

THE THERMOPHYSICAL PROPERTIES OF AUSTRALIAN OPAL

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ABSTRACT

The characterisation of the surface area and porosity of opals derived from Tintenbar, a volcanic environment, and Lightning Ridge, a sedimentary environment, using nitrogen gas adsorption at -196°C is reported. Both opal types were found to have relatively low surface areas and displayed little porosity. The low surface areas observed is indicative of the ability of silica to infill voids and interstices. Thermogravimetric analysis of the samples before and after degassing was carried out to determine the amount of water removed by the degassing process. Negligible difference was found in the water content before and after degassing in the case of the Lightning Ridge sedimentary opal, while the Tintenbar volcanic opal was found to have lost more than 60% of its water during the degassing process. These differences were ascribed to the differences in the silica structure of the opals with the Lightning Ridge opal having a more dense cage structure which traps the molecular water while a more open structure is postulated for the Tintenbar opal allowing the water to be relatively easily removed.

KEYWORDS: Opal, nitrogen adsorption, thermogravimetric analysis, volcanic, sedimentary

INTRODUCTION

Potch or common opal and precious opal exhibiting play of colour (POC) or the dancing colours for which precious, gem opal is prized, is found in two geologically distinct environments in Australia and worldwide and can be generally defined as sedimentary or volcanic in nature. In Australia, the sedimentary environment is characterised by an association with the Great Australian (Artesian) Basin (GAB). In Lightning Ridge NSW, for example, the opal-bearing strata consist mostly of sandstones and claystones that form a system of low lying north east trending ridges along the south eastern margin of the GAB (Watkins 1985). Opal is found associated with the chemically weathered rocks that comprise the Griman Creek Formation within the Rolling Downs Group and is of early Cretaceous age. The two major stratigraphic units are the intensely weathered and bleached Wallangulla sandstone and an unweathered to partly weathered claystone known as the finch clay facies. Opal is most often found at the interface between these two stratigraphic units. Whilst this may be a simplified description of opal occurrence in the sedimentary environment, there is a good correlation between these weathered profiles and those observed in the South Australian opal fields (Barnes et al 1992).

The main occurrence of volcanic opal in Australia is in the Tintenbar district of northeastern NSW. The opal deposit at Tintenbar represents, commercially, the largest producing district of volcanic environment precious opal in Australia. In Tintenbar, the opal is associated with the decomposed basalt of the Lismore Basalt and part of the Lamington Volcanics of Miocene age. In this area, the Lismore volcanics consist of three distinct volcanic flows. The precious opal occurs mainly near the junction of the first and second basalt flows as loose nodules in the soil and as amygdales in the weathered vesicular basalt (MacNevin and Holmes 1979, Mumme et al 1975).

Although both potch and precious (POC) opals may be found in both environment types, the physical properties of the opals derived from each of these environment types are distinct and environment type specific (Table 1). A significant difference is the degree and type of order observed at the atomic level (Figure 1 (Smallwood et al 2008)). The x-ray diffraction (XRD) pattern of the volcanic opal derived from Tintenbar has distinct peaks which, based on the

original classification by Jones and Segnet (1971), correspond to the partially crystalline opal-CT containing cristobalite-tridymite lattice intergrowth while the sedimentary opal belongs to the opal-A classification (later described by Langer and Flörke (1974) as opal-AG), as only a broad amorphous hump is observed in the diffraction pattern.

A number of other physical properties listed in Table 1, differentiating the volcanic and sedimentary opals, are also noteworthy. Although the volcanic opal has an apparently higher degree of order at the atomic scale, a lower density is observed. The lower density is consistent with the higher water content, most of which is molecular water trapped in cages in the silica structure (Iler 1979, Langer and Flörke 1974), and a lower refractive index (Phillips and Griffin 1981). The lower density is also consistent with the reported proportion of silicon atoms with zero (Q^4), one (Q^3) and two (Q^2) silanol (Si-OH) groups attached where volcanic opals have been observed to have more Q^2 and Q^3 silicon atoms (i.e. more silanol groups through the bulk of the structure) than the sedimentary opal indicating a more open and, hence, less dense structure (Brown et al (2003)).

