranges by mineral acids. Additionally, partially digested and amorphous siliceous reaction rims surrounded some of the larger undissolved quartz grains, and the presence of such rims should not be precluded from the SRM, where they could ultimately influence the diffraction intensity distributions. The quartz SRM, although not intended for use as a particle size reference material because of its tendency to agglomerate, is composed of particles in the respirable size range with many nonrespirable agglomerates. The equivalent spherical diameters as determined by a sedimentation method were found to be 0.33 to 5 μm (95% by mass of the particles). The mass mean equivalent spherical diameter as determined from these measurements is 1.62 μm (*24*).

The cristobalite SRM was prepared by an NIST contractor from similarly labeled commercially available quartzose material according to information listed on JCPDS-ICDD Card 39-1425 (*14*, *15*). The contractor apparently heated 2-kg quartz batches to 1,600 °C and maintained this cycle for 8 hours. The batches were then air-quenched, treated with 6$\underline{N}$ HCl, and jet-milled with the subsequent plus 325-mesh fraction removed by sieving. The earlier discussions on the quartzose material and the quartz SRM are probably applicable to this SRM cristobalite.

The limitations for ambient stable and metastable standards are amplified later in the text. However, it should be noted that the use of one quartz and cristobalite quantification standard in conjunction with test samples of dissimilar materials exhibiting a wide range of spatial and chemical disorder would be difficult at best. The effect of disorder on quantitative determination and on the definition of crystallinity itself is addressed at more appropriate sections of the text.

Analytical Techniques

The maximum 0.1% crystalline silica criterion was derived from governmental regulations dealing with potentially carcinogenic materials and not from limitations of the accepted analytical methods. The established techniques applicable to the determinations are reviewed by Hamilton, Peletis, and Miles (*10*). These authors reviewed the established analytical techniques, such as modal analysis by optical microscopy, particle counting by electron microscopy and thermal analysis, selective dissolution, separation based on density, infrared absorption spectroscopy, and X-ray diffraction. Except for the X-ray diffraction technique, all the above techniques were judged by these authors to be unacceptable for determining crystalline silica at the 0.1% level. In using the infrared method, although it was sensitive to small amounts of crystalline silica, matrix effects restricted the practical limit of the determination of the crystalline silica content to 1%. The infrared techniques are covered in National Institute of Occupational Safety and Health (NIOSH) method 7601 (*27*) and by the British Health and Safety Executive (*39*).

The X-ray diffraction techniques are generally acknowledged to hold the greatest promise for determining crystalline silica at the 0.1% level. The advances in instrumentation and automation of data gathering and processing over the past decade have enabled analysts to concentrate their efforts on resolving the major problems of sample preparation, matrix effects, and characterization of spectral overlap and/or interfering peaks. These methods and procedures, including the foundations for quantitative X-ray diffractometry, are detailed by Alexander and Klug (*1*) and Klug and Alexander (*19*). This present work is limited to the quantitative analysis of crystalline silica by X-ray diffractometry.

Quantitative X-ray Diffractometry

X-ray diffraction techniques enable the distinction between crystalline and amorphous material. Crystalline materials diffract coherently by yielding well-defined peaks, lines, reflections, or maxima at angles given by Bragg's Law from which unambiguous crystallographic parameters, such as unit cell dimensions and diffraction intensities, can be readily calculated and used in both positive phase identification and quantification. Amorphous materials scatter X-rays incoherently into broad diffuse peaks or reflections, thereby precluding positive calculation of crystallographic parameters required not only for positive phase identification but also for the necessary intensity measurements on which to base a meaningful quantitative analysis.

It must also be pointed out that determining small amounts of crystalline silica associated with only one or two other minerals or phases is significantly different from determining small amounts of crystalline silica in multiphase systems. Earlier successes in quantification in multiphase systems, such as commercial paints, were successfully accomplished for paint films solely because of the intimate knowledge of the limited number of pigments used in manufacturing (*18*). Unknowns in uncharacterized multiphase systems containing natural and synthetic materials would be significantly more difficult or impossible to analyze. In addition, metastable ambient phases, such as cristobalite and tridymite, although quenched from their high-temperature fields of stability, may not be 100% of either, since metastability implies not only instability but also amorphousness, and poorly crystalline transitional phases and/or polymorphic mixtures that vary with months or years. Theoretically, the metastable tridymite and cristobalite are not perfectly crystalline but rather composed of mixed domains of hexagonal and cubic close-packed structures and possibly amorphous domains which collectively give nontypical X-ray diffraction patterns. The X-ray diffraction technique, generally discussed earlier, requires a nearly perfect crystalline standard, such as quartz, to be viable. In the instance of quartz, optical-quality single crystals, usually of high purity, would be ideal as an internal standard, thereby making possible the discrimination of intensity contributions from amorphous scattering and background. Ideally, as shown by Jackson, Huggins, and Ampian (*13*), either a synthesized or an acquired internal standard with a similar half-width added in known amounts to an equivalent matrix would minimize analytical difficulties. The internal standard should have similar peak half-widths, $\beta_{1/2,2\theta}$,[6] to those of the silica phase being quantified.

The recent work by Flynn, Rosal, and Kinsala (*7*) on the effects of time and temperature on the cristobalite formation in diatomaceous earths clearly illustrates the impact of a mismatched internal standard from either crystallinity and/or particle-size considerations. The authors reported cristobalite contents in excess of 100%, with one sample containing 110% in their well-crystallized, unfluxed, selected freshwater French diatomites when heated between 1,000° and 1,200 °C. The X-ray diffraction analysis was based on a standard curve prepared from NIST SRM 1879 cristobalite blended with the natural diatomites to minimize matrix effects.

NIOSH method 7500 (*26*) for the quantitative X-ray diffraction technique for crystalline silica is generally considered the most practical method advanced. Briefly, this method (also used by MSHA) uses X-ray diffractometry to determine the amount of crystalline silica deposited on a silver membrane filter (*36*). The approach enables the quantification of the crystalline silica content of the airborne dust and hence enables compliance with all regulatory parameters, including the OSHA HCS. The dust is collected on a polyvinyl chloride (PVC) filter and transferred to a silver filter using a dissolution technique. The silver filter also serves as an internal standard. The useful range of this analysis is usually between 5 and 200 mg, and matrix effects are not a problem if the dust collected is represented by a thin film on the silver membrane. The Health and Safety Executive (*38*) maintains that this method is suitable up to a limit of approximately 2 mg when the dust is deposited on a 25-mm-diameter filter. Difficulties, however, may be encountered with overloaded samples because of deviation from linearity due to matrix absorption effects. This fact is critical because quantification by X-ray techniques is calculated on the assumption that a linear relationship exists between the X-ray diffraction peak intensity and crystalline silica concentration. Additionally, samples with a very high mass absorption coefficient, such as hematite- or magnetite-bearing iron ore samples, may cause difficulties, which are usually corrected by lighter loadings. The lighter loadings minimize this phenomenon experienced with CuKα radiation. Generally, the remedies for correcting these matrix absorption effects are not advocated because they further complicate the analysis and may result in major overcorrections. Inherent problems with the NIOSH method that warrant additional attention are preferred orientation, causing changes in the intensity of the major quartz peak (3.34Å), found in samples of thin layers of respirable quartz, and the shadowing of the smaller respirable particles by the rough surface of the silver membrane from the X-ray radiation. Edmonds, Hensle, and Guerra (*5*) maintain that errors up to 300% of the quartz present may be commonplace in such environments. The present authors maintain that an appropriately sized standard matching the particle size distribution of the monitor sample would mitigate the problem. The preferred orientation problem,

---

[6] The measured breadth of a reflection at half maximum.

on the other hand, eliminated by heavier loading because of a more random orientation of particles, is unfortunately accentuated by lighter loadings, as in the instance of iron-bearing materials. Other complications inherent in the technique—chiefly overlap or peak interference with crystalline silica peaks by other phases present, and the suitability of the standard reference crystalline silica standards in both particle size range and degree of crystallinity—remain as the principal shortcomings. These shortcomings will be amplified later in the figure discussions.

Other approaches, such as peak deconvolution (*11*) and full pattern matching (*34*), have been evolving in recent years to accommodate the increasingly complex spectra from spectroscopy and chromatography, including X-ray diffraction patterns. These new and sophisticated analytical techniques with their enhanced processing and data collection capabilities are encouraging development of new mathematical solutions to resolve complex spectra. The full pattern matching technique holds the most promise for analyzing difficult multiphase systems. These new techniques account for noise, background, and multiphases and make use of data from the entire pattern instead of relying on a single peak, scan, or limited region of 2θ. Allowances for poor crystallinity, interfering peaks from other phases, and amorphous material are also reportedly possible. Several X-ray diffraction problems not minimized by these techniques and deserving attention are particle statistics, preferred orientation, microabsorption, and extinction (*28*). These techniques, while holding considerable promise for determining major phases in multiphase systems, are yet to be proven at very low concentrations, such as in the 0.1% HCS quartz limitation. Despite the formidable problems confronting the analyst, as mentioned earlier, scrupulous attention to fundamentals has increased the overall precision and sensitivity of quantitative X-ray diffraction techniques for low levels of crystalline silica in some relatively direct and well-characterized materials. Carter, Hatcher, and Di Carlo (*2*), using an internal standard method and mass-absorption coefficient correction methods to compensate for sample absorption effect, were successful in determining quartz and cristobalite approaching 0.01% and 0.03%, respectively, in beneficiated and treated bentonitic clays. Salter and Riley (*32*) conclude that the analysis of quartz in kaolin clay products is possible at the 0.1% level when interfering mica peaks are not present to overlap the 3.34Å principal quartz (101 hkl) reflection. Otherwise, they were prohibited from using the most sensitive and/or intensive quartz line. The principal problems associated with their analyses were (1) peak overlaps from kaolinite and mica minerals, (2) detection of the main quartz line above background, and (3) data reduction of the scanning region of interest to collect reproducible peak areas. The direct determination of quartz in a well-crystallized dolomite matrix was shown by Emig and Smith (*6*) to be possible below 0.1%. These authors discussed methods for handling matrix and spectral overlap effects. In other works, Hamilton and Peletis (*9*), Hamilton, Peletis, and Miles (*10*), and Miles and Hamilton (*22*) researched the determination of quartz in perlite to below the 0.1% level where matrix absorption was not a major factor. The authors concentrated their attention on correcting statistics and very low peak-to-background ratios normally associated with glassy, highly scattering matrices. The careful work by Hamilton and others was substantiated by McKee, Renault, and Barker (*21*) on several New Mexican perlites.

