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Distinguishing well ordered opal-CT and opal-C from high temperature cristobalite by x-ray diffraction

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Abstract

A critical step in quantifying the amount of crystalline silica in mineral deposits is the accurate identification of all mineral constituents. It is particularly important to correctly identify the low-temperature opaline silica polymorphs opal-C and opal-CT which, depending on degree of ordering, can be mistaken for α-cristobalite in standard x-ray diffraction patterns. Misidentification occurs because there is limited x-ray diffraction data available from the literature and because these minerals have diffraction maxima that coincide with those of high temperature cristobalite. X-ray diffraction patterns of opal have been collected in 20 bentonite, fuller's earth, and diatomaceous earth deposits to illustrate the range in ordering that naturally occurs in these polymorphs. Two opaline silica polymorphs are commonly observed. Opal-C is characterized by sharp, intense (101) reflections centered near 4.0 Å with peak widths ranging from 0.222 to 0.453 Å and opal-CT is characterized by broader, less intense (101) reflections centered near 4.07 to 4.10 Å with peak widths ranging from 0.506 to 0.883 Å. Opal-A was observed in one sample. Opal-A is easily distinguished from the other opaline silica polymorphs and from α-cristobalite using x-ray diffraction. Opal-C and opal-CT, however, are not as readily distinguished from α-cristobalite. The position and width of the (101) peak can be used to distinguish these polymorphs from one another or a simple heating test can be used. Because opaline silica is hydrated, the position of the (101) reflection shifts and sharpens as a result of heating. When α-cristobalite is heated no change in peak position is observed. It has also been found that opaline silica, when reacted with phosphoric acid, potassium pyrosulfate, and sodium sulfide solutions, is considerably more chemically reactive than the crystalline silica minerals. Based on results of the heating test and the position and width of the 4 Å peak of the unheated sample, none of the 20 bentonite, fuller's earths, or diatomaceous earth deposits analyzed contain high temperature α-cristobalite.

Keywords: X-ray diffraction; Cristobalite; Crystalline silica; Opal-CT; Opal-C

In 1987, the International Agency for Research on Cancer (IARC) declared crystalline silica a probable human carcinogen. This classification triggered OSHA's Hazard Communication Standard which requires that any material containing > 0.1% crystalline silica be appropriately labelled. Minerals that are specifically regulated include quartz, cristobalite, and tridymite. In addition to these polymorphs, there are other forms

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TABLE 1

Hydrous and non-hydrous forms of SiO_2

Polymorph	Crystallinity
α-Quartz (low T°)	SiO_2
β-Quartz (high T°)	SiO_2
α-Cristobalite (low T°)	SiO_2
β-Cristobalite(high T°)	SiO_2
α-Tridymite (low T°)	SiO_2
β-Tridymite (high T°)	SiO_2
Coesite	SiO_2
Stishovite	SiO_2
Melanophlogite	SiO_2
Keatite	SiO_2
Silica glass	$SiO_2 \cdot H_2O$
Opal-A	$SiO_2 \cdot H_2O$
Opal-CT	$SiO_2 \cdot H_2O$
Opal-C	$SiO_2 \cdot H_2O$

of silicon dioxide including several hydrated forms (Table 1).

The most common naturally occurring hydrated silica polymorphs are the opaline silicas, which have a composition given by the formula $SiO_2 \cdot nH_2O$. These minerals are found in economically important deposits such as bentonite, fuller's earth, flint kaolin and diatomaceous earth. Deposits containing these secondary silica minerals are found in the United States, Japan, Canada, Indonesia, Italy, Spain, Greece, Yugoslavia, Czechoslovakia, Australia and Turkey [1]. In the United States opaline silica-bearing bentonites are located in Alaska [2], Texas [3], Georgia [1], Alabama [4], Idaho, Utah, Nevada and Wyoming [5]. These minerals, which are considered non-crystalline from a regulatory point of view, have been and are confused with high temperature cristobalite.

The confusion between opaline silicas and α-cristobalite is based on several factors. One is that the term "cristobalite" is often interchangeably used with "opal-CT", "opal-cristobalite", "opaline silica" and various other names. This ambiguous terminology is commonly found in older publications [e.g., 2,6–8] and less often in more recent literature [e.g., 9–11]. The other factor that has contributed to this confusion is the similarity between the x-ray diffraction patterns of well-ordered low temperature opal-CT and opal-C and high temperature α-cristobalite (Fig. 1).