The SEM images of the hydrofluoric acid (HF) vapour etched fracture surfaces of a precious (POC) sedimentary Lightning Ridge opal and a precious (POC) volcanic Tintenbar opal are shown in Figure 2. Significant differences between the opal types are again observed. The Lightning Ridge opal shows the characteristic structure of monodispersed spheres aligned in ordered arrays upon which the Bragg diffraction of visible light occurs resulting in POC (Jones et al 1964, Darragh et al 1976). The spheres are observed in this image because the silica cement, infilling the voids between the ordered stacking spheres, has been removed by the etching process. For the Tintenbar opal the view is reversed with the spheres being etched resulting in an ordered array of voids in the silica cement. Fritsch et al (2002) have reported similar observations for volcanic opal for Mexican and Ethiopian opals.

The differences in the morphologies of these two opal types have also been exemplified by thermogravimetric analysis (Thomas et al 2007, 2008). Transparent Lightning Ridge opal has been observed to be morphologically relatively homogenous, while Tintenbar opal has been observed to contain two morphologies ascribed to the cement and sphere silica. Thermal analysis

has also identified the different degrees of entrapment of the molecular water in the silica again suggesting that the Tintenbar opal contains a more open network structure than the Lightning Ridge opal.

Although the volcanic opal has a higher degree of order at the atomic level, it is more crystalline and has a more open, less dense silica network suggesting a greater degree of porosity. In order to verify this postulation, characterisation of the porosity and surface area of patch or common opal derived from Tintenbar and Lightning Ridge using nitrogen adsorption at -196°C was carried out and the results are reported in this paper. As nitrogen adsorption requires the thorough removal of surface volatiles through the degassing of the sample under high vacuum, thermogravimetric analysis of both untreated and degassed opal powders was also carried out to determine proportion of water that was removed as a result of the degassing process.

Experimental

Specimens of a transparent (or crystal) patch opal derived from Tintenbar and a black patch opal from Lightning Ridge were collected and hand ground to a powder. These patch specimens were used for this study, as relatively large, inexpensive and homogenous specimens were available for characterisation. Approximately 5 g were placed in a sample tube of a Micrometrics ASAP2020 surface area and porosity characterisation facility. The samples were degassed at 50°C for 24 hours below $10\ \mu\text{mHg}$. The adsorption isotherms were measured at -196°C in a bath of liquid nitrogen using nitrogen gas as the adsorptive and using an isotherm that was skewed logarithmically to lower pressure to enable data from $10^{-7} p/p_0$ to p_0 to be determined (where p is the pressure and p_0 is the saturation pressure). The value of p_0 was measured at two hourly intervals. The volume of the apparatus was measured using non-adsorbing helium. The controlling software for the ASAP2020 also provided a model fitting routine which was used to analyse the data. The surface area was measured using the BET method (Brunauer et al 1938). The pore size, pore volume and limiting pore surface area were calculated using the method of Dubinin and Astakhov (1971).

TG experiments were carried out on 20 mg portions of opal before and after the degassing and adsorption experiments using a TA instruments SDT2960 simultaneous TG-DTA at a heating rate of $1^{\circ}\text{C min}^{-1}$ to 1200°C in flowing air atmosphere with a flow rate of 15mL min^{-1} .

Results and Discussion

The data for the adsorption of nitrogen at -196°C are shown in Figure 3 for the Tintenbar and Lightning Ridge opals. The volume of gas adsorbed was observed to be greater for the Tintenbar volcanic opal suggesting a higher surface area or larger total pore volume. Using BET analysis, the surface area was calculated in the relative pressure range 0.05 to 0.3 p/p_0 (Table 2, Figure 4) and was found to be higher for the Tintenbar specimen. The higher surface area is consistent with the lower density and higher concentration of linkage breaks, observed for Tintenbar as well as other volcanic opals. The magnitudes of the surface areas for both opals are, however, relatively small for materials that have been deposited by a dissolution precipitation mechanism.

From the adsorption curve it is possible to estimate the pore size and size distribution. In the current study, the Dubinin-Astakhov approach was selected to estimate the pore size, volume and limiting surface areas which are listed in Table 2 (Dubinin and Astakhov 1971). The pore size distribution based on this method is shown in Figure 5. Both opals appear to be mesoporous with pore widths of approximately 17\AA . The porosity is, however, very limited and contributes less than half the total surface area for each opal.

