

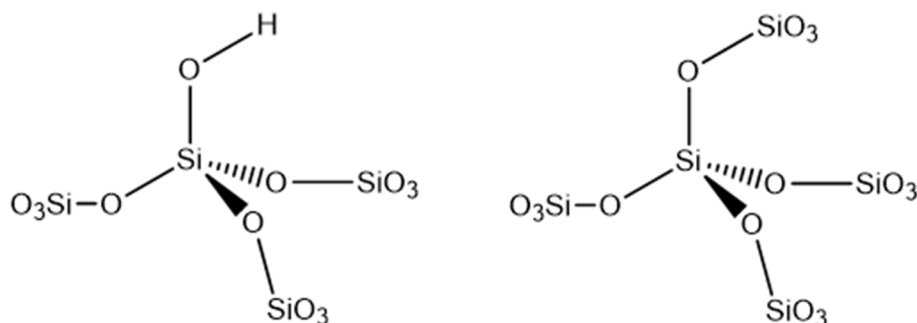
## Opal chemistry: classification and characterisation

### A Compilation of Techniques and Representative Patterns and Spectra

Prepared by Neville J Curtis (Flinders University) for the International Opal Academy as a reference for opaleers everywhere

#### Introduction

A simple description of opal is that it is wet, impure silica, with formula  $\text{SiO}_2 \cdot n\text{H}_2\text{O} \cdot x$ . Most of it is in the form of  $\text{Q}_3$  and  $\text{Q}_4$  based on tetrahedral silicon.



*Partially bridged silica ( $\text{Q}_3$  with silanol) on left with full bridged ( $\text{Q}_4$ ) on right*

The chemist's basket of techniques can help us to classify and characterise opal:

- x-ray diffraction
- vibrational spectroscopy (Raman and infra-red)
- nuclear magnetic resonance spectroscopy ( $^1\text{H}$  and  $^{29}\text{Si}$ )
- scanning electron microscopy
- elemental analysis
- inelastic neutron scattering
- thermal analysis

What follows below is a summary of what we've seen with some of these techniques. The examples given are taken from our extensive database (>250) of worldwide samples. Data in xy Excel format are available for comparisons. Our database is constantly being updated with new samples.

At present, the listing comprises x-ray diffraction, Raman and infra-red spectroscopy and some Scanning Electron Microscopy. Some explanatory information on the techniques is given.

#### (Powder) X-ray Diffraction

*This is a standard method of characterising and identifying minerals (and other crystalline materials). The method measures the distances between atoms. For a regular, well-defined mineral, such as quartz, you get a set of characteristic sharp peaks which give a lot of information about structure.*

*The technique involves grinding 100-200 mg of sample into a fine powder. The sample is placed on flat plate and scanned by monochromatic x-rays at increasing angles (theta,  $\vartheta$ ), usually starting at 5 to 10° and going up to 65°. For a crystalline compound, when the numbers are right there will be constructive interference and the x-rays will be diffracted at an angle of 2 theta. The detector picks these up. There will be several ways in which the atoms may line up to produce diffraction peaks. The product is thus a set of peaks, as a function of 2 theta, which for many compounds is as characteristic as a fingerprint.*

The Bragg equation can be used to determine the distance (*d*-spacing) between the atoms that causes the effect. Crystallographers tend to use the Ångstrom unit (Å) as the distances are usually between 1 and 10. It equates to 0.1 nm (or 100pm).

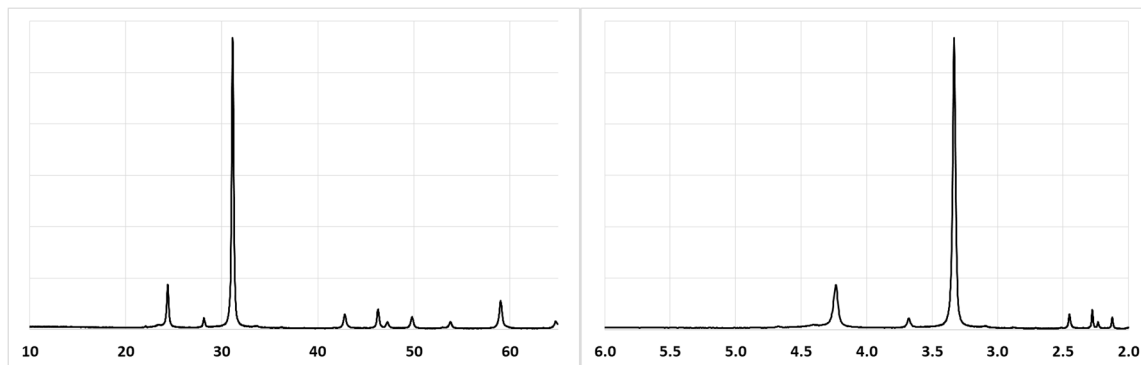
Commercial XRD instruments are widespread. There is usually a choice of sources: copper (Cu) or cobalt (Co) though molybdenum (Mo) is sometimes used. We use cobalt. We prefer to present as *d*-spacing (in Å) for the x-axis rather than 2 theta as Co and Cu sourced scans look a little different on the x axis though the features are the same.

### X-ray diffraction (XRD) of opals

If you have access to an instrument do this technique first as it provides primary information for classification and purity.

For reference, the XRD pattern of quartz is characteristic and an example of what the technique can produce.

XRD scan 1: Quartz (labelled G15914 common opal from Botswana(!))



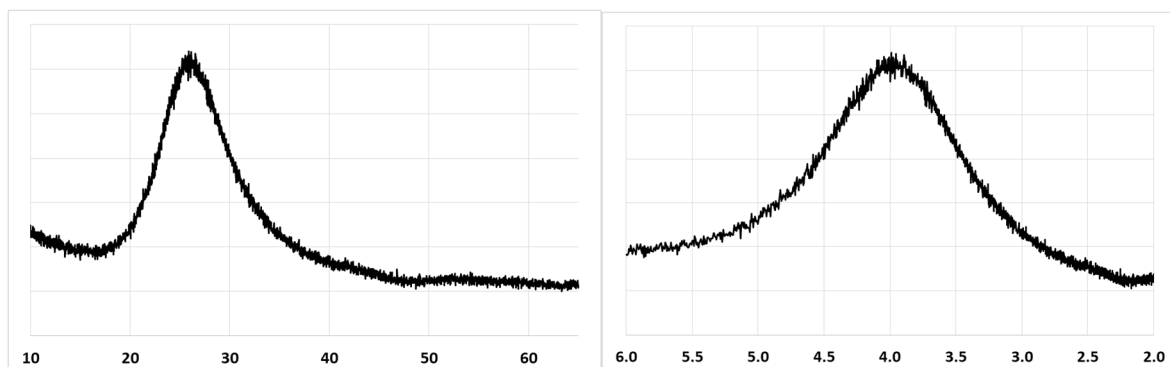
XRD pattern of quartz. Initial scan on left with *d*-spacing on right.

Opal is not a well-defined mineral (and usually called a mineraloid) so the XRD pattern is less informative. Opal can be classified into three major types by XRD:

- Opal-A
- Opal-CT
- Opal-C

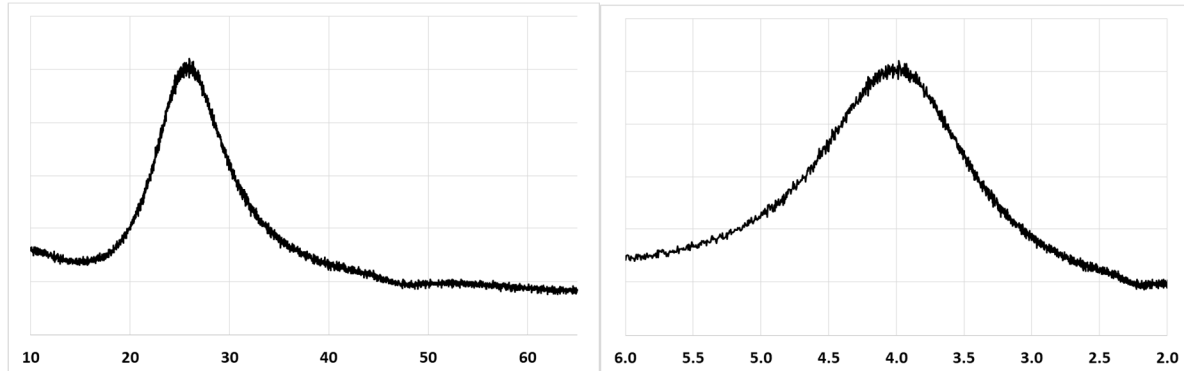
**Opal-A** is the least structured by XRD.

XRD scan 2: play of colour opal (opal-AG) from Coober Pedy, South Australia



XRD pattern of G9593 (Cooper Pedy). Initial scan on left with d-spacing on right.

XRD scan 3: hyalite (opal-AN) from Mount Cora, New South Wales



XRD pattern of G1419 (Mount Cora). Initial scan on left with d-spacing on right.

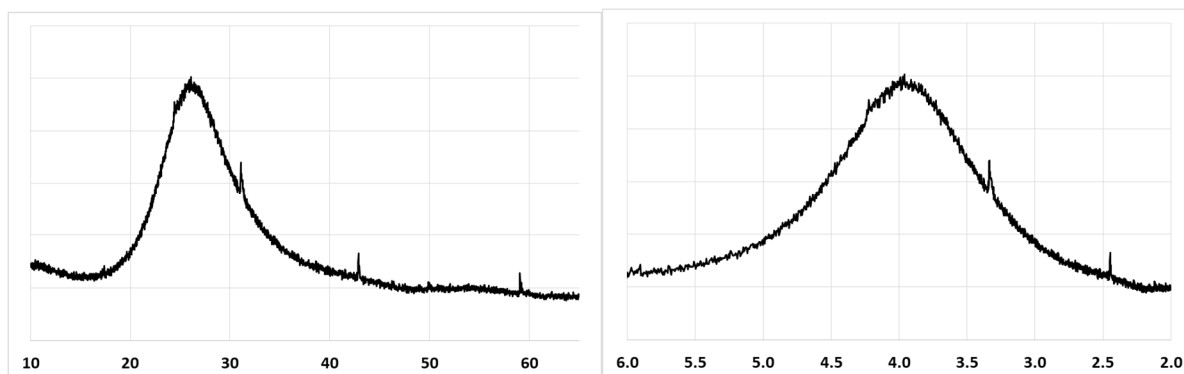
These were classified as opal-A (amorphous) by Jones and Segnit in the 1970s. A further delineation is that under the scanning electron microscope (see later) the Cooper Pedy ones shows spheres while the hyalite shows little at all. Respectively they are opal-AG and opal-AN. The names derive from *amorphous with gel or network*.