Cristobalite is generally considered a high temperature phase and is often associated with volcanic rocks. The opal minerals, with perhaps the exception of opal-C, form at low temperatures, usually below 100°C. These minerals may form under a number of different geologic conditions. For example opal-A may be precipitated by marine organisms as skeletal material or it may precipitate from silica saturated solutions formed as a result of water interacting with silica-rich rocks such as volcanic ash or tuff. This genetic association explains why opal-CT and opal-C commonly occur in bentonite deposits which form by the alteration of volcanic ash. Opal-A converts to opal-CT during diagenesis.

The common association of secondary opal-CT and opal-C with bentonite has led to the interpretation that these minerals form simultaneously with smectite during ash alteration [12]. However, Henderson et al. [6] demonstrated that authigenic opal-cristobalite (opal-CT) in the Helms bentonite did not precipitate with smectite, but formed much later and in contact with meteoric water. Other investigators have proposed that, in some cases, cristobalite was a component of the original ash and is therefore a high temperature phase that has no genetic relationship to the smectite [13]. Mount St. Helens ash, for instance, contained up to 2 weight percent α-cristobalite [14].

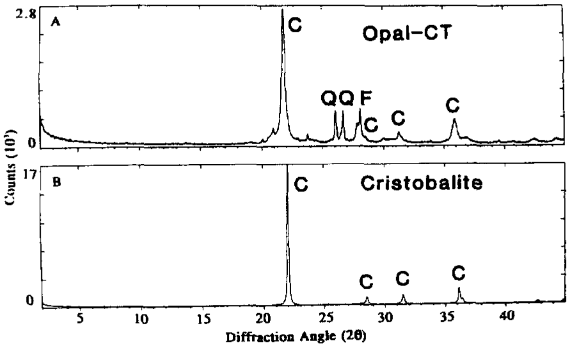

Fig. 1. X-ray diffraction patterns of opal-CT (top) and α-cristobalite (bottom). Peaks marked with the letter "C" are cristobalite peaks. Those marked with "Q" are quartz peaks (α and β) and those marked with "F" are feldspar peaks.

This paper attempts to eliminate the confusion surrounding these minerals by characterizing the low temperature hydrated silica polymorphs commonly found in commercial grade clay deposits and describing a simple test for distinguishing well-ordered opaline silica from α-cristobalite.

CLASSIFICATION OF LOW-TEMPERATURE SILICA POLYMORPHS

A large number of experimental, theoretical and descriptive studies of low-temperature silica phases are described in the literature. A review of this literature indicates that the classification of hydrous silica proposed by Jones and Segnit [15] is currently widely accepted by the geologic community. They propose a three-fold classification based on atomic structure. X-ray diffraction, infrared spectroscopy and differential thermal analyses data all support this classification scheme. According to this classification, the naturally occurring hydrous silica polymorphs are grouped as opal-A, opal-CT, and opal-C.

Opal-A is a highly disordered near amorphous polymorph and includes precious opal, all biogenically precipitated opal and geyserities. When analyzed by x-ray diffraction it produces a single diffuse band centered at approximately 4.1 Å (Fig. 2). Biogenic opal-A may occur as radiolarian tests, diatom frustules, or sponge spicules. Inorganically precipitated opal-A forms when a solution becomes saturated with respect to silica causing silicic acid polymers to precipitate. These polymers then grow by Ostwald ripening to form colloidal sols and gels [16,17].

