Comparative Analysis of Sedimentary and Volcanic Precious Opals from Australia

A.G. Smallwood, P.S. Thomas and A.S. Ray

Department of Chemistry, Materials and Forensic Science, University of Technology, Sydney,
PO Box 123, Broadway NSW 2007Australia

Email: tony@adgems.com.au

Available Online at: www.austceram.com/ACS-Journal-2008vol2.asp

Abstract
Precious opal is Australia's national gemstone, with Australian opal fields providing 90% of world production. The sedimentary geological environment, associated with Cretaceous sediments of the Great Artesian Basin, is the source of most precious opals in Australia. The deposit of precious opal at Tintenbar in northern New South Wales is the only known commercial occurrence of precious opal in volcanic environment in Australia. Differences in silica structure of opal previously classified by x-ray diffraction (XRD) in the 1960's by Jones and Segnit identified three types of opal structure – amorphous opal-A, opal-CT with a poorly crystalline intergrowth cristobalite and tridymite and opal-C showing the cristobalite structure. Recent papers have suggested that all precious opal from a sedimentary environment is Opal-A, and all precious opal from the volcanic environment is opal-CT. This paper examines the differences between sedimentary precious opals from Coober Pedy, South Australia, and volcanic precious opal from Tintenbar, NSW using XRD, scanning electron microscopy and thermal analysis.

Keywords: Precious opal, scanning electron microscopy, x-ray diffraction, thermogravimetric analysis

INTRODUCTION

The origins of the flashes of spectral colour seen in precious gem opal known as play-of-colour (POC), have been an enigma for a long time. Although much of the mineralogy has been known since Roman times, the structure within the opal responsible for the POC was not revealed until the mid 20th century. Jones *et al*, in their original transmission electron microscope (TEM) study, identified the cause of the POC in precious opal to be the result of diffraction of visible light from a three dimensional array of close packed mono-dispersed spheres in the size range of 150 – 350nm [1]. The microstructure of opal was, therefore, identified as having the unusual hierarchy of low structural order at the atomic level (i.e. x-ray amorphous silica) while a high degree of order is produced in the secondary structure (i.e. mono-dispersed amorphous silica spheres packed in ordered arrays). To explain the origins of the formation of such an interesting natural structure, a number of models have been proposed [2-5]. The models take on a number of forms, but all need a supply of silica for the formation of the opal. In sedimentary environments, which dominate opal occurrences in Australia, the silica is most likely to be derived from the sandstones associated with the Great Artesian Basin (GAB) by the chemical weathering of relatively soluble silicates such as the feldspars contained in these sediments. Using a typical potassium felspar as an example, the chemical weathering occurs by dissolution of the feldspar:

$$2KAlSi_3O_8 + 3H_2O$$
$$\rightarrow Al_2Si_2O_5(OH)_4 + 2KOH + 4SiO_2$$
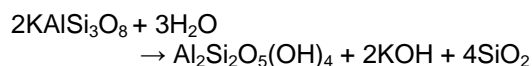
by the permeation of ground water through the sediments resulting in kaolinite and dissolved silica, aided by an increase in pH (8-10) through the release

of potassium hydroxide. Once the silica is in solution, the enrichment of the solution can occur, for example, by evaporation. An increasing in the concentration of the silica solution coupled with a lowering of the pH through alkali ion exchange with the surrounding clays allows the nucleation of primary silica spheres and, subsequent, sphere growth as more silica is supplied to the system. As the supply of silica in the solution is a cyclic process generations of growth rings are produced and the thickness controlled by the process of Ostwald-Ripening. Once a critical sphere size has been reached sedimentation occurs, which under suitable and, evidently, rare conditions results in the formation of an ordered array and, hence, precious opal exhibiting POC [6-7].

Opaline silica, a natural hydrous silica with the general formula $SiO_2.nH_2O$, has been found to occur with a range of morphologies depending on the environment in which the opal is found. Based on x-ray diffraction (XRD) measurements Jones and Segnit originally divided opaline silica into three categories; Opal-C, Opal-CT and Opal A [8].

Opal-C is a "well ordered α-cristobalite" structure as seen by its distinctive XRD pattern. These opals are commonly found associated with lava flows.

Opal-CT is a combination of "disordered α-cristobalite and disordered α-tridymite structure. These opals are usually described as "common opals". Rare occurrences of precious opal, derived from volcanic geological environments, fall into this category.

Opal-A is a "highly disordered near amorphous", structure showing only an amorphous 'hump' in XRD. Subsequent analysis by Langer and Flörke [9] sub-divided opal-A into two further categories, opal-AN and opal-AG.