Spectral Overlap

The X-ray diffraction maxima from minerals that are commonly associated with quartz in mining, milling, processing, and manufacturing situations may overlap one or more of the three principal quartz diffraction lines. Table 4 lists several minerals and materials that the present authors have encountered in the past. In simple systems, as mentioned earlier, with amorphous and/or relatively few crystalline materials, the interfering peaks may not present an insurmountable problem. Unfortunately, multimineralic systems are commonplace in rocks. Usually, the secondary or weak quartz diffraction peaks, such as those listed in table 5 (4.26Å, and 1.82Å), or a combination of other unlisted less desirable peaks are used for quantification. This approach, while useful in simple systems, is severely limited in multiphase systems because these relatively weak secondary quartz peaks would significantly limit sensitivity.

The regulatory entities, such as OSHA, MSHA, NIOSH, and the British Health and Safety Executive, recognizing the seriousness of the overlap problem, recommend qualitatively scanning each sample in order to select a quartz line free from interference from other phases. In practice, however, this requirement is usually omitted in the press for time to simply quantifying additional peaks, and the results are simply accepted if within some arbitrary limits. This approach, while outwardly appearing reasonable for a major interfering phase, would be totally unacceptable for a minor constituent, such as mica, and would lead to erroneous results because minor variations and/or discrepancies between peaks are usually attributed to simple statistical fluctuations in line positioning and intensity and not to a minor interfering phase peak. In addition, the spatial and chemical disorders commonplace in minerals, along with solid-solution phenomena found in minerals such as micas and feldspars, affect the minerals' crystallographic composition and lattice dimensions, which ultimately determine the positioning and intensities of the diffraction peaks in the pattern. In complex rock-dust systems it may even be impossible to find an interference-free principal quartz peak to even attempt quantification. To better illustrate these points, a series of X-ray diffraction patterns (figs. 3-13) has been prepared; each figure deals with a different aspect of the analytical approach discussed earlier.

Table 5.—Interfering peaks of minerals and materials overlapping the three strongest alpha-quartz diffraction maxima

Mineral	JCPDS-ICDD	hkl	k,Å	I/I_{100}	hkl	k,Å	I/I_{100}	hkl	d,Å	I/I_{100}
Quartz	33-116	100	4.26	22	101	3.34	100	112	1.82	14
					INTERFERING PEAKS					
Albite	19-1184	$2\overline{01}$	4.03	100	$1\overline{12}$	3.37	14	$\underline{0\overline{62}}$ $3\overline{51}$	1.830	11
Graphite	25-284	—	—	—	002	3.35	100	—	—	—
Gypsum	33-311	021	4.28	100	—	—	—	062	1.81	13
Kaolinite	14-164	$1\overline{11}$	4.19	45	002	3.58	80	$1\overline{14}$ $2\overline{23}$	1.81	20
Kyanite	11-46A	011 $1\overline{11}$	4.30	25	200	3.35	65	—	—	—
Muscovite	6-263	—	—	—	006	3.32	100	—	—	—
Wollastonite	27-1064	—	—	—	$\overline{1}02$	3.31	100	401	1.81	11
Barite	24-1035	101	4.34	30	$\underline{021}$ 20	$\underline{3.45}$ 3.32	$\underline{100}$ 70	—	—	—

D = Doublet.

DISCUSSION OF FIGURES

Figure 3

Figure 3 illustrates the actual X-ray diffraction pattern of the NIST respirable alpha-quartz standard obtained with the equipment and constant instrument settings described above. The principal d-spacings in angstroms (Å) are included in the figures for ready reference. The strongest quartz maxima listed in table 5 at 4.26Å (I_{22}/I_{100}),[7] 3.34Å (I_{100}/I_{100}), and 1.82Å (I_{14}/I_{100}) are also indicated in figure 3. The instrumental settings were maximized to obtain the optimum peak-to-background ratio necessary for illustration purposes, with the exception of figure 12, which was obtained at the more sensitive 1,000-intensity-count scale. All other data were recorded at the less sensitive 6,000-intensity-count scale. The purpose for the intensity scale changes for figure 10 is discussed later in the text.

Powder X-ray diffraction patterns used by this investigation for both the positive identification and characterization of the materials and minerals cited in table 4 and the crystallographic data tested in table 5 were obtained exclusively from the JCPDS-ICDD file (*14, 15*). The protocol cited in the JCPDS file also was followed for the positive identification of constituents and as to the reliability of selected published powder diffraction patterns. The reliability of opal-CT, discussed later, was the only phase in this entire investigation that was judged to be both amorphous and unreliable by JCPDS. This classification by the Committee is not surprising considering the very diffuse nature of the diffraction pattern reproduced on JCPDS-ICDD card 38-448 (*15*), which clearly indicates a highly disordered or near amorphous state.

Figures 4 and 5

The crystalline forms of silica included in this overview are the alpha-quartz (fig. 4*D*) and cristobalite (fig. 4*A*) varieties. The tridymite polymorph, although included in the HCS, is only observed in high-temperature natural and synthetic siliceous products. Both cristobalite and tridymite, as described earlier, are high-temperature polymorphs of silica and exist metastably at ambient temperatures. Cristobalite, the phase appearing in certain diatomite materials, usually flux calcined between 1,100° and 1,200 °C, is stabilized on cooling with soda ash mineralizers or fluxes (*22*). Diffraction patterns of this material are isostructural with the NIST cristobalite standard and compare favorably with its diffraction pattern listed in figure 4*A*. The tridymite polymorph apparently does not persist metastably at ambient temperatures on quenching from high-temperature diatomite and soda ash samples cited above, even though this heating cycle is in the field of stability or high-temperature range for tridymite. Cristobalite patterns similar to the cristobalite standard were not encountered in any of the natural samples (table 4) studied by X-ray diffractometric analysis.

Figure 4 also contains other X-ray patterns of forms of naturally occurring crystalline silica and/or quartz. The diffraction patterns of chert (fig. 4*C*) and tripoli (fig. 4*B*), both microcrystalline varieties listed in figure 4, reveal that these materials also are composed chiefly of quartz. Other common quartz microcrystalline varieties such as agate, jasper, and chalcedony, as well as the macrocrystalline varieties rose quartz, citrine, and amethyst, give identical quartz diffraction patterns. The microcrystalline (crystals

---

[7] I/I_{100} - the ratio of the strongest line arbitrarily set at 100 to the peak listed.

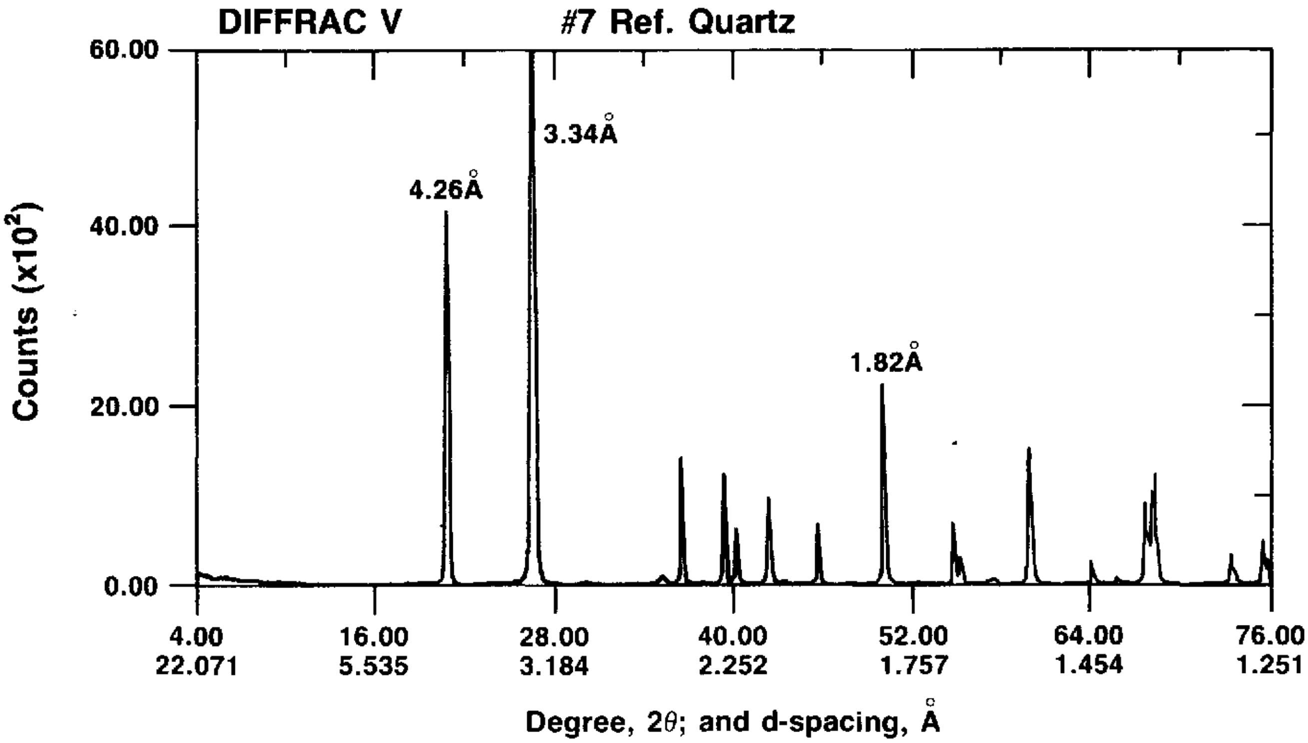


Figure 3.—NIST quartz standard. Example of typical X-ray diffraction pattern with constant instrument settings.

too small to see with the eye; aggregates of single crystals) and macrocrystalline (crystals large enough to see with the eye; nonaggregates) nature of the quartz can only be determined microscopically. The poorly crystalline and/or amorphous varieties of silica listed in table 4 are shown in figure 5. The silica types included in figure 5 follow; *5D*—glassy, synthetic; *5E*—natural volcanic obsidian; *5C*—natural perlite; *5B*—gem opal, a material characterized by its finely divided particle size; *5A*—opaline silica from diatomite (opalized diatomite). The opaline silica or opal is formed essentially from colloidal silica, while obsidian and perlite are basically highly siliceous glassy rhyolitic-type rock materials. The obsidians are usually either devoid of water or contain very low amounts of combined water. The glassy materials in figure 5 (*C*, *D*,and *E*) all reveal characteristic amorphous scattering exhibited by highly disordered material in the low 2θ region. This type of amorphous matrix possesses little or no periodicity or long-range order required for diffraction and/or crystallinity. The diffraction patterns from the quartz and cristobalite listed in figures 2 and 3 are examples of better crystalline or crystallized material. Although these materials in figures 4 and 5 may have similar free silica content or chemical compositions, the amorphous and glassy material is considered as noncrystalline and the quartz, chert, tripoli, and cristobalite are considered as crystalline. The pattern for opaline silica from diatomite (*5A*), although still disordered, has some short-range order exemplified by two broad peaks labeled SRO (short-range order). This material is referred to by some as opal-CT (*16*).

