

Water in opal – what can it tell us?

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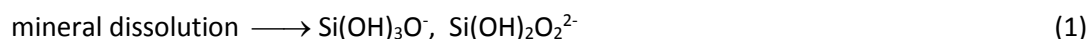
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Introduction

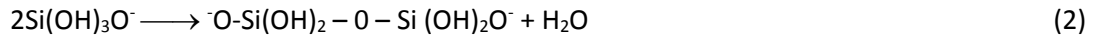
Opal is a hydrous silica composed of predominantly silicon dioxide and water. The chemical composition of opal is normally described by the general formula $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The formula indicates that opal contains water and the value of 'n' is variable so the water content is variable and is known to range widely. Such a simple formula hides much of the important characteristics of how water is contained in opal and the variability in the water content and states of water is intricately involved in the formation of opal and may influence properties of the opal as a gemstone. The understanding of the states of water in opal is therefore of importance. The way in which the water is contained provides clues to the mechanisms of formation of opal. The water contained may also be used as a probe to help elucidate the complex microstructure beyond the sphere array structure in which precious opal, in particular, is described. This article will outline the types of water present in opal that displays play-of colour (POC) and how these types have been determined using chemical and physical laboratory characterisation techniques.

Why does opal contain water?

In order to understand and characterise the types of water that are present in opal, the first step is to have a basic model for the formation of opal. The origin of the silica remains disputed, but it is generally agreed that opal formation is based on a dissolution-precipitation mechanism with water as the medium (Iler 1979). For opal to form by this diagenetic process, the first step must be dissolution of silica through the weathering of silica bearing minerals:



$\text{Si(OH)}_3\text{O}^-$, $\text{Si(OH)}_2\text{O}_2^{2-}$ species are the individual silica species formed in solution on the weathering of silica rich minerals. As the dissolution process proceeds more silica is dissolved until the solution becomes saturated, or even supersaturated. A supersaturated solution is a solution where the water contains more dissolved silica than it should be able to dissolve and that is energetically favourable and so the solution is in a *meta-stable* state and is ripe for precipitating the silica. In a supersaturated solution, the silica species react together in a process of polymerisation to produce larger species:



This polymerisation process continues until colloidal particles are formed. The chemical process can be described by the generalised reaction:



This generalised equation does not give a visual impression of how the silica is bonded. As silica has a valence of 4, each silica atom bonds to 4 oxygen atoms which form the Si-O-Si bridges between the silicon atoms. As there are 4 of these bridges per silicon atom, a three dimensional network is formed as outlined in Figure 1.

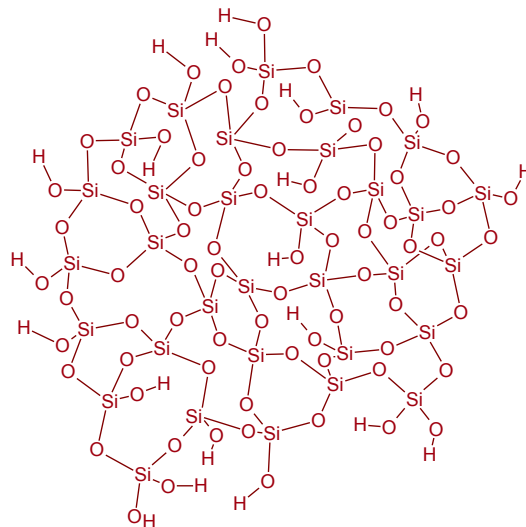


Figure 1. Schematic of the three dimensional network of polymerised silica which forms the sphere particles in the colloid initially formed by precipitation.

The silica network continues to grow as long as the supply of silica continues resulting in the formation of colloidal particles in the water. This growth process continues until, in the formation of precious opal, a monodispersed colloid of large spherical particles (circa 200 to 400 nm with a size variation that should be less than 5%) are formed (Iler, 1979). The colloid then concentrates and the

spherical particles ‘crystallise’ to form an ordered array of silica spheres. An example of such an array is shown Figure 2.

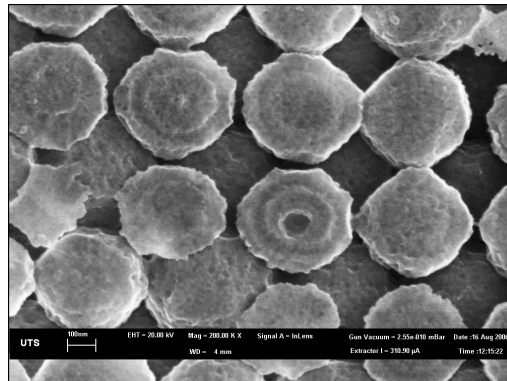


Figure 2. Coober Pedy play of colour opal showing ordered arrays of spheres after etching with hydrofluoric acid. (Smallwood et al, 2008a)

The final step in the formation of the opal is the cementing of the spheres with a silica cement as, prior to this step, the opal will remain porous allowing the diffusion of water through the array. The cementing process binds the spheres together through the precipitation of silica in the voids between spheres. The microstructure in Figure 2 is therefore only observed if this silica cement is etched away using hydrofluoric acid.