Opal-AG is opal that is formed from solution by a process of slow concentration of the silica followed by the precipitation of the colloidal particles. Precious opal derived from the sedimentary fields of the GAB in Australia fall into this category.

Opal-AN is opaline silica that is deposited in thin botryoidal crusts on volcanic rocks by quenching from high temperature silica fluids. Opal-AN, although a natural hydrous silica, has a much lower water content that opal-AG and has properties that are much more akin to silica glasses. Examples of this type of silica are hyalite or 'Libyan desert glass'.

Precious opal exhibiting POC is found in two geologically distinct environments, generally defined as sedimentary or volcanic in nature, and, hence, falls into the opal-AG and opal-CT categories. In Australia, the commercial production of precious opal occurs mainly in the sedimentary environments and accounts for as much as 90% of total world precious opal production [10]. Precious opal is also found in volcanic environments in Australia, although the extent of their commercial production is limited. Production of opal from outside Australia is almost exclusively derived from the volcanic environment.

The Australian sedimentary geological environment is characterised by an association with the Great Artesian Basin (GAB), and opal formation is intimately associated with weathered sedimentary profiles that make up the GAB. In Coober Pedy, South Australia, the opal-bearing strata consist mostly of sandstones that form the Stuart Range, an east facing escarpment along the western margin of the GAB. Opal is found associated with the chemically weathered rocks that comprise the Bulldog Shale which is part of the Marree formation and is of early Cretaceous age. The Bulldog Shale is subdivided into two stratigraphic units; an intensely weathered and bleached claystone (called sandstone by the miners) and an unweathered to partly weathered claystone. Precious opal is most often found at the interface between these two stratigraphic units suggesting that the silica required for opal formation is derived from the weathering of the stratigraphic unit above the opal deposit. Whilst this remains a simplified description of opal occurrence there remains a correlation between these weathered profiles in the other South Australian, the Lightning Ridge (NSW) and White Cliffs (NSW) opal fields [11].

The occurrence of 'volcanic' opal in the Tintenbar district of north eastern NSW represents commercially the largest producing district of volcanic environment precious opal in Australia. In Tintenbar, 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 decomposed vesicular basalt [12-13].

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	[8,9]
Crystallinity	Amorphous	Partially crystalline	[8,9]
Density	~ 2.15	~ 2.00	[19,20]
NMR	Less Q^2, Q^3	More Q^2, Q^3	[7,14]
Water content	4% – 9%	9%-18%	[9,15]
Water Types - Silanol	More silanol - OH	Less Silanol - OH	[7,9,14]
Water Types - Molecular	Less Molecular – H_2O	More Molecular – H_2O	[7,9,14]
Refractive Index	1.42 -1.45	1.40 – 1.42	[15,20]
Photoluminescence	Strong Emission @ 2.65eV, Excitation @ 5.0eV	Negligible	[19]

Although precious opal derived from the two classes of geological environment appear similar as gemstones, a number of differences in their physical properties have been observed (Table 1). The first notable difference is that the opal from the sedimentary environment is amorphous Opal AG where as the volcanic opal is of the poorly crystalline opal CT class. While volcanic opal is more crystalline than sedimentary opal, volcanic opal is of lower density, a fact that might be explained by the higher water contents observed. This is also supported by the reported proportion of silicon atoms with zero (Q^4), one (Q^3) and two (Q^2) silanol (Si-OH) groups attached. 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 [14].

Another physical property related to water content is the refractive index. The refractive index of opal diminishes as water content increases [9-15]. Hence, the refractive index is also lower for the volcanic opals. It is also interesting to note that sedimentary opals tend to be fluorescent while volcanic opals are not. These consistent differences, between precious opal specimens derived from volcanic environments, both in Australia and worldwide, and the Australian sedimentary opal specimens, indicate that the environment is an important factor in controlling the dissolution, precipitation and subsequent sedimentation of the mono-dispersed colloidal sol

that forms the ordered arrays that are required for the deposition of precious opal. Developing an understanding of the origins of these differences may provide the key to the mechanisms of formation that are currently not well understood. This paper, therefore, furthers this endeavour by reporting the results of an investigation into the morphological characteristics of precious opals derived from the volcanic environment at Tintenbar and from the sedimentary environment at Coober Pedy.