Jones and Segnit (*16*) proposed that the natural hydrous silicas, such as opal and opalized diatomite, be classified as either opal or opaline silica. They further subdivided these materials as opal-A, which is highly disordered, amorphous, and equivalent to the gem opal cited in figure *5B*, and opaline silica-diatomite (fig. *6D*); opal-CT, which is disordered and amorphous with some short-range ordering of α-cristobalite and α-tridymite type structure, shown by opalized diatomite in figures *5A* and *6C*; and opal-C, which is better ordered or crystallized α-cristobalite and equivalent to the NIST standard illustrated in figures *4A* and *6A*. The shoulder on the SRO (short-range order) peak in figures *5A* and *6C*, according to the Jones and Segnit classification, would be ascribed to some α-tridymite ordering. The present authors support the unreliable amorphous group designation recommended for the opal-CT and -C phases by the JCPDS-ICDD (*15*). This designation was based on both the failure and inability of the diffraction data to be indexed unambiguously so as to give calculated lattice dimensions. Additionally, the presence of only two broad peaks for identification of any specimen is counter to the recommended procedure advanced by the Joint Committee on positively identifying species—that you cannot positively identify with one or two peaks. The committee stipulates a minimum of three strong peaks to permit a positive identification based on an

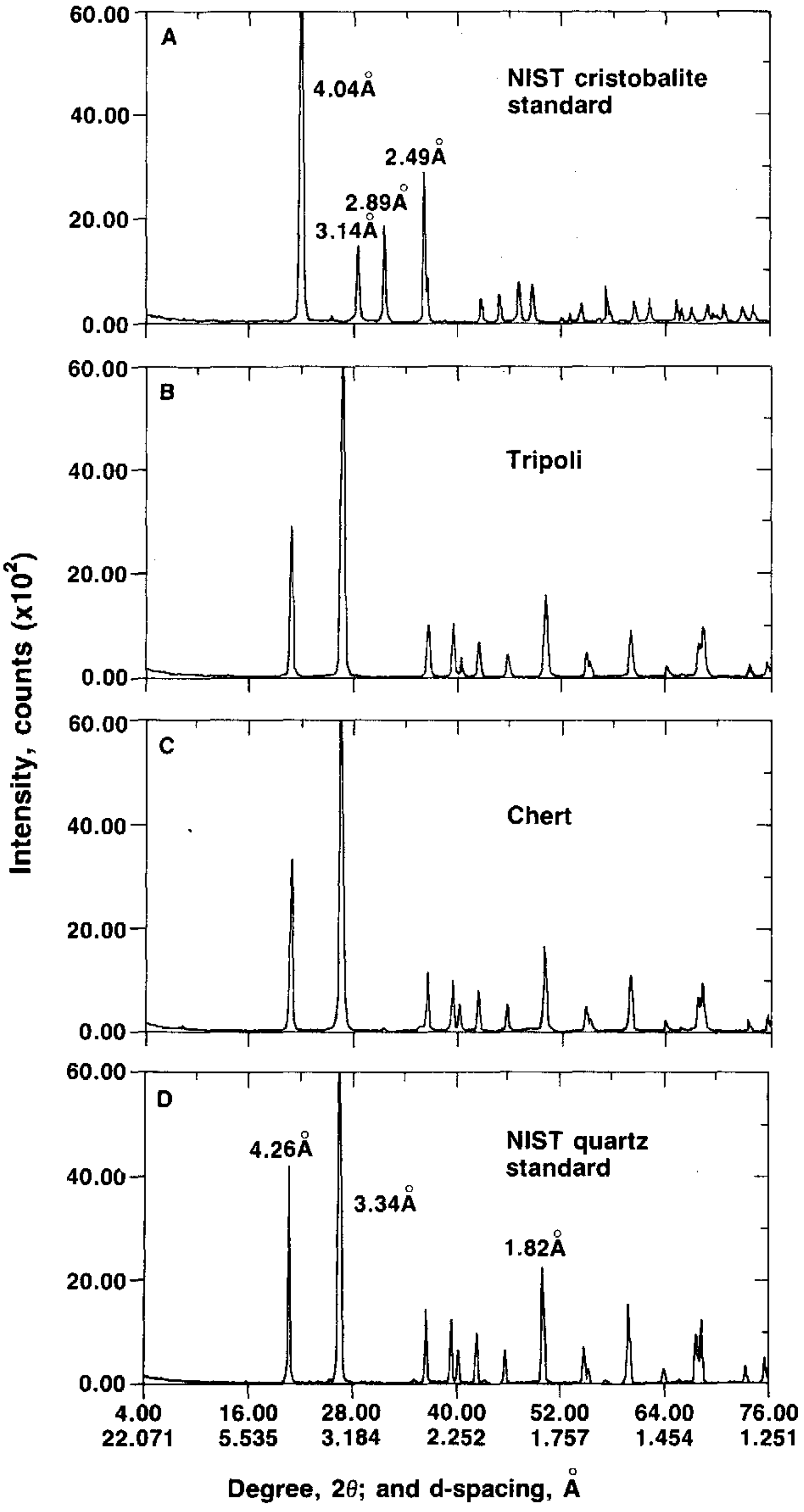
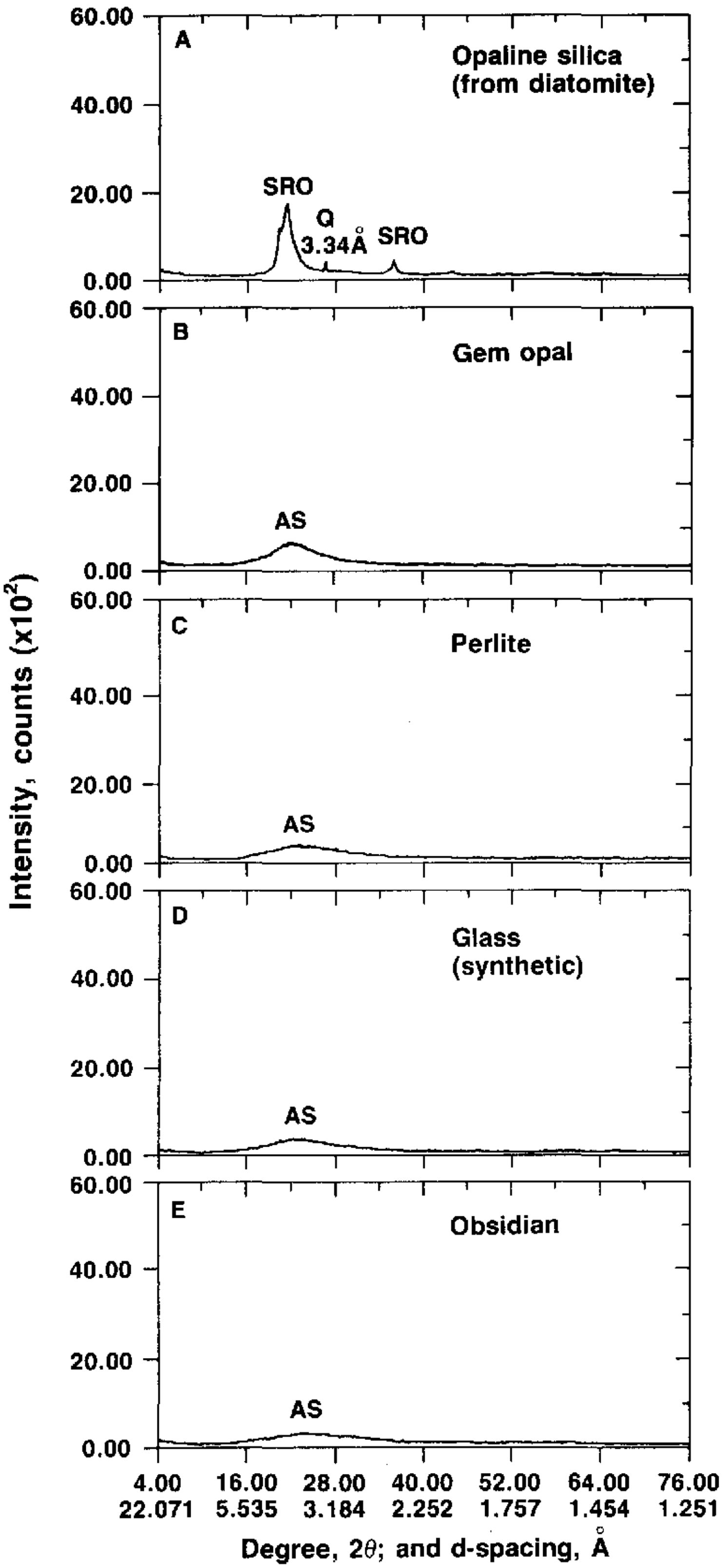


Figure 4.—Crystalline forms of silica.



Q = quartz, SRO = short-range order, AS = amorphous scattering

Figure 5.—Amorphous forms of silica.

acceptable and/or recommended powder diffraction pattern or card containing an adequate range of intensities and a certain composition. An adequate range of intensities and constant diffraction maxima, unencumbered by polytypes (e.g., a melange of α- and β-cristobalites and tridymites), as discussed earlier and reinforced later, is the basis for meaningful quantitative determination by the X-ray diffraction known-additions internal standard method. Deviations from this optimum procedure, discussed earlier, may even result in a greater than 100% content of a respirable crystalline phase content, or for that matter, any other size range. The present authors have no problem with either the Jones and Segnit designation or definitions of opal-A, opal-C, and opal-CT, although they lack the JCPDS-ICDD specifications cited above for recognition of crystalline phases, but cannot recommend the use of Jones and Segnit's varieties as accredited crystalline phases. In all probability Jones and Segnit never intended that their very diffuse patterns, indicating the transitory evolution from a highly disordered or near-amorphous opal-A (fig. 5*A*) to a higher degree of order in opal-C (fig. 6*A*), would be used for crystallographic or regulatory purposes. Constant reference is made by them to the multiphase, polytypism, and contamination exhibited by the opal samples they investigated.

