Characterisation of Australian Opals

A thesis submitted for
the award of Ph.D.

by

Leslie Dean Brown, BSc. (Mat. Sci.) Hon 1

University of
Technology, Sydney
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STATUTORY DECLARATION

I hereby declare that this submission is my own work and that to the best of my knowledge and belief, it contains no material previously published or written by another person (nor material to which to a certain extent has been excepted for the award of any other degree or diploma of the university or other institute of higher learning), except where due acknowledgment is made.

Leslie Brown

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GLOSSARY OF TERMINOLOGY

Agglomeration	Collect into a mass; accumulate in a disorderly way.
Aggregation	A term used for all the ways in which colloidal particles are linked together. This includes gelling, coagulation and flocculation.
Aluminium silicate	Octahedrally coordinated aluminium within silica.
Aluminosilicate	Tetrahedrally coordinated aluminium within silica.
BCC	Body Centred Cubic stacking sequence.
Coacervate	Primary particles accreting around a nucleus to form a much larger secondary particle.
Coagel	Fully dehydrated precipitate of a sol or gel.
Coagulation	Particles that come together into relatively close-packed clumps as a result of the inability of a colloidal system to maintain its dispersed sate. This is usually an irreversible process.
Coagulum	An aggregate of colloidal particles having a relatively tight, dense structure. A coagulum cannot easily be distinguished from a floc.
Coalesce	The process of eliminating the negative radius of curvature at the point where spheres contact each other (similar to sintering, but at low temperatures).
Co-coagulation	See heterocoagulation.
Colloidal system	A system which contains a dispersed phase, which is finely divided and distributed evenly throughout a medium (the continuous phase). The particle size is just larger than that of a true molecular solution but less than a coarse suspension. Usually it is between 1nm and 1μm.
Common opal	A type of opal that is not associated with precious opal.
α-Cristobalite	A crystalline phase in which the silica tetrahedra of adjacent silicate sheets occur in the 'trans' structural arrangement.
Critical coagulant concentration (c.c.c.)	The specific concentration of coagulant required to initiate rapid coagulation of all colloids in a sol.
Cryptocrystalline	A crystalline substance that contains crystallites which are too small to be observable with the microscope.
CSA	Chemical Shift Anisotropy.
CTE	Coefficient of Thermal Expansion.
Decrepitation	When a mineral, such as opal, "breaks up" (fractures) on heating.

EDX	Energy Dispersive X-Ray Spectroscopy.
Electrical double layer	The variation in electrical potential that is generated at various distances from a charged surface.
EPS/ESR	Electron Paramagnetic Spectroscopy / Electron Spin Resonance.
FCC	Face Centred Cubic stacking sequence.
Floc	Particles linked together by bridges of the flocculating agent that are sufficiently long so that the aggregated structure remains relatively open and voluminous. A floc cannot easily be distinguished from a coagulate.
Flocculation	The process of forming flocs.
FWHM	Full Width of a peak at Half its Maximum height.
Gel	Particles which are linked together in branched chains that fill the whole volume of the original sol so that there is no increase in the concentration of the dispersed phase in any macroscopic region in the medium. A gel can easily be distinguished from a floc or a coagulate.
Gelling	Process of forming a gel.
Geminal silanol	Twin hydroxyls (Q^2 resonance).
HCP	Hexagonal close-packed stacking sequence.
Heterocoagulation	The simultaneous coagulation of two oppositely charged colloids.
Homodisperse	See monodisperse.
HRTEM	High-Resolution Transmission Electron Microscopy.
Hydrophilic	"water loving"
Isodisperse	See monodisperse.
Isoelectric point (IEP)	pH of zero ζ potential, interpreted as the point of zero charge at the shear plane. The IEP is not necessarily the ZPC.
LA-ICPMS	Laser Ablation Inductively-Coupled-Plasma Mass Spectrometry.
LDG	Libyan Desert Glass.
Lyogel	A type of gel where the colloids are sterically but not dynamically separated by layers of liquid.
Macropores	Pores with a diameter greater than 2000Å.
Mesopores	Pores with a diameter between 20 and 2000Å.
Metastable	To exist in a state which is not thermodynamically stable.
Microcrystalline	A crystalline substance in which the crystallites are

	resolvable in the standard optical petrographic microscope.
Micropores	Pores with a diameter less than 20Å.
Monodisperse	A colloidal system containing particles of uniform dimensions.
Monosilicic acid	$Si(OH)_4$
MRJ	Maximally Random Jammed structure; state that minimises disorder among all statistically homogeneous and isotropic jammed structures.
Network colloid	Systems that contain two inter-penetrating networks. Technically speaking, opal-AG is a network colloid.
NMR	Nuclear Magnetic Resonance spectroscopy.
Octahedral aluminium	Aluminium atoms in a six-fold co-ordination. Sometimes this is written as Al^{o} or ^{VI}Al.
Opal-A	Amorphous opal.
Opal-AG	Amorphous opal, with a colloidal microstructure.
Opal-AN	Amorphous opal with a glassy, network-like structure.
Opal-C	Paracrystalline opal with a predominantly cristobalite molecular structure.
Opal-CT	Paracrystalline opal containing both cristobalite and tridymite stacking sequences, but still predominantly amorphous.
Paracrystalline	A term which implies partial ordering in a disordered matrix, while still constituting a continuous network.
Poc	Play of colour.
Polydisperse	A colloidal system that contains particles of various sizes.
Polysilicic acid (oligomers)	SiO_2 polymers with molecular weights up to about 100,000.
Potch	Opal that lacks a play of colour.
Precious opal	Opal that displays a play of colour.
RCP	Random Close-packing; the maximum density that a large, random collection of spheres can attain = 0.64.
RF	Radio Frequency.
RMS	Root Mean Square, a statistical measure of the magnitude of a varying quantity. Also referred to as the quadratic mean.
SANS	Small Angle Neutron Scattering
Sedimentation	Natural process of microscopic solid particles (usually in a fluid phase) falling to the bottom of a container