The microstructure observed in Figure 2 is responsible for the POC in opal. The POC is based on the diffraction of light off ordered arrays of monodispersed silica spheres (Sanders, 1968; Darrah et al, 1976). The size of the spheres defines the colour of light that is observed as diffraction is based on the path length that light travels between the planes of spheres and the colour by the wavelength of light. The larger the spheres the longer the path length light can travel and hence the longer the wavelength of light that is observed. In the white light spectrum blue is at the short wavelength end of the spectrum and is observed for smaller sphere sized opal (200 to 250 nm in diameter) while at the long wavelength end of the spectrum red is observed for larger sized sphere (roughly in the range 250 to 400 nm).

Opal – A and Opal – CT

The three dimensional silica network at the atomic scale is composed of SiO_4 tetrahedra (Figure 1) that are bonded together in a random network as is the case for opal – A (amorphous) or with a more ordered network (but not highly ordered) as in opal – CT (cristobalite-tridymite). X-ray diffraction (XRD) is a useful tool for the discrimination of opal – A and opal – CT. The tetrahedra in opal – A are randomly stacked and only a broad hump or halo is observed (Figure 3(a)). On the other hand, opal – CT is partially crystalline and contains a partially ordered arrangement of silica tetrahedra which produce definite peaks in the diffraction pattern corresponding to the ordering exhibited by cristobalite (C) with tridymite stacking faults (T) (Figure 3(b)). In fact, X-ray diffraction formed the original basis for the nomenclature of opaline silica (Jones and Sanders, 1968; Langer and Flörke, 1974).

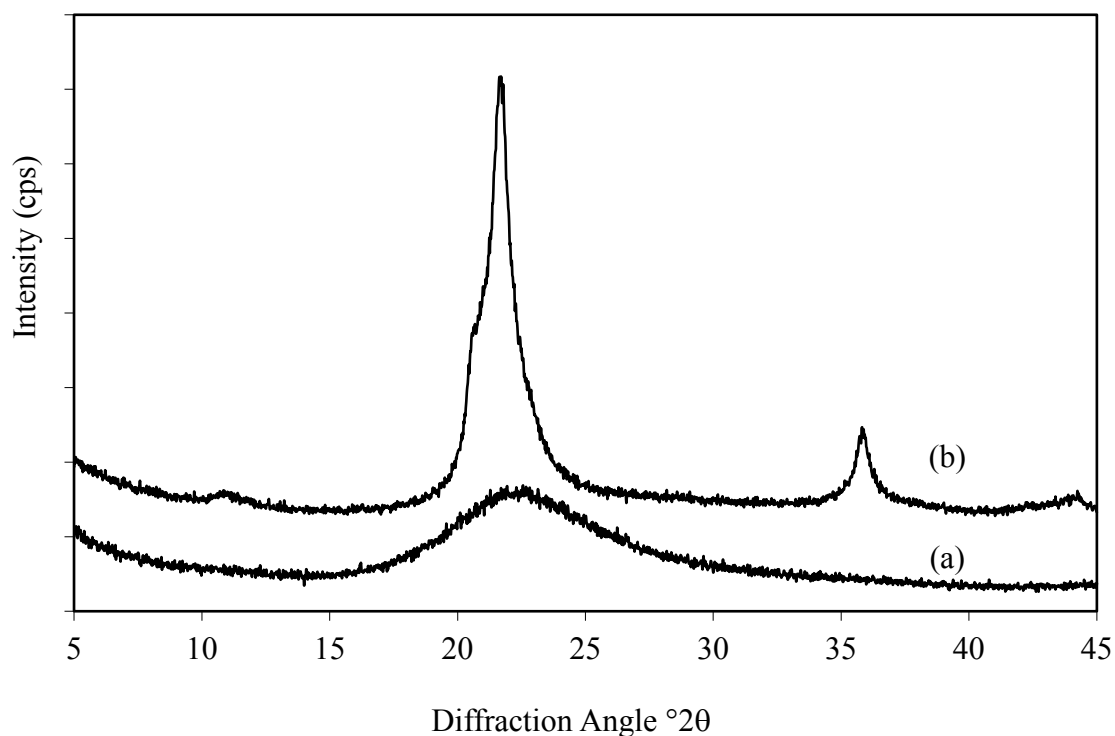


Figure 3. X-ray diffraction pattern of (a) opal – A from Coober Pedy and (b) opal – CT from Tintenbar (Smallwood et al, 2008b).

