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ESTIMATION OF THE DIFFUSION COEFFICIENT OF WATER EVOLVED DURING THE NON-ISOTHERMAL DEHYDRATION OF AUSTRALIAN SEDIMENTARY OPAL

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The dehydration of an opal specimen was investigated by thermogravimetric analysis (TG) in powder and bulk forms. The change in geometry resulted in a significant difference in the temperature range in which dehydration occurred with peak temperatures in the differential TG (DTG) curve for the hand ground opal at 203°C and for the bulk opal at 340°C. This difference was attributed to time taken for diffusion of free water in the bulk opal to the specimen surface prior to evolution as a registered mass loss. A model was proposed to account for the diffusion of water and was used to estimate the diffusion coefficient.

Keywords: *amorphous silica, dehydration, diffusion coefficient, Fickian diffusion, opal, thermogravimetric analysis*

Introduction

Opal, an amorphous hydrous silica with the general formula $SiO_2\cdot nH_2O$, is formed naturally through the diagenisis of inorganic silica. Although the mechanism of opal formation remains the subject of debate, much of the evidence suggests a mechanism of the dissolution of inorganic silica followed by the precipitation of colloidal spheres (100 to 350 nm in diameter) which sediment into the ordered arrays responsible for the play of colour that is characteristic of precious opal [1, 2].

In Australia, the majority of precious opal is derived from sedimentary environments which are located around the Great Artesian Basin stretching over several thousand kilometres from north western Queensland to New South Wales (NSW) and South Australia (SA). Although opal is found over such a range, the physical and chemical properties of opal derived from the Australian sedimentary opal fields are very similar resulting in few distinguishing features and making the differentiation of opals derived from each region by chemical or physical means (other than visual inspection!) difficult. Indeed, to date, only thermal analysis has been successful in differentiating between opals derived from opal fields in SA and NSW [3]. The regional differentiation of the opals characterised in [3] was based on the rate of removal of water suggesting that morphological differences in the opal structure or differences in the water types is responsible for the observed differentiation.

The water contents of opal have been measured in the range 1 to 21% [4], and for the sedimentary Australian opal, the subject of the current paper, between 6 and 10% [3]. 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]. These types of water exist in such a range of energetic states, and with diffusion being a factor limiting the rate of water loss, the identification of these types of water by thermal methods has not been possible. The sensitivity of the thermal analysis to regional differences is, therefore, likely to be due to differences in morphology between samples. In order to apply thermal analysis to the characterisation of the morphology of the opal, the process of water removal from the opal must first be considered. A model has, therefore, been proposed and applied to the characterisation of the water loss measured by thermogravimetric analysis (TG) from a typical specimen of opal sourced from Lightning Ridge in New South Wales.

Theory

The model is based on the removal of water in three states, 'bound', 'free' and 'liberated', from an opal specimen in two different forms, bulk and powdered. The term bound water, defined here, does not refer to the chemical state of the water, just that it is immobilised in the opal specimen in a condensed state and in-

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cludes all four types of water described above. Free water is water in the vapour state and refers to immobilised, or bound, water that has been released from the opal substrate into pores within the opal structure by thermal activation. The free water must then diffuse to the surface to be liberated and, hence, registered as a mass loss. Therefore, in the context of the model, the types of water are defined as; bound water, free water and liberated water following the process of Eq. (1).

$$\text{bound water}\rightarrow\text{free water}\rightarrow\text{liberated (registered) water} \quad (1)$$

The two forms of the specimen described are; a hand ground powder and fractured lumps of opal. The hand ground powder sample is considered to have no bulk and, therefore, diffusion of water to the surface of the specimen does not contribute to the mechanism of dehydration. Given that diffusion does not inhibit water loss in the hand ground specimen, any water loss observed is ascribed directly to the removal of bound water from the opal and is instantly registered as mass loss by the TG balance. As the powder opal contains only bound water, the process of dehydration may be described by Eq. (2).

$$SiO_2{\cdot}nH_2O\text{ (bound)}\rightarrow SiO_2+nH_2O\text{ (liberated)} \quad (2)$$

The lumps of opal are considered to be 'bulk' specimens. The mass loss mechanism is, therefore, a combination of the conversion of bound water into 'free' molecular water followed by diffusion to the surface before the water is liberated and registered as mass loss by the balance:

$$SiO_2{\cdot}nH_2O\text{ (bound)}\rightarrow SiO_2+nH_2O\text{ (free)}\rightarrow SiO_2+nH_2O\text{ (liberated)} \quad (3)$$

Based on these assumptions, the proportion of bound water can be determined and, hence, the delay in mass loss from the bulk specimens is associated solely with diffusion of free water to the surface. In the current model, steady state diffusion is assumed (Fick's 1st law) from infinite plane of the thickness of 2δ.