Vertical scales are not shown here but they reveal that the signals are relatively weak and noisy. The baselines tend to slope and in some cases you can see the non-linear effect of the silicon plate showing through.

All the samples of opal-AG and opal-AN look more or less the same with similar peak maxima and full width half maximum (FWHM), subject to the variations in noise and baselines. There is no difference between play of colour opal-AG and potch. Australian seam and boulder opals, opalised mollusc fossils and overseas samples (e.g. Slovakian and Virgin Valley) all look similar.

Small amounts of quartz sometimes show:

XRD scan 4: honey potch (opal-AG) from Mintabie, South Australia

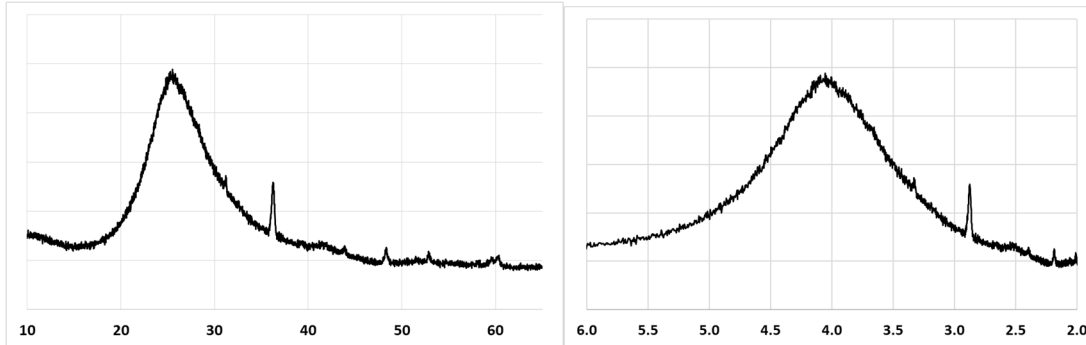


XRD pattern of G13962 (Mintabie). Initial scan on left with d-spacing on right.

This is probably a very minor level of quartz as it gives a much better response by XRD.

This is not the complete story for opal-A as we can propose two (and no doubt others) other members, on the basis of other measurements (see later sections), though they all have the same XRD pattern.

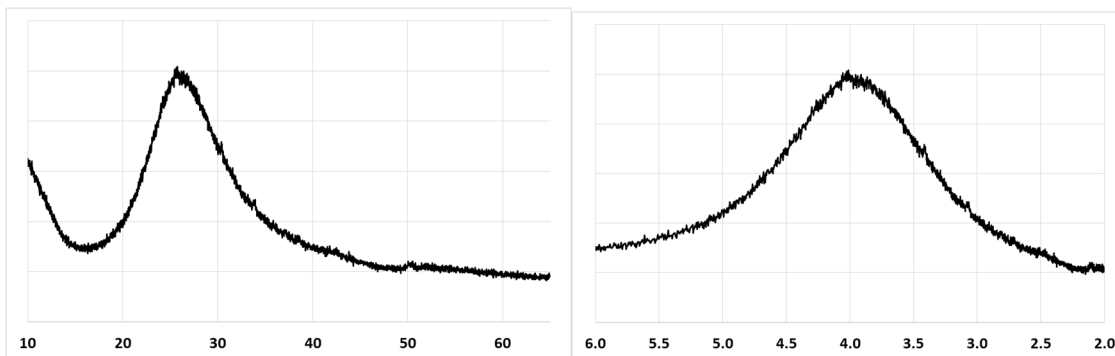
XRD scan 5: ninot from Caldes de Malavella, La Selva, Girona, Catalonia, Spain



*XRD pattern of G NEW23 (Girona, Spain). Initial scan on left with d-spacing on right.*

These are sold as menilites (see MINDAT for comments on grey and brown menilites) and are opaque and nodular. The local name is ninot (Catalan for doll). The impurity pattern seems consistent (though we'll need more examples) and is not purely quartz.

XRD scan 6: hot springs sinter (or geyselite) from Rotorua, New Zealand



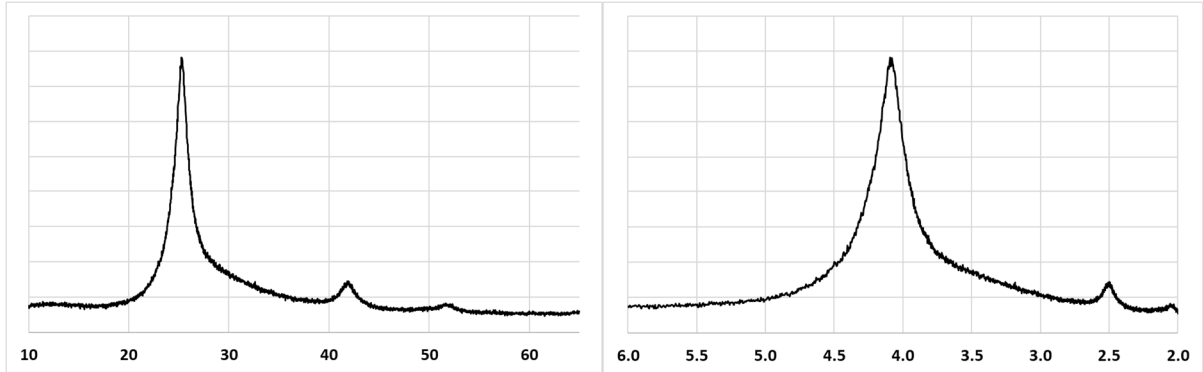
*XRD pattern of G21471 (Rotorua, New Zealand). Initial scan on left with d-spacing on right.*

This a crumbly white mass. We only have ones from NZ though the literature suggests others have similar XRD patterns. Fiorite may be similar.

**Opal-CT** provides a range of responses. Opal-CT may show play of colour though most do not show this property. Samples could be clear, translucent or opaque, and may be in a variety of colours. For instance, fire opals are orange and clear. Other samples may be considered as “mineral specimens” though they can come from exotic locations such as Madagascar.

In general, opal-CT patterns are more intense (typically the main peak is five times higher) than for opal-AG and opal-AN. The name comes from the notion that it was thought to be a mix of *cristobalite* and *tridymite*, which are polymorphs of silica. The following 5 scans show that there is considerable variation with the class. This can be described as an increase in structure and delineation.

XRD scan 7: Play of colour opal-CT.

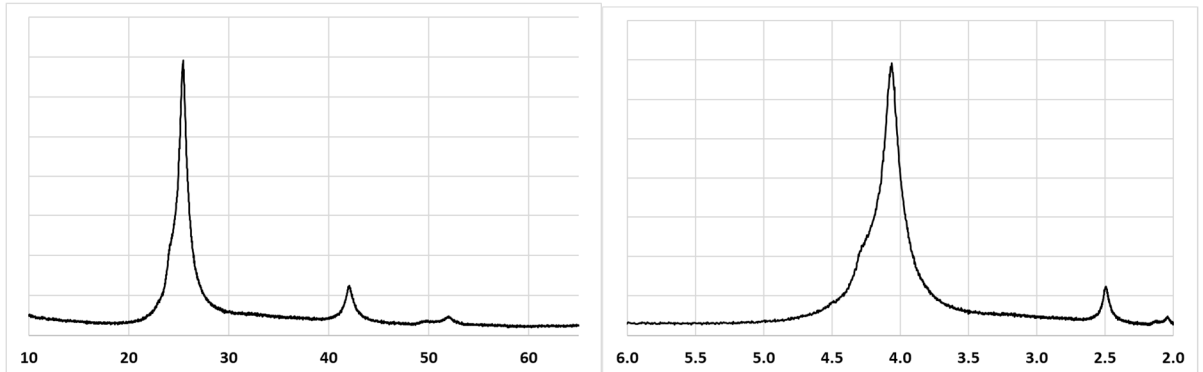


*XRD pattern of G32752 POC (Afar, Ethiopia). Initial scan on left with d-spacing on right.*

Peaks are sharper than for opal-A but still broad. The peak at 2.5Å is characteristic. Several non play of colour opals also show this sort of scan. The main peak may show some asymmetry.

The main peak may be more complicated as the following examples progressively show.

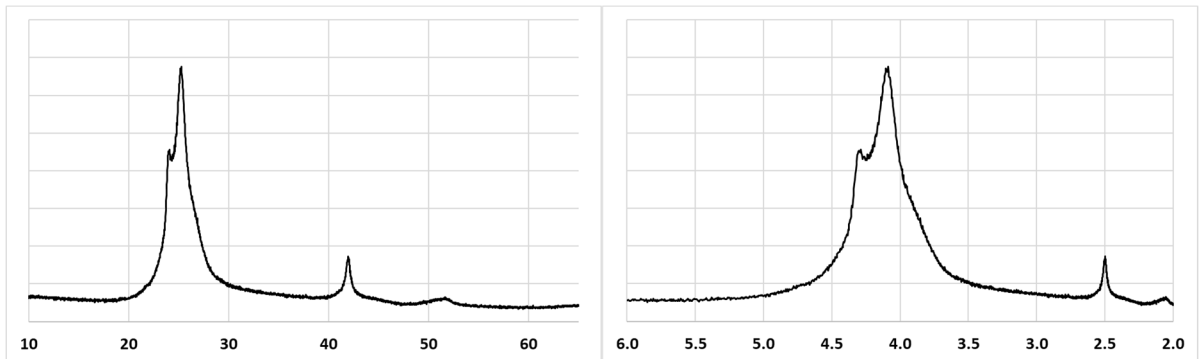
*XRD scan 8: Jelly opal (cloudy with play of colour)*



*XRD pattern of G9964 (Murwillumbah). Initial scan on left with d-spacing on right.*

There is now more obvious asymmetry in the main peak and peak at 2.5Å is sharper.

*XRD scan 9: Fire opal*

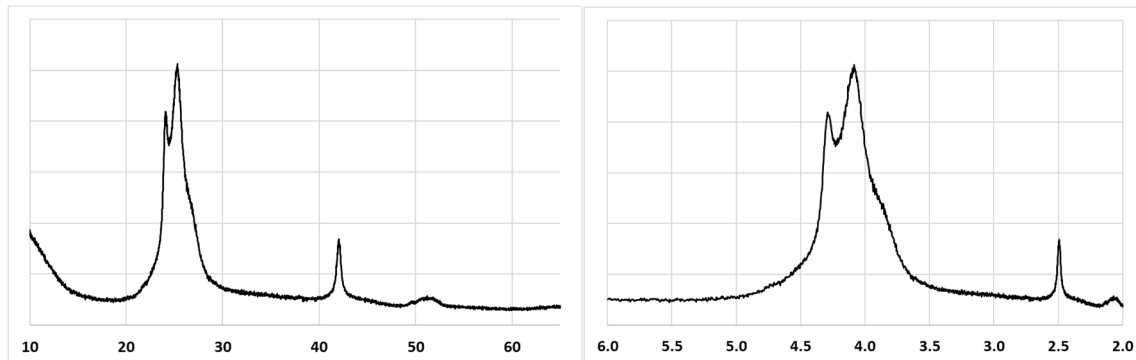


*XRD pattern of M21798 (Zimapanan, Mexico). Initial scan on left with d-spacing on right.*

The peaks at 4.3 and 4.1Å are now better defined. Several opals look like this including translucent and opaque samples. Colour does not influence the pattern.

