

EP Minerals New Test Method for determining crystalline silica in diatomite products

There are distinguishing characteristics between opal-C (and/or opal-CT) and cristobalite that can be measured, albeit not always precisely. Opals always contain some water existing as internal or attached silanol groups, while cristobalite is anhydrous. Thus, it is possible to perform a “loss on ignition test” to see if water of hydration exists in a sample. Such a test should be carried out at high temperature (for example 980°C- 1200°C) for a sufficient time (at least 1 hour) so that chemically-bound water has a chance to disassociate and volatilize. Precise measurement of sample mass (to the nearest 0.1mg) before and after this treatment allows quantification of volatiles, including the water of hydration, with a resolution to better than 0.01%. American Society for Testing and Materials (ASTM) method C571 provides a suitable protocol for determination of loss on ignition of samples comprising diatomite. Samples that are determined to contain measurable (generally over 0.1 wt%) loss on ignition have the potential to be opal-C (and/or opal-CT).

Bulk powder XRD can also be used to differentiate between opal-C and α -cristobalite. The diffraction pattern of cristobalite contains sharp Bragg's peaks, most notably at 22.02°, 36.17°, 31.50°, and 28.49° 2 θ . The diffraction pattern of opal-C (and/or opal-CT) is less well-defined as compared to cristobalite, with broader and fewer peaks that may be indicative of radial scattering and not true Bragg's peaks. The locations of the primary and secondary peaks are similar to that of cristobalite, but the peaks at 31.50° and 28.49° 2 θ are missing or very poorly developed. To summarize, the opal-C (and/or opal-CT) diffraction pattern differs from that of α -cristobalite in the following ways: the primary peak (22°) and the secondary peak (36°) are at higher d-spacing (lower 2 θ angle), there is a broader primary peak for opal-C (and/or opal-CT) as measured using the “Full Width at Half Maximum” (FWHM) statistic, opal-C (and/or opal-CT) has poorly-defined peaks at 31.50° and 28.49° 2 θ , and a much more significant amorphous background.

Differentiating opal-C from β -cristobalite using XRD is more difficult. However, Chao and Lu demonstrated that by grinding samples of β -cristobalite with alumina content less than 10 wt% to fine particle size, most of the β -cristobalite is inverted to the α -cristobalite phase with corresponding XRD pattern peak shifts. This does not occur when diatomite products comprising opal-C (and/or opal-CT) are finely ground and then analyzed using XRD – there is no peak shift. As a matter of standard practice with diatomite, all samples should be finely milled prior to bulk powder X-ray Diffraction analysis.

Where differentiation based just on XRD pattern is difficult, Miles et al. advocate a twenty-four-hour thermal treatment of the sample at very high temperature (1050 °C). Theoretically, opal-C will de-hydrate and re-crystallize as cristobalite. Diffraction peaks will become sharper, more intense, and will shift. Sharper diffraction peaks are indicative of increasing long-range molecular order (larger crystallite size). Increasing peak intensity indicates an increasing quantity of the crystalline phase represented by the peak. A shift in peak location indicates a change in crystal structure with associated increase or reduction in d-spacing. If cristobalite is present in the original sample, the diffraction pattern will not change significantly.

The potential problem with this technique is where a sample is comprised of individual particles, some of which could be opaline and others of which could be composed of cristobalite. Heating of such a sample would convert the opaline phase to cristobalite but not affect the cristobalite, and not much of an argument can subsequently be made that cristobalite was not also present in the original sample.

Another problem exists with the chemical dissolution techniques of Miles, Hillier, and others. Hillier et al. successfully demonstrated the efficacy of a sodium hydroxide digest in determining whether various clay samples contained opaline phases or cristobalite. NaOH is capable of dissolving all forms of silica but requires more contact time for the crystalline varieties in comparison to the opals. When used on diatomite samples (natural, straight-calcined, and flux-calcined), Hillier's method was not found to entirely remove the opaline phases, including opal-A. This is most likely because diatomite particles are coated with chemically-resistant precipitates in the natural state (such as limonite), iron oxides when straight-calcined, and a sodium-rich vitreous or glass-like phase when flux-calcined. While extending the NaOH contact time does increase the dissolution of the opaline phases, results can be inconsistent between diatomaceous product samples produced using varying processes and from different raw materials.

One relatively simple way to confirm the absence of cristobalite within a sample is to spike the sample (add a known amount of) with cristobalite standard reference material (i.e. National Institute of Standards and Technology (NIST) Standard Reference Material 1879A), run XRD analysis on the spiked sample and then compare the original un-spiked sample diffraction pattern with the spiked sample pattern. If the spiked sample diffraction pattern simply increases the intensity of the primary and secondary peaks but does not show a position shift or show additional peaks, then the original sample most likely contains cristobalite. If the primary peak shifts, broadens or resolves into two separate peaks, and secondary peaks appear or become much better defined, then opal-C (and/or opal-CT) and not cristobalite is present in the original sample.

