Application of a Fickian model of diffusion to the dehydration of graded specimens of a precious Australian sedimentary opal derived from Coober Pedy

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Abstract A model developed for the estimation of the diffusion coefficient based on Fickian diffusion is applied to the dehydration of a Coober Pedy white play of colour (precious) opal using thermogravimetric analysis (TG). The model was originally applied to bulk and powdered opal (opal with no bulk). In this paper the opal was graded prior to TG analysis. The diffusion coefficient was calculated and is reported up to the critical point of water.

Keywords Amorphous silica · Diffusion coefficient · Opal · Dehydration
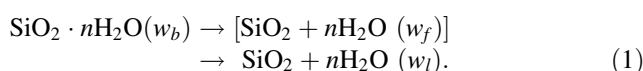
Introduction

Australian sedimentary opal is an amorphous hydrous silica with the general formula $SiO_2 \cdot nH_2O$. Although there is some conjecture in the literature, opal is most likely formed by the diagenisis of inorganic silica through the dissolution of silicate minerals such as feldspar followed by the precipitation of colloidal monodispersed silica spheres (150 to 350 nm in diameter) which sediment into the ordered arrays responsible for the play of colour (POC) that is characteristic of precious opal [1, 2 and references therein].

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The process of opal formation results in relatively high water contents which have been measured in the range 1–21% [3], and for the sedimentary Australian opal, 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]. Although silanol water has been observed by nuclear magnetic resonance [5, 6] and infrared spectroscopy [7], the water in opal is predominantly molecular water trapped in silica cages [7, 8] and, as a consequence, the water is removed at relatively high temperature (200–500 °C in a standard thermogravimetric (TG) analysis experiment at heating rates of 0.25–2 °C/min [4, 8–10]). The temperature at which this water can be removed can be significantly altered by the state of the opal sample under investigation. Higher temperatures of dehydration are observed for relatively large pieces of opal ('lumps' of mm size). Much lower temperatures of dehydration are observed for hand ground powdered specimens of opal [8, 9].

Based on the differences in the dehydration rate of opal in lump and powder forms as measured by TG, a model for the diffusion of water in opal has been developed [9]. The lumps of opal are considered to be 'bulk' specimens. For these bulk specimens, the first step in the dehydration process is considered to be the volatilisation of bound water (either molecular or silanol) to free water. In this process a change of state occurs, but no mass loss is registered by the balance. For mass loss to be registered the free water must first diffuse to the surface of the particle. Once a water molecule has arrived at the surface, the molecule can then be liberated into the atmosphere. During the liberation process, the balance registers a mass loss. Three types of water are, therefore, defined in this model; bound water, w_b, free water, w_f, and liberated water, w_l, with the process of dehydration of bulk specimens of opal being described by Eq. 1:

$$SiO_2 \cdot nH_2O(w_b) \rightarrow [SiO_2 + nH_2O \ (w_f)]$$
$$\rightarrow \ SiO_2 + nH_2O \ (w_l). \tag{1}$$

Hand ground powder specimens are considered to be opal specimens which have no bulk as the path length of diffusion is significantly reduced by the reduction in particle size. Hand grinding the opal does not appear to affect the water content and, hence, the mass loss measured in a TG experiment [4, 8–10]. As the powder specimens are considered to have no bulk, diffusion of water to the surface of the specimen is considered not to contribute to the mechanism of dehydration. Any water loss observed is, therefore, ascribed directly to the removal of bound water from the opal and is instantly registered as mass loss by the TG balance:

$$SiO_2 \cdot nH_2O(w_b) \rightarrow \ SiO_2 + nH_2O \ (w_l). \tag{2}$$
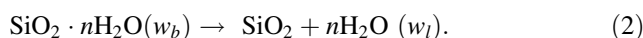
The proportion of bound water in an opal specimen can, therefore, be determined from Eq. 2 and Eq. 1 yields the proportion of liberated water. As the initial amount of water in the bulk opal should be equal to the sum of amounts of bound (w_b), free (w_f) and liberated (w_l) water:

$$w_i = w_b + w_f + w_l \tag{3}$$

the proportion of free water may be determined.

Given that the rate of dehydration of bulk opal is governed by the diffusion of free water to the opal surface prior to liberation, at low heating rates the dehydration of bulk opal may be assumed to conform to steady state diffusion (Fick's 1st law) from infinite plane of the thickness of 2δ yielding Eq. 4 [9]:

$$D = \beta \frac{2\delta^2 \rho dw_l}{Mp \ dT} \tag{4}$$

where D is the diffusion coefficient, β is the heating rate, ρ is the density of silica, M is the molecular mass of water, T is the temperature and p is the vapour pressure of water which based on the relative free volume in Australian opal is assumed to be above the saturation vapour pressure [9, 10].