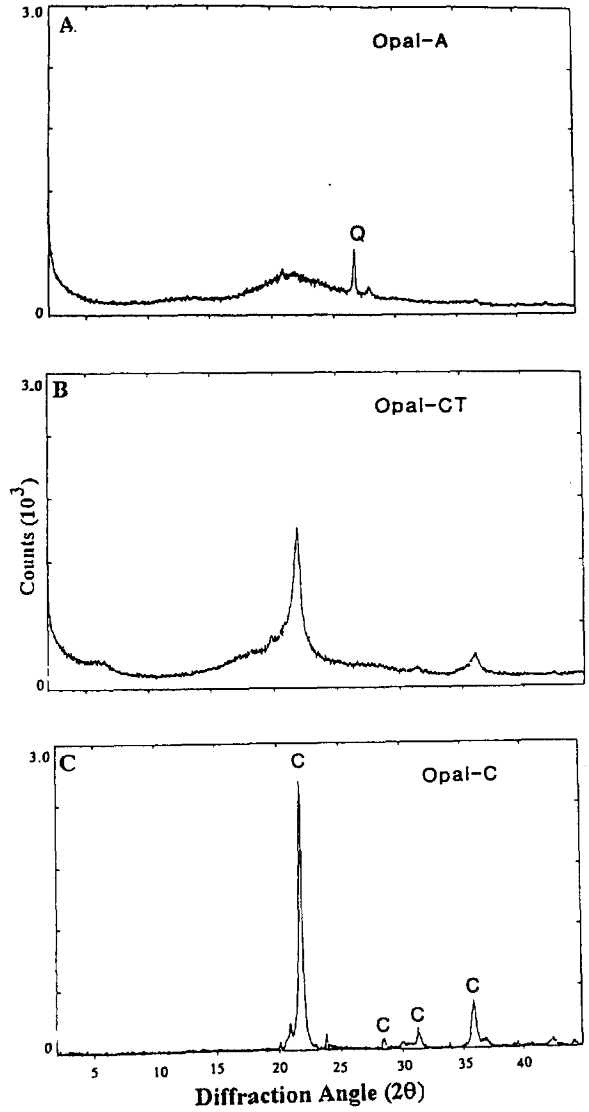

Fig. 2. X-ray diffraction patterns of opal-A, opal-CT and opal-C.

Opal-CT is interpreted as disordered microcrystallites of α-cristobalite in a matrix of amorphous silica. These crystallites exhibit varying degrees of stacking disorder, which may lead to the appearance of x-ray maxima that coincide with those of α-tridymite [18]. Opal-CT has an XRD pattern characterized by two broad reflections in the 4.05 to 4.10 Å and 2.50 Å regions and a single small reflection at 4.25 to 4.35 Å (Fig. 2). Opal-CT typically occurs as lepispheres composed of bladed crystals. Fibrous crystals of opal-CT have also been observed [19]. Opal-CT exhibits a range of ordering that is most clearly documented in sediments, such as the Monterey Formation, that have undergone burial diagenesis. It has been observed in these and other sediments that opal-CT becomes better ordered during diagenesis [20]. This increased ordering manifests itself as sharper more intense x-ray diffraction maxima that are often slightly shifted in position relative to the unaltered silica.

It has been suggested that opal-CT may be reinterpreted as disordered α-tridymite [21]; however, this reinterpretation does not appear to have been widely accepted. Only one report of disordered low tridymite, identified in diatomaceous sediments from Japan where it was precipitated as lepispheres from percolating groundwater, was found in the literature [22].

Recently, de Jong et al. [23] have challenged the idea that opal-CT is a mixture of cristobalite–tridymite microcrystallites in an amorphous silica matrix. In their study the structures of both opal-CT and opal-A were re-examined using XRD and ^{29}Si MAS NMR. Conclusions drawn from these data suggest that opal-CT is not comprised of cristobalite-tridymite microcrystallites but instead exhibits long-range ordering of oxygen atoms followed by short-range ordering of silicon atoms. Opal-CT has a ^{29}Si MAS NMR spectrum much more like that of amorphous silica than that of cristobalite or tridymite.

Opal-C closely resembles cristobalite and is recognized by major reflections occurring as sharp, symmetrical peaks centered at 4.04, 3.13, 2.84, and 2.47 Å (Fig. 2). Opals associated with lava flows and other high temperature environments commonly occur as opal-C. However, reports of authigenic well-ordered opal-C [22,24], suggest that high temperatures may not be required for the formation of this phase. Although, this mineral is structurally similar to α-cristobalite it is not true α-cristobalite. This conclusion is based on the fact that the x-ray diffraction pattern of opal-C may show minor tridymite peaks, and when heated does not convert to β-cristobalite [25].

Alpha-cristobalite is metastable under 268°C and persists at lower temperature due to strong Si–O bonds [15]. Structurally, cristobalite is built of layers consisting of 6-membered rings of silicon and oxygen tetrahedra that are vertically stacked. These layers are linked by the vertices of tetrahedra that alternately point up and down. This ring structure is a low energy structure and, therefore, promotes the metastable precipitation of cristobalite over other crystalline silica polymorphs [26].

CHARACTERIZATION OF LOW-TEMPERATURE HYDROUS SILICA POLYMORPHS

Sample materials and methods

Twenty samples of commercially mined minerals that commonly contain opaline silica were examined by a number of analytical techniques including optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray diffraction.

