

## TMA AND SEM CHARACTERIZATION OF THE THERMAL DEHYDRATION OF AUSTRALIAN SEDIMENTARY OPAL

A. Smallwood<sup>1</sup>, P. S. Thomas<sup>1\*</sup>, A. S. Ray<sup>1</sup> and P. Šimon<sup>2</sup>

<sup>1</sup>Department of Chemistry, Materials and Forensic Sciences, University of Technology Sydney, P. O. Box 123, Broadway NSW 20007, Australia

<sup>2</sup>Department of Physical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology Radlinského 9, 812 37 Bratislava, Slovak Republic

The dehydration of samples of a Coober Pedy, South Australian sedimentary white opal, displaying play of colour, was investigated using TMA by heating the samples of the specimen to a range of temperatures between room temperature and 1000 at 200°C intervals followed by cooling to room temperature. Etched fracture surfaces of the samples were then examined using SEM. The samples showed the typical expansion at low temperature up to 210°C before contraction was observed. The contraction of the opals was ascribed to both sintering, supported by morphological change observed in the SEM micrographs, and dehydroxylation of the silanol groups producing silicon-oxygen-silicon bridges resulting in a more dense silica network.

**Keywords:** amorphous silica, dehydration, opal, SEM, TMA

### Introduction

Opal is a hydrated amorphous silica, with the general formula  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , and is formed naturally through a process of dissolution of felspathic aluminosilicates followed by the precipitation of the silica as a colloidal sol of monodispersed spheres with a size range of 100 to 450 nm [1, 2 and references therein]. The monodispersed silica spheres are then flocculated and sedimented into ordered arrays which diffract visible light producing the play of colour that is characteristic of the precious opal. This process of diagenesis of inorganic silica results in the incorporation of significant amounts of water in the opal. Water contents of opal have been measured in the range 1 to 21% [3], and for the sedimentary Australian opal, the subject of the current paper, between 6 and 10% [4]. Four types of water have been identified in opal; surface adsorbed water, molecular water trapped in silica cages in the bulk of the opal, surface silanol and bulk silanol water [1]. Thermal methods have so far not been able to differentiate between these water types as the water is contained in sites with a range of energetics and due to the necessity for diffusion of the water out of the opal during dehydration.

Thermal methods, applied to the characterisation of the dehydration of opal, have, however, successfully differentiated between specimens of opal derived from three regions of Australia, Andamooka and Coober Pedy in South Australia and Lightning Ridge in New

South Wales [4]. This regional differentiation was based on the rate and temperature at which water loss occurred during dehydration measured by thermogravimetric analysis (TG) and by dimensional change using thermal mechanical analysis (TMA). In the TG, the differentiation is observed in the position of the maximum of the water loss peak in the DTG curve. In the TMA, an expansion in the opal specimen is observed up to a peak whereupon on further heating contraction is observed. The differentiation was based on the position of the peak. This differentiation is valuable as it furthers the understanding of opal as a material, it aids the further understanding of the origins or genesis of opal and is important as other physical and chemical test methods (e.g. trace element distribution [2]) have not found clear differences between opals derived from the different regions in Australia (although, it should be noted that, to the trained eye, the origin of an opal specimen can generally be identified by visual inspection!). This paper, therefore, furthers the investigation into the thermal characteristics of opal by characterising a specimen of colour (or precious) opal derived from Coober Pedy by thermally treating the opal specimen using TMA and characterising the effect of the thermal treatment using electron microscopy (SEM).

\* Author for correspondence: paul.thomas@uts.edu.au

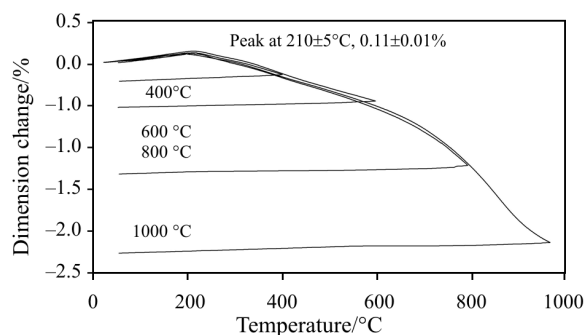
## Experimental

A relatively large homogenous specimen of Coober Pedy seam opal displaying play of colour was cut into 'logs' approximately 10×3×3 mm using a diamond impregnated wafering blade and water as the lubricant. The ends of the long dimension were then 'faceted' parallel to each other, for analysis in the TMA, by polishing the ends on a 400 grit diamond impregnated 8 inch (250 mm) lap on an Imahashi polishing machine.

Thermal analysis was carried out on a TA Instruments TMA 2940 Thermo-mechanical Analyser using the instrument as a dilatometer. Specimens were heated at a heating rate of 0.5°C min<sup>-1</sup>, in a static air atmosphere, to 200, 400, 600, 800 and 980°C and then cooled to room temperature at 5°C min<sup>-1</sup>. The specimens were recovered from the TMA experiments and fractured. The fracture surfaces were etched with hydrofluoric acid vapour and platinum coated before mounting and placing in a LEO Supra 55VP SEM for micro-structural analysis. Images of the fracture surface were collected using the in-lens detector with an accelerating of 20 kV.