The lack of porosity in the microporous range and the low specific surface area for each of these opal specimens suggests that the opal (whether volcanic or sedimentary) has a fairly compact silica network structure. Any interstice or void produced by the stacking of spheres (random packing for the opals studied here as both opal specimens were potch opal) is in-filled with a silica cement of low porosity. The opal is, however, known to contain significant quantities of water which is predominantly in molecular form (Iler 1979, Langer and Flörke 1974) and, especially in the case of the Tintenbar opal, is relatively easy to remove (Thomas et al 2008). Given that the opals were subject to relatively stringent degassing regimes ($<10\ \mu\text{mHg}$, 50°C , 24 hours), the effect of degassing on the water content was investigated by thermogravimetric analysis (TG) (Figure 6). Within experimental error (circa $\pm 0.2\%$), little or none of the bulk water

contained in the Lightning Ridge opal was removed during degassing. This suggests, as does the relatively high temperature at which the water is removed (circa 200°C), that the molecular water is trapped in a tight cage structure. A significant amount of water (61% of the total water) is, however, removed from the Tintenbar opal during the degassing procedure. The volcanic opal is again demonstrated to have a more open network which allows the removal of the molecular water under vacuum while the sedimentary opal contains a tighter network of silica cages which traps the molecular water.

Although a more open network is the ascribed description of the Tintenbar silica network, this description has a relative meaning. It is apparent that this more open network cannot be detected by nitrogen adsorption at -196°C. There are two possible reasons why this is the case. Firstly, the degassing occurs at 50°C, whereas the nitrogen adsorption occurs at -196°C. The significantly lower temperatures used in the adsorption experiments will result in lower specific volumes of the opal with a consequent reduction in the size of the pores which may now not be penetrable by the adsorbing nitrogen molecules. Secondly, the cross-sectional areas of water and nitrogen molecules are 12.5 and 16.2 Å², respectively (McClellan and Harnsberger 1967). This difference in cross-sectional area indicates that the pore size may be too small for the ingress of nitrogen molecules but is large enough, in the case of the Tintenbar opal, to allow for the diffusion and loss of molecular water under the degassing conditions.

Given that the differences in the properties of sedimentary and volcanic opal listed in Table 1 are general for both precious and potch opal derived from a wide variety of sources worldwide, coupled with the data presented in this paper furthering the distinction between opals sourced from volcanic and sedimentary environments, it is likely that the origins of these differences are due to the geological environment or host rock in which the opal is found. The volcanic opal is more crystalline, but less dense and contains more water resulting in a more open silica network than is observed in the sedimentary opal. The more open network of the volcanic opal may be associated with a higher pH coupled with higher concentrations of electrolyte in the solution in which the colloid is formed. A higher equilibrium temperature for the dissolution and precipitation may also explain these differences. Both of these factors could contribute to the more open network and lower density of the volcanic opal. Identification of the specific origins

of the more open network from the results presented in this paper would, however, be speculative and further characterisation of opals from both environments is required before a relationship between property and environment can be established.

CONCLUSIONS

Opals of both sedimentary and volcanic origin were observed to have very low specific surface areas with little porosity present. The low surface area is linked to the ability of silica to fill in voids with relative ease. The surface area was, however, found to be higher for the volcanic opal which is consistent with its lower density. The process of degassing the two opal types also resulted in differing behaviour. The Tintenbar opal was found to lose a significant proportion of its water (compared to little or no water loss from the sedimentary opal) suggesting that the opal has a more open silica network. This is also consistent with previously reported data such as the proportion of Q² and Q³ silicon atoms as determined by ²⁹Si NMR. Although speculative, the origins of these differences are likely to be in their environments, in particular, the host rock, in which the opals are found leading to differences in the pH and electrolyte concentration of the saturated silica solutions, or in an elevated temperature of the solution, from which the colloidal particles that form the opal grow.

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Table 1.

Comparison of the physical properties of opals derived from sedimentary and volcanic environments.

	Sedimentary Opal	Volcanic Opal	Refs.
X-ray Diffraction (XRD)	Opal - A	Opal-CT	[a,b]
Crystallinity	Amorphous	Partially crystalline	[a,b]
Density	~ 2.15	~ 2.00	[c]
NMR	Less Q ² , Q ³	More Q ² , Q ³	[d]
Water content	4% – 9%	9%-18%	[b,e]
Water Types - Silanol	More silanol - OH	Less Silanol - OH	[b,d]
Water Types - Molecular	Less Molecular – H ₂ O	More Molecular – H ₂ O	[b,d]
Refractive Index	1.42 -1.45	1.40 – 1.42	[e]
Photoluminescence	Strong Emission @ 2.65eV, Excitation @ 5.0eV	Negligible	[c]

[a] Jones and Segnit 1971, [b] Langer and Flörke 1974, [c] Smallwood 1999, [d] Brown et al 2003, [e] Phillips and Griffin 1981.