Results

From these data two opaline silica polymorphs were recognized based on chemistry, particle size, particle shape and structure (Table 2). These polymorphs are distinguished from one another primarily on the basis of x-ray diffraction data including peak position, intensity and width (Table 3 and Fig. 3) and correspond to opal-C and opal-CT as described by Jones and Segnit [15]. Only one sample contained opal-A.

In these samples the (101) peak of opal-C occurs at lower d-spacings and tends to have narrower peaks than opal-CT (Fig. 4). Opal-C is characterized by a relatively sharp intense 4 Å peak with a d-spacing close to 4.04 Å. Opal-CT exhibits a range of x-ray diffraction peak intensities and positions (Fig. 4) and appears to be less ordered. In general, the position of the most intense peak of this phase varies from 4.07 to 4.09 Å. It is interesting to note that the degree of ordering in these polymorphs, as measured by dividing the peak width at half height by peak position (FWHM/d (101) Å), appears to increase with age of the deposit (Fig. 5).

TABLE 2

Distinguishing characteristics of two opaline silica polymorphs

Polymorph 1	Polymorph 2
Sharp, intense (101) reflection ≈ 4.04 Å	Broad, less intense (101) reflection ≈ 4.07 to 4.10 Å
Large crystallites along edges of clay grains	Smaller crystallites, large agglomerates and lepispheres
Si + trace amounts of Al and Fe	Si only
Opal-C	Opal-CT

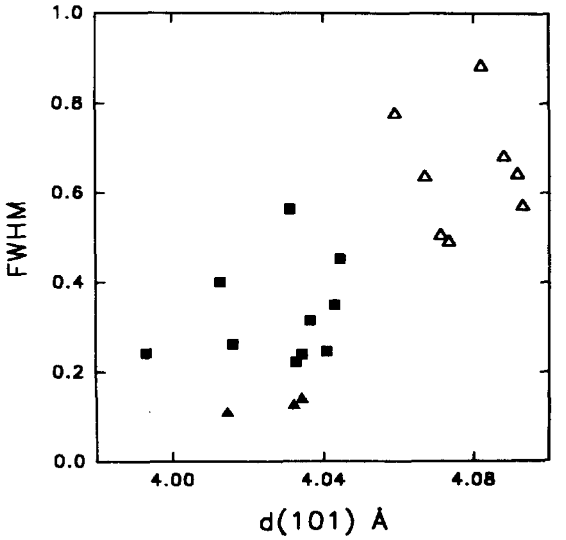

Fig. 3. Plot of peak width at half height (FWHM) vs position of the 4 Å peak (d(101)) for the two opaline silica polymorphs.

Scanning and electron microscopy reveals some other differences between these polymorphs. Opal-C tends to form large crystallites that aggre-

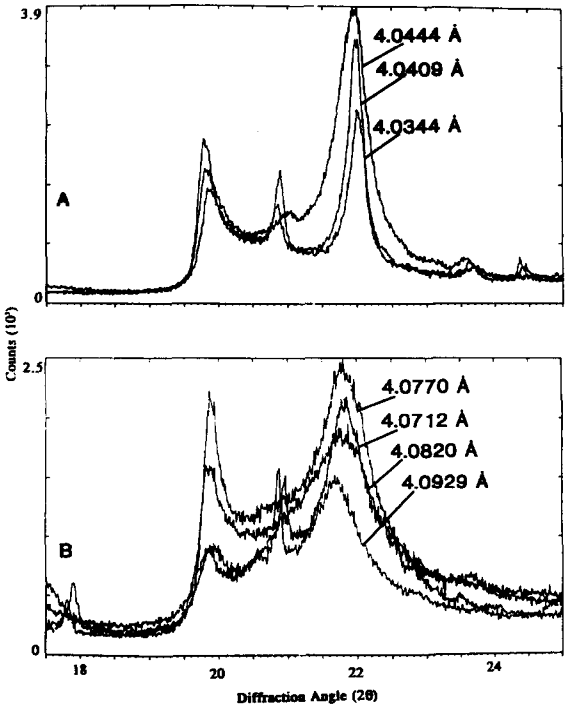

Fig. 4. X-ray diffraction patterns of opal-C (A) and opal-CT (B).