## Results and discussion

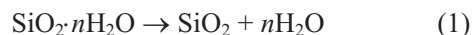
TMA measurements were carried out up to limiting temperatures which were set at 200°C intervals between room temperature and 1000°C in order to determine the effect of heating on the morphology of the opal (Fig. 1). Expansion was observed to a maximum of 0.11±0.01% at a temperature of 210±5°C before contraction was observed correlating with the data previously published [4]. The total degree of contraction for each of the heat treated samples is listed in Table 1. Expansion coefficients, for each sample run, were measured over 100°C range at 200°C intervals and are also listed in Table 1. All specimens were observed to have similar expansion coefficients throughout the testing range suggesting good homogeneity in the opal sample tested. The contraction rates were observed to increase as the temperature increased, although close to 1000°C the rate of expansion decreases markedly, suggesting that the processes occurring which cause the large decrease in the linear dimension (up to a maximum of 2.25% (Table 1)) are close to completion. For the cooling segment of each experimental run, the expansion coefficients, for specimens heated to above 200°C, are all fairly similar with some scatter observed in the data rather than any observable trend. For the sample heated to 200°C, a temperature below the transition temperature from expansion to contraction, the contraction followed the expansion curve fairly closely suggesting reversibility of the thermal expansion.



**Fig. 1** TMA curves for 'logs' of Coober Pedy colour opal heated in a static air atmosphere at 0.5°C min<sup>-1</sup> to the temperatures indicated followed by cooling to room temperature at 5°C min<sup>-1</sup>. The 200°C specimen is included, but as the expansion below the peak is reversible, its cooling curve simply follows the heating curve

SEM images of each specimen, at 100,000 times magnification, are shown in Fig. 2a to f. The untreated specimen (Fig. 2a) is observed to have the distinct opaline structure of monodispersed silica spheres, with a diameter of approximately 420 nm, packed in ordered arrays. The specimen heated to 200°C also shows the distinct silica sphere structure (Fig. 2b). There is a difference in the apparent degree of etching that is observed which could be associated with a change in the character of the 'cement' which holds the spheres together. On heating to 400°C, the outline of the spheres remains visible, however, the fine structure within the spheres begins to disappear. Above 400°C, sintering of the structure appears to occur. Etching reveals less and less of the fine structure of the opals with only voids observed for the higher temperatures.

Based on the SEM and the TMA data, the dehydration of opal to high temperature is accompanied by a sintering of the opal. As the silica is in a hydrated form, the dehydration process results in the removal of all types of water contained in the specimen.



For bound water, the removal of water results in the formation of silicon-oxygen-silicon bridges.