The three dimensional network defines the atomic scale structure of the silica, but not the microstructure which results in the POC. The structure of opal at the atomic scale does, however, influence the amount of water contained in the opal and the type of water present. We will first discuss the amount and then we will address the types of water present in opal.

Water content of Opal

As the formation of opal is a dissolution-precipitation process, water becomes trapped in the opal as it is being formed. Opal can therefore contain significant amounts of water, from 2 to 20 %, but typically the quantity of water contained in opal is 6 to 10 %. Measurement of the amount of water in opal is usually carried out by thermogravimetric analysis (TG) where a sample (typically 20 to 50 mg) is heated at a constant rate (typically 1°C/min) to 1000°C to drive off the water. The amount of water contained can then be determined from the mass change. Some typical data is shown in Figure 4 and total water contents using this technique are listed in Table 1 along with their XRD classification.

Table 1. Water contents of opals determined using thermogravimetric analysis by heating the opals to 1000°C at a rate of 1°C/min supported on a balance in a furnace. The type of opal (opal – A or opal – CT) is listed based on XRD pattern (unpublished data).

Origin	XRD Classification	Water Content / %
Andamooka Black Boy	A	6.90
Andamooka Honey Opal	A	6.11
Argentina Lemon Opal	A	5.33
Brazil Lemon Opal	A	5.32
Brazil Light Opal	A	5.80
Coober Pedy 14 Mile	A	7.05
Coober Pedy 9 Mile	A	6.60
Coober Pedy Alans Rise	A	6.82
Coober Pedy Olympic	A	6.90
Ethiopian Fire Opal	CT	7.05
Ethiopian Shewa Brown POC	CT	9.09
Ethiopian Shewa Colourless	CT	12.86
Ethiopian Wollo Lumps	CT	8.04
Indonesian Java Faint POC	CT	3.01
Lambina	A	6.74
Lightning Ridge Sun Flash	A	5.88
Mali Lemon Opal	CT	5.14
Mexican Orange	CT	9.91
Mexican POC	CT	8.36
Mintabie Grey POC	A	6.01
QLD Boulder Blue POC	A	6.05
Slovak Opal	A	8.39
Tintenbar POC	CT	9.10
White Cliffs	A	6.52

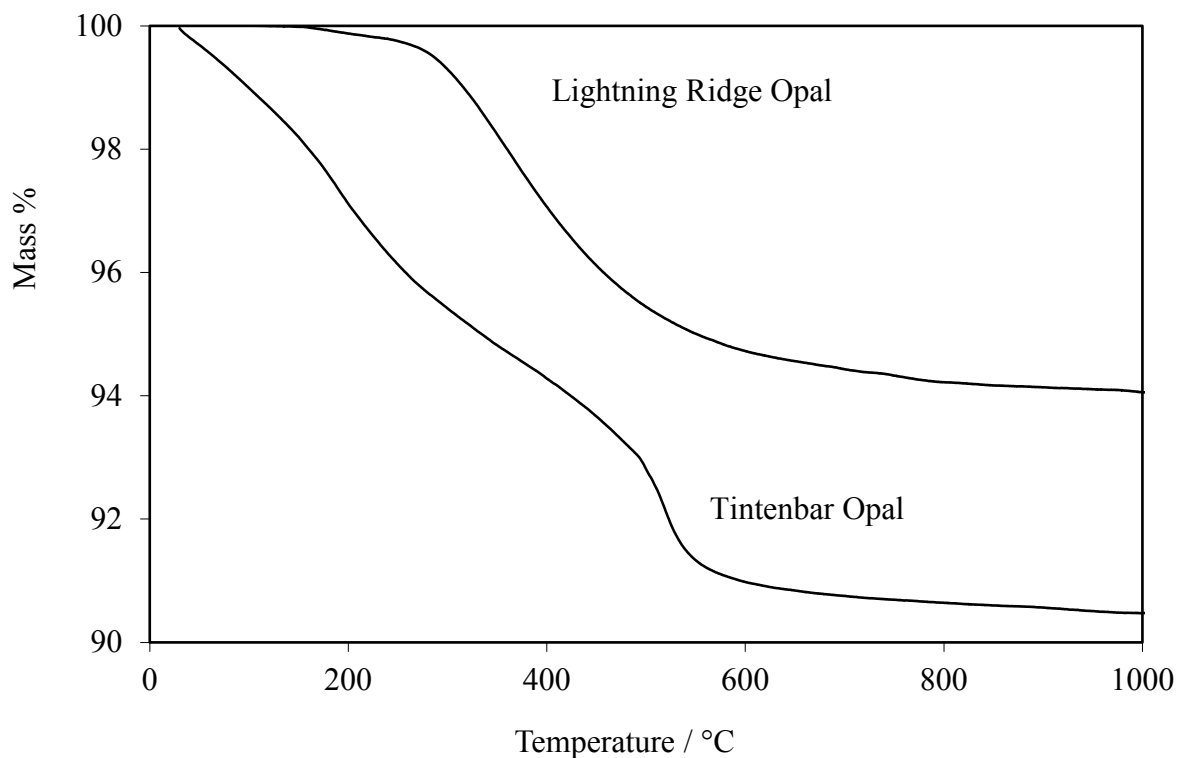


Figure 4. Mass % (TG) curves representing the mass change during heating resulting from water loss from a Lightning Ridge patch opal containing 5.9 % total water and a Tintenbar crystal opal containing 9.5 % water (Smallwood et al, 2008) .