In summary, to determine whether a sample of a product that includes diatomite contains cristobalite or opal-C (and/or opal-CT) then to quantify the opal-C (and/or opal-CT) and/or crystalline silica content involves a number of steps according to the method referred to as the "EP Method", (may also be referred to as the LH Method).

First, it is determined whether the sample contains water of hydration via high-temperature loss on ignition (LOI) testing. A representative split of the sample (previously dried) is obtained, and loss on ignition testing is performed on the split (i.e., ASTM C571). If the LOI is < 0.1%, then the phases present are not opaline. If it is > 0.1%, then there is a chance that opaline phases are present.

Second, bulk powder X-ray Diffraction is performed, and the resulting (first) diffraction pattern inspected. Another representative split (dry) of the sample is milled prior to XRD. Milling contact surfaces should be compatible with no chance for crystalline silica contamination. The milled split should be at least 99% minus 400 mesh (37um) prior to XRD.

The resulting diffraction pattern is analyzed for the presence or absence of opal-C (and/or opal-CT) and cristobalite. The diffraction pattern may also be analyzed for the presence or absence of other crystalline silica phases (for example, quartz and tridymite). As discussed, the opal-C (and/or opal-CT) diffraction pattern differs from that of α -cristobalite in the following ways: the primary peak (22°) and the secondary peak (36°) are at higher d-spacing (4.06 to 4.11 for the primary peak as opposed to 4.02 to 4.04 for well-ordered cristobalite), there is a broader primary peak for opal-C (and/or opal-CT) as measured using the "Full Width at Half Maximum" (FWHM) statistic (usually > 0.35), opal-C (and/or opal-CT) has poorly-defined peaks at 31.50° and $28.49^\circ 2\theta$, and a much more significant amorphous background.

If the diffraction pattern is questionable with regard to whether opal-C (and/or opal-CT) and/or cristobalite is present, then according to the EP Method a second XRD analysis is performed to determine whether opal-C (and/or opal-CT) and/or cristobalite is present. This time, the analysis is performed on another representative portion of the sample spiked with cristobalite standard reference material (NIST 1879a). A (representative) third split of the sample is obtained and then spiked with cristobalite standard reference material (NIST 1879A).

After co-milling and dispersion of the standard within the sample, XRD is performed on the third split. The resulting diffraction pattern is analyzed. If the original sample comprises opal-C (and/or opal-CT), the cristobalite spike significantly modifies the original diffraction pattern with additional peaks identifiable at 22.02° and $36.17^\circ 2\theta$, along with more prominent peaks at 31.50° and $28.49^\circ 2\theta$. If the original sample comprises cristobalite, then addition of the cristobalite spike only results in increased peak intensity and no other significant change from the first diffraction pattern. Figures 1 and 2 show the diffraction patterns of spiked samples. Figure 1 shows the pattern of a sample comprising opal-C, and figure 2 shows the pattern of a sample comprising cristobalite.