EXPERIMENTAL METHODS

Precious opal samples were sourced from the Coober Pedy opal fields in South Australia, representing the sedimentary environment, and from Tintenbar New South Wales, representing the volcanic environment. For the microstructural analysis, samples of each opal were mechanically fractured to provide a fresh clean surface. This fractured surface was then etched in the vapour of concentrated hydrofluoric acid for approximately 30 seconds. The etched surfaces were then platinum coated by vapour deposition. Electron micrographs were obtained by placing the prepared specimens in a Zeiss Supra 55 VP scanning electron microscope with images collected using an in lens detector with an accelerating voltage of 20kV.

Powder X-ray diffraction (XRD) analysis was carried out on samples of opal which were ground, by hand, to a powder using a pestle and mortar before mounting in a Siemens D5000 X-ray diffractometer using CuK α radiation between 4° and 45° 2θ with a step size of 0.02° and an acquisition time of 8 seconds
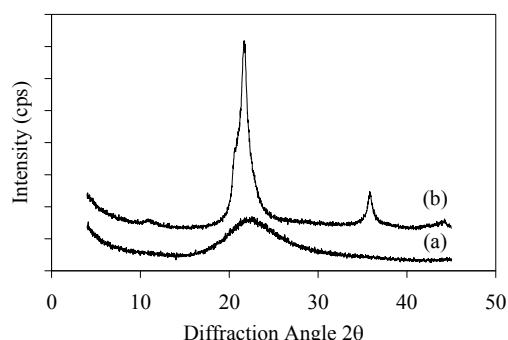
Fig. 1. XRD patterns of ground specimens of (a) Coober Pedy sedimentary opal and (b) Tintenbar volcanic opal.

per step. Thermogravimentric analysis (TG) was carried out on fractured lumps of opal weighing approximately 25 mg by loading the specimens in a TA Instruments SDT 2960 simultaneous TG-DTA, heating at a rate of 1°C min^{-1} to 1200°C in flowing air atmosphere with a flow rate of 15mL min^{-1}.

RESULTS AND DISCUSSION

The XRD data for the two opal classes are shown in Fig. 1. These data are typical for amorphous opal-AG derived from the sedimentary environment of Coober Pedy and the partially crystalline opal-CT derived from the volcanic environment, and are in good agreement reported data [8].

SEM micrographs are shown in Figs. 2 and 3. In both micrographs there is evidence of ordered sphere structure, however, the sphere structure is observed in two distinct ways for the two classes of opal. In the sedimentary opal, Fig. 2, the cement infill between the spheres is etched away by the HF etching process [16]. Concentric rings are observed in the structure of

the spheres with a nucleating primary sphere observed at the centre. These concentric rings represent the generational growth of the opal with each ring representing a single step in the dissolution-precipitation cycle.

By contrast, the Tintenbar volcanic opal shows the superstructure of the infilling cement with the spheres themselves having been etched away by the HF treatment (Fig. 3). As the more chemically reactive material will be removed by the etching process, the process of etching identifies, effectively, the less dense medium which for the case of the Coober Pedy opal is the infilling cement while, for the Tintenbar opal, it is the spheres themselves. As both opal types contain ordered arrays in their secondary structures, both opal types display POC.

The thermogravimetric (TG) and differential TG (DTG) curves are shown in Figs. 4 and 5, respectively. The mass loss for each opal, represented as a mass % in Fig. 4, is due to the loss of water as the specimen is heated. The final mass loss, therefore, corresponds to the water content of the opals which for Coober Pedy opal was found to be 7.8±0.3% while the water content for the Tintenbar opal was 9.8±0.2%. For both opals, these values fit into the expected ranges (Table 1.), although the Tintenbar opal is at the low end of the volcanic range. The shape of the TG curves, reflected as peaks in the DTG curves (Fig.5.), for each opal type is quite distinct. Mass loss is observed in a single step for the Coober Pedy opal with the centre of mass of the peak in the DTG curve at approximately 285°C. Mass loss in the Tintenbar sample occurs through two main processes with centres of mass at 212°C and 531°C. A shoulder on the 531°C peak is also observed at 494°C.
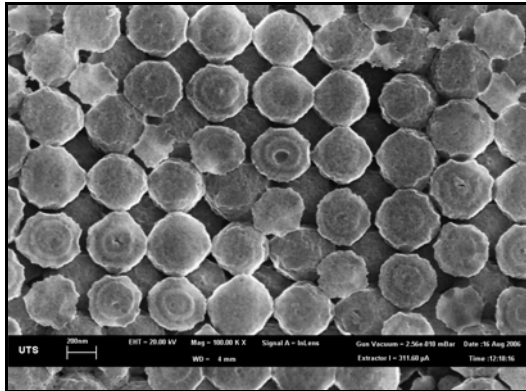
Fig. 2. SEM micrograph of a Coober Pedy precious opal showing the ordered stacking of monodispersed silica spheres. Width of view is 3.5 μm.
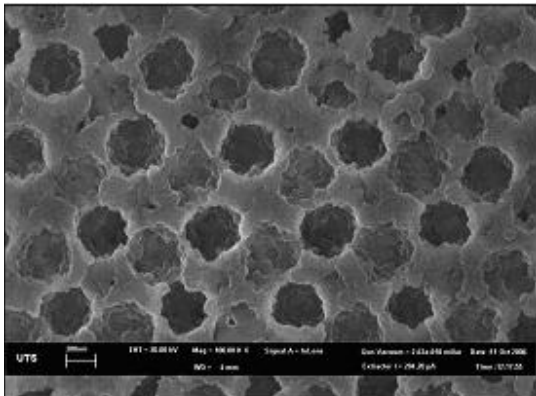