The total amount of water is an important measure as it is the basis for the status of opal as a hydrous silica with the notional formula of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. Measurement of the amount of water provides a value for 'n', but it does not in itself help to understand how the water is contained in the opal. In order to understand how water is contained in opal, the types of water need to be identified and characterised.

Types of Water in Opal

The formation mechanisms are important in defining how water is contained in opal. As opal is formed through the polymerisation of silica in water, two generic types of water are, therefore, contained in the structure, molecular water and bound silanol water. Molecular water is literally water molecules that are physically contained or trapped in the opal whilst silanol water is water that is chemically bound in the form of Si-OH groups in the opal network at internal or external surfaces. The types of water are schematically shown in Figure 5 and are discussed below.

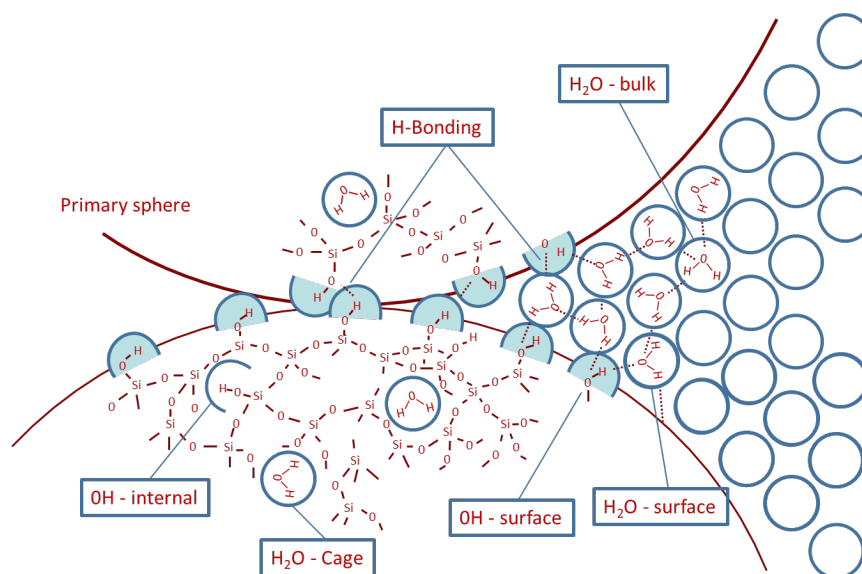


Figure 5. Schematic of the environments of water in opal (after Langer and Florke, 1974).

Molecular Water

Molecular water is literally molecules of water molecules physically contained in the opal. Due to the nature of the formation process, molecular water is contained in a number of environments within the opal. These are identified in Figure 5 as *bulk*, *surface adsorbed* and *cage* water. The presence of molecular water in opal has given rise to the term opal – A_G or amorphous gel like opal as oppose to hyalites which are also amorphous, but contain negligible quantities of water and have the designation opal – A_N or network like opal (Langer and Flörke, 1974). We will limit the discussion to opal – A_G and will simply refer to these types of opal as opal – A.

(i) Bulk water

Bulk water is defined as water where large quantities of molecules are trapped together in voids or inclusions in the opal. This type of water has all the characteristics of liquid water as each water molecule experiences an environment where they are surrounded by lots of other water molecules. Although bulk water can be contained in large inclusions, most of the bulk water is contained in defects in the arrays or in the voids or spaces between spheres.

As spheres do not tessellate when packing voids may occur between the spheres. If these voids are not infilled by the silica cement the voids are likely to be filled with water. An example of this phenomenon is shown Figure 6 where a micrograph of an unetched fracture surface of a Coober Pedy opal is shown.

