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Review

The structure of opal-CT revisited

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Highlights

- Opal-CT structure is best explained by tridymite-dominant paracrystalline model.

- Paracrystalline model is supported by various spectroscopic methods.

- XRD and electron microscope evidence are reconciled with paracrystalline model.

- Paracrystalline model has implications for nomenclature of silica polymorphs.

Abstract

There is a conflict of evidence with regard to the structure of the silica polymorph known as opal-CT. The current widely accepted interpretation of the structure views opal-CT as made up essentially of a disordered interlayering of crystalline cristobalitic and tridymitic

stacking units, in about equal proportions where the d spacing of the diffraction maximum is close to 4.11 Å, but becoming progressively more ordered and cristobalitic as this spacing decreases in value and approaches the $d_{(101)}$ reflection at 4.04 Å of α-cristobalite. The most compelling evidence for this interpretation comes from matching calculated and experimental XRD profiles, HRTEM lattice images and SAED patterns. This interpretation is here described as the "crystalline" model. However, the crystalline model is not supported by a variety of spectroscopic techniques that can be used to probe both long-range and short-range order. In general, these techniques which include FTIR, Raman, NMR and XANES spectroscopies are more consistent with a structure, especially where the diffraction maximum approaches 4.11 Å, as being dominated by disordered material similar to amorphous opal (opal-A) but containing a small volume of crystalline stacking units which are mainly (sometimes exclusively) of a tridymitic nature. This interpretation is referred to as the "paracrystalline" model. From a critical review of the literature, suggestions are made as to how these two conflicting strands of evidence can be reconciled, as well as matters concerning appropriate nomenclature of opaline materials.

Introduction

In a paper that has since been recognized as a landmark contribution, Jones and Segnit [1] classified hydrous silicas, described as opaline, into three categories based upon their atomic structures, namely opal-C, consisting of well-ordered α-cristobalite, opal-CT, consisting of disordered α-cristobalite and α-tridymite, and opal-A, which was highly disordered and near amorphous. This classification has been widely accepted and is now well-embedded within the literature. As is well-known, the X-ray diffraction (XRD) powder pattern yielded by opal-CT is characterized by three broad reflections (Fig. 1), the most intense of which occurs at about 4.12 to 4.05 Å (21.74 to 22.00°2Θ CuKα), with a subsidiary peak or shoulder at about 4.32 Å (20.72°). There is also a weaker reflection at about 2.50 Å (35.90°). [1] concurred with the earlier interpretation of [2] that such patterns "essentially result from α-cristobalite with varying degrees of stacking disorder leading to the appearance of maxima which can be attributed to tridymite". This interpretation has received substantial support through the application of other investigative techniques, particularly those involving calculated XRD profiles, as well as lattice images revealed by high resolution transmission electron microscopy (HRTEM).

Thus, [3] showed simulated XRD powder patterns derived from cristobalitic and tridymitic units stacked in a disordered way. In this instance, the crystallographic parameters of the structures of high cristobalite and tridymite were used to calculate the diffraction profile, (not the low-temperature form found in opal-CT) but nevertheless the model successfully

simulated the relative intensities of the two major diffraction maxima found in opal-CT for a stacking sequence with equal amounts of cristobalite and tridymite units. Broadening the diffraction maxima between 19 and 26° achieved a close similarity between calculated and experimental profiles for such a stacking sequence. [4] also modelled the XRD pattern of opal-CT, again using the high-temperature structures of cristobalite and tridymite, but taking into account the relative proportions of the two components, maximum crystallite size in three dimensions and an ordering coefficient describing the probability of randomness or regularity of the layer stacking. The model used was a modified version of the Wildfire program which has successfully simulated the experimental diffraction profiles of mixed-layer clay minerals [5]. An impressive match between calculated and experimental profiles for opal-CT was achieved, assuming about equal proportions of the two silica components.

HRTEM lattice image studies have also tended to support the view that opal-CT consists essentially of cristobalite and tridymite units stacked in a disordered way. For example, [6] showed lattice images from opal-CT samples taken from bentonite and silicified kaolinite which were interpreted as providing "direct evidence that opal-CT is comprised of interlayered cristobalite and tridymite stacking sequences" consistent with the model originally proposed by [2]. Both types of stacking were illustrated, and while it was conceded that estimation of their relative proportions on the basis of lattice images from a few samples was problematical, it was nevertheless inferred that substantial cristobalite stacking was always present, even in samples yielding d spacings close to 4.11 Å, the most intense reflection of α-tridymite.