Fig. 3. SEM micrograph of a Tintenbar precious opal showing an ordered arrangement of voids representing the positions of the monodispersed silica spheres prior to HF etching. Width of view is 3.5 μm.

Mass loss, although solely attributable to the loss of water from the opal specimen during heating in a TG experiment is not a simple process. The mechanism of water loss from an opal specimen has been proposed to occur through a two step process of volatilisation of bound water followed by diffusion of the water vapour to the surface of the opal before it is liberated and, hence, registered as a mass loss by the balance [17]. Therefore, the temperature at which water is observed to be evolved is a combination of the energetics of the volatilisation and a diffusion component. The diffusion rate is also complicated by
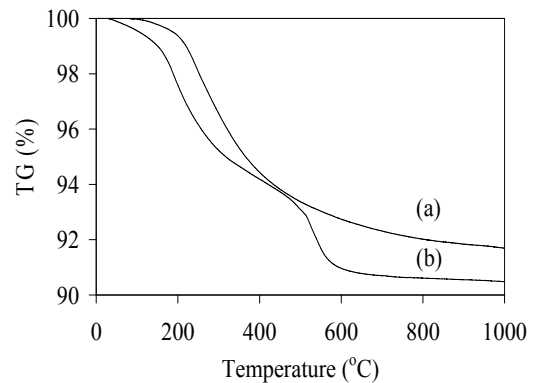

Fig. 4. TG Curves of (a) Coober Pedy and (b) Tintenbar opals.

a change in the opal structure as the temperature is increased as, as the silanol water is driven off, a more dense structure is produced due to the formation of new Si-O-Si bridges [18]. Additionally, sintering is observed which also increases the density of the system. These two processes may be the cause of the asymmetric shape of the DTG peaks. Mass loss can, therefore, be attributed to both the morphology of the opal and the environment in which the water is present in the opal (e.g. silanol, surface adsorbed, cage water etc.). It is, however, most likely that diffusion is dominating the evolution of water and, hence, the two peaks in the Tintenbar opal are characteristic of two types of silica; one of greater density and one of lower density (i.e. the sphere materials and the cementing material between the spheres). It is likely that in the Tintenbar opal, the sphere material corresponds to the lower temperature evolution as this is the material that is more readily removed during HF etching. A similar analysis may be applied to the Coober Pedy opal, but with only one silica type present resulting in a single mass loss step.

CONCLUSIONS
Precious opal derived from volcanic and sedimentary geological environments have been characterised to identify the morphological characteristics that differentiate them. The Coober Pedy sedimentary opal was found to be x-ray amorphous opal-AG, while the Tintenbar opal was found to have some semblance of crystallinity in accordance with the opal-CT classification. Characterisation of the morphology of these opals by SEM using a fracture plus HF etching technique of sample preparation showed distinct differences between these opal types
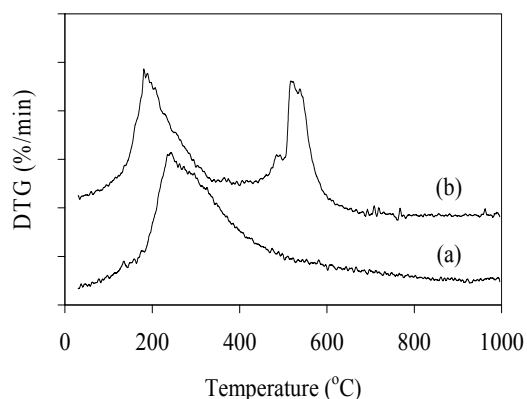
Fig. 5. DTG Curves of (a) Coober Pedy and (b) Tintenbar opals.

with the cementing material between the spheres being etched by the HF in the Coober Pedy opal while it was the spheres themselves which were etched away in the Tintenbar opal. The thermal analysis also identified some significant differences between the opal morphologies. These differences are evidence that the different environments of formation of the opals have an influence on the morphology and, hence, provide a basis for the further characterisation of the opals with a view to gaining a greater understanding of the mechanisms of formation.