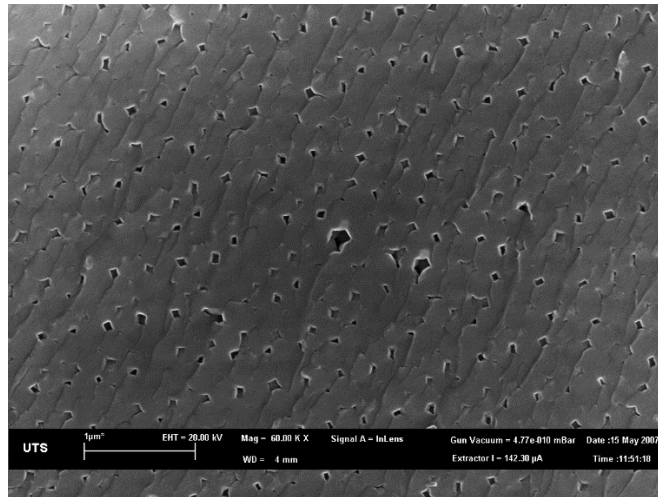


Figure 6. SEM micrograph of the fresh fracture surface of a precious play-of-colour Coober Pedy opal (without etching) showing distinct arrays of voids between spheres (Thomas et al, 2013).

As bulk water contained in the opal has the properties of liquid water, it can be frozen by cooling to below 0°C. Once the opal has been cooled to sub-zero temperatures and the water crystallised, the crystallised water can be melted again by heating to above 0°C. This type of crystallisation-melting process has been carried out using the technique of differential scanning calorimetry (DSC) where on heating the frozen water, the melting process can be followed and is observed as a negative peak in the scan as the melting of water is endothermic (it takes energy to melt the crystals). The size of the peak is proportional to the amount of crystallisable water present in the opal. DSC curves are shown in Figure 7 for a variety of opals from Australia and a Mexican opal (Thomas et al, 2013).

Two aspects of the DSC curves help to characterise the opal. The temperature at which the water melts indicates size of the void or capillary in which the water is contained (the lower the temperature, the smaller the void or capillary) and the area of the peak is proportional to the amount of crystallisable water (Landry, 2005). The data in Figure 7 can be separated into two groups, the opal – A group and the opal – CT group (although only two opals are included in the latter group). For opal – A, opal that is sourced from the Great Australian Basin (GAB), the melting begins around -10°C, but most of the water melts around zero which suggests that the water is contained in relatively large pores (estimated to be in the range 8 to >50 nm in diameter based on the method outlined in Landry (2005)) which is consistent with the voids shown in Figure 6. For opal – CT from Tintenbar, all of the water melts below zero in the range -40 to -10°C suggesting that the pores are much smaller (we have estimated them to be of the order of 2 to 8 nm in diameter using the method of Landry (2005)). The opal from Mexico has characteristics of both capillary water and void water. The small size of the pores which contain water in the opal – CT are smaller than the voids between spheres. This suggests that the pores are more like capillaries and are formed during the polymerisation of the spheres themselves. Figure 8 is a schematic of the types of cavity which contain the water in opal.