Table 2. Data derived from the nitrogen adsorption and the thermogravimetric analysis on each opal type.

	Tintenbar Crystal Opal	Lightning Ridge Black Potch Opal
BET [†] Surface Area (m ² /g)	1.30	0.72
DA [‡] Mean Pore Diameter (Å)	16.8	16.6
DA Limiting Pore Volume (cm ³ /g)	3.3 x 10 ⁻⁴	1.9 x 10 ⁻⁴
DA Equivalent Pore Surface Area (m ² /g)	0.78	0.40
% water by mass before degassing	9.8	5.7
% water by mass after degassing	3.8	5.6

[†]BET – Brunauer, Emmett and Teller Model (Brunaur et al 1938)

[‡]DA – Dubinin-Astakov Model (Dubinin and Astakov 1971)

Figures (also attached as separate files)

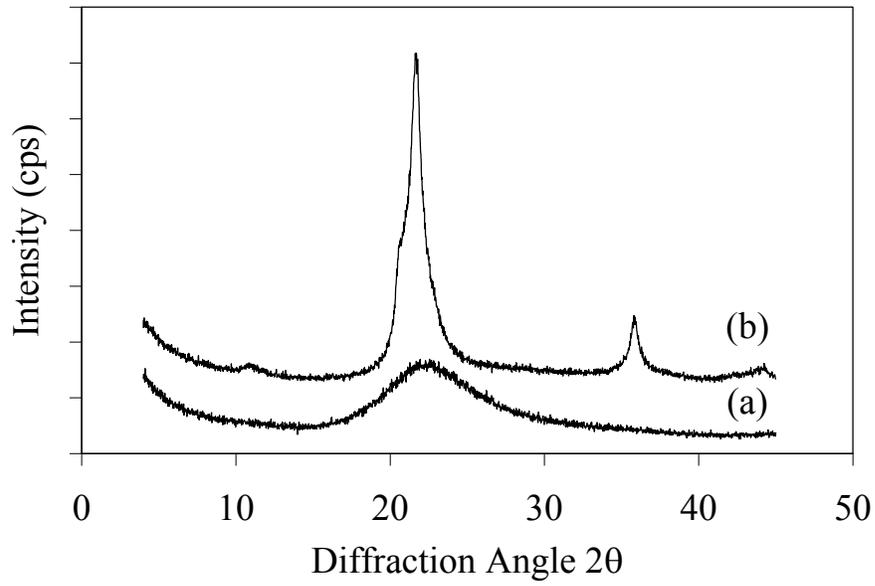
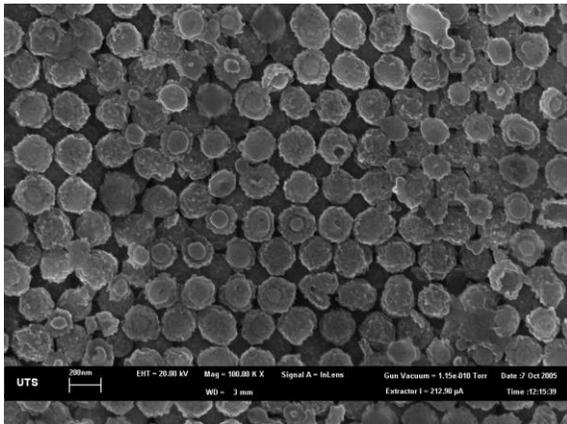
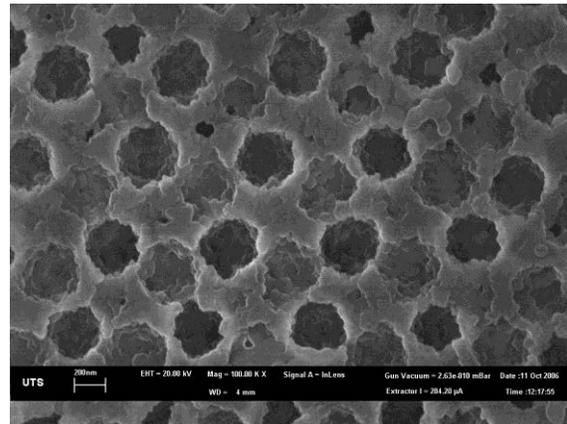


Figure 1.