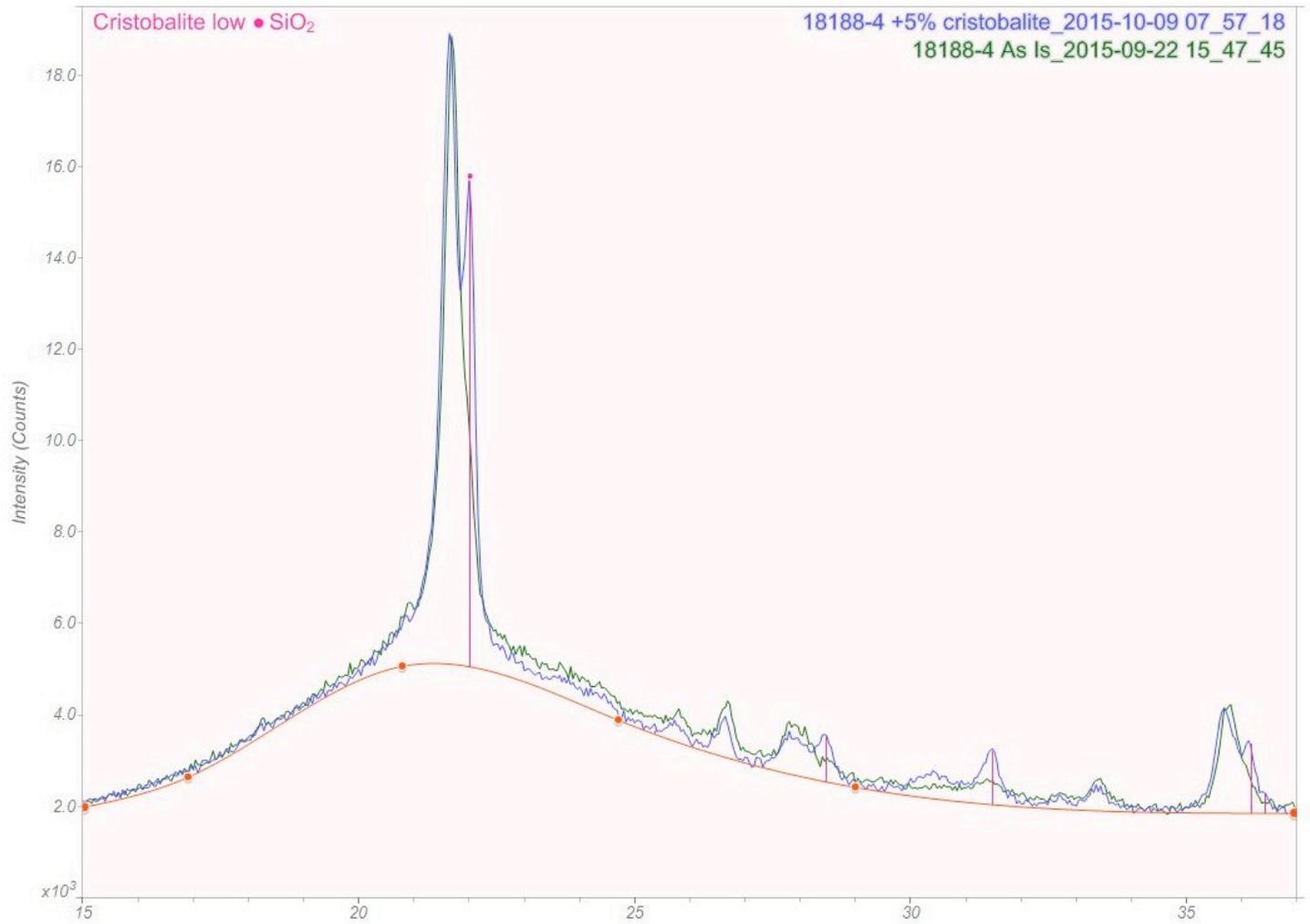


Figure 1: Flux-calcined DE with and without 5% 1879a Spike showing Opal-C

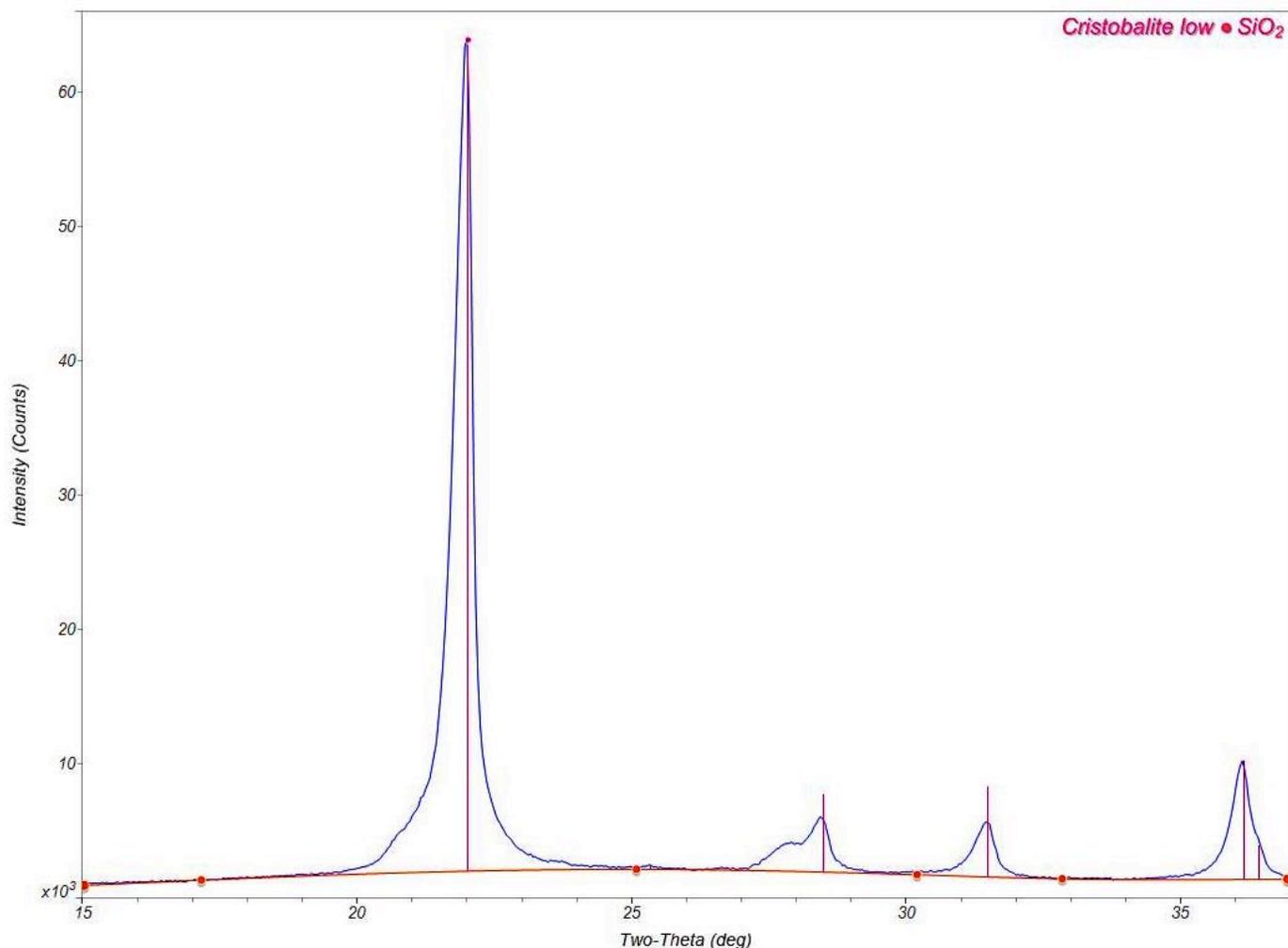


Figure 2: Flux-calcined DE with 28% 1879a Spike showing Cristobalite

Quantifying the opal-C (and/or opal-CT) content of a diatomite sample can be complicated as its diffraction pattern is a combination of broad peaks and amorphous background, and diatomite products often contain other x-ray amorphous phases in addition to opal. According to the EP Method, an estimate of the quantity is obtained by treating the opal-C peaks of the first diffraction pattern as if they are cristobalite and quantifying against cristobalite standards such as NIST 1879a. This method of quantification of opal-C (and/or opal-CT), which we call the XRD Method, will usually underestimate the opal-C (and/or opal-CT) content but is effective for a number of purposes, such as manufacturing quality control. Alternatively, a measure may be obtained by heating a representative split of the sample at very high temperature (e.g., 1050 °C) for an extended period of 24 to 48 hours until that heated portion is fully dehydrated. This completely dehydrates opaline phases and forms cristobalite (reduces amorphous background component). XRD analysis is then performed on the dehydrated split and the cristobalite in the resulting diffraction pattern can be quantified against the cristobalite standards to give an estimate of original opal-C (and/or opal-CT) content.

As long as additional flux is not added prior to heating the selected split, and the temperature is kept below 1400 °C, any quartz present in the sample split will not be converted to cristobalite.