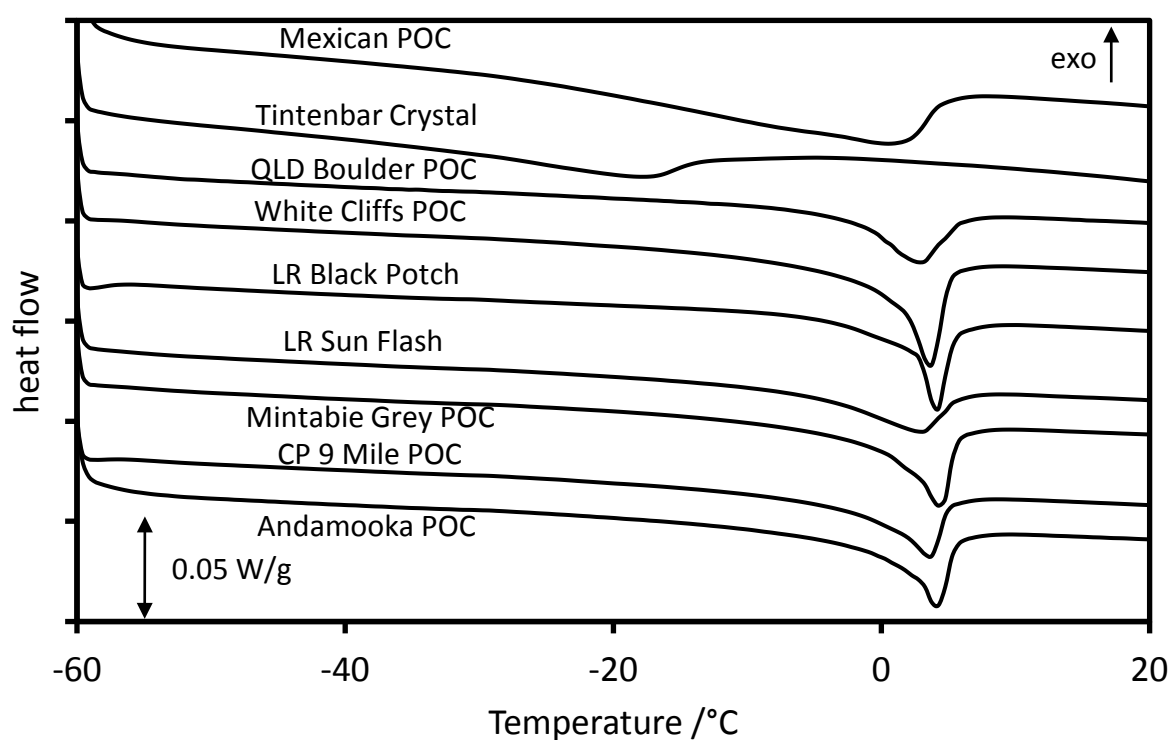


Figure 7. DSC curves showing the melting behaviour of bulk water in specimens of opal (Thomas et al, 2013).

Table 2. List of water contents of the opal samples characterised which were used to determine the percentage of crystallisable water present in the opal as a percent of the total water content (Thomas et al, 2013).

Sample	Total Water content (mass loss at 1000°C) as a % of opal mass	Crystallisable water present as a % of opal mass	Crystallisable water as a % of total water content
Andamooka POC (SA)	6.7	0.63	9.4
Coober Pedy (CP) 9 Mile POC (SA)	7.2	0.74	10.2
Mintabie Grey POC (SA)	6.3	0.89	14.1
Queensland (QLD) Boulder POC	6.5	0.56	8.6
Lightning Ridge (LR) Black Potch (NSW)	6.1	0.67	10.9
Lightning Ridge (LR) Sun Flash POC (NSW)	8	0.58	7.3

White Cliffs POC (NSW)	6.6	0.96	14.5
Tintenbar POC (NSW)	9.1	1.16	12.8
Mexican Fire Opal	8.8	2.05	23.3

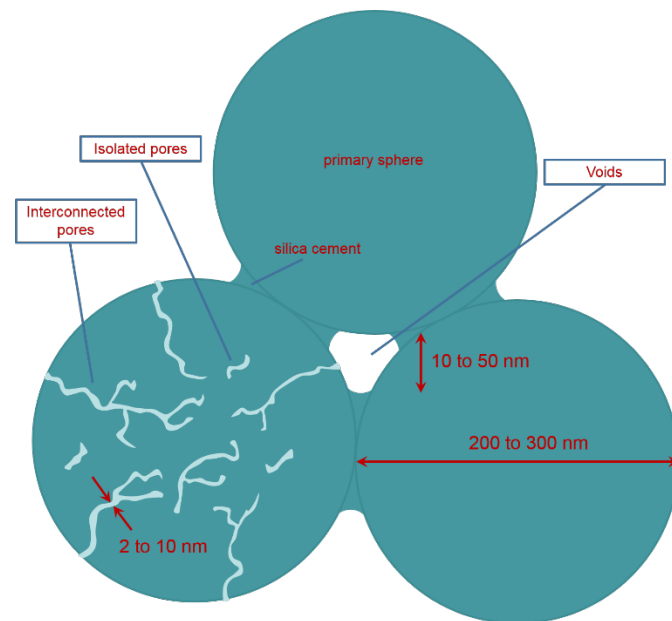


Figure 8. Schematic of the voids and capillaries that contain crystallisable water. The crystallisable water in opal – A is contained predominantly in the voids while, for opal – CT, the water is predominantly contained in capillary pores.

Based on the area of the melting peaks, the amount of crystallisable water ranges from 10 to 25 % (Table 2), although that range has been expanded in recent work on going in our laboratories. This suggests that the between 75 and 90% of the water is not crystallisable and is contained elsewhere in the opal.

(ii) *Adsorbed water*

The second type of molecular water contained in opal is adsorbed water. Adsorbed water is molecular water that is physically adsorbed to the silica surface. Adsorbed water does not have the characteristics of bulk water as it is not as free to diffuse and is interacting with silanol (Si-OH) groups in the surface. As adsorbed water is interacting with the solid surface, the water does not freeze and so is not crystallisable. The effect of the surface on the water molecules is not limited to the water molecules directly adsorbed to the surface, it also influences water molecules adsorbed to water molecules adsorbed to the surface. The thickness of the adsorbed layer has been estimated by experimental studies on synthetic mesoporous silicas and is estimated to be circa 1.1 nm (Landry,

2005). Potentially, a significant portion of the water can be adsorbed, but this type of water is difficult to identify and therefore quantify. The proportion of this type of water will increase for smaller pores as the surface area to volume ratio of the capillary pores increases with reducing pore diameter. Based on the size of pores contained in the opal – CT determined from the data in Figure 7, it is estimated that opal – CT has a greater proportion of this type of water than opal – A. It should also be noted that, if the pores are less than 2 nm in diameter, the water contained in the pores is just adsorbed water. If the pores are less than 1 nm in diameter they are approaching the size of the water molecules and water therein contained can be considered to be cage water.