XRD data for (a) Coober Pedy precious opal and (b) a Tintenbar transparent opal.



(a)



(b)

Figure 2.

SEM images of platinum coated hydrofluoric acid etched fracture surfaces of (a) Lightning Ridge and (b) Tintenbar precious (POC) opals. Width of view is 3.5 μm .

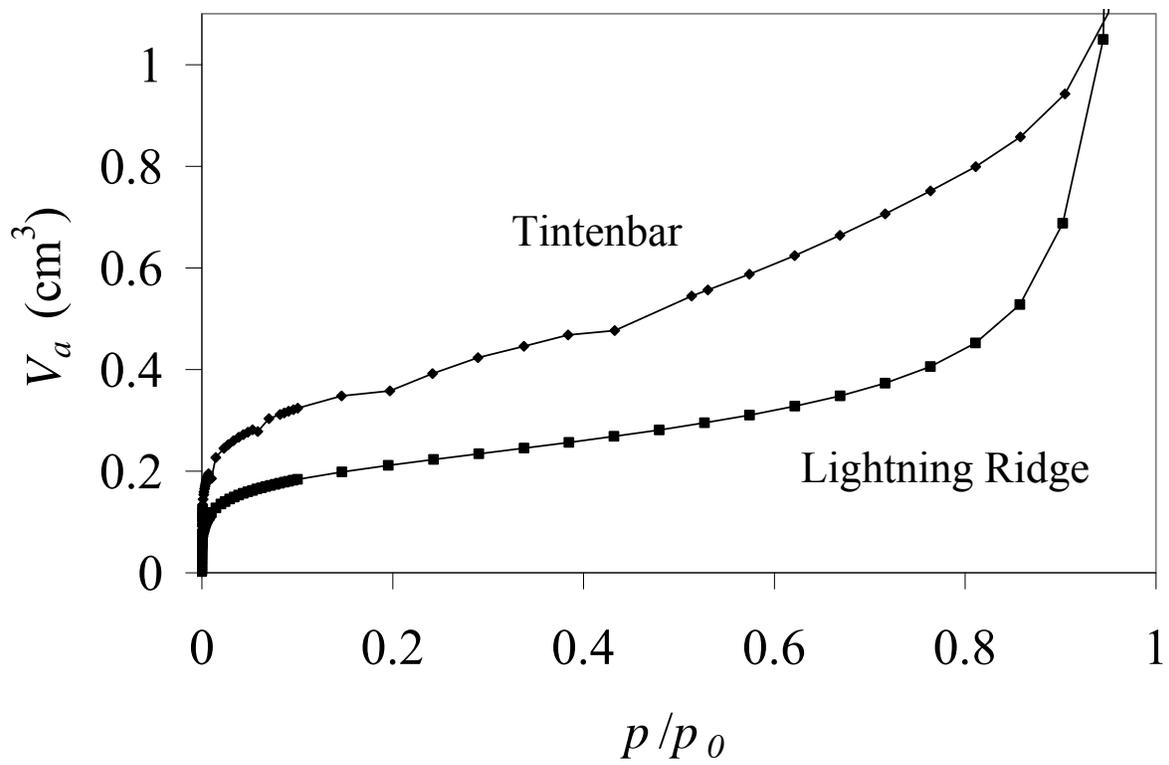


Figure 3.
Nitrogen adsorption data on Lightning Ridge and Tintenbar patch opals acquired at -196°C .