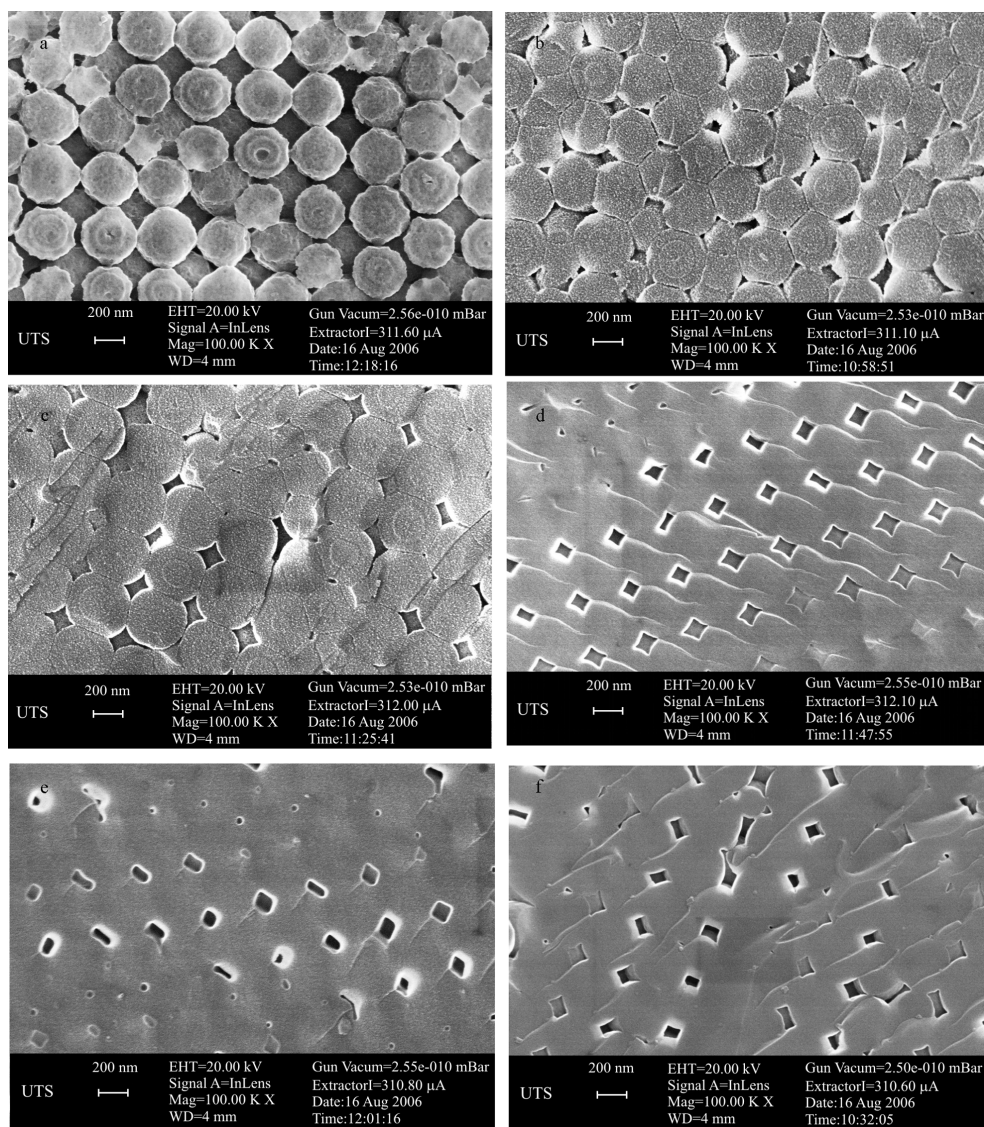


The removal of silanol groups from the structure will result in the contraction in volume. Therefore, two processes are likely to be involved in the contraction process; sintering of the amorphous silica is likely to result in fusion of the particles, as is observed in the SEM images, and contraction associated with the elimination of bound water (silanol groups) resulting in the formation of silica bridges and a reduction of the volume of the system. The latter process has been observed by <sup>29</sup>Si NMR for the dehydration of opal heated to 1000°C [5].

**Table 1** Expansion coefficient data for the specimens heat treated in Fig. 1

Sample	Peak/ $^{\circ}\text{C}$	Heating slope RT to $150^{\circ}\text{C}$ ( $\times 10^3\%$ $^{\circ}\text{C}^{-1}$ )	Heating slope $300$ to $400^{\circ}\text{C}$ ( $\times 10^3\%$ $^{\circ}\text{C}^{-1}$ )	Heating slope $500$ to $600^{\circ}\text{C}$ ( $\times 10^3\%$ $^{\circ}\text{C}^{-1}$ )	Heating slope $700$ to $800^{\circ}\text{C}$ ( $\times 10^3\%$ $^{\circ}\text{C}^{-1}$ )	Heating slope $900$ to $1000^{\circ}\text{C}$ ( $\times 10^3\%$ $^{\circ}\text{C}^{-1}$ )	Cooling slope $150^{\circ}\text{C}$ to RT ( $\times 10^3\%$ $^{\circ}\text{C}^{-1}$ )	Change in length after heating/%
$200^{\circ}\text{C}$	—	0.63	—	—	—	—	0.67*	-0.003
$400^{\circ}\text{C}$	209	0.63	-1.6	—	—	—	0.22	-0.22
$600^{\circ}\text{C}$	213	0.74	-1.8	-1.5	—	—	0.11	-0.53
$800^{\circ}\text{C}$	214	0.55	-1.6	-2.0	-4.3	—	0.17	-1.32
$1000^{\circ}\text{C}$	203	0.64	-1.7	-1.8	-4.5	-5.1	0.16	-2.26

\*Expansion coefficient for this sample is measured without heating to the peak temperature, thus contraction follows the original expansion



**Fig. 2** SEM images of the specimens heat treated in Fig. 1. The specimens are: a – no heat treatment, and samples heated to b – 200°C, c – 400°C, d – 600°C, e – 800°C and f – 980°C

## Conclusions

A homogenous specimen of seam opal derived from Coober Pedy was thermally treated by heating samples to a series of elevated temperatures. Analysis of the microstructure of the opal after thermal treatment indicated that the shape of the TMA curve was first associated with typical reversible thermal expansion of the opal followed by dehydration through the dehydroxylation of the silanol groups in the hydrated opal. This dehydroxylation coupled with the sintering of the amorphous silica, resulted in significant contraction of the specimens.

## References

- 1 R. K. Iler, 'The Chemistry of Silica, Solubility, Polymerisation, Colloid and Surface Properties, and Biochemistry', 2<sup>nd</sup> Ed., John Wiley and Sons, Inc, New York, 1979.
- 2 P. S. Thomas, L. D. Brown, A. S. Ray and K. E. Prince, *N. Jb. Miner. Abh.*, 182 (2006) 193.
- 3 R. Webster, 'Gems, Their Sources Descriptions and Identification', Butterworths, 3<sup>rd</sup> Ed., London (2000).
- 4 L. D. Brown, A. S. Ray, P. S. Thomas and J. P. Guerbois, *J. Therm. Anal. Cal.*, 68 (2002) 31.
- 5 L. D. Brown, A. S. Ray and P. S. Thomas, *J. Non-Cryst. Solids*, 332 (2003) 242.

DOI: 10.1007/s10973-006-8136-7