(iii) Cage Water

The third type of molecular water is cage water. This is water that is trapped in the three dimensional silica network (Figure 5). As in the case for adsorbed water, cage water is also difficult to identify directly. Experimental comparisons between opal – A and opal – CT suggest that opal – A has more cage water than opal – CT. Work currently being carried out by our group on the diffusion rates of molecular water using quasi-elastic neutron scattering (QENS – where neutrons hit the water molecules to determine their mobility in a similar fashion to a cue ball hitting the pool balls). QENS has shown that the mobility of water in opal – A is greater than that of opal – CT (water molecules move on average faster in opal – A). This greater mobility is ascribed to isolated molecules in cages. If the molecules are isolated they are freer to move. If the water molecules are bonded to other water molecules or silanol groups (this type of bonding is known as *hydrogen-bonding* and is the way that water molecules interact with each other), they are less free to move and so have less mobility. This difference can also be seen in near-infrared spectrum of the water in opal (Chauviré B. et al, 2017). Peaks in the spectrum are sharper and more skewed to higher wavenumber when they are less associated with other water molecules or silanol groups (Figure 9). Greater interaction between water molecules results in broader peaks which are extended to lower wavenumber.

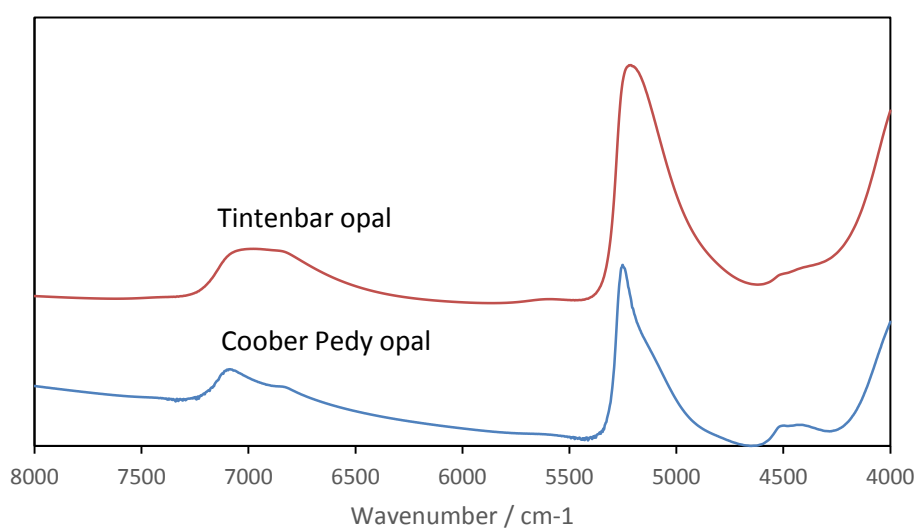


Figure 9. Near infrared spectra of a Coober Pedy and a Tintenbar opal showing the characteristic differences in the water contained in these opals (unpublished data).

Silanol Water

Silanol water is water that is chemically bound in the silica network. Silanol water corresponds to the presence of broken bridges in the silica network (Adams et al, 1991; Brown et al, 2003; Langer and Flörke, 1974). Silanols can be found at both internal (e.g. capillary pores) and external surfaces or as isolated broken bridges in the 3D silica network (Figure 5). Each Si atom has a valance of 4 and is therefore bonded to 4 oxygen atoms. In pure silica each of these oxygen atoms is bonded to another Si atom creating the 3D network (Figure 1). The process of opal formation is a 'condensation reaction' as describe by Equation 3 above, but the process is imprecise and depends on the pH. The higher the pH the more likely there are to be broken Si-O-Si bridges and the more silanol (Si-OH) or bound water present. The proportion of broken bridges can be determined from ^{29}Si nuclear magnetic resonance (nmr) spectroscopy as this technique is sensitive to the environment of the atoms and can detect how many bridges (or broken bridges) are present per Si atom. Figure 10 shows the ^1H cross polarisation ^{29}Si nmr spectra (i.e. it accentuates the Si-OH functionalities present) of opal – A from the GAB and opal – CT from Tintenbar and Mexico. It is clear that the peak at -102 ppm is bigger for the opal – CT specimens indicating that these opals have a greater amount of silanol water per silicon atom. These results correlate with the greater capillary porosity of opal – CT and suggest that the environment is key to the type of opal that is formed. Opal – A is formed in sedimentary rocks of the GAB. These sedimentary rocks are kaolinite rich and have the potential to ion exchange with the pore waters thus reducing pH. Opal – CT, on the other hand is normally found in weathered tuffs and at closer proximity to weathered rocks that are the source of the silica resulting in an elevated pH and a greater proportion of silanol groups.