The peak at 4.3Å can be more prominent.

### XRD scan 10: Translucent vermilion opal

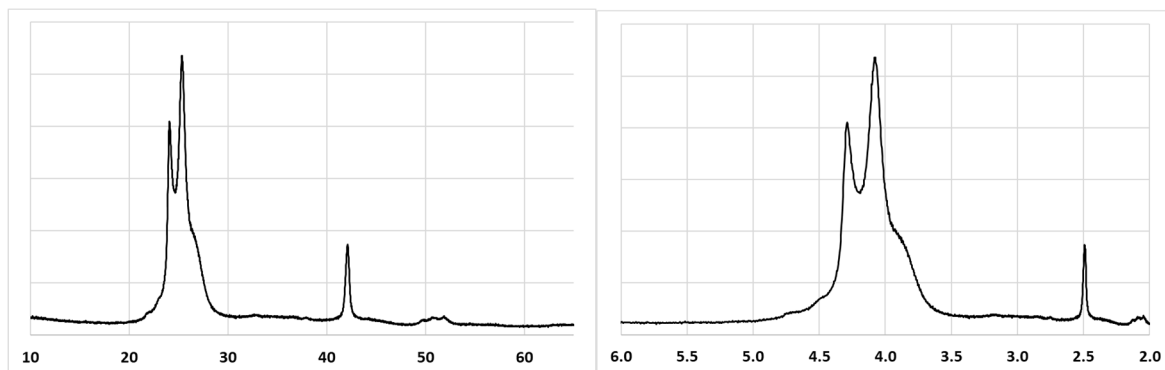


*XRD pattern of G32925 (Zelinograd, Qazaqstan). Initial scan on left with d-spacing on right.*

The peak at 4.3Å is more separated with sharpening of the one at 2.5Å. The (shoulder) peak at 3.9Å is more apparent. A wide range of translucent and opaque samples of many colours look like this.

Some samples are more defined, and while not as sharp as the patterns for quartz, imply much more structure and regularity.

### XRD scan 11: translucent off-white opal



*XRD pattern of G32226 (St Austell, England). Initial scan on left with d-spacing on right.*

This is a very pronounced example showing the three components of the main peak. Again this is a common result.

All opal-CT samples can be placed within this range of patterns though it may not be obvious what any opal will look like before scanning. As a general rule, if the sample shows play of colour then it will have a simpler pattern. Building up a library of patterns may show location characteristics.

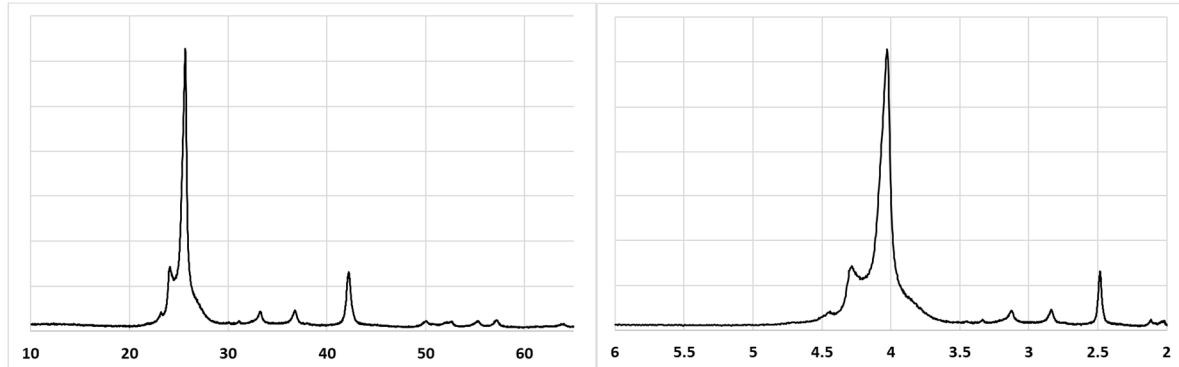
We can infer that there is a trend from less to more structured XRD patterns. We might propose that there is a correlation with crystallinity in the opals. Baselines are sufficiently regular for curve-fitting of the peaks at 4.3, 4.1, 3.9 and 2.5Å. It looks like there are least two progressions occurring rather than a single less to more complex trend. This may indicate a gradual transformation with aging though without experimentation (unambiguous accelerated aging) this is speculative. It may also simply represent the local conditions when the opal formed.

Opal-CT samples also suffer from quartz "impurities". Peaks can be quite significant (and interfere with the composite centred at 4.1Å) and it is hard to determine the real composition of the complex of peaks. There is an example of this in the Raman section. Quartz peaks may also be variable

depending on which part of the sample was used. Again it is difficult to determine the origin of the quartz, in particular, if it came from the opal or from a separate event.

**Opal-C** presents distinctive XRD patterns. As for opal-CT, the patterns are relatively intense.

XRD scan 12: an opal-C



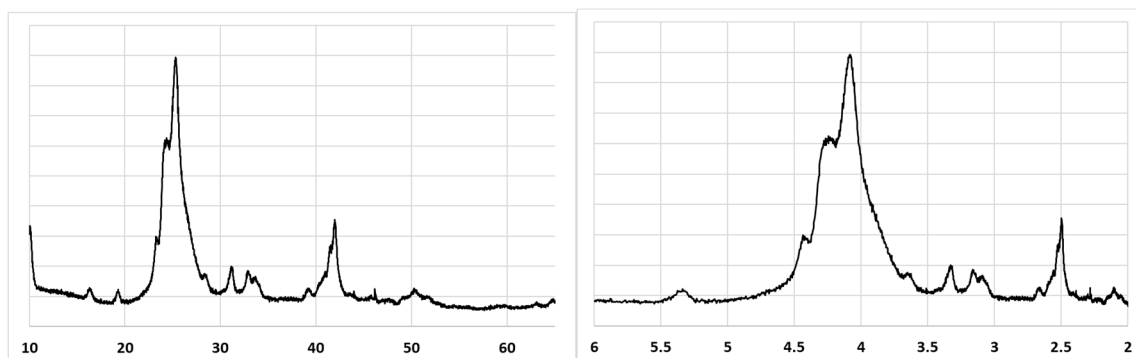
*XRD pattern of G34327 (Guanajuato, Mexico). Initial scan on left with d-spacing on right.*

The most obvious feature is the pair of small peaks either side of  $3\text{\AA}$ . This pattern matches that for cristobalite. The major peak is slightly displaced from that for opal-CT. We note that there is never any evidence for doubling of the major peak for opal-CT. The feature at  $2.5\text{\AA}$  is common to opal-CT and opal-C. The above sample contains orange glass and opaque sections though both have identical XRD patterns. We have only seen four examples of opal-C.

### Other insights

Some further features are revealed by XRD. For instance, Peruvian pink “opal” is readily shown not to be pure.

XRD scan 13: a Peruvian pink opal

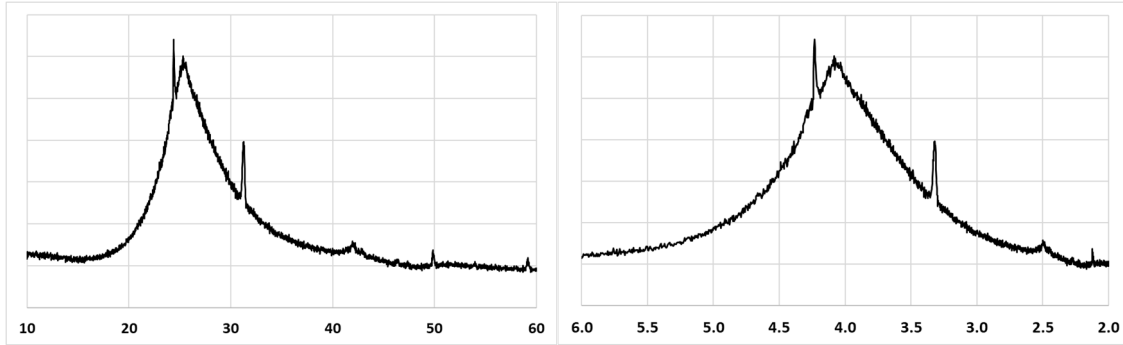


*XRD pattern of G NEW21 (Peru). Initial scan on left with d-spacing on right.*

We have 2 samples of this with the other having more palygorskite. The peaks at  $4.1$  and  $2.5\text{\AA}$  imply that it is probably opal-CT. The actual opal content is of course unknown as palygorskite presumably gives an intense signal. Other examples of Peruvian opal-CT (white and blue) seem free of palygorskite.

Next, we can identify opals that have characteristics of more than one class. First, a few appear to be between opal-AG and opal-CT.

XRD scan 14: a “transitional” opal-AG to opal-CT.



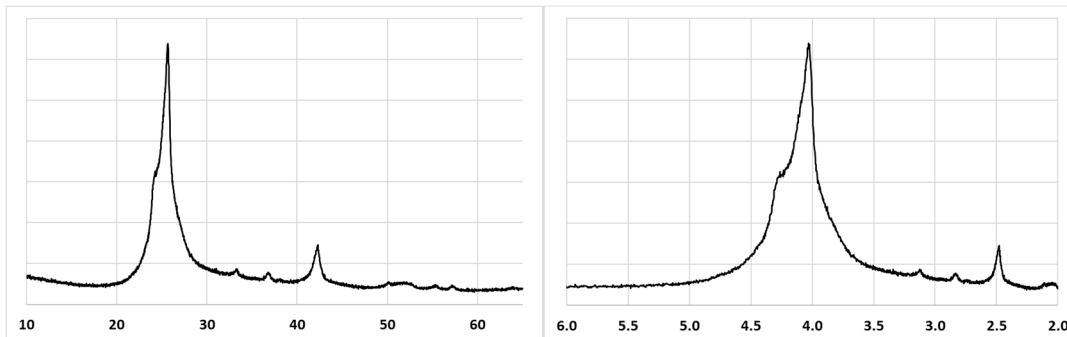
*XRD pattern of G14581 (Andamooka). Initial scan on left with d-spacing on right. The sample shows some play of colour*

This is a play of colour opal from Andamooka. In comparison with opal-AG the main peak is narrower and there is a hint of a peak at 2.5Å. The XRD varies according to which part is sampled, particularly the quartz-like “impurities” at 4.2 and 3.3Å.