Experimental

A white POC seam opal specimen derived from Coober Pedy, South Australia was selected for this study as a large volume of relatively homogenous specimen was available. The opal was first fractured into small pieces and then roughly ground by hand using an agate pestle and mortar. The aim of hand grinding was to minimise the energy (and, hence, heat) imparted to the opal during grinding. The ground material was then graded using a small sample sieve stack sizing the opal into fractions with >1.18 (S1),

Table 1 List of gradings, measured peak positions and estimated values of δ for a Coober Pedy opal displaying play of colour

Sieve grading	Sieve size (mm)	DTG peak (°C)	Free water (w_f) peak (°C)	Estimated value of δ (mm)
S1	>1.18	267	233	0.185
S2	1.18–1.14	266	236	0.170
S3	1.14–0.55	271	241	0.155
S4	0.55–0.41	252	239	0.113
S5	0.41–0.38	226	212	0.098
S6	<0.38	190	–	–

1.18 to 1.14 (S2), 1.14 to 0.55 (S3), 0.55 to 0.41 (S4), 0.41 to 0.38 (S5), and <0.38 mm (linear dimension) particle size (Table 1).

TG was carried out on a TA Instruments SDT2960 simultaneous TG-DTA instrument by placing 22–23 mg of graded opal into a platinum crucible and heating at a rate of 1 °C/min to 1,200 °C in an air atmosphere with a purge gas flow rate of 20 mL/min.

Results and discussion

The differential TG (DTG) curves for dehydration of the Coober Pedy white POC opal are shown in Fig. 1 with the peak positions, based on the centre of mass, listed in Table 1. The centre of mass was taken as the measure of the peak position as it is apparent that the curves show two overlapping peaks around 230 and 280 °C which develop as the grading size increases suggesting that the dehydration processes of this POC seam opal changes as the temperature is increased. The change in the process of dehydration is likely to be associated with a change in the bulk structure of the opal. Previously it has been reported that a peak in the expansion curve is observed at approximately 211 °C as the Coober Pedy white POC opal dehydrates [11]. Initially, linear expansion is observed.
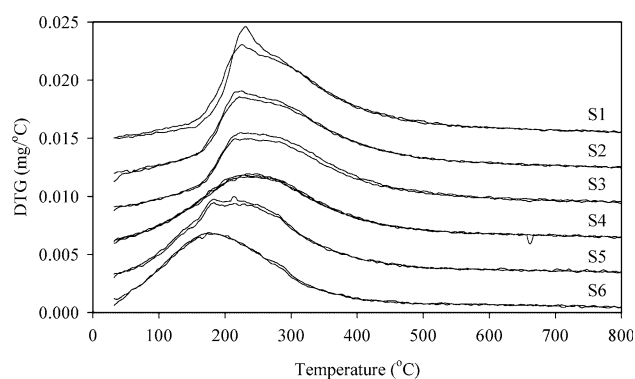

Fig. 1 DTG curves for graded samples of a Coober Pedy opal displaying play of colour

Above 211 °C, however, a significant decrease in the linear dimensions is observed. The contraction was ascribed to the sintering of the opal as well as the removal of silanol water reducing the free volume and, hence, the available pore structure for diffusion. This change in pore structure is likely to be responsible for a change in the ease of diffusion of water through the opal resulting in asymmetry of the DTG peak. Despite the development of two peaks in the DTG data, the general trend is for that of an increase in the dehydration temperature as the grading size is increased up to the S3 grade.