Figure 6

Figure 6 includes patterns of selected amorphous diatomite (fig. 6*D*) with quartz and feldspar and the NIST quartz (fig. 6*B*) and cristobalite standards (6*A*). The contrast between the range of crystallinity for the silicas is readily apparent: The better crystallized standards (figs. 6*A* and 6*B*) versus the highly disordered amorphous silica (fig. 6*D*) with amorphous scattering and the disordered opalized diatomite (fig. 6*C*) with short-range ordering. Assigning an unambiguous d-spacing and 2θ angle, required for precise line intensity measurements employed in conjunction with a well-crystallized internal standard, is mandatory for the quantitative analytical method to succeed. The presence of SRO diatomite peaks (fig. 6*C*) alone would preclude long-range crystallinity. Additionally, the strongest cristobalite 101 hkl line from JCPDS-ICDD card 39-1425 for the NIST cristobalite standard at 4.040Å is not even equivalent to the present SR0 peak in figure 6*C*. In addition, Jones and Signet show that the cristobalite 101 hkl peak obtained from either opal-A or opal-CT (depending on annealing temperatures from 925° to 1,300 °C for up to 97 days) ranges from 4.056Å to 4.114Å. The similar discrepancies obtained in this present work and that of Jones and Segnit in d-spacing between the NIST standard and the samples alone would indicate either polytypism, compositional differences, or different materials. In any event, using the internal standard method for these SRO samples with the present crystallized standard would be precluded.

Figure 7

Figure 7 shows X-ray diffraction patterns from typical regional soils from Florida (fig. 7*D*), Illinois (fig. 7*C*), Kansas (fig. 7*B*), and Montana (fig. 7*A*) (kindly supplied by the National Soil Survey Center, U.S. Department of Agriculture, Lincoln, NE). The ubiquitousness of crystalline silica, undoubtedly in the respirable particle size range, is clearly evident in each of the soils analyzed.[8] Except for the Montana soil sample, which also contains small amounts of poorly crystalline cristobalite and/or amorphous silica, quartz (crystalline silica) is a major component of each soil. Kaolin in the Montana soil, feldspar in the Montana, Kansas, and Illinois soils, and mica-illite in the Montana and Kansas soils were also detected as major phases. All of these minerals can interfere with the peak intensities of quartz and cristobalite and therefore with the quantification of crystalline silica.

Figure 8

Some typical ores and/or common rocks are shown in figure 8 to illustrate the omnipresence of crystalline silica-quartz in the everyday environment. The diffraction pattern of the mica schist (fig. 8*D*) listed is similar to that of the crystalline basement rocks constituting Manhattan Island in New York City. The schist is composed predominantly of quartz, feldspar, and mica. The presence of quartz in another schistose rock, graphitic schist (fig. 8*C*), is also an essential mineralogical component. The two schists shown also reveal the peak overlapping problem mentioned earlier in the text. The principal quartz maximum used in the quantitative analytical peak is interfered with and/or reinforced by mica and graphite. The quantitative detection of quartz would be difficult at best even with a comprehensive knowledge of the mineralogy of these rocks. The clay samples depicted—ball clay (fig. 8*E*), bentonite (fig. 8*B*), and claystone (fig. 8*A*)—reveal a similar interference problem, with the mica and illite peaks also overlapping the major quartz line at 3.34Å. Quantitative analysis for quartz under these conditions also would be difficult, even if the analyst is well versed in the mineralogical makeup of these clays. The claystone also contains small amounts of SRO opaline silica, designated in the figure as SRO, further complicating the analytical approach. The poorly crystalline habit of the kaolin component in the ball clay, essential for ball clay's unique rheological properties of plasticity, and its impact on the determination of its quartz and the glycerol method for positive smectite identification, further complicating the analytical approach, will be discussed later.

---

[8] The pedon narrative descriptions for these soils supplied by the NSSC are available from the present authors.

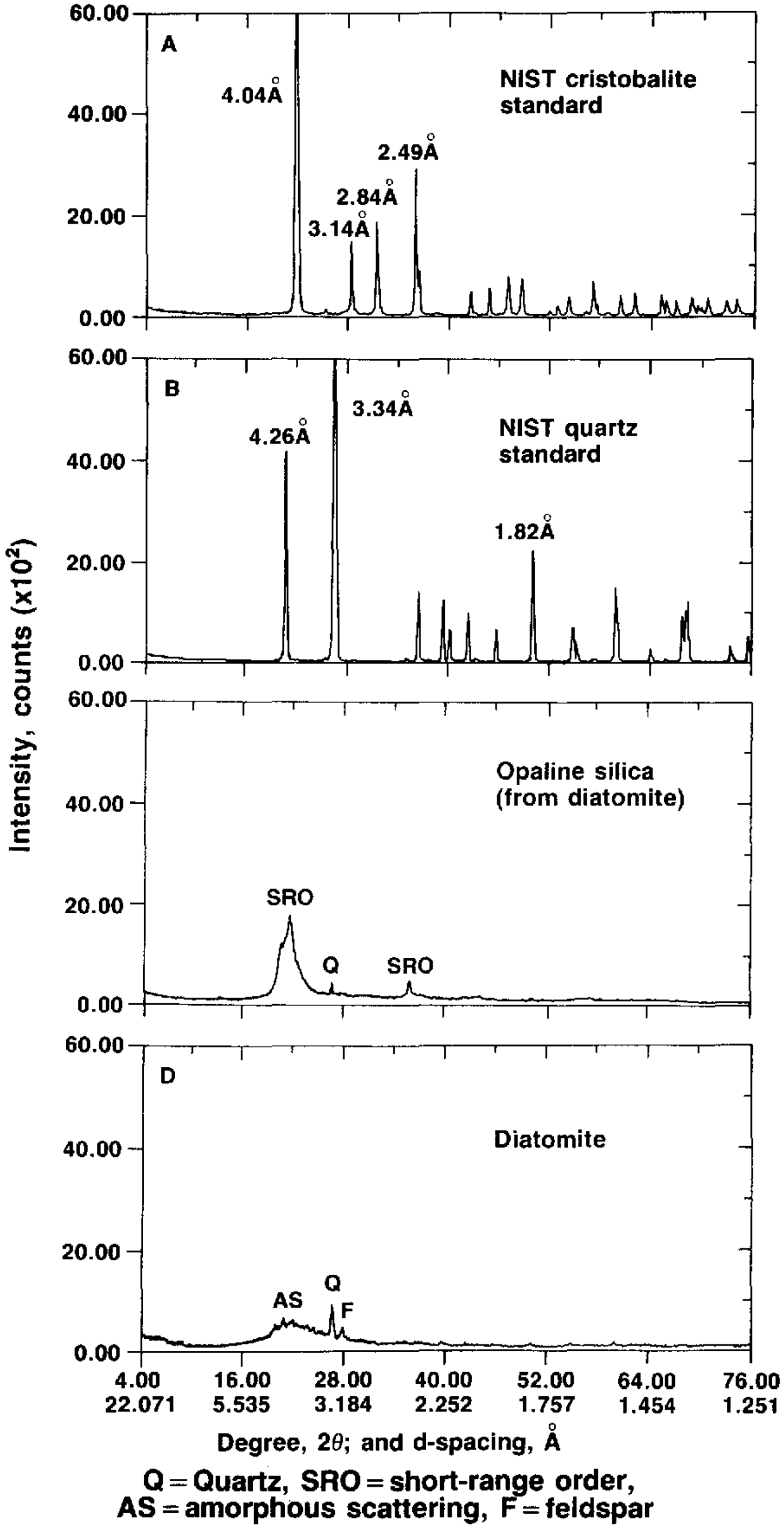


Figure 6.—Selected silica patterns.