TABLE 3

Summary of x-ray diffraction data for opaline silica polymorphs

Name/location	Rock type	d(101)Å	FWHM	Heated d(101)Å	Heated FWHM	Polymorph
Australia	Bentonite	4.0344	0.239	4.0781	0.248	opal-C
Nevada	Bentonite	4.0444	0.453	4.0921	0.244	opal-C
Commercial Bed, WY	Bentonite	4.0409	0.246	4.0761	0.193	opal-C
Lower Mowry, WY	Bentonite	4.0127	0.401	–	–	opal-C
Yellow CB, WY	Bentonite	4.0328	0.222	4.0766	0.202	opal-C
Blue CB, WY	Bentonite	4.0161	0.262	4.0818	0.283	opal-C
Yellow New Castle, WY	Bentonite	4.0365	0.315	4.0628	0.352	opal-C
Upper Bed, Lovell, WY	Bentonite	4.0430	0.350	4.0713	0.362	opal-C
D-Bed, Lovell, WY	Bentonite	3.9932	0.242	4.0834	0.242	opal-C
Utah	Fuller's Earth	4.0313	0.564	4.0737	0.3135	opal-C
Flux Calcined Diatomite	DE	4.0734	0.491	4.05286	0.305	opal-CT
Texas	Bentonite	4.0770	0.681	4.0837	0.349	opal-CT
Chalk Hills Fm, ID	Bentonite	4.0590	0.776	4.0927	0.222	opal-CT
Turkey	Bentonite	4.0820	0.883	4.0497	0.215	opal-CT
Mozambique	Bentonite	4.0670	0.636	4.0904	0.447	opal-CT
Porters Creek	Fuller's Earth	4.0929	0.571	4.1007	0.402	opal-CT
Mississippi	Fuller's Earth	4.0712	0.506	4.0761	0.343	opal-CT
Monterey	DE	4.0915	0.642	4.0769	0.390	opal-CT

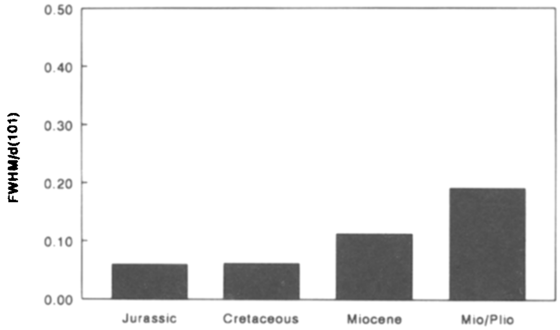

Fig. 5. Bar graph showing the relationship between peak width and age. Younger deposits contain less ordered opaline silica compared to older deposits.

gate along the edges of clay flakes (Fig. 6). Opal-CT is characterized by small crystallites that commonly form lepispheres and agglomerates (Fig. 7).

DISTINGUISHING WELL-ORDERED OPALINE SILICA FROM α-CRISTOBALITE

X-Ray diffraction

Although the x-ray diffraction pattern of cristobalite is distinct from that of opal-A and poorly ordered opal-CT, it can be confused with that of well-ordered opal-CT and opal-C particularly if only the 4 Å peak is examined. This is because these minerals have diffraction maxima that are almost identical to those of α-cristobalite. Despite these shortcomings, x-ray diffraction is the best method for routinely distinguishing between these minerals.

Because peak position cannot be used as a diagnostic tool to distinguish α-cristobalite from the opal minerals, peak shape must be considered as an alternative means for identification. Typi-