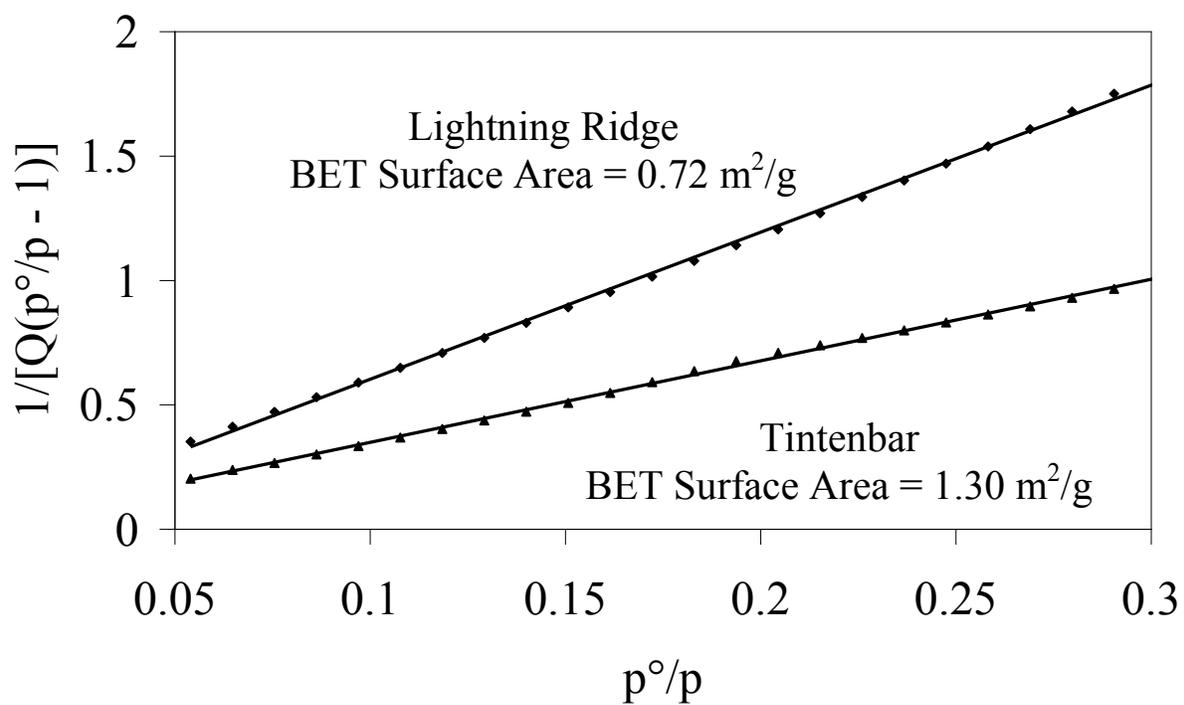


Figure 4.

BET fit (Brunauer et al 1938) to the adsorption data presented in Figure 4.