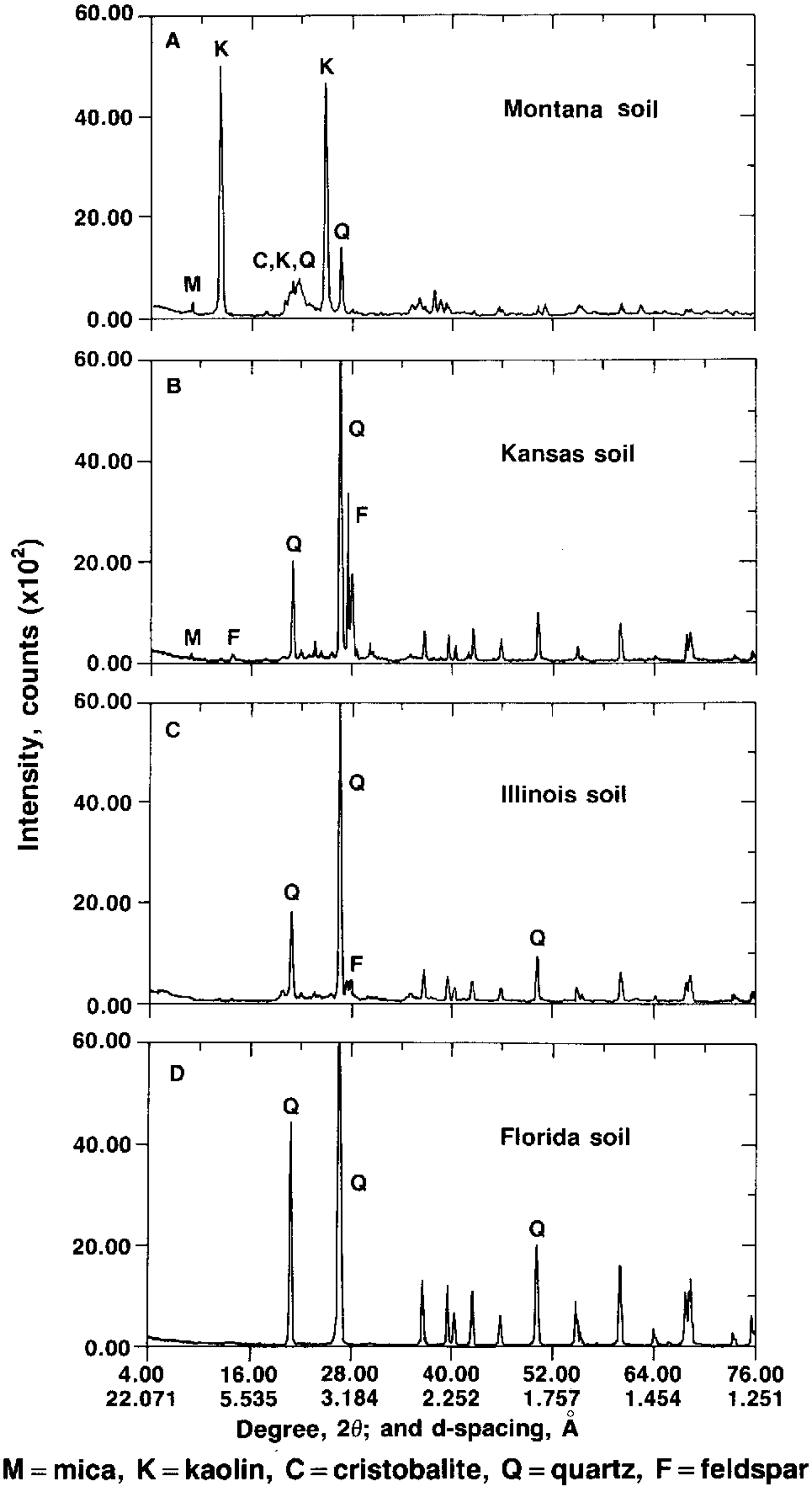


Figure 7.—Typical domestic soils.

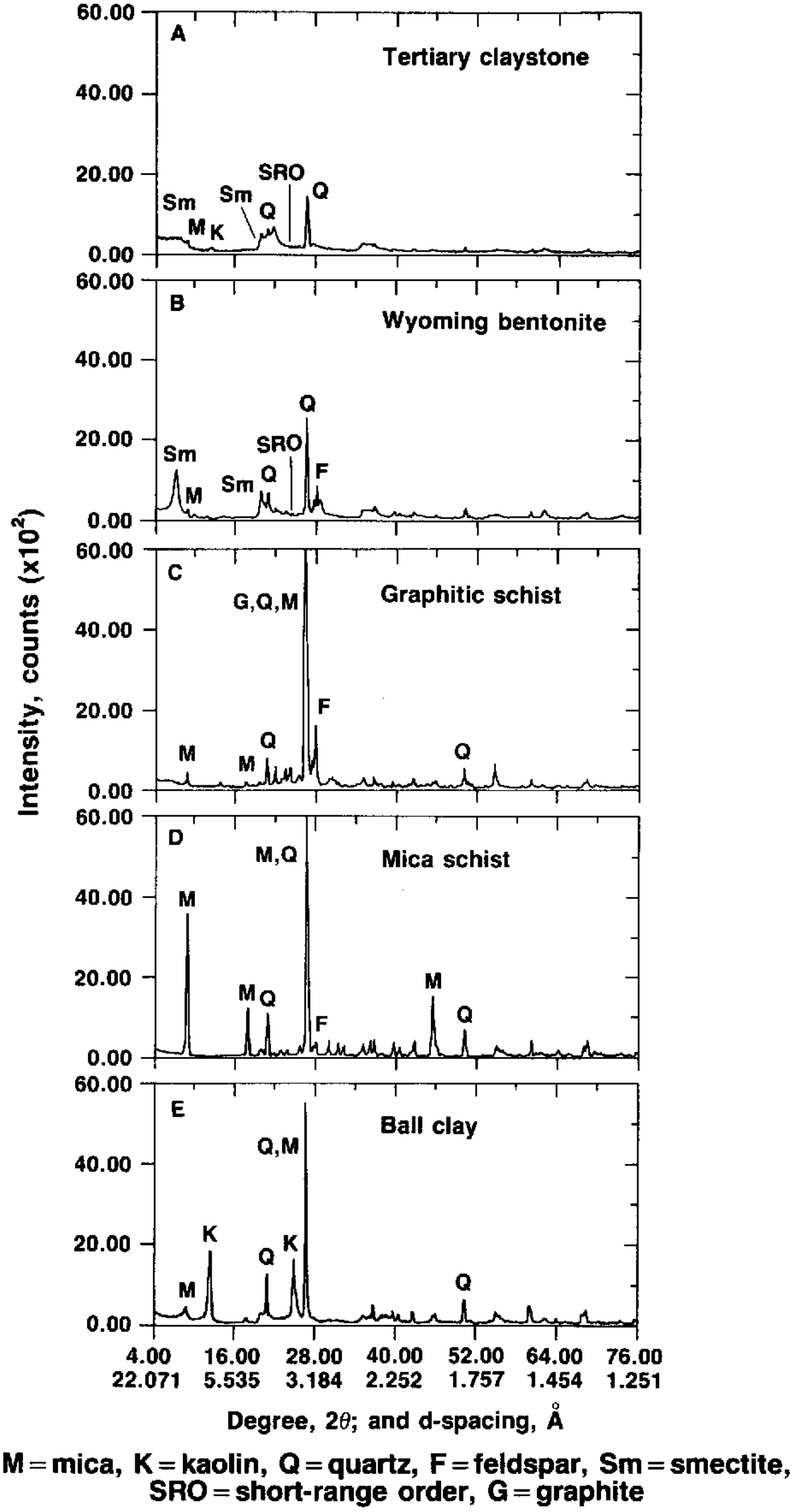


Figure 8.—Typical ores containing crystalline silica.

Figures 9 and 10

Figures 9 and 10 compare the X-ray diffraction patterns of selected minerals routinely encountered by the regulatory entities (table 5) along with the NIST standard quartz pattern (figs. 9*D* and 10*D*). These minerals, which have peaks that overlap one or more quartz standard peaks, include both concentrates and commercially available products. These figures not only graphically demonstrate the overlap problem with the strong 3.34Å quartz reflection but also indicate the inherent difficulties encountered in quartz quantification in multiphase systems containing small amounts of either quartz and/or interfering minerals.

Small amounts of quartz and mica, shown in several complete mineral patterns and discussed earlier, will be illustrated and amplified in the final three figures, 11, 12, and 13. Theoretically or geochemically, except for wollastonite (an undersaturated silica-bearing rock that is incompatible with nonchemically combined or free silica), all these minerals and rocks are commonly associated with quartz mineralization. The wollastonite concentrates occasionally contain crystalline silica owing to contamination from country and/or contact rocks or introduced during subsequent metamorphic activity.

Figures 11 and 12

Figures 11 and 12 are X-ray diffraction patterns obtained from silver membrane filters from specially prepared monitor samples. The samples were run either at the standard 6,000 intensity-count scale (figs. 11*A* and 11*B*) used for all the other previous patterns or on an abbreviated scan from 16° 2θ to 40° 2θ at the more sensitive 1,000-count scale (figs. 12*A* and 12*B*). The silver membrane mounts were prepared according to the MSHA and NIOSH techniques referred to earlier, and with the NIST respirable quartz standard material.[9] The two membranes contained either 27 μg (fig. 11*A*) or 52 μg (fig. 11*B*) of quartz, with the latter samples barely out of compliance with the OSHA permissible exposure level (PEL) of 50 μg for an 8-hr workday. The quartz content of the membranes is readily quantifiable in this simple system by X-ray diffraction techniques even with the less sensitive scale used in figure 11. The weak 4.26Å and 1.82Å quartz peaks, indicated by Q, in both samples (figs. 11*A* and 11*B*) are barely discernible, and both the determinations and positive identifications were based on a single quartz reflection: The strongest 3.34Å quartz maxima. An undesirable condition in known samples then becomes an intolerable situation in unknown samples, or for routine regulatory monitoring of the workplace.

The abbreviated and more sensitive patterns shown in figure 12 reveal another disturbing situation. The more sensitive scale factor, while advantageously accentuating the 3.34Å and 4.26Å quartz line intensities, has additionally altered the peak-to-background ratio. In the instance of the 27 μg sample (fig. 12*A*), it is difficult to separate the noise and/or background from the actual diffraction maxima intensities for the 4.26Å. This peak is also used in tandem with the 3.34Å peak for quantification in this simple single-phase system. The noise-background peak or spike labeled by a question mark on the pattern from the 52 μg sample (fig. 12*B*), but missing from the 27-μg pattern, is roughly equivalent in line intensity with the weaker labeled quartz and silver peaks. This random spike could unduly complicate both determination and positive identification schemes. An analyst again would be relegated to guessing. Clearly, in difficult situations with unknown phases of this nature, a complete qualitative scan would be essential, even though positive phase identifications on which to base a quantitative analysis for quartz might still be impossible.

Figure 13

The patterns shown in figure 13 were designed to point out the difficulties in both determining and positively identifying minor constituents at the 0.1% HCS levels in specially prepared marble-calcite matrices or samples determined to be devoid of crystalline silica quartz contamination. Unfortunately, the lack of intensity and/or resolution of the quartz, mica, and graphite peaks at the 0.1% HCS levels for each mineral in this selected matrix, at the constant instrumental settings used, precluded any experiments at the total 0.3% contamination level. Positive phase identification and quartz quantification were impossible, as was the meaningful representation of their diffraction peaks for illustrative purposes. Therefore, the marble samples, except for the 2% graphite-bearing sample (fig. 13*D*), required admixtures at the total 1% level for ready presentation of the single-peak, quartz-determination, and positive-identification dilemmas discussed earlier. Collectively these patterns also substantiate the intensity-sensitivity problems discussed in figures 11 and 12. The analyst would be hard put to use the 3.34Å peak for any determinations and still achieve meaningful results in each of the marble samples depicted—the 2% graphite (fig. 13*D*), the 1% NIST quartz standard (fig. 13*C*), the 0.5% mica and 0.5% quartz standard (fig. 13*B*), and the 0.33% quartz, 0.33% mica, and 0.33% graphite samples (fig. 13*A*). For the marble sample in figure 13*D*, devoid of quartz but containing 2% graphite, a mineral that interferes with the 3.34Å quartz peak, the analyst could not, by X-ray diffractometry alone, make a proper analytical judgment with any certainty. In fact, the

---

[9] The weak silver diffraction peak intensities listed in figure 10 as SKβ are due to unfiltered CuKβ radiation.