We have another example similar to this (from Mazaron, Spain) and several more which suggest a spectrum ranging into the less developed opal-CT patterns as in XRD scan 7. We propose that G14581 is more likely to be opal-AG trending towards opal-CT rather than opal-C. The XRD scan itself, of course, can give no information if the samples formed like this or are transforming.

Some opal-CT samples show peaks which could be consistent with the presence of cristobalite (or opal-C).

XRD scan 15: opal-CT with cristobalite (or opal-C)



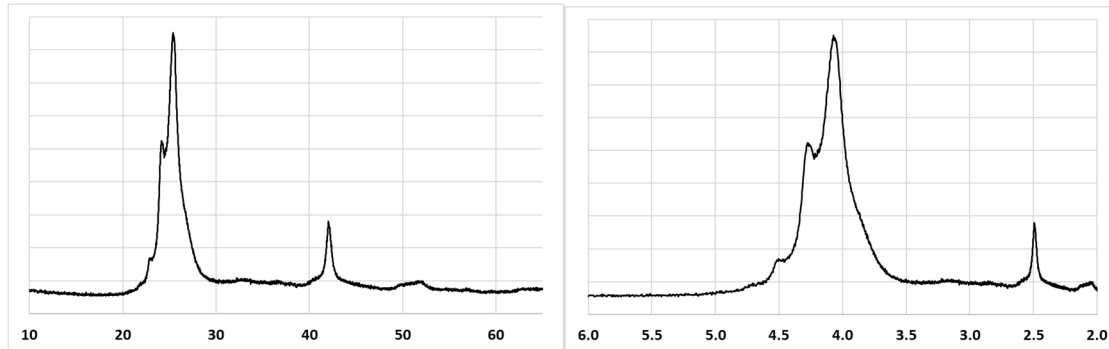
*XRD pattern of GNEW18 (Oregon). Initial scan on left with d-spacing on right.*

This looks like a poorly structured opal-CT XRD pattern though the two peaks either side of 3Å are characteristic of cristobalite. Raman and IR (see later) also suggest cristobalite. Recently we have seen two more looking this: from Boi Morto, Brazil and Butte, Montana.

Additional peaks may also be seen which could be characteristic of location or mechanism of formation.

XRD scan 14: Opal-CT with additional peaks





*XRD pattern of GNEW4 (Mt Lyobo, Tanzania). Initial scan on left with d-spacing on right.*

This has an extra peak at 4.5Å. Another “prase opal” sample from this location is similar.

XRD is thus a ready means to classify opals (at least into opal-A, opal-CT and opal-C) and to assess what impurities (such as quartz) are present. Routine measurement should be made of samples, particularly from new sites. Apart from opal-C which looks like cristobalite, XRD does not provide the necessary information to propose feasible structures for opal; sporting methods (as below) will be needed.

### **Vibrational spectroscopy**

*This gives information on chemical bonds and arrangement of atoms. It can identify (or show the absence of) specific functional groups or arrangements of atoms but will not provide the complete picture.*

*All chemical compounds vibrate. The energy involved is in the infra-red (IR) region, at longer wavelengths than visible light. It is important to note that it is not “one band to one bond” as a group of atoms may vibrate in a few ways which is dictated by symmetry. These include stretches (lengthening/shortening of bonds) and bends (opening/closing of the bond angle at the centre of three joined atoms). With three or more atoms, stretches may be symmetric (all lengthening/shortening together) or asymmetric (one lengthens while another shortens).*

*Parts of larger molecules also act in an isolated manner and for instance we can expect characteristic patterns associated with the silicate units.*

*There are two techniques available: Raman and IR. The Raman effect causes scattering of optical light and shifts the photons to a lower energy at infra-red wavelengths. IR is more conventional in context as it involves scanning a range of energies. When the right energy is reached, energy is absorbed by the vibration and a peak is seen. Selection rules dictate whether a vibration will be Raman or IR active.*

*This compilation only includes far- and mid- range spectra. Near IR is the preserve of water and silanol overtones and combination bands.*

*Spectroscopists and chemists usually express things in terms of reciprocal centimeters ( $\text{cm}^{-1}$ ) or wavenumbers ( $\text{wn}$ ) as the numbers are sensible and reflect the usual limit of resolution. Energy units are more appropriate in this case and may be divided into far ( $100\text{-}400\text{ cm}^{-1}$ ), mid ( $400\text{-}4000\text{ cm}^{-1}$ ) and near ( $>4000\text{ cm}^{-1}$ ) ranges.*

## Raman spectroscopy of opals

Raman also provides additional confirmatory evidence for classification as opal-A, opal-CT and opal-C. Differences between types are more apparent than for infra-red (see later). While it has the advantage that grinding of the sample is not required, Raman may not work owing to overwhelming fluorescence. This is probably due to transition metal ions.

Standard Raman instruments will give you choice of laser wavelengths (typically red, green and blue). Raman is a bit of an art so preferences on laser, resolution, scanning range and number of scans may be a personal or institutional thing. We've done most our work with a red laser at 786 nm. Some instruments offer the ability to do a baseline correction as the region of interest has significant absorbance and curves sharply. We don't do this and have concerns about the effectiveness of doing so.

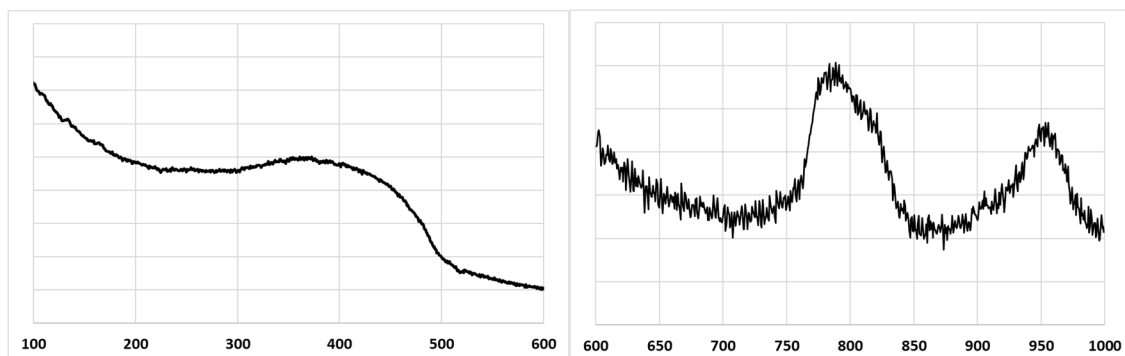
It should be noted that laser spot size is small. Thus any measurement is of a localised area that may be different to other zones. Several different measurements should be made as a precaution. This is different to the bulk measurements made for XRD. We have also noted that many spectra show minor peaks superimposed on the major absorbance. This isn't something that we've looked at in detail though some may be common and again could be characteristic of location. The actual levels of the "impurities" are hard to judge but if they are not apparent in the XRD patterns they will be minor.

For opals, the major region of interest is 100 to 1000 wn. The signals are stronger in the 100 to 600 wn range with lesser peaks above 600 wn. Opal-A, opal-CT and opal-C all present different spectra. We have not explored the region above 1000 wn in detail.

These spectra are from our initial study. Flinders University has now acquired a more sensitive machine with better to signal to noise qualities. Some of the below samples, but not all, have been run on the new instrument, and at different laser wavelengths. We will update the presentation in due course.

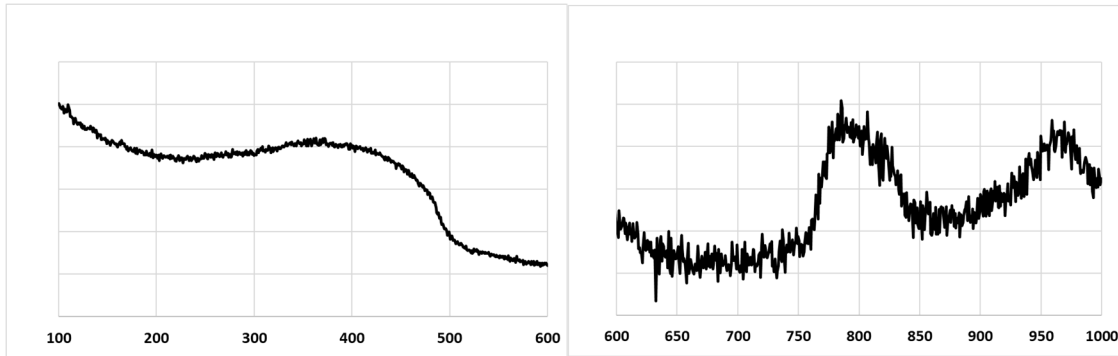
Spectra for **opal-AG** and **opal-AN** are mostly featureless with a broad absorption between 200 and 520 wn. There is lesser absorption in the 600 to 1000 wn range.

Raman spectrum 1: play of colour opal (opal-AG) from Coober Pedy, South Australia



*Raman spectrum of G9593 (Coober Pedy). 100-600 wn on left, 600-1000 wn (with expanded y axis) on right*

Raman spectrum 2: hyalite (opal-AN) from Mount Cora, New South Wales

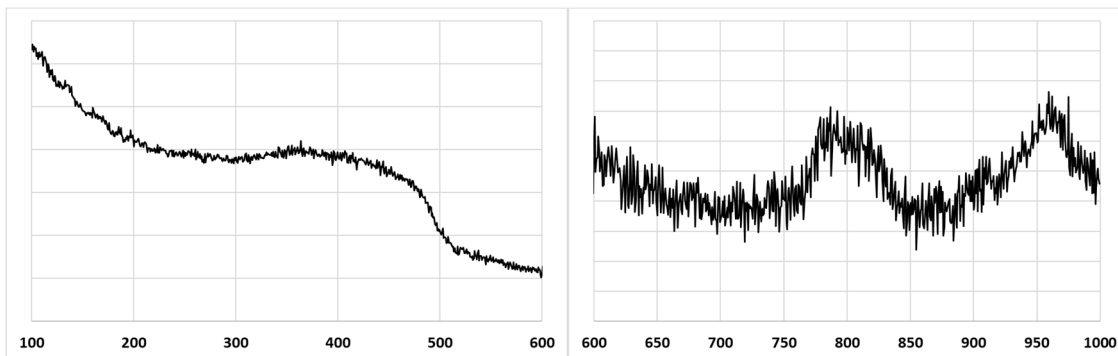


*Raman spectrum of G1419 (Mt Cora). 100-600 wn on left, 600-1000 wn (with expanded y axis) on right*

All opal-A samples look like the 100-600 wn spectra shown above though there is no obvious set of peaks for correlation with reference spectra, such as for silica polymorphs. There is, however, a slight difference in the peak position between opal-AG and opal-AN of the minor band at 950-970 wn. This is likely to be related to silanol and gives an indication of different chemistry.