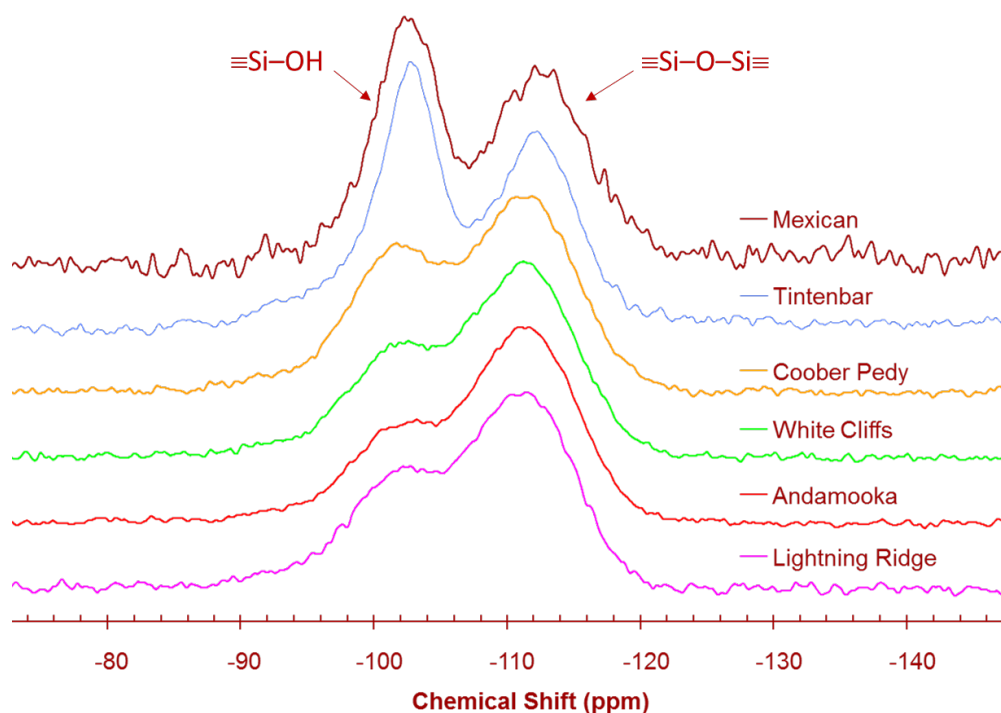


Figure 10. ^1H cross polarisation ^{29}Si nmr spectra for opal – A specimens from the GAB and opal – CT specimens from Tintenbar, NSW and Mexico. The peak at -102 ppm indicates the proportion of silanol (Si-OH) water present (Brown et al, 2003).

General Remarks

Two types of water have been identified in opal, molecular water and chemically bound silanol water. These types of water can be subdivided further into water contained in the silica network (cage water and internal silanol water) and water that is contained in capillaries and voids in the opal (surface adsorbed and bulk water and surface silanols). The presence of these types of water results from the formation mechanism of opal – that is – opal is formed through the dissolution and reprecipitation of silica.

The atomic structure and the microstructure of the opal can be influenced by the environment in which the opal is formed. Certainly there are significant differences between the water contained in opal and the morphological type of opal (i.e. whether the opal is opal – A or – CT) and in the total water content (opal – A is generally found to contain less water than that of opal – CT). Both the molecular water and the silanol water in opal can be differentiated between opal – A and – CT. The molecular water in Opal – A is contained in voids between spheres or is distributed through the silica cage network whilst in Opal – CT the molecular water is contained in small capillary pores. Opal – CT is observed to contain more silanol or bound water than opal – A. These differences suggest differences in the environment in which the opal is formed and from the perspective of the proportion of silanol groups in opal – CT, opal – CT is expected to be formed at a higher pH than opal – A, though still within the bounds suggested by Iler (1979); a pH of 8 to 10.

The presence of water and how water is contained has been implicated in the physical properties of opal as well. Water has been linked to whitening and crazing of opal through water loss (Pearson, 1985; Aguilar-Reyes et al, 2005; Rondeau et al, 2011). Understanding the microstructure and the states of water in the microstructure of opal can therefore help to understand the mechanism of crazing and hence has the potential to help identify stones which might be susceptible to crazing. At this stage, the correlation is based on water content, but the more information we attain from characterising the water content and the types of water in opal, the closer we will be to achieving the goal of being able to identify susceptible material.

Finally, not only does opal provide us with the aesthetic pleasure of the beauty and uniqueness of the gem stone and the magnificence of the chemical and physical processes that underpin the formation of this beautiful gem, opal and its dissolution-precipitation mechanism of formation has also helped to identify the presence of water on Mars (Milliken et al, 2008). Opal is helping to understand the environment of Mars and understanding the nature of the water in terrestrial opal will aid the understanding of the formation of Martian opal and the environment in which it is formed. Opal is out of this world!

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