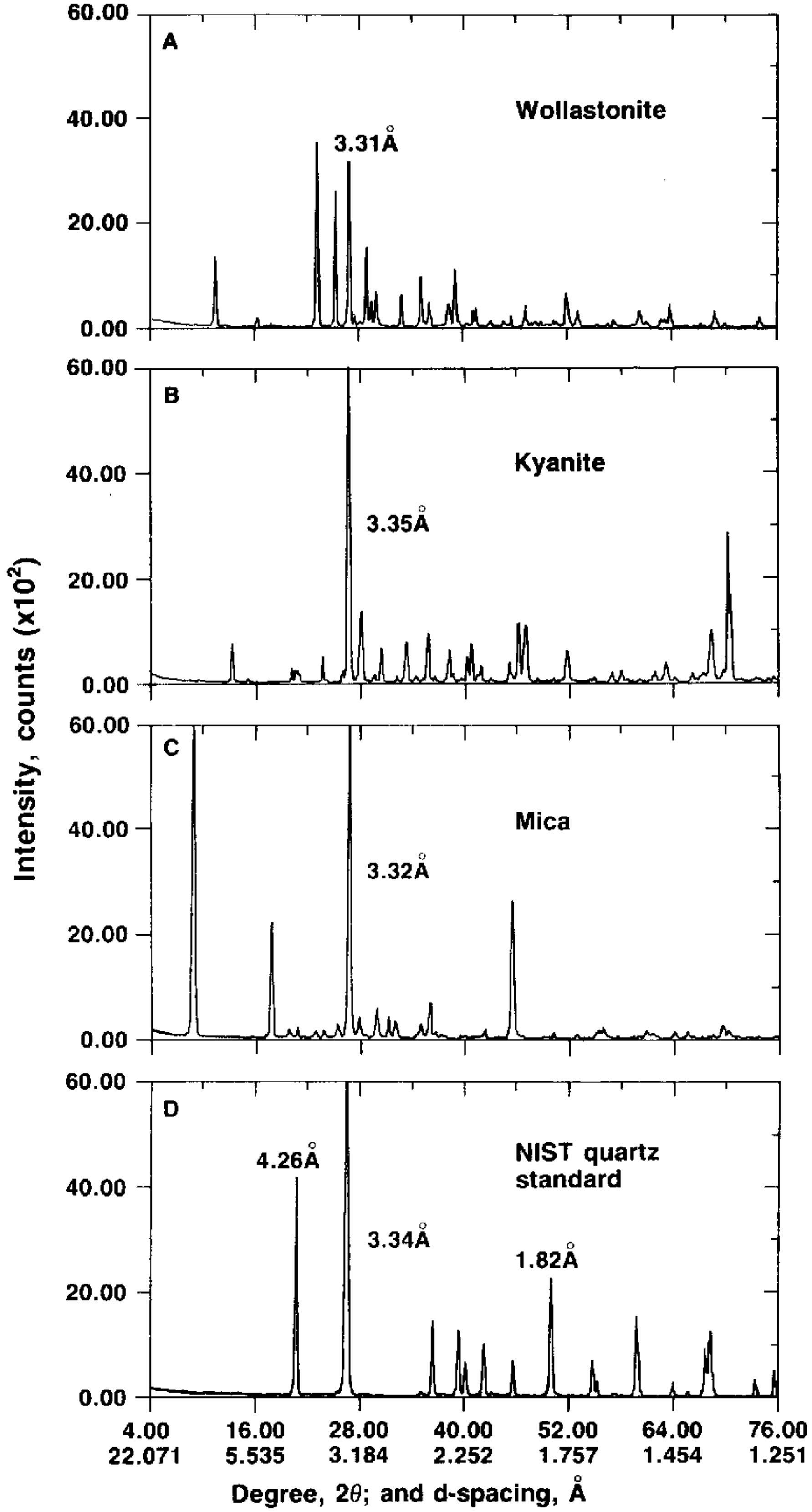


Figure 9.—NIST quartz standard and selected interfering minerals—muscovite mica, kyanite, and wollastonite.

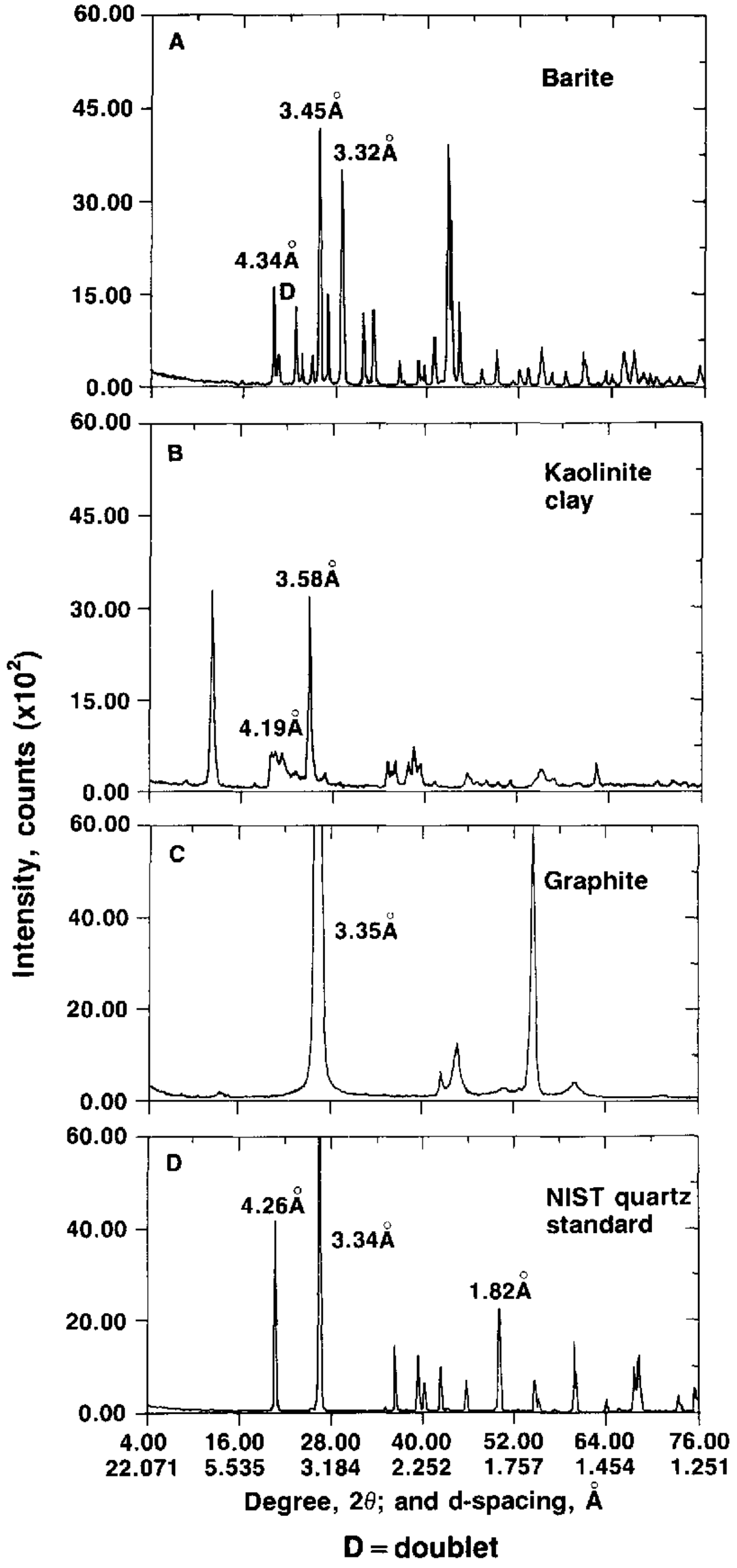


Figure 10.—NIST quartz standard and selected interfering minerals—graphite, kaolin, and barite.

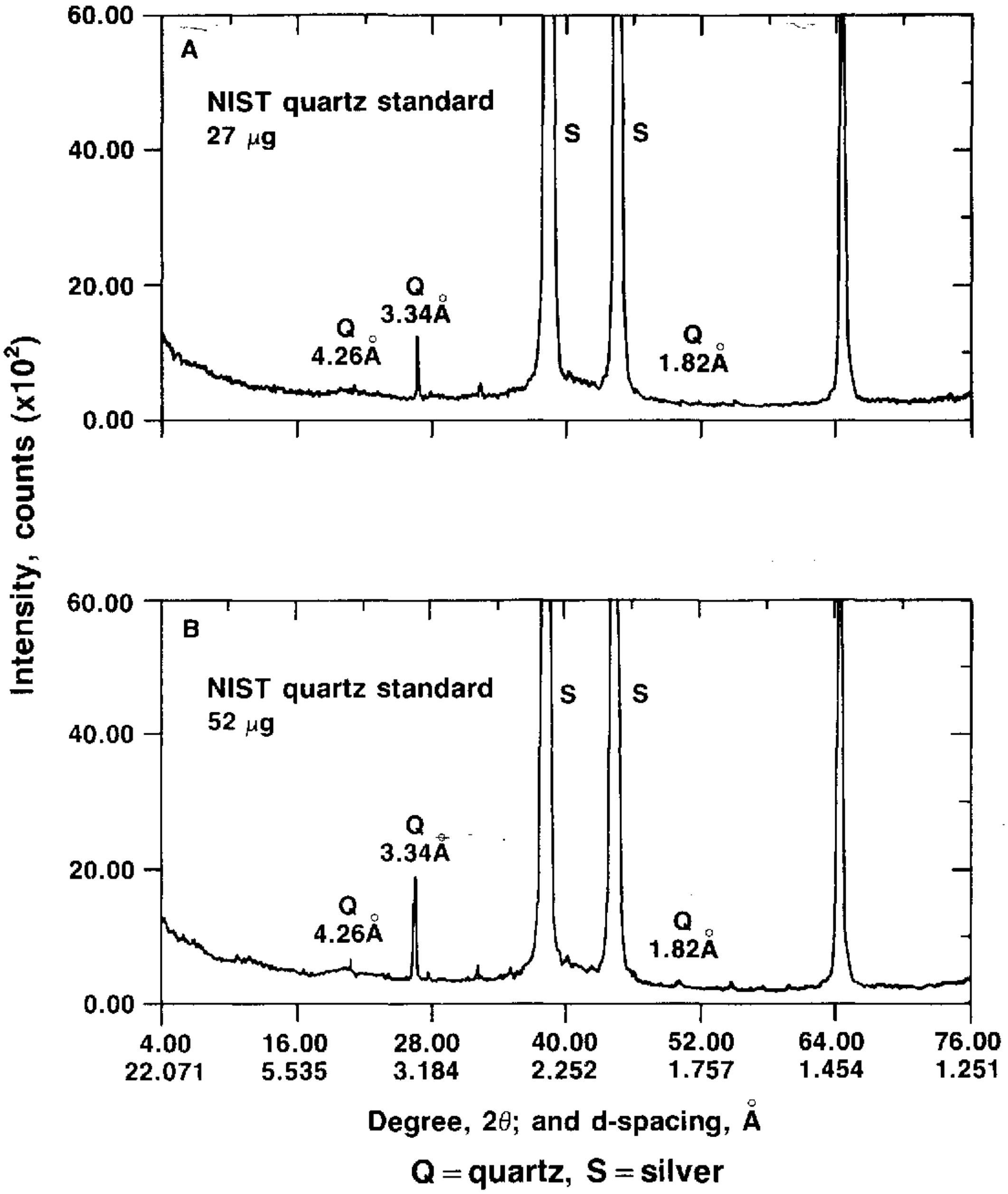


Figure 11.—Full patterns of typical silver-membrane-loaded respirable silica samples.