The mass loss determined from the TG measurements was found to be 8.0 ± 0.2%. No relationship between sieve size and mass loss was observed suggesting that the grinding process did not significantly affect the water content of the opal. As some variation in the absolute mass loss was observed between TG measurements, in order to apply the diffusion model to the data, the TG data for the graded specimens of opal were first normalised to the averaged measured water content (7.97%) based on the mass loss at 800 °C. A ten point linear smoothing (equivalent to 2 °C) was also applied to the data in order to reduce the noise developed through further manipulation of the data. The normalised water loss curves are shown in Fig. 2 and are labelled as bound water (w_b). The liberated water (w_l) data were calculated from the bound water data and are also shown in Fig. 2. These data also demonstrate that the rate of dehydration is a function of particle size up to, apparently, the S4 grade. Above this grade, the particle size appears to have little influence on the rate of dehydration as the curves for the S1, S2 and S3 grades all appear to overlap. Based on Eq. 3 and using the S6 grade as the powder sample containing no bulk, the proportion of free water (w_f) was determined for the S1 to S5 grades (Fig. 3). As is the case in the bound water curves, the grading size effect is apparent up to the S4 grade; the curves for the S3 to S1 are observed to overlap.
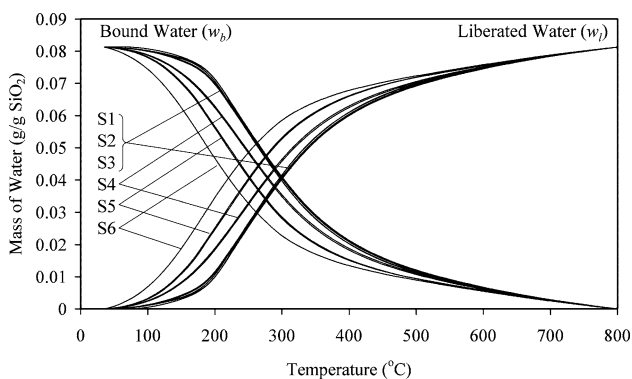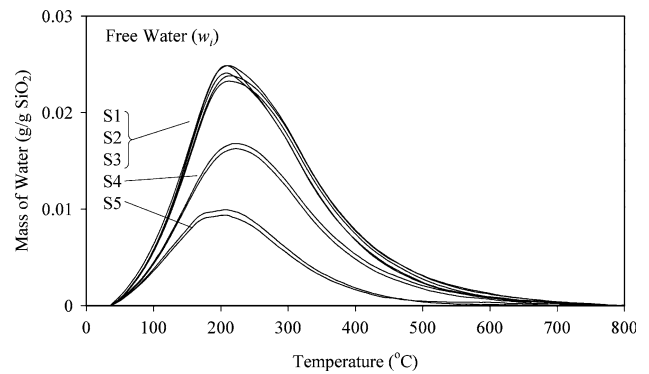

Fig. 3 Free (w_f) water curves for graded samples of the Coober Pedy opal

The diffusion coefficient defined by Eq. 4 was determined for each of the sieve sizes and is plotted as a function of temperature in Fig. 4. In calculating the diffusion coefficient, the value of δ was estimated to be equal to a quarter of the sieve size. The diffusion coefficient is observed to decrease with temperature in each case. A peak is also observed in the S1, S2 and S3 data. The peak position is centred around 210 °C for the S1 and S2 samples and 200 °C for the S3. These temperatures correlate with the peak expansion curve observed at 211 °C in the TMA data [11]. The change in the diffusion coefficient is, therefore, consistent with the densification process that is occurring in the specimen. This is exemplified by the Log(D) versus T plot (Fig. 5) which shows a step in the exponential dependence of the diffusion coefficient. Based on this interpretation, it is now apparent that the shape of the diffusion coefficient temperature curve for the Lightning Ridge specimen studied in Ref [9] is associated with a similar densification process.

The magnitude of the parameter δ was estimated as being equal to the sieve size divided by four. Given that the calculated diffusion coefficient apparently increases with
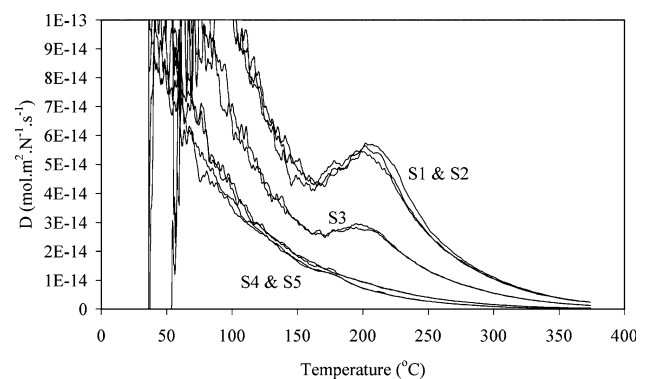

Fig. 2 Bound (w_b) and liberated (w_l) water curves for graded samples of the Coober Pedy opal