[7] also investigated the structure of opal-CT by HRTEM. The samples were from banded chert and porcelanite in the Monterey Formation of California and were described as microcrystalline. Many samples showed a distinct fibrous structure and were identified as corresponding to opal-C in some cases and in others to lussatite, a variety of opal made up of tiny fibrous particles and exhibiting birefringence under the polarizing microscope. Both types yielded lattice fringe spacings at about 4.1 Å and were characterized by many defects and manifestations of disorder. Other samples were described as "opal-CT crystals with incoherently interstratified lamellar domains" and were characterized by such stacking disorder that identification of the different layer types was uncertain. In one sample, however, pseudo-orthorhombic tridymite was identified in the matrix of an opal-CT porcelanite on the basis of a single-crystal type optical diffraction pattern generated from a lattice image. It was concluded that HRTEM observations of lussatite type opal-CT in general provided direct evidence for the structure of opal-CT originally proposed by [2], although no

conclusions were drawn concerning the incoherently interstratified opal-CT mentioned above.

Perhaps the clearest illustration of the structure of opal-CT has been provided by the study of samples from the Hosaka opal mine, Japan, by [8]. It may be noted, however, that this material is of volcanogenic origin and may not be directly comparable to the sedimentary type of opal-CT discussed so far. It yielded an intense diffraction maximum over a rather small range (4.055 to 4.072 Å), but with a mean value of about 4.063 Å, and always contained domains of ordered cristobalite. These domains often surround disordered domains of cristobalite, the inter-domain boundary being of a coherent nature. It was suggested that the d-value of the diffraction maximum was related to the volume ratio of ordered to disordered cristobalite and that the proportion of ordered cristobalite increased as the value of the diffraction maximum decreased. It was also commented that volcanogenic opal-CT almost always contained such ordered domains to a greater extent than sedimentary-type opal-CT.

It may be concluded that the studies cited above, as well as many other complementary investigations and reviews [3], [9], [10], [11], [12], [13], [14] generally concur that opal-CT is of a crystalline nature consisting essentially of a disordered interlayering of cristobalitic and tridymitic stacking units, in about equal proportions where the d spacing of the diffraction maximum is close to 4.11 Å, but becoming progressively more ordered and cristobalitic as this spacing decreases in value and approaches the $d_{(101)}$ reflection at 4.05 Å of α-cristobalite.

Section snippets

An alternative structural model

Although a central issue in the papers briefly reviewed above revolves around the question of the relative proportion of the cristobalite and tridymite components in opal-CT, an equally important issue is the relative volume fraction in opal-CT that can be described as disordered and ordered respectively. Smith (1998) [15] addressed this question and pointed out that strictly speaking opal-CT should be referred to as paracrystalline, a description which implies that there is "partial ordering…

Evidence from spectroscopic methods

XRD and electron diffraction methods have limited application with respect to substances that lack long-range order, in contrast to spectroscopic techniques which respond to short-range energetic vibrations of the various structural components of the material being investigated. For this reason, the results of various spectroscopic techniques, including Fourier Transform Infrared, Raman, Nuclear Magnetic Resonance, and X-ray Absorption spectroscopies, will be reviewed, particularly as they have …

Reconciling spectroscopic results with those of XRD and HRTEM

In general, the results from all the spectroscopic techniques briefly reviewed above are consistent with a structure for opal-CT which is of a paracrystalline nature, as suggested by [15], where disordered domains are predominant. In addition, the crystalline domains that occur within this disordered matrix are predominantly tridymitic where the main X-ray diffraction maximum occurs at about 4.10Å. The question therefore arises as to how these conclusions can be reconciled with the XRD and…

Comments on nomenclature

The nomenclature proposed for opaline silica by [1] has been widely accepted and is currently in general use. However, if the paracrystalline structure of opal-CT as described above is correct then it may be that some modification of nomenclature is desirable. Thus, if it is found that the diffraction maximum of a sample occurs at the high end of the 4.04 to 4.12Å range (say 4.08 to 4.12Å) then it would seem appropriate to designate such material as opal-TC, inasmuch as the spectroscopic…

Conclusions

A variety of spectroscopic methods used to probe the structure of opal-CT yielding an X-ray diffraction maximum at about 4.10Å, consistently indicate a predominance of non-crystalline material. The spectra obtained by these methods are similar to that of opal-A but with indications of minor amounts of crystalline material which appears to consist largely of tridymite. The spectroscopic results are generally in line with the paracrystalline model for opal-CT suggested by [15] but contrasts with…

Acknowledgements

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2021, Sedimentary Geology

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> …Etching with HF showed that many of these spheres had a nucleus 20 to 50 nm in diameter (Liesegang and Milke, 2014). Basic descriptions of opal-CT include (1) "low-cristobalite unidimensionally disordered by stacking of randomly interstratified tridymite layers" (Kano and Taguchi, 1982), (2) "disordered microcrystallites of α-cristobalite in a matrix of amorphous silica" with varying degrees of stacking order, that may include tridymite (Elzea et al., 1994), (3) a disordered α-cristobalite, α-tridymite (Smith, 1998), and (4) the "paracrystalline" model that involves a small volume of tridymite-like units among disordered material that is akin to opal-A (Wilson, 2014). Fröhlich (2020) argued that the opal-CT in sedimentary rocks is formed of nanoparticles, ~ 3 nm thick, with a monoclinic, crystalline tridymite domain that passes into a non-crystalline domain.…

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2021, Geochimica et Cosmochimica Acta

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