If it is determined by the EP Method that cristobalite is present, the cristobalite seen in the (first) diffraction pattern may be compared to its respective standard (for example NIST 1879a) for quantification of the content, or be quantified through the use of an internal standard (such as corundum) and applicable relative intensity ratios. In the case where there is both opal-C (or opal-CT) and cristobalite present, and the primary peak of the opal-C (or opal-CT) cannot be differentiated or de-convoluted from that of cristobalite, the opal-C (or opal-CT) and cristobalite are quantified as one phase and reported as cristobalite. The quantity of cristobalite thus reported will be higher than the actual quantity in the sample.

Bulk powder XRD equipment and instrumental parameters are not expressly fixed, but should provide good resolution and sufficient counts for quantification. EP Minerals' internal analyses are performed using a Siemens[®]D5000 diffractometer controlled with MDI[™] Datascan5 software, with CuK α radiation, sample spinning, graphite monochromator, and scintillation detector. Power settings were at 50KV and 36mA, with step size at 0.04° and 4 seconds per step. JADE[™] (2010) software was used for analyses of XRD scans. Sample preparation included SPEX[®] milling in zirconia vials with zirconia grinding media.

Citations:

Chao, Chin-Hsiao, Lu, Hong-Yang, 2002, "Stress-induced β to α -cristobalite phase transformation in (Na₂O + Al₂O₃)-codoped silica", Materials Science and Engineering, A328, 267-276.

J.M. Elzea, I.E. Odom, W.J. Miles, "Distinguishing well-ordered opal-CT and opal-C from high-temperature cristobalite by x-ray diffraction", Anal. Chim. Acta 286 (1994) 107-116.

Hillier, S., and D.G. Lumsdon. "Distinguishing opaline silica from cristobalite in bentonites: a practical procedure and perspective based on NaOH dissolution," Clay Minerals (2008) 43, 477-486.