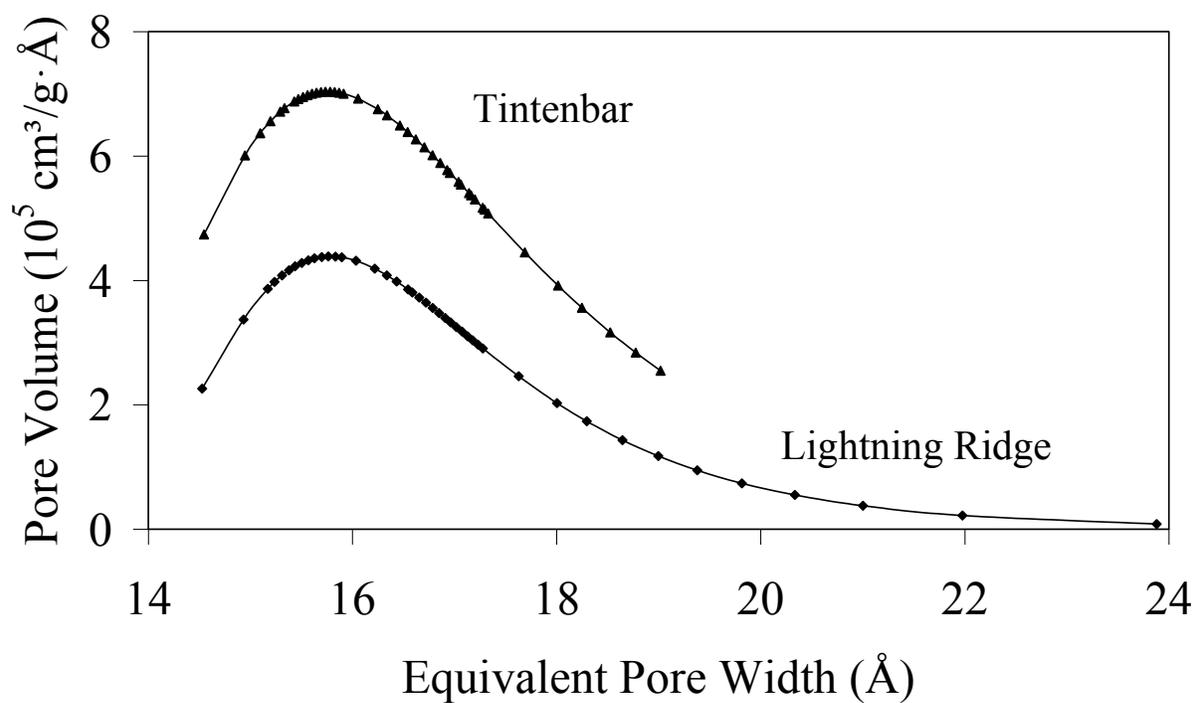


Figure 5.

Pore size distribution of Lightning ridge and Tintenbar patch opals determined using the method of Dubinin and Astakhov (1971).

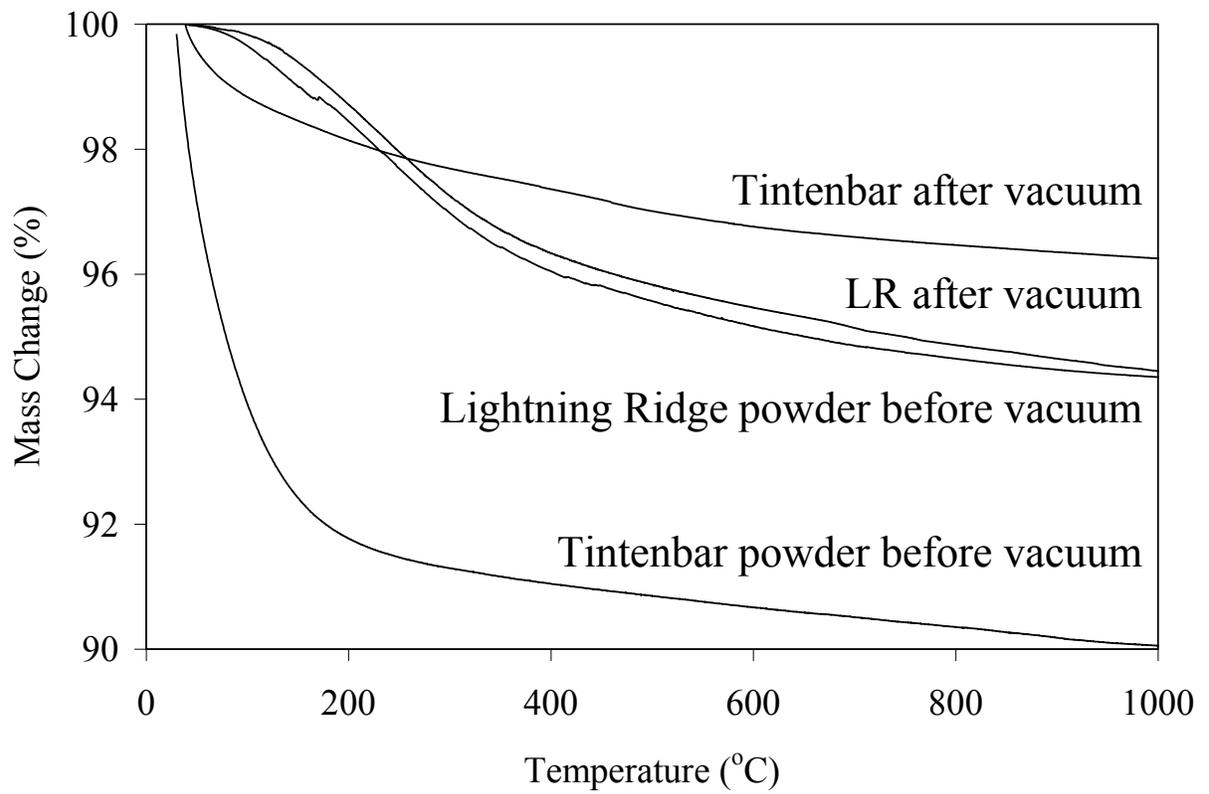


Figure 6.

Thermogravimetric data for Lightning Ridge and Tintenbar patch opals acquired before and after degassing of the samples.