Samples of ninot fluoresce, however geysirites may be measured.

Raman spectrum 3: Hot springs sinters (or geyserite) from Rotorua, New Zealand

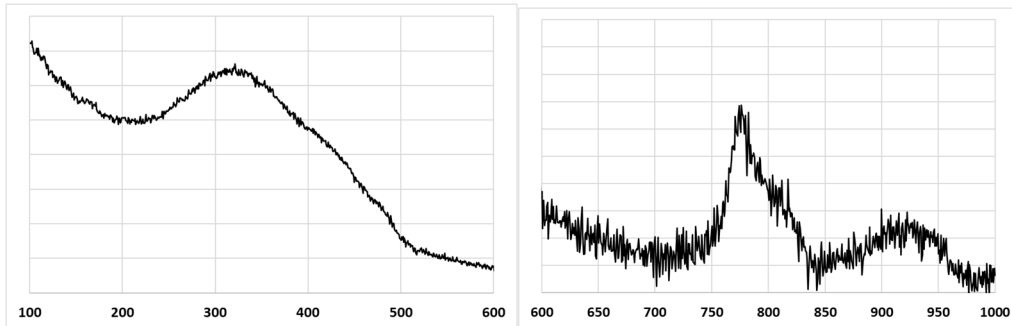


*Raman spectrum of T1665 (Rotorua, NZ). 100-600 wn on left, 600-1000 wn (with expanded y axis) on right*

Another sample of geyserite (G21471, also from Rotorua) shows a slight difference at 480 wn but is otherwise similar. This is probably an example where a very minor component gives a misleadingly large signal. The minor peak at 950-970 wn seems more like opal-AN.

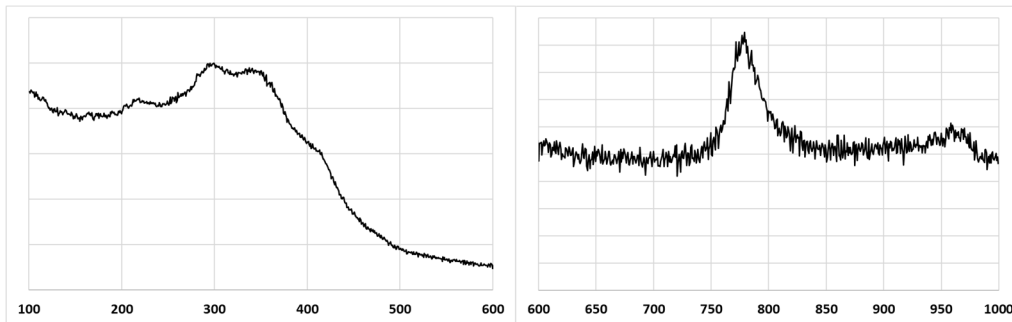
Raman spectra for **opal-CT** are distinct to those for opal-A with the absorption focussed at less than 400 wn rather above it. Similar to XRD, spectra of opal-CT show a progressive sharpening and definition of the peaks. This is an easy, non-destructive means of differentiating play of colour opal-AG from opal-CT.

Raman spectrum 4: Play of colour opal-CT



*Raman spectrum of G32752 POC (Afar, Ethiopia). 100-600 wn on left, 600-1000 wn (with expanded y axis) on right*

#### Raman spectrum 5: translucent off-white opal



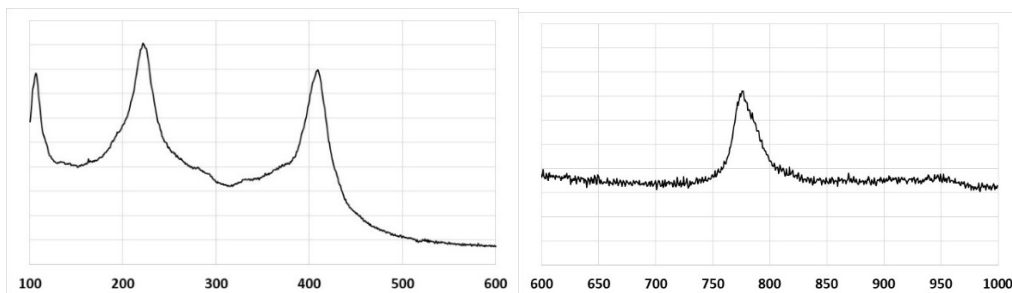
*Raman spectrum of G32226 (St Austell, England). 100-600 wn on left, 600-1000 wn (with expanded y axis) on right*

Four peaks emerge with better definition. Subject to any baseline correction these are at about 220, 300, 360 and 420 wn. Attempts have been made to correlate these spectra with those for tridymite which shows 4 peaks in similar positions. The minor peaks at 950-970 wn are variable in intensity and this area needs more work. There is a loose (but not exact) correlation of sharpness of Raman spectra with XRD pattern.

Raman does not support the notion that opal-CT is a mix of tridymite and cristobalite. A bit further down you'll see cases where there appears to be some cristobalite.

In contrast, a strong case may be made for cristobalite in **opal-C** with the characteristic three peaks seen.

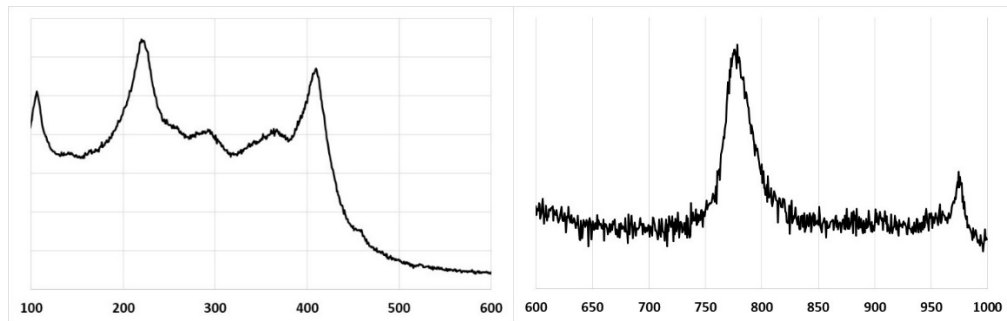
#### Raman spectrum 6: opal-C



*Raman spectrum of M5081 (Iceland). 100-600 wn on left, 600-1000 wn (with expanded y axis) on right*

Other examples (though we don't have many) show more features (probably containing something other than cristobalite).

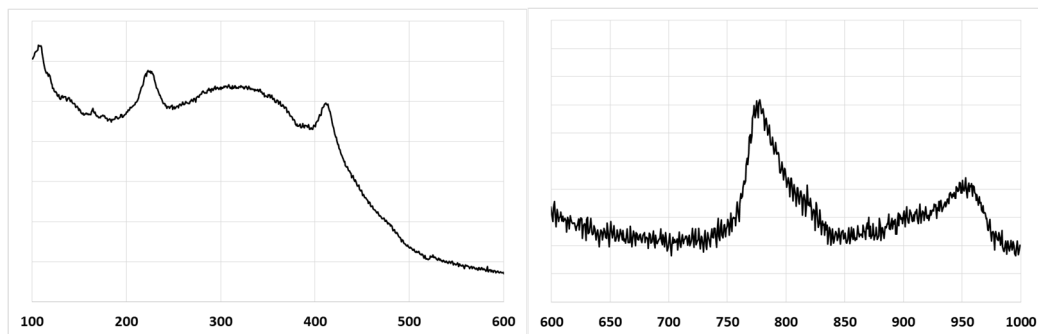
Raman spectrum 7: another opal-C



Raman spectrum of G34246 (Czerwenita, Hungary). 100-600 wavenumbers on left, 600-1000 wavenumbers (with expanded y axis) on right

Raman spectra reproduce the possibility of cristobalite seen in XRD patterns for some opal-CT samples. So far, we've only seen this for examples where the opal spectra shows little structure.

Raman spectrum 8: opal-CT showing (presumably) cristobalite

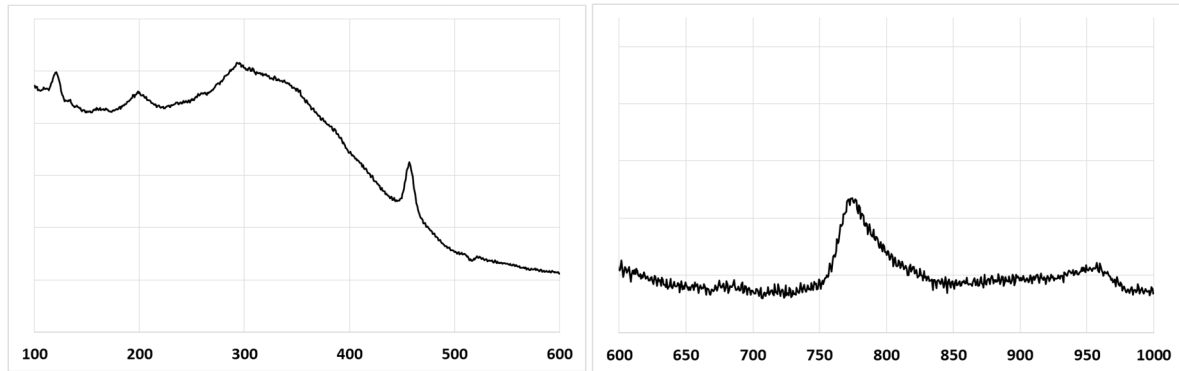


Raman spectrum of GNEW18 (Oregon). 100-600 wavenumbers on left, 600-1000 wavenumbers (with expanded y axis) on right

This looks like cristobalite superimposed on opal-CT (maximum more towards 300 rather than 400 wavenumbers) giving a "batman" appearance. The prominence of the "cristobalite" peaks may be compared with the minor contribution seen in XRD patterns.