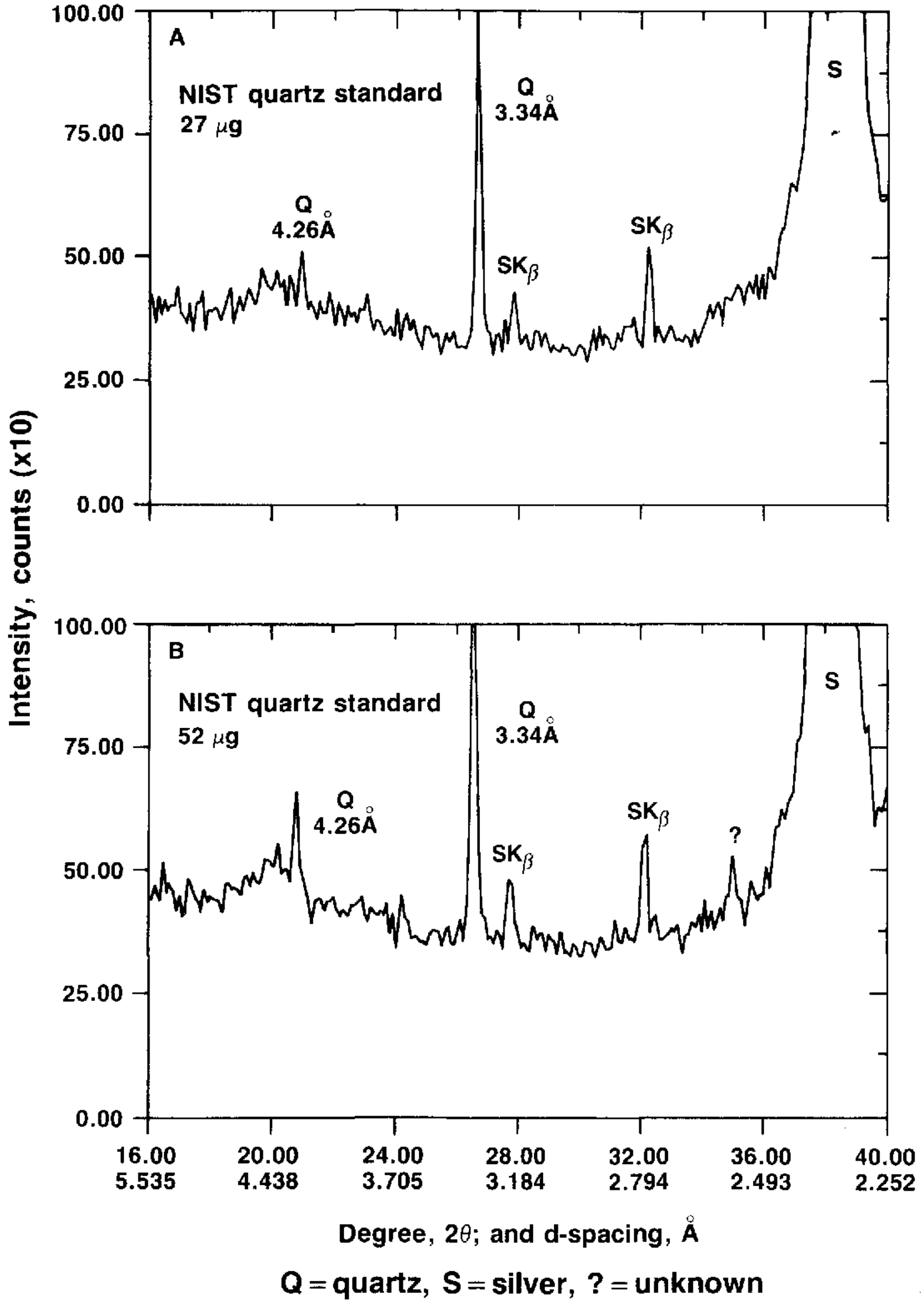
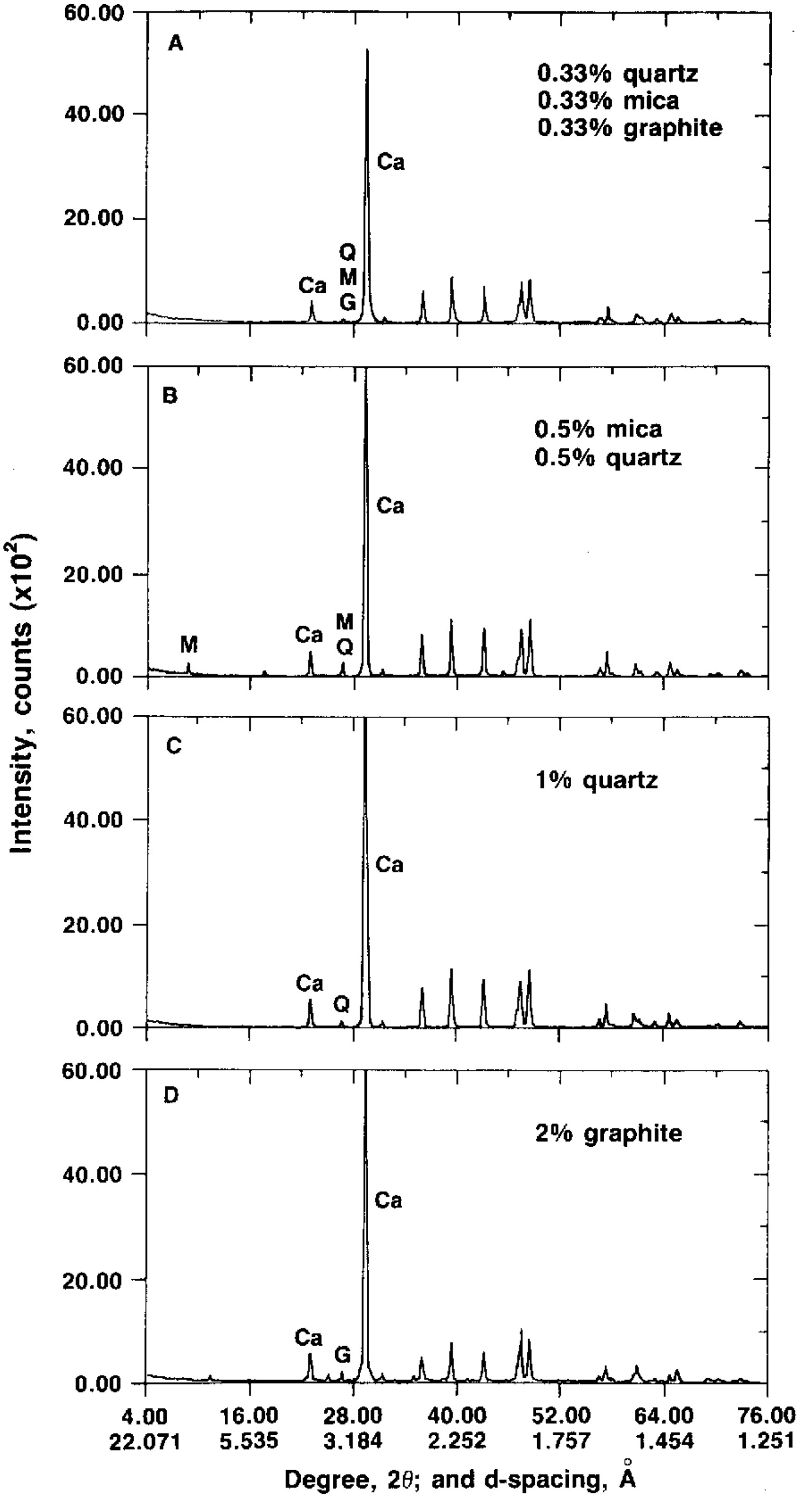


Figure 12.—Limited and more sensitive scan of the typical silver-membrane-loaded respirable silica samples.



Ca = calcite, M = mica, G = graphite, Q = quartz

Figure 13—X-ray patterns of prepared marble samples (with interfering minerals, graphite, muscovite mica, and quartz at the total 1-weight percent level).

1% quartz sample immediately above (fig. 13*C*), containing no graphite additions at all, is identical to the quartz-free pattern in figure 13*D*. In each of the patterns obtained from the out-of-compliance 0.33%, 0.5%, and 1% quartz admixtures, the analyst could not with any degree of certainty make meaningful determinations of a known material with the possible exception of the 0.5% mica sample, and this would be possible only if a full qualitative diffraction scan of bulk material was studied earlier. Any quantitative determinations of quartz from a single peak represented by the marble patterns studied, 2% graphite, 0.5% quartz, and 0.33% quartz, would be scientifically incorrect, and worse, damaging to the employee and employer alike.