	due to the force of gravity.
SEM	Scanning Electron Microscopy.
Shear plane	A very thin region just outside the stern layer, where the viscosity effects change rapidly.
Silanol	Si–OH bond
Silica	Silica occurs in a variety of polymorphs, such as: cristobalite, tridymite, chalcedony, amorphous silica, opal and quartz.
Siloxane	Si–O–Si bond
SIMS	Secondary Ion Mass Spectrometry.
Sol	A solid dispersion of small particles in a liquid medium. See "colloidal system".
SSA	Specific Surface Area
Stern layer	A small space separating the ionic atmosphere near an interface, the diffuse double layer, from the steric "wall" of the charged plane just adjacent to the interface. Ions in the stern layer remain with the surface.
Tectosilicate	Fully polymerised (or condensed) silica, where each of the four corners of the silica tetrahedra are connected to other tetrahedra (Silicon in the Q^4 configuration).
Tetrahedral aluminium	Aluminium atoms in a four-fold co-ordination. Sometimes this is written as Al^t or ^{IV}Al.
TGA	Thermogravimetric Analysis.
TMA	Thermomechanical Analysis.
Transition temperature	The temperature at which the opal changes from a positive to a negative thermal expansion coefficient (the point where the thermal expansion coefficient equals zero).
α-Tridymite	A crystalline phase in which the silica tetrahedra of adjacent silicate sheets occur in the 'cis' structural arrangement.
Vicinal silanol	Single hydroxyl (Q^3 resonance).
XAS	X-Ray Absorption Spectroscopy
Xerogel	A gel in which the micelles are in direct contact with each other.
XRD	X-Ray Diffraction.
Zeta (ζ) potential	Potential at the shear plane. Also referred to as the electrokinetic potential.
ZPC	Point of Zero Charge.

ABSTRACT

Australia is the world's largest producer of precious opals, contributing more than $1 billion per annum to the GDP. However, to date little fundamental research has been carried out on banded opals, which are potentially the most valuable of all opal varieties. Opal is also Australia's national gemstone; yet for such an important resource, it is surprising that the mechanisms of opal formation remain in dispute, in particular for banded opals. The focus of this study is to understand the formation of opal by investigating the chemistry and microstructure of banded and non-banded opals. Opals from several regions of Australia (Coober Pedy, Lightning Ridge, Andamooka and Tintenbar), in addition to opals from Mexico, were thus investigated in detail using a range of techniques.

Evaluation of the trace element chemistry of opals was carried out by employing a combination of experimental techniques, including Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS) and Secondary Ion Mass Spectrometry (SIMS). Darker-coloured bands contained significantly higher concentrations of certain transition elements (Ti, V, Co, Ni, Cu, Zn and Y) and rare-earth elements (La, Ce) than the lighter-coloured bands. The concentrations of other elements (Mg, Ca, Al, Fe and Mn) were in most cases found to be similar between bands. Some elements (Ti, Cr, Cu, Zn, Co and Zr) were found to be distributed more heterogeneously than others (Na, Ca, Mg, K, Al and Fe). Based on this evidence, a solution depletion model was proposed to explain the formation of banded opals, involving the charge-neutralisation of silica colloids by highly-charged transition metal cations.

The microstructural characteristics of several Australian opal-AG (amorphous, gel-like opal) specimens were studied using a number of experimental techniques such as porosity measurement, thermomechanical analysis (TMA) and thermogravimetric analysis (TGA). An initial expansion followed by contraction was observed in TMA. The temperature at which this 'transition' occurred ranged from 200 to 400°C and was found to be region dependent. TGA revealed that the temperature range, from 215 to 350°C,

over which the maximum rate of dehydration occurred, was again region dependent, consistent with the TMA data. A dehydroxylation–sintering mechanism was proposed to account for these results. Porosity measurement yielded a greater degree of porosity in the opaque white samples than the transparent ones; the additional voids consequently scatter light internally, rendering the opal opaque.

^{29}Si NMR and ^{27}Al NMR experiments were undertaken to characterise the relative disorder, silanol content and the coordination state of Al within opal-AG and opal-CT (cristobalite-tridymite opal). The comparison of ^{29}Si NMR spectra demonstrated that opal-CT samples contained a higher proportion of both geminal (Q^2) and vicinal silanol groups (Q^3) than opal-AG. This result was attributed to the large internal surface area of opal-CT compared to that of opal-AG. Since Al was found to exist in a tetrahedral coordination within the opal structure, incorporation of Al occurred through substitution of Si during the period of colloidal growth. As the concentration of Al in banded opals was similar, the colloids within each band are considered to have formed at similar times.