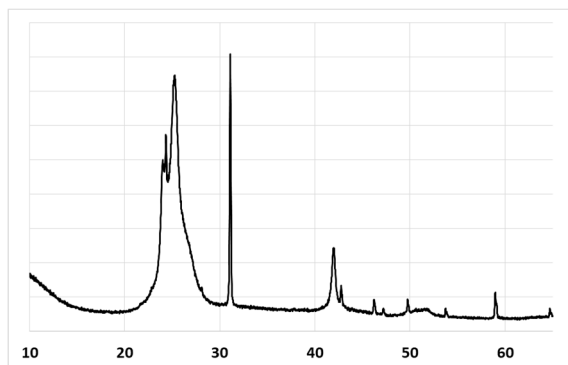
Raman shows the *presence* of additional components rather than an indication of their *abundance*. If there is enough quartz in the sample, peaks for this will show up.

Raman spectrum 9: opal-CT showing the presence of quartz



Raman spectrum of G15293 (Dampier). 100-600 wn on left, 600-1000 wn with (expanded y axis) on right

The XRD pattern for this shows quartz:



Expect the peaks for quartz to be variable if there is uneven distribution about the sample.

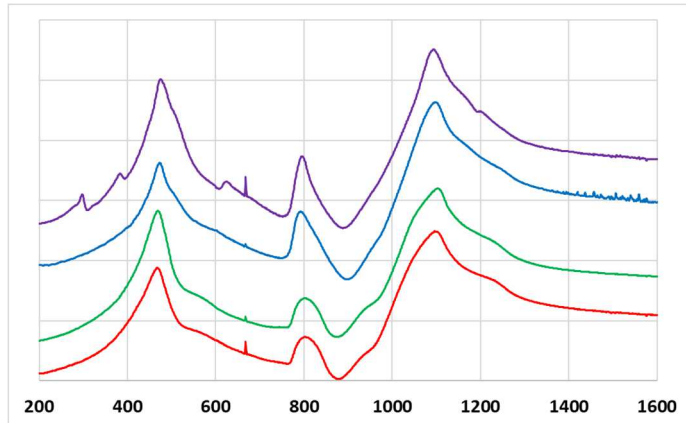
In summary, Raman is best used as a classification tool. Opal-C again looks like (wet and impure) cristobalite while opal-CT has similarities with tridymite. Opal-A is still a puzzle but there are indications that there are differences between opal-AG and opal-AN.

### Infra-red (IR) spectroscopy

If you do not have access to XRD and if you can grind the sample then this is a viable means of classification. Grinding and mixing probably eliminates the sampling issue seen for Raman. A base-level instrument will give sound classification in a few minutes. Any sample may be measured, unlike for Raman.

The purist's method for IR analysis is in transmission mode. A 1% suspension in dry KBr or CsI is finely ground and pressed into a thin transparent disc and scanned in the range 100 to 4000 wn (i.e. IR passes through the sample). The range 100 to 400 wn is usually outside of the scope of the regular benchtop instrument though enough information will be gained by stopping at 400 wn. It also means that KBr can be used rather than CsI. Spectra of **opal-AG**, **opal-AN**, **opal-CT** and **opal-C** are more similar in IR than Raman though are still distinguishable. We find little evidence for differences within each class.

Infra-red spectrum 1: composite of opal-AG, opal-AN, opal-CT and opal-C in transmission mode.



*Transmission mode IR spectra of opal-AG (red, G13771 White Cliffs), opal-AN (green, G32740 Valec Czechia), opal-CT (blue, G9942 Angaston) and opal-C (violet, M5081 Iceland)*

Opal-C may be distinguished by the small peak at 625 wn, as is found for cristobalite. There are also peaks in the far IR (<400 wn). Opal-AG and opal-AN show a shoulder at 550 wn and a characteristically broad band at around 800 wn. To some extent, opal-CT is indicated by not being opal-A or opal-C. Typically, three transverse optical (TO) bands are recognised at around 470, 800 and 1000 wn though as can be seen more are apparent.

There is no major change seen when comparing opal-CT samples with simple XRD patterns and Raman spectra to those with more structured features, though the quality of the baselines may make this difficult to examine.

While transmission mode may be the preferred mode for simplicity of the spectra, it is not the most convenient because of sample preparation. We also find that the baselines present difficulties possibly as a result of fogging of the plates due to moisture. Water is present in opal anyway evidenced to a greater or lesser extent at around 1600 wn. Nowadays, attenuated total reflectance (ATR) is the preferred option because of ease of use. For this a very small amount of powdered sample is crushed onto a diamond plate illuminated from below. The reflected signal is analysed.

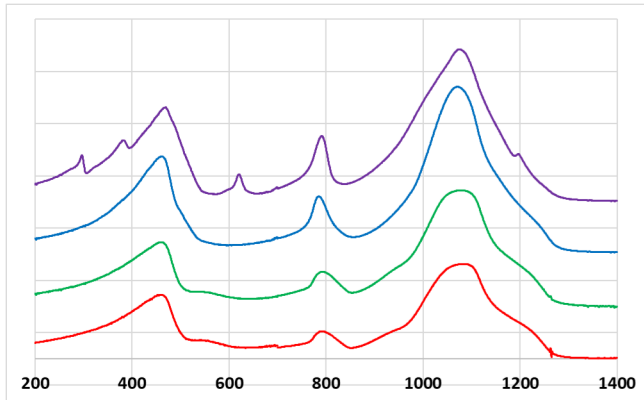
However, somewhat surprisingly, the refractive index (RI) at energies close to the peaks is very high with figures up to 6 seen. This greatly exceeds that for diamond (2.46) so in theory the conditions for ATR do not hold.

The second issue with ATR is that another set of bands comes into play: longitudinal optical (LO). The combination of LO bands and theoretically unsound procedures leads to variability of spectra. Nevertheless, ATR provides a ready means of classification using a basic instrument as the key differences found in transmission mode still hold.

ATR spectra are usually corrected for variable depth penetration as a function of wavelength. The instrument will do this for you, but it doesn't make much difference.

We also found that the degree of grinding could affect the spectra probably affecting the mix of TO and LO contributions. The diagram below is for finely ground samples of **opal-AG**, **opal-AN**, **opal-CT** and **opal-C**. It is best to ignore any differences you see around 1100 wn.

Infra-red spectrum 2: composite of opal-AG, opal-AN, opal-CT and opal-C in ATR mode.



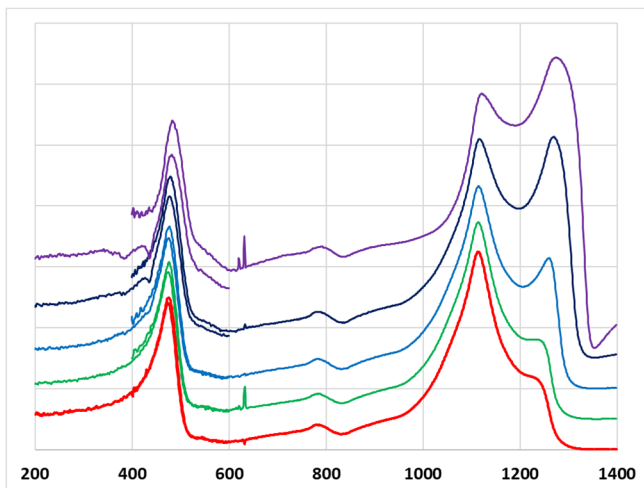
ATR mode IR spectra of opal-AG (red, GNEW22 Lambina), opal-AN (green, G8877 Dalby), opal-CT (blue, G9942 Angaston) and opal-C (violet, T1664 Guanajuato Mexico)

The general differences between opal types seen in transmission mode are seen again here and classification is straightforward. ATR IR also confirms the presence of small amounts of cristobalite that were seen in the opal-CT samples mentioned above. The presence of quartz is not as apparent as for Raman.

We have only had limited success with ATR of unground samples, such as faceted opal, as contact needs to be good. Pressing the sample down on the diamond plate seems to help. However, the possibility of variable LO contributions can lead to confusion.

A high-end IR instrument can provide additional research information into structure. For instance, we have prepared several polished flat segments for specular reflectance measurement. As long as there is a flat area of at least 10mm square and you can put the sample in the holder you can get this data. The technique involves shining the IR beam onto the surface with the plate set at angles from 15 to 75° off the vertical.

Infra-red spectrum 3: specular reflectance of a polished plate of opal-AG



Specular reflectance of CP-2 (Coober Pedy) at incident (off vertical) angles from 15° (red) to 75° (violet)

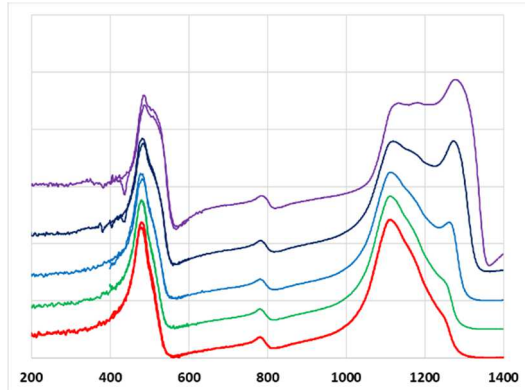
We can see that the LO bands become more prominent, particularly in the 1000 to 1300 wavenumber range, at higher incident angles. We note that the band at 800 wavenumber is far smaller than in (powder) transmission and ATR spectra. There's also more data to be had through using polarisation. With some



mathematical jiggery-pokery (which the instrument does for you) you can get the peaks positions of all three TO and LO bands.

The LO bands are more visible for opal-CT.

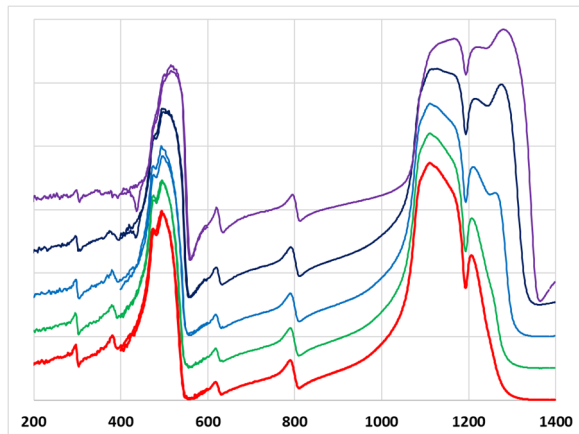
Infra-red spectrum 4: specular reflectance of a polished plate of opal-CT



*Specular reflectance of G9942 (Angaston) at angles from 15° (red) to 75°(violet)*

Opal-C is similarly complicated. Again the peak at 625 wn shows.