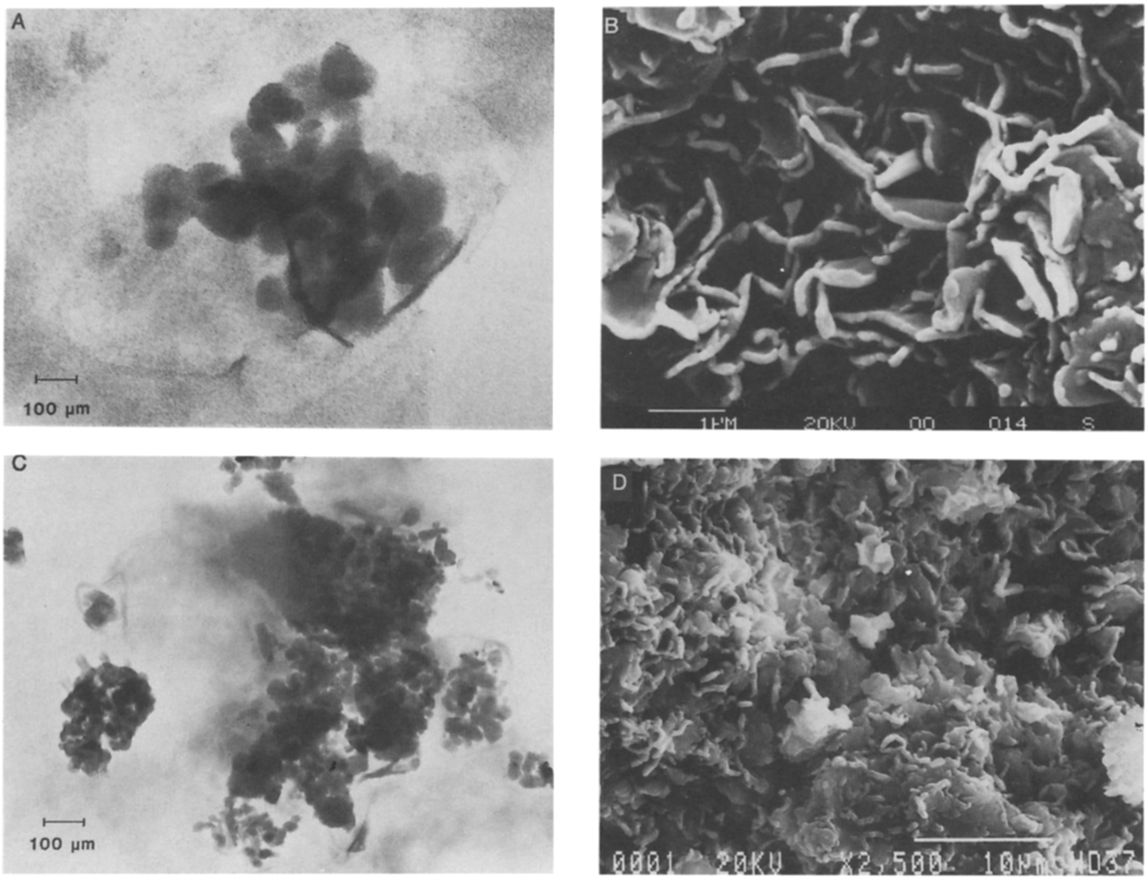

Fig. 6. TEM (a and c) and SEM (b and d) images of opal-C.