CONCLUSIONS AND RECOMMENDATIONS

One major concern with OHSA's HCS is the widespread occurrence of crystalline silica in nature and the effect that it has had on the mining industry. Crystalline silica is present in most rocks and soils in concentrations ranging from trace to major. Most ore is mined from silica-bearing rock. Consequently, most mined materials will contain at least trace amounts of crystalline silica. Clay, crushed stone, diatomite, dimension stone, industrial sand, perlite, pumice, pyrophyllite, sand and gravel, and talc are some of the commodities that will be most affected by OSHA's HCS. Sampling, analysis, and labeling costs that will be incurred can be predicted. Costs associated with sales losses and liability issues cannot be predicted.

OSHA's HCS affects a limited number of operations. If MSHA's proposed HCS is enacted, the most mining operations would have to monitor to ensure compliance. For either regulation, crystalline silica can be quantified in air monitor and bulk sample by X-ray diffractometry at the 0.1% HCS levels only in simple one-, two-, and possibly three-phase systems if-

- It is uncontaminated with minerals and/or materials yielding overlapping and/or interfering peaks with the principal crystalline silica reflections.
- Standard reference materials equivalent in peak half-widths and particle size distribution (crystallinity) are available for comparison with the mineral or material sample under study.
- Periodic positive phase identifications of the mineral and/or material suites under investigation are determined by a qualified mineralogist or petrologist from representative bulk and monitor samples.

Quantitative mineralogy for "real world" mineral samples is only possible where standards of each mineral to be quantified match the crystallinity and the specific crystallite size distribution of the material under stady. This is preferably accomplished by separating the individual minerals from the ore or material to be quantified and developing calibration standards by the addition of the separated minerals and/or synthesized equivalent materials back into the original matrix. This is particularly true of clay minerals derived from altered volcanic ashes and glasses (smectites, perlites, etc.).

In certain instances, the mineral technicians may simply be unable, with any degree of confidence, to quantify crystalline silica at the 0.1% HCS level for a myriad of technical reasons, both cited above and described earlier in the text and figures. The dual dilemmas of whether a silica polymorph is crystalline or not and the use of a metastable standard are perplexing problems deserving more attention.

REFERENCES

1. Alexander, L. E., and H. P. Klug. Basic Aspects of X-ray Absorption in Quantitative Diffraction Analysis of Powder Mixtures. Powder Diffraction, v. 4, No. 2, June 1989, pp. 66-69.
2. Carter, J. R., M. T. Hatcher, and L. Di Carlo. Quantitative Analysis of Quartz and Cristobalite in Bentonite Clay Based Products by X-ray Diffraction. Anal. Chem., v. 59, No. 3, Mar. 1987, pp. 513-519.
3. Clarke, F. The Data of Geochemistry. U.S. Geol. Surv. Bull. 588, 1914, pp. 13, 36.
4. Deer, W., R. Howie, and J. Zussman. Rock-Forming Minerals, v. 4 - Framework Silicates. Longman, 9th ed., 1976, p. 192.
5. Edmonds, J. W., W. W. Henslee, and R. E. Guerra. Particle Size Effects in the Determination of Respirable β-Quartz by X-ray Diffraction. Anal. Chem., v. 49, No. 14, Dec. 1977, pp. 2196-2203.
6. Emig, J. A., and D. K. Smith. The Detection and Quantification of Low Concentrations of Quartz in Dolostone by X-ray Powder Diffraction. Powder Diffraction, v. 4, No. 4, Dec. 1989, pp. 209-213.
7. Flynn, P. T., Jr., A. T. Rosol, and S. D. Kinsala. Cristobalite Formation in Diatomaceous Earth. Ch. 48 in Proceeding of the Symposium on Environmental Management for the 1990's, ed. by D. J. Lootens, W. M. Greenslade, and J. M. Barker. Soc. Min. Metall. and Exp., Denver, CO, pp. 367-371.
8. Goldberg, S. A., and M. Jacobson. Bureau of Mines Procedure for Evaluating Quartz Content of Respirable Coal Mine Dust. BuMines IC 8545, 1972, 10 pp.

9. Hamilton, R. D., and N. G. Peletis. The Determination of Quartz in Perlite by X-ray Diffraction. Ch. in Advances in X-ray Analysis, v. 33, ed. by C.S. Barrett. Plenum 1990, pp. 493-497.

10. Hamilton, R. D., N. G. Peletis, and W. J. Miles. Detection and Measurement of Crystalline Silica in Minerals and Chemicals. Soc. Min. Metal and Exp. AIME/SME preprint "Silica," Regulation of Crystalline Silica Symposium, Washington, DC, Apr. 9, 1990, 6pp.

11. Howard, S. A., and K. D. Preston. Profile Fitting of Powder Diffraction Data. Ch. in Reviews in Mineralogy, v. 20, Modern Powder Diffraction, ed. by D. L. Bish and J. E. Post, Mineralogical Society of America, Washington, DC, 1989, pp. 217-275.

12. Hurlbut, C. Dana's Manual of Mineralogy. Wiley, 18th ed., 1971, pp. 368, 446-458.

13. Jackson, J., Jr., C. W. Huggins, and S. G. Ampian. Synthesis and Characterization of Dawsonite. BuMines RI 7664, 1972, 14 pp.

14. Joint Committee on Powder Diffraction Standards. International Centre for Diffraction Data Mineral Data Book. 1986. 1396 pp. Available from Powder Diffraction File, 1601 Park Lane, Swarthmore, PA 19081-2389.

15. ____. Mineral Data Book, 1990 in press. Available from Powder Diffraction File, 1601 Park Lane, Swarthmore, PA 19081-2389.

16. Jones, J. B., and E. R. Segnit. The Nature of Opal. I. Nomenclature and Constituent Phases. J. Geol. Soc. Australia, v. 18, No. 1, 1971, pp. 57-68.

17. Kadey, F. L., Jr. Diatomite. Ch. in Industrial Minerals and Rocks, ed. by S. LeFond. AIME, 5th ed., 1983, pp. 677-708.

18. Kamarchik, P., Jr. Quantitative Crystalline Pigment Analysis by X-ray Diffraction. J. Coat. Technol., v. 52, No. 666, July 1980, pp. 79-82.

19. Klug, H. P., and L. E. Alexander. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. 2d ed., pp. 531-561.

20. Lyon, T. L., and H. O. Buckman. The Nature and Properties of Soils. Macmillan, 1949, p. 9.

21. McKee, C., J. Renault, and J. M. Barker. Quantitative Analysis of Quartz in Perlite by X-ray Diffraction. Soc. Min. Metal. and Exp., Denver, CO. SME/AIME Preprint 90-166. Available from New Mexico Bureau of Mines and Minerals Resources, Socorro, NM 87801, Open File Report 364.

22. Miles, W. J., and R. D. Hamilton. Detection and Measurement of Crystalline Silica in Minerals. Ch. 43 in Proceedings of the Symposium on Environmental Management for the 1990's, ed. by D. J. Lootens, W. M. Greenslade, and J. M. Barker, Soc. of Min. Metal and Exp., Denver, CO., pp. 329-333.

23. Murray, H. H. Occurrence and Uses of Silica and Siliceous Materials. Soc. Min. Eng. AIME preprint "Silica," 1990, p. 1.

24. National Bureau of Standards (now National Institute of Standards and Technology). Certificate of Analysis. Standard Reference Material 1878, Respirable Alpha Quartz. Nov. 3, 1983, 2 pp.

25. ____. Certificate of Analysis Standard Reference Material 1879, Respirable Cristobalite. Jan. 22, 1988, 2 pp.

26. National Institute of Occupational Safety and Health. NIOSH Manual of Analytical Methods, Silica: Crystalline-Respirable, Method 7500, rev. #1, May 15, 1989, 9 pp.

27. ____. NIOSH Manual of Analytical Methods, Silica: Crystalline-Respirable, Method 7601, Feb. 15, 1984, 5 pp.

28. Pawloski, G. A. Quantitative Determination of Mineral Content of Geological Samples by X-ray Diffraction. Am. Mineral., v. 70, 1985, pp. 663-667.

29. Pearl, R. M. Geology. Barnes & Noble, 1966, 262 pp.

30. Pettijohn, F. J. Sedimentary Rocks. Harper and Row, 3d ed., 1975, p. 202.

31. Reed, W. P. Private Communication, 1991. Available from W. P. Reed, National Institute of Science and Technology, Gaithersburg, MD.

32. Salter, T. L., and W. E. Riley. Quartz Determination by X-ray Diffraction in Processed Kaolin. 1991. Available from T. L. Salter, Thiele Kaolin Co., Sandersville, GA.

33. Silicosis and Silicate Disease Committee. Diseases Associated With Exposure to Silica and Nonfibrous Silicate Minerals. Arch. Pathol. Lab. Med., v. 112, July 1988, pp. 673-720.

34. Smith, D. K., G. G. Johnson, A. Scheible, A. M. Wims, J. L. Johnson, and G. Ullmann. Quantitative X-ray Powder Diffraction Method Using Full Diffraction Pattern. Powder Diffraction, v. 2, No.1, Mar. 1987, pp. 73-77.

35. Sorrell, C., and G. Sandstrom. Minerals of the World. Golden, 1973, p. 154.

36. Thatcher, J. W. The Determination of Free Silica in Airborne Dust Collection Membrane Filters MESA (now MSHA), IR 1021, 1975, 16pp.

37. Travis, R. B. Classification of Rocks. Q. Colorado Sch. Mines, v. 50, No. 1, 1955, 98 pp.

38. United Kingdom. Occupational Medicine and Hygiene. Health and Safety Executive. Quartz in Respirable Airborne Dusts. Laboratory Method Using X-ray Diffraction (Direct Method). Methods for the Determination of Hazardous Substances 51/2, Mar. 1988, ISBNO-7176-02559.

39. ____. Laboratory Method Using Infra-Red Spectroscopy (Direct Method). Methods for the Determination of Hazardous Substances 37, Nov. 1987 (revised), 7 pp.

40. U.S. Bureau of Mines. A Dictionary of Mining, Mineral, and Related Terms. Spec. Publ., 1968, p. 1012.

41. U.S. Bureau of Mines. Mineral Commodities Summary 1990. 199 pp.

42. Velde, B. Clay Minerals. Elsevier, 1985, p. 50.

43. World Health Organization. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Silica and Some Silicates, v. 42. IARC Working Group on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Lyons, France, June 10-17, 1986, pp. 109-112.

U.S.G.P.O.: 5-13-92/611-007/60030/2000

INT.BU.OF MINES,PGH.,PA 29553