Acknowledgements

References

1. J. B. Jones, J. V. Sanders, and E. R. Segnit. (1964). The structure of opal. Nature 4962, pp 991.
2. P. J. Darragh, A. J. Gaskin, J. V. Sanders. (1976). Opals. Scientific American. 234/4, pp84.
3. H.J. Behr, K. Behr, J.J Watkins. (2000). Cretaceous microbes – producer of black opal at Lightning Ridge, NSW, Australia. Geological Abstracts No. 59. 15th Australian Geological Convention. Sydney July 2000.
4. S.R Pecover. (1996). A new Genetic model for the origin of precious opal. Extended Abstracts No. 43. Mesozoic geology of Eastern Australia plate conference. Geological Society of Australia. pp450-454.
5. B. Devison. (2004). The origin of precious opal – a new model. Australian Gemmologist Vol 22, No. 2. pp50-58.
6. R.K. Iler. (1979). The Chemistry of Silica, Solubility, Polymerisation, Colloid and Surface Properties, and Biochemistry. John Wiley and Sons Inc. New York.
7. L. D. Brown. (2005). Characterisation of Australian Opals. PhD Thesis University of Technology Sydney.
8. J. B. Jones, E. R. Segnit. (1971). The Nature of Opal. I. Nomenclature and Constituent Phases. Journal of the Geological Society of Australia. 18/1. pp57
9. K. Langer, O. W. Flörke. (1974). Near Infrared Absorption Spectra (4000-9000cm^{-1}) of Opals and the Role of Water in these $SiO_2.nH_2O$ Minerals. Fortschrite der Mineralogie 52/1. pp17-51.
10. J.G Olliver, I.J Townsend. (1993) Gemstones in Australia. Australian Gemstone Industry Council, Australian Government Publishing Service, Canberra, Australia. pp3-18.
11. L. C. Barnes, I. J. Townsend, R.S. Robertson, D.C. Scott. (1992) Opal South Australia's Gemstone. Handbook No. 5 Revised edition. Department of Mines and Energy Geological Survey of South Australia.
12. A. A. MacNevin and G. G. Holmes. (1979). Notes on Precious Opal and its Occurrence in NSW. Geological Survey Report GS 1979/268. Geological Survey of NSW. p 64.
13. I. A. Mumme, L. Seibright, R. Ball, On the Origin of Volcanic Opal from Houghlahan's Creek (near Teven). (1975). The Australian Gemmologist. Vol12. No 8. p235.
14. L. D. Brown, A. S. Ray, P. S. Thomas. (2003). ^{29}Si and ^{27}Al NMR Study of Amorphous and Paracrystalline Opals from Australia. Journal of Non-crystalline Solids 332. pp242-248.
15. . R. Phillips, D.T. Griffin. (1981). Optical Mineralogy, the Non Opaque Minerals. W.H Freeman and Company. San Francisco. p326.
16. E. Fritsch, M.Ostrooumov, B. Rondeau, A. Barreau, D. Albertini, A.M. Marie, B. Lasnier, J. Wery. Mexican Gem Opals. Nano- and Micro-structure, Origin of Colour, Comparison with Other Common Opals of Gemmological Significance. (2002). Australian Gemmologist. Vol 21, No. 6. pp 230.
17. P. S. Thomas, P. Šimon, A. Smallwood, A. S. Ray (2007). Estimation of the Diffusion Coefficient of Water Evolved During the Non-isothermal Dehydration of Australian Sedimentary Opal. J. Therm. Anal. Cal. Vol 88 No. 1. pp231-235.
18. A. G. Smallwood, P. S. Thomas, A. S. Ray, P. Šimon (2007). TMA and SEM characterisation of the Thermal Dehydration of Australian Sedimentary Opal. Vol 88 No. 1. pp185-188.
19. A. G. Smallwood. (1999) Chemical and Physical Evaluation of Australian Precious Opal. MSc. Thesis. University of Technology Sydney.
20. A.G. Smallwood.(2003). 35 years on a New Look at Synthetic Opal. Australian Gemmologist. Vol 21. No 11. pp438-447.