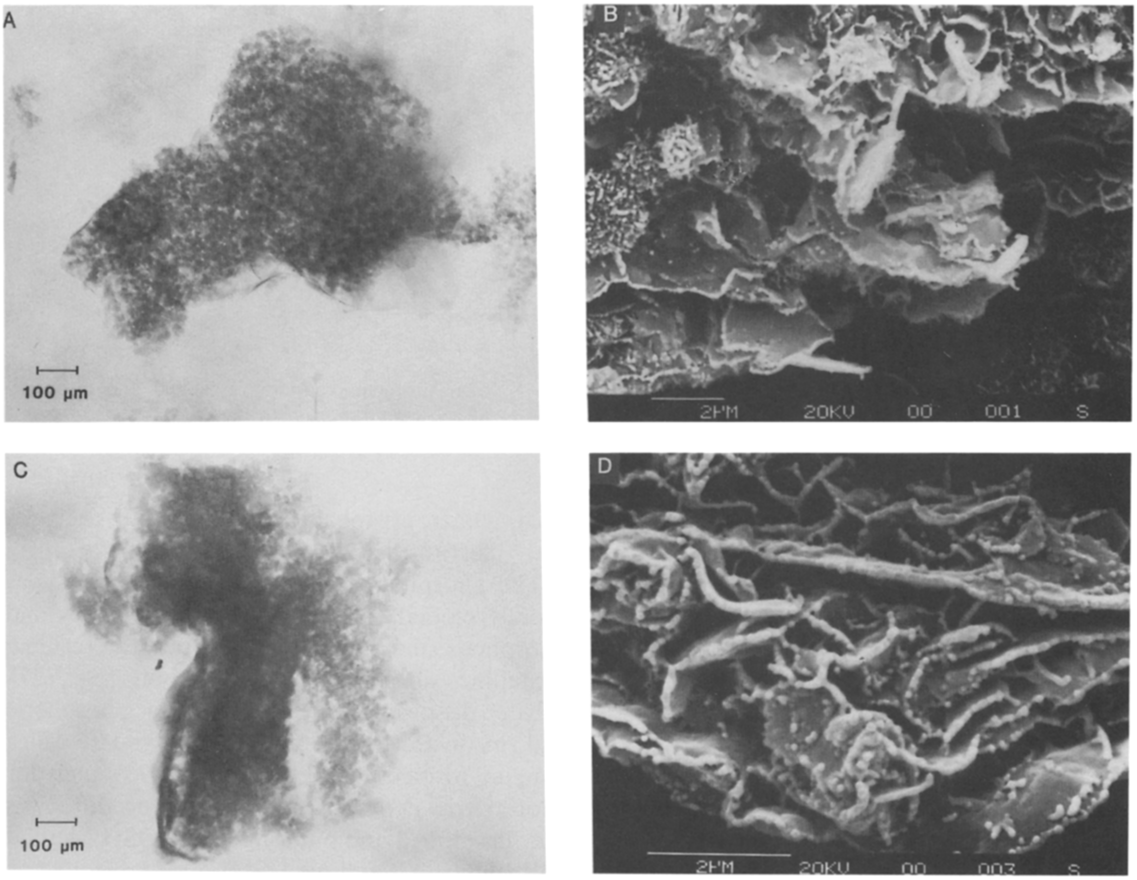

Fig. 7. TEM (a and c) and SEM (b and d) images of opal-CT.

cally opal minerals exhibit line broadening due to their very small crystallite size. An examination of three cristobalite standards indicates that cristobalite does not exhibit line broadening (Table 4). Therefore, a quick check of the peak width at half height (FWHM) has the potential for indicating whether opal or cristobalite is present.

TABLE 4

Peak width at half height (FWHM) for opal-A, opal-CT, opal-C, and cristobalite

FWHM	Opal-A	Opal-CT	Opal-C	Cristobalite
Minimum	3.492	0.506	0.222	0.109
Maximum	3.492	0.883	0.453	0.140
Mean	3.492	0.671	0.306	0.125
n	1	8	10	3

Another way to distinguish the opaline silica minerals from cristobalite is to x-ray the sample before and after heating. Approximately 2 g of powdered clay were heated for 24 h at 1050°C in a platinum crucible. The sample was then x-rayed from 17.5 to 25.0° 2θ and the results were compared to those obtained for the unheated sample. For both opal-CT and opal-C an increase in

TABLE 5

X-Ray diffraction data for α-cristobalite

Standard	d(101) Å	FWHM	Heated d(101) Å	Heated FWHM
NIOSH CB-25	4.0321	0.126	4.0320	0.126
NBS SRM 1879	4.0145	0.109	4.0279	0.109
D. Smith	4.0343	0.140	4.0341	0.140

intensity of approximately 10 000 counts per second and as much as a 0.09 Å shift in the position of the (101) peak (Fig. 8) were observed. This shift may be attributed to dehydration and/or an increase in ordering. The change in peak shape and intensity is probably due to recrystallization accompanied by an increase in crystallite size. By contrast, the diffraction pattern of high temperature α-cristobalite does not change with heating (Table 4, Fig. 9). This test, therefore, provides a relatively simple way to differentiate the hydrated opaline silica minerals from the crystalline silica minerals.

Chemical reactivity

Opaline silica differs from the anhydrous crystalline silicas not only in chemical composition but also in chemical reactivity. Amorphous and opal silica are much more reactive than crystalline silica with refluxing phosphoric acid, potassium pyrosulfate fluxes, and refluxing sodium sulfide solutions. The crystalline forms of silica, quartz, cristobalite, and tridymite, are relatively inert to these chemical reagents.

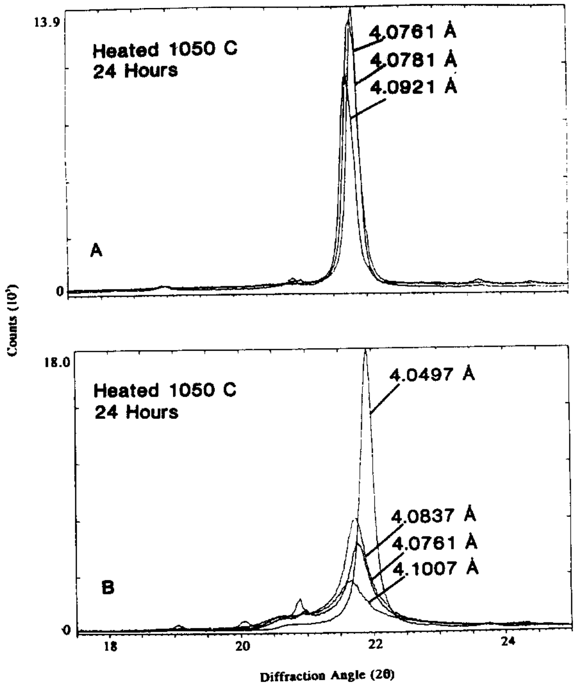

Fig. 8. Patterns obtained after heating opal-C (A) for 24 h and opal-CT (B) for 24 h.