Infra-red spectrum 4: specular reflectance of a polished plate of opal-C



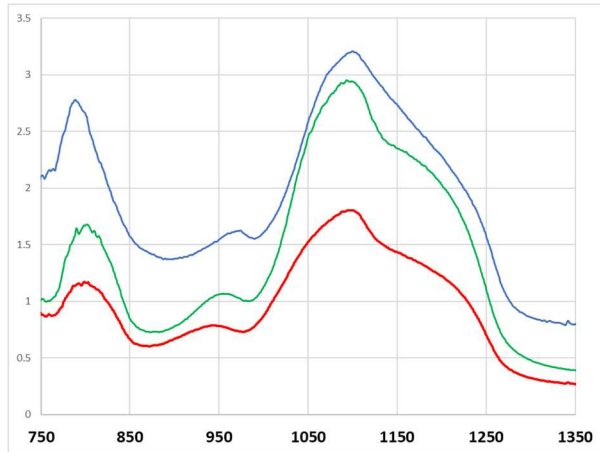
*Specular reflectance of T1664 (Guanajuato Mexico) at angles from 15° (red) to 75°(violet)*

There is a probably a lot more that can be teased out using specular reflectance. It does, of course, require a large enough piece of opal and the ability to prepare the flat slice.

The next technique is diffuse reflectance. This requires a 5% suspension of powdered opal in dry KBr. Since the cell is quite large this involves a substantial amount of sample which can't be recovered. This involves a specialised attachment in the form of a gold lined sphere. IR radiation is directed at the sample which scattered by the opal/KBr mix. The scattered light is collected at a detector.

Again, different things are highlighted.

Infra-red spectrum 5: comparative diffuse reflectance of opal-AG, opal-AN and opal-CT

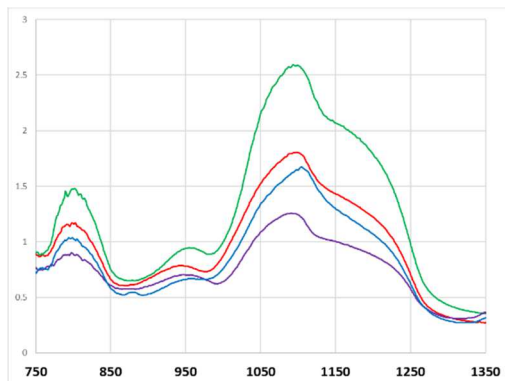


*Diffuse reflectance of opal-AG (red, G NEW22 Lambina), opal-AN (green, MS-4 Mt Squaretop) and opal-CT (blue, G9887 Curdimurka)*

In this, the peak at around 950 wavenumbers becomes well delineated. This is in the same place as the presumed silanol feature in Raman with opal-AG at lower wavenumbers than opal-AN.

Subtle differences are also seen for the different types of opal-A.

Infra-red spectrum 6: comparative diffuse reflectance of opal-AG, opal-AN, ninot and geyselite



*Diffuse reflectance of opal-AG (red, G NEW22 Lambina), opal-AN (green, MS-4 Mt Squaretop), ninot (blue, G NEW23 Girona, Spain) and geyselite (violet, G21471, Rotorua, NZ)*

This probably needs more investigation, in particular the region around 950 wavenumbers, to see if the four samples here do indeed represent different sub-classes of opal-A. The extra peak for the ninot was seen for another sample. Curve-fitting to find out the actual peak positions was difficult because of the baseline.

The specialised equipment can also be used to analyse flat samples by placing on an opened port at the top of the globe. LO bands are apparent though small as the technique corresponds to a zero degree angle of incidence.

Infra-red spectroscopy has potential both as an easy classification tool and for structural analysis. Consistent support for opal-C containing cristobalite is maintained. Detailed comparison of authentic tridymite with opal-CT, using the techniques above, may prove fruitful. Minor differences between opal-AG and opal-AN are again seen. Analysis of all this is difficult. We hope that a theoretician will be able to use this material to propose possible structures (presumably patterns of mixed Q<sub>3</sub> and Q<sub>4</sub> composition).

## Scanning Electron Microscopy (SEM)

*Microscopy shows the physical structure of the surface of material.*

*SEM and optical microscopy are similar in concept in that both give a top down view of the surface or near surface. In SEM, electrons are focussed on the substrate which produces a range of responses such as back-scattered electrons, secondary electrons and x-rays. Usually, secondary electrons are analysed as they originate from close to the surface and give good resolution (typically 2 nm) and better surface morphology. Images are scalable with magnifications of 100 000 readily accessible. The set up also allows a 3D effect to be shown. Because of charge build up issues, which affect image stability, samples are usually thinly coated with a conductive film such as carbon, gold or platinum.*

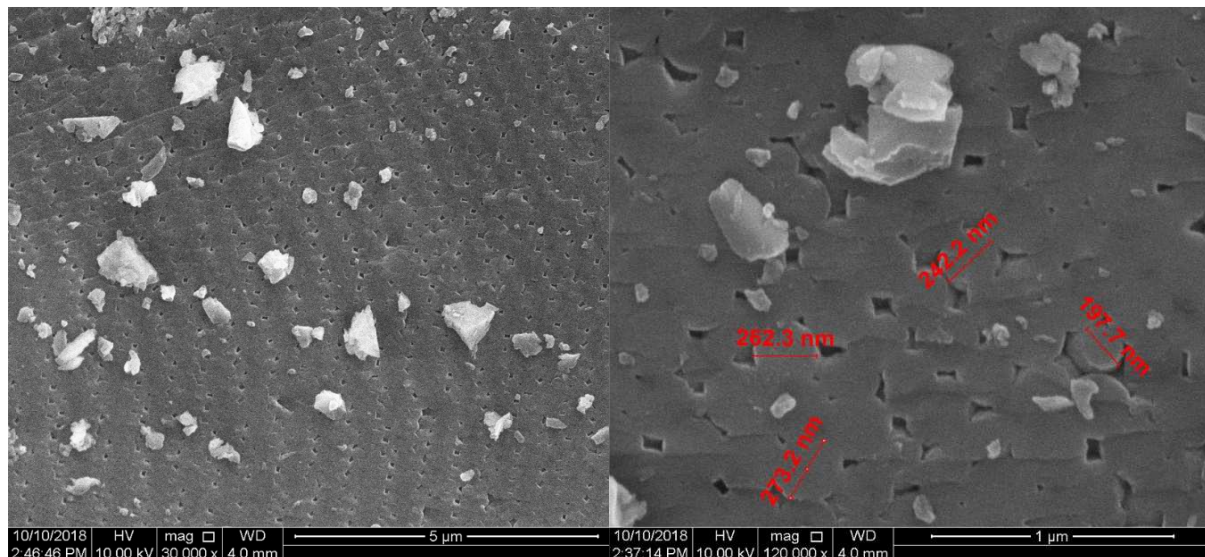
### Scanning electron microscopy (SEM) of opals

The images below show some of the observations we have made on opal-A samples but are not systematic nor comprehensive. All are produced from freshly ground samples. The literature also contains images from HF (the chemical not a radio source) etched samples which look different overall. We have not attempted this.

A cautionary note should be made here. The images represent the best features seen in a SEM study as the sample is scanned for stable and “interesting” zones.

SEM examination of opal can produce spectacular images, particularly for showing the causes of play of colour in **opal-AG**.

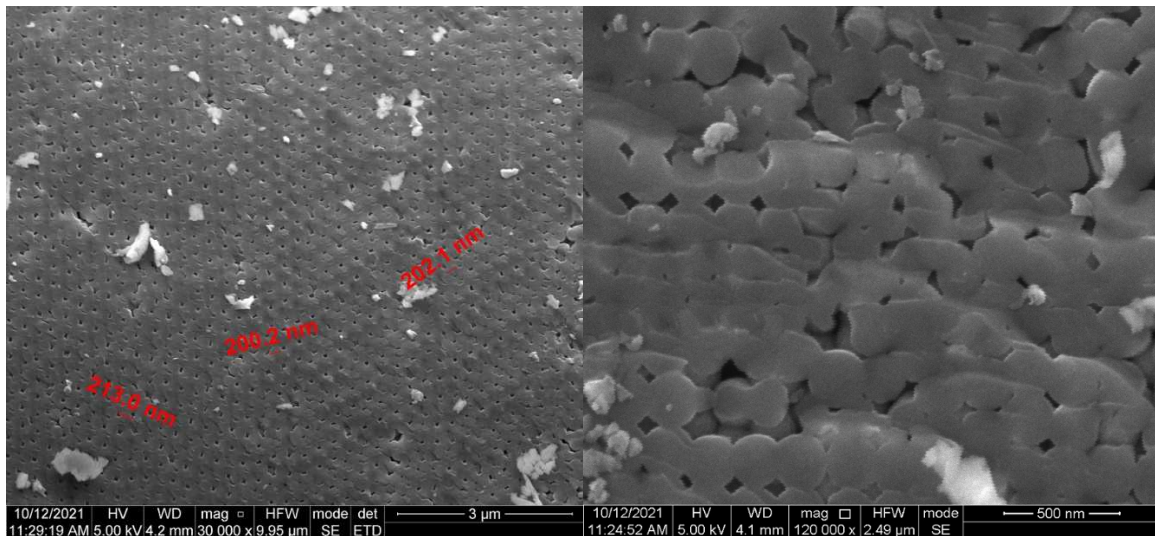
Scanning electron microscopy image 1: a play of colour seam opal-AG



*G7534 a white play of colour opal-AG from Coober Pedy*

Play of colour is proposed to occur when there is a regular array of the right size of spheres. For G7534 there is a regular pattern (LHS) with spheres of about 200 nm (RHS). This is compatible with diffraction at optical wavelengths from 400 nm (violet) to 700 nm (red). This is the same Bragg diffraction seen in XRD but with different wavelengths and particle sizes. As the sample is ground, it is not possible to correlate the image with play of colour properties.

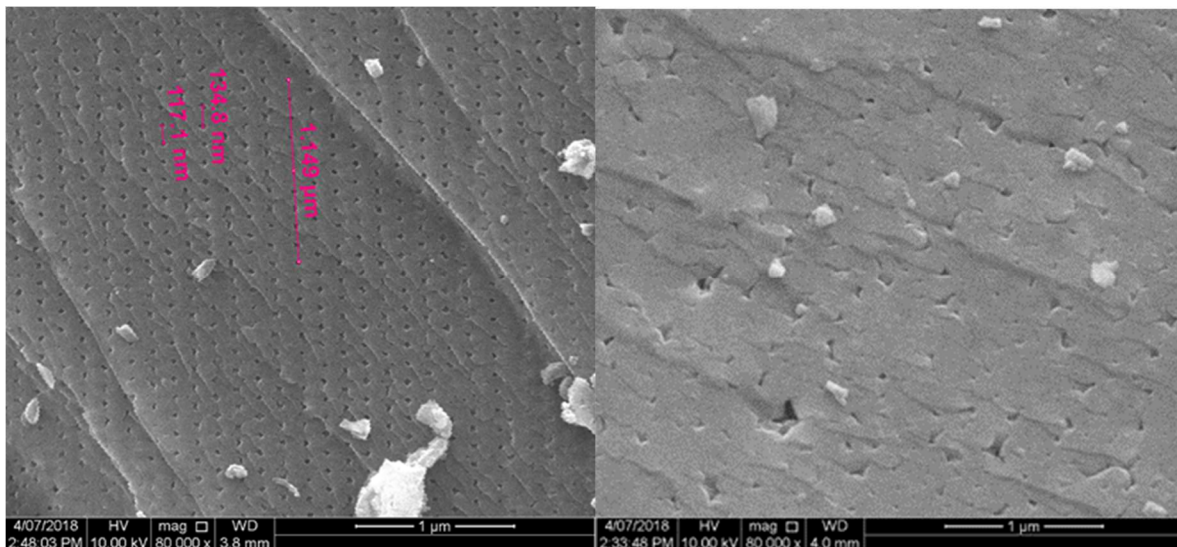
Scanning electron microscopy image 2: a play of colour boulder opal-AG



*WBO1 - an offcut from a jeweller's play of colour opal-AG from Winton*

All opal-AG samples show these features and it possible to construct a rationale of why play of colour may or may not (as follows) occur.