Fig. 4 Temperature dependence of the diffusion coefficient using values of δ based on the sieve size divided by four
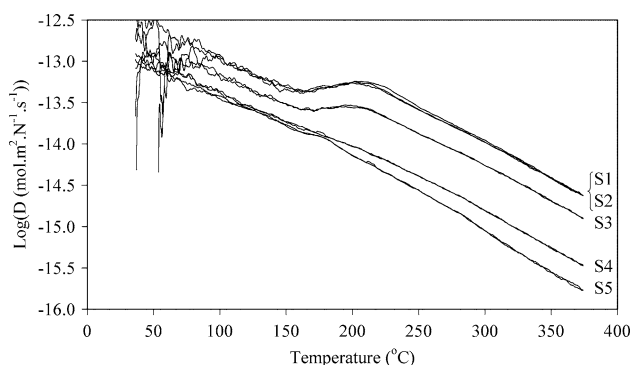
Fig. 5 Temperature dependence of the log of the diffusion coefficient using values of δ based on the sieve size divided by four
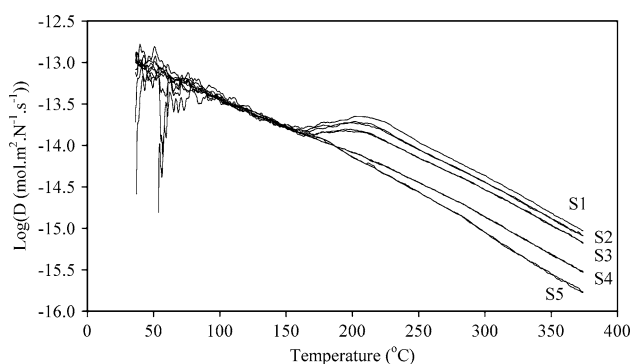

Fig. 6 Temperature dependence of the log of the diffusion coefficient using values of δ estimated to give equivalent values of D below 200 °C

increasing grading size, this estimate of δ must, to some extent, be in error. If the size grading for S5 is taken as the reference, the overestimate of the values of δ have been made for the S1 to S4 grades may be accounted for by reducing the value until overlap of the curves is achieved in the region below 200 °C. Accordingly, the data shown in Fig. 6 is achieved by reducing the magnitude of δ to the values listed in Table 1. Reducing the value of δ also separates the S1 grade from the S2 grade in the high temperature diffusion regime. It should also be noted that, although it is likely that the value of δ is overestimated, a shift in the data may also arise from the fact that the powdered opal, S6, has a finite average particle size and is not infinitely fine as is assumed in the application of Eqs. 1 to 3 in determining the proportion of bound, liberated and free water.

Conclusions

A model based on the steady state diffusion from infinite plane (Fick's 1st law) has been applied to a graded Coober Pedy white play of colour opal. Based on the application of this model two regimes of diffusion with exponential temperature dependences have been identified in the dehydration of the opal. The presence of two regimes correlates with a dehydration model that results in sintering of the opal. A limitation of the model is in the estimation of the characteristic diffusion path length; however, the sensitivity of the method to the particle size suggests that, using the volatilised water as a probe, this method may be a useful method for the characterisation of the morphology of opals or other amorphous substances.

References

1. Iler RK. The chemistry of silica, solubility, polymerisation, colloid and surface properties, and biochemistry. 2nd ed. New York: Wiley; 1979.
2. Thomas PS, Brown LD, Ray AS, Prince KE. A SIMS study of the transition metal element distribution between bands in banded Australian sedimentary opal from the lightning ridge locality. N Jb Miner Abh. 2006;182(2):193–9.
3. Webster R. Gems, their sources descriptions and identification. 3rd ed. London: Butterworths; 2000.
4. Brown LD, Ray AS, Thomas PS, Guerbois JP. Thermal characteristics of Australian sedimentary opals. J Therm Anal Calorim. 2002;68:31–6.
5. Brown LD, Ray AS, Thomas PS. ^{29}Si and ^{27}Al NMR study of amorphous and paracrystalline opals from Australia. J Non-cryst Solids. 2003;332:242–8.
6. Paris M, Fritsch E, Reyes BO. ^{1}H, ^{29}Si and ^{27}Al NMR study of the destabilization process of a paracrystalline opal from Mexico. J Non-cryst Solids. 2007;353:1650–6.
7. Langer K, Flörke OW. Near infrared absorption spectra (4000–9000 cm^{-1}) of opals and the role of water in these $SiO_2.nH_2O$ minerals. Fortschrite der Mineralogie. 1974;52(1):17–51.
8. Smallwood AG, Thomas PS, Ray AS. Thermal characterisation of Australian sedimentary and volcanic precious opal. J Therm Anal Calorim. 2008;92:91–5.
9. Thomas PS, Šimon P, Smallwood AG, Ray AS. Estimation of the diffusion coefficient of water during the non-isothermal dehydration of Australian sedimentary opal. J Therm Anal Calorim. 2007;88:231–5.
10. Wagner W, Pruss A. International equations for the saturation properties of ordinary water substance. Revised according to the international temperature scale of 1990. Addendum to J. Phys. Chem. Ref. Data 16, 893 (1987). J Phys Chem. Reference data. 1993;22:783–7.
11. Smallwood AG, Thomas PS, Ray AS, Šimon P. TMA and SEM characterisation of the thermal dehydration of Australian sedimentary opal. J Therm Anal Calorim. 2007;88:185–8.