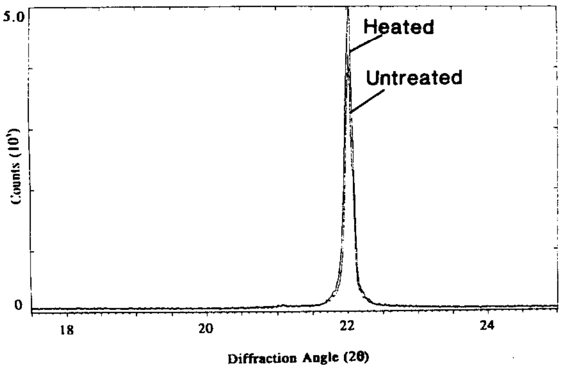

Fig. 9. X-ray diffraction pattern of heated and untreated α-cristobalite.

The phosphoric acid digestion of silicates was first developed to remove reactive silicates and amorphous silicas and to concentrate the residual crystalline silica for further analysis [e.g., 27]. Talvite dissolved the residue from phosphoric acid in hydrofluoric acid. A molybdate–silica complex formed as a result of this treatment for calorimetric determination. This procedure was later developed and published as NIOSH Method 7601 "Silica, Crystalline [28]."

The NIOSH method suffers in that there are a number of partially or completely insoluble silicate minerals that create positive interferences and errors unless the mineralogy is completely identified and appropriate corrections are made. Amorphous silica of volcanic origin or inorganic origin, such as perlite and obsidian, are particularly slow to react with the refluxing phosphoric acid. Miles and Hamilton [30] have shown that phosphoric acid digestion can be used as a concentration technique for crystalline silica, followed by subsequent x-ray diffraction analysis for the quantitative determination of crystalline silicas. The opal silicas, including opal-C and opal-CT, exhibit almost complete reactivity and solubility in refluxing phosphoric acid under the conditions specified in NIOSH analytical Method 7601, while quartz and cristobalite of high temperature origin exhibit slight solubilities of approximately 10% for respirable sized particles.

In other unpublished work, Miles has concentrated opal-CT from a Mozambique bentonite and removed clay components from opal-CT in the Monterey formation of California. He has confirmed that the silica is hydrated opal by determining loss on ignition and index of refraction. Both silica concentrates give x-ray patterns that are consistent with opal-CT.

Other methods

Other methods that can be used to differentiate these minerals include differential thermal analysis [15], infrared spectroscopy [29] and under some circumstances, light microscopy. In general, light microscopy is not possible to use because these minerals often have particle sizes of less than 0.5 Å. If individual particles are large enough for optical examination then refractive index measurements can be used to identify cristobalite, which has a higher refractive index than opal.

Conclusions

Twenty samples of bentonite, fuller's earth and diatomaceous earth were examined by x-ray diffraction, TEM and SEM to characterize the opaline silica phase(s) in these deposits. One purpose of this characterization was to determine whether or not α-cristobalite occurs in these deposits. Numerous references to the presence of cristobalite in bentonite, for instance, can be found in a number of publications. A careful examination of the mineral that has often been referred to as "cristobalite" indicates that it is actually opaline silica. Part of the reason that this mineral has been misidentified as cristobalite is because of the similarity between the diffraction patterns of some opals and cristobalite. Because x-ray diffraction is the most commonly used method for quantifying crystalline silica, it is critical that anyone analyzing a bentonite, or any other deposit of low temperature origin, for crystalline silica be aware of the fact that opaline silica, which forms and is stable at low temperatures, is more likely to occur in these deposits than is α-cristobalite which is a high temperature phase.

In many cases opaline silica is relatively easy to distinguish from α-cristobalite, especially if it is poorly ordered. There are, however, many examples of deposits containing well-ordered opaline silica that can be mistaken for α-cristobalite based on x-ray diffraction patterns. The simple heating test described in this paper will quickly reveal whether the mineral in question is opaline silica or cristobalite. It is recommended that this heating test be performed on all bentonite, fuller's earth and diatomaceous earth samples whenever there is a question concerning the identification of the silica minerals.

Thus far, no true α-cristobalite has been identified in any of the bentonite and fuller's earth deposits examined for this study. Samples used in this investigation were collected from deposits from around the world. These deposits range in age from Jurassic to Miocene, represent a range of compositions, and were formed under a variety of geologic environments.

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