Scanning electron microscopy image 3: non play of colour seam opal-AG



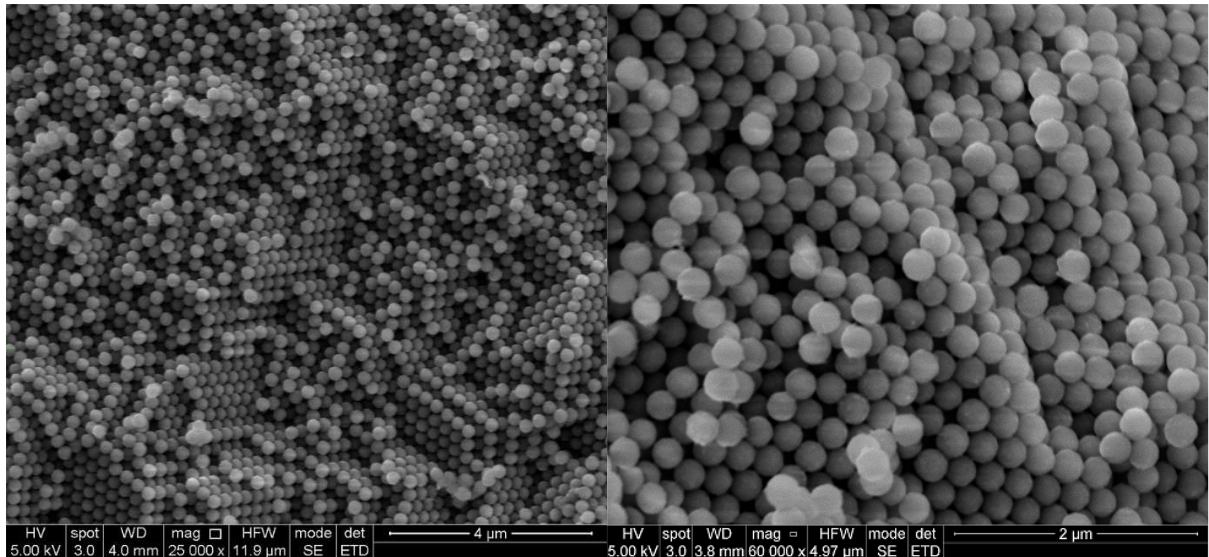
*Lightning Ridge samples (G13767): clear orange (LHS) and opaque blue (RHS)*

Possibly, the clear orange glass has spheres that are too small and the blue opaque sample does not have regular enough spheres.

Gilson synthetic opals are readily distinguishable by SEM.

Scanning electron microscopy image 4: Gilson synthetic opal

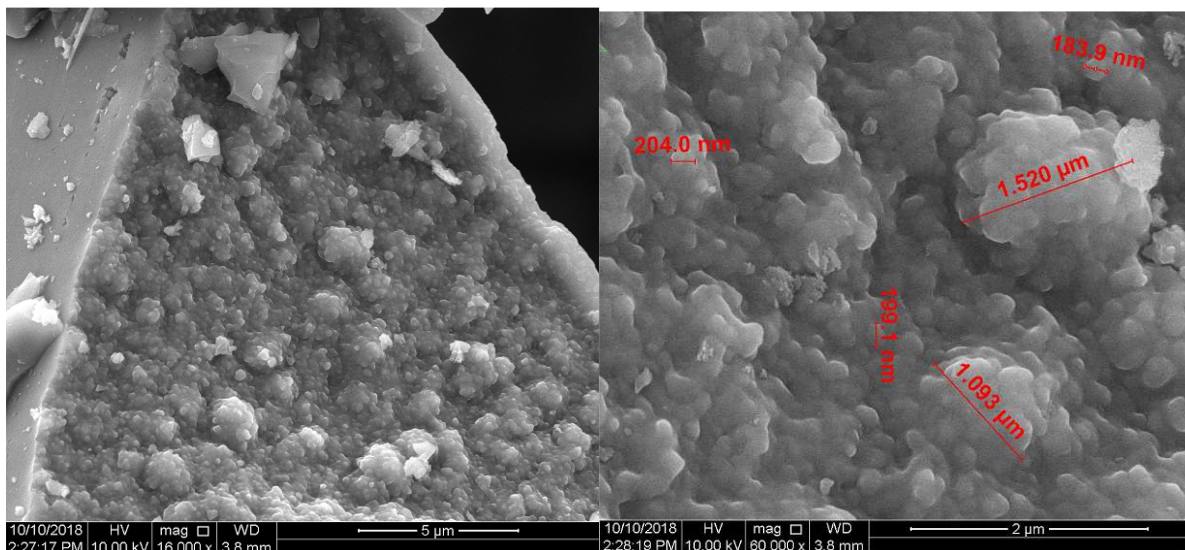




*Gilson synthetic opal (from about 30 years ago)*

Other forms of opal-AG give different images.

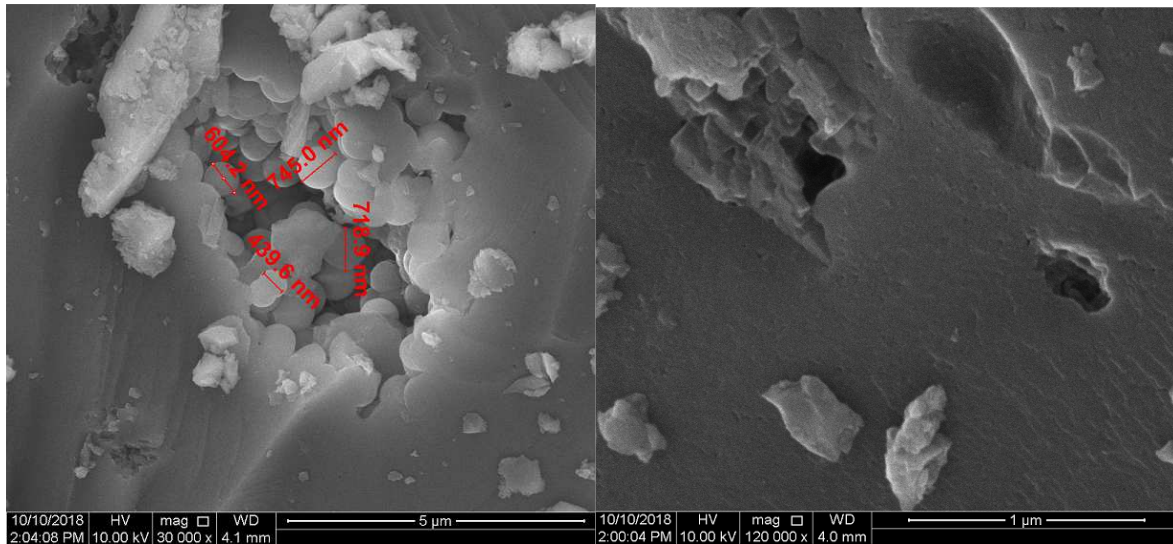
Scanning electron microscopy image 5: geysirite (hot springs sinter)



*G21471 from Rotorua, New Zealand*

This is an example of opal-AG by XRD, and Raman and IR spectroscopy. While it does show spheres they are not linear. It is also an example of a non-uniform lay-out with much of surface featureless as in the top left of the left hand image.

Scanning electron microscopy image 6: ninot

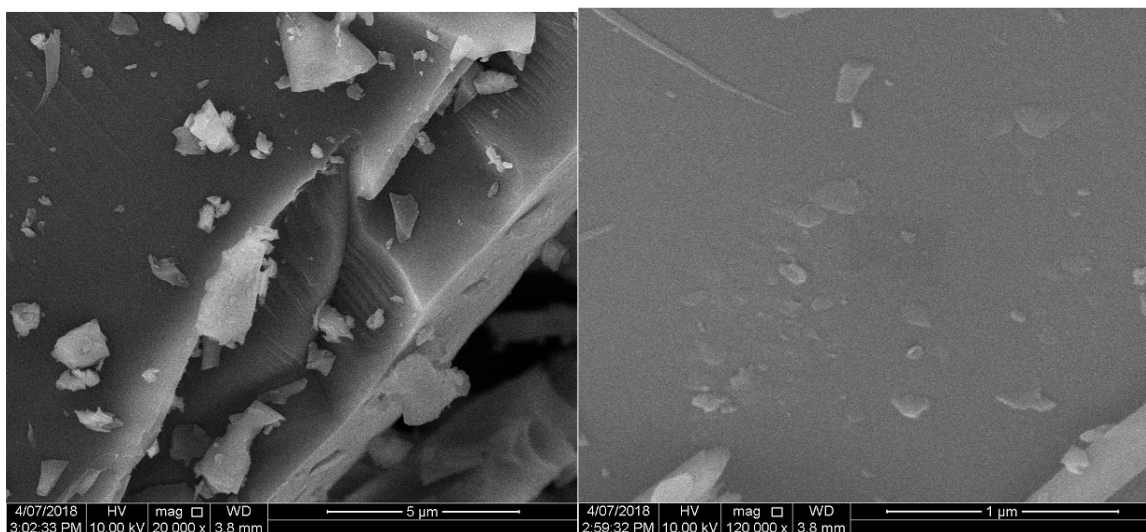


*GNEW23 ninot from Caldes de Malavella, Spain*

While much of the surface is relatively bland there are pockets of spheres present.

**Opal-AN** is relatively featureless.

Scanning electron microscopy image 7: opal-AN



*G32740 opal-AN from Valec Czechia*

The striations seen here are also found for other examples of opal-AN and will be due to the grinding process.