Expressions for bound, free and liberated water in opal

As the amount of silica during opal dehydration is constant, the mass change or water loss is best expressed as a relative mass fraction, relative to the amount of silica present (i.e. the final mass loss):

$$w=\frac{m}{m_{sil}} \quad (4)$$

where m is the mass of water and m_{sil} is the mass of silica. In TG, residual mass fraction (r) is measured and can be expressed as:

$$r=\frac{m_{sil}+m}{m_{sil}+m_i} \quad (5)$$

where m_i is the initial mass of water contained in the opal which can be expressed in terms of the amount of silica present:

$$r=\frac{1+w}{1+w_i} \quad (6)$$

where w_i is the initial relative mass fraction of water. At the end of experiment, temperature is so high that there is no water in the opal sample, i.e., w=0:

$$r_\infty=\frac{1}{1+w_i} \quad (7)$$

where r_∞ is the residual mass fraction at the end of the experiment. Combination of Eqs (6) and (7) yields:

$$w=\frac{r-r_\infty}{r_\infty} \quad (8)$$

Given that for the powdered sample the water is liberated immediately it becomes free (Eq. (2)), the relative mass fraction of bound water (w_b) can be expressed from the residual mass fraction of the powder opal:

$$w_b=\frac{r_p-r_{p\infty}}{r_{p\infty}} \quad (9)$$

where r_p and $r_{p\infty}$ stand for actual and final residual mass fractions for the powder opal. The relative mass fraction of liberated water can be expressed by rearranging Eq. (5):

$$r=\frac{m_{sil}+m_i-(m_i-m)}{m_{sil}+m_i} \quad (10)$$

The term (m_i–m) in Eq. (10) is the mass of the liberated water. Dividing Eq. (10) by m_{sil} and combining it with Eq. (7) yields:

$$w_l=\frac{1-r}{r_\infty} \quad (11)$$

where w_l is the mass fraction of liberated water. The initial amount of water (w_i) in the bulk opal should be equal to the sum of amounts of bound (w_b), free (w_f) and liberated (w_l) water.

$$w_i=w_b+w_f+w_l \quad (12)$$

The relative mass fraction of free water, w_f, can thus be expressed as:

$$w_f=w_i-w_b-w_l \quad (13)$$

The relative mass fractions of bound, free and liberated water in the bulk opal can, therefore, be calculated from Eqs (9), (11) and (13), respectively.

Expression for water diffusion in opal

For the bulk opal specimen, the bound water is first converted to free water, but in order for the free water to be liberated and registered as a mass loss, the water must first diffuse through the opal to the surface. The rate of diffusion can be described by Fick's 1st law of diffusion:

$$J=\frac{\mathrm{d}n_\mathrm{f}}{S\mathrm{d}t}=-D\frac{\partial p}{\partial x} \tag{14}$$

where n_f is the number of moles of free water, S is the surface area, p is the pressure of water vapour in bulk opal, x is the distance and D is diffusion coefficient. Given the condition of steady state diffusion Eq. (14) can be rearranged to:

$$\frac{\mathrm{d}m_\mathrm{f}}{\mathrm{d}t}=DSM\frac{p}{\delta} \tag{15}$$

where m_f is the mass of free water, M is the molar mass of water and δ is the length of the diffusion path (the diffusion length). Dividing Eq. (15) by the mass of silica present and rearranging in terms of the diffusion coefficient yields:

$$D=\frac{m_\mathrm{sil}\delta}{SMp}\frac{\mathrm{d}w_\mathrm{f}}{\mathrm{d}t} \tag{16}$$

The mass of silica can be defined in terms of the diffusion length:

$$m_\mathrm{sil}=2\delta S\rho \tag{17}$$

where ρ is the density of silica. Given the linear relationship between temperature and time

$$T=T_0+\beta t \tag{18}$$

where T is the sample temperature, T_0 is the starting temperature and β is the heating rate and combining Eqs (16)–(18), the diffusion coefficient can be related to the non-isothermal dehydration data:

$$D=\beta\frac{2\delta^2\rho}{Mp}\frac{\mathrm{d}w_\mathrm{f}}{\mathrm{d}T} \tag{19}$$

Pressure of water vapour

In order to estimate the diffusion coefficient, the pressure of the water vapour in the opal specimen needs to be determined. Using the relative densities of Australian sedimentary opal (2.1 g cm^{-3}) and crystalline quartz (2.66 g cm^{-3}) a rudimentary estimation of the free volume in the opal may be used to estimate the pressure exerted by the free water, w_f present. As the estimated pressures were calculated to be significantly greater than the saturation vapour pressure, it was concluded that the atmosphere in the opal bulk was at saturation and, hence, the pressure exerted was determined from [5]:

$$\ln(p/p_\mathrm{c})=(a_1\tau+a_2\tau^{1.5}+a_3\tau^3+a_4\tau^{3.5}+a_5\tau^4+a_6\tau^{7.5})(T_\mathrm{c}/T) \tag{20}$$

where T is absolute temperature and subscript c indicates the values at the critical point and $\tau=1-T/T_\mathrm{c}$. The values for substitution in the equation are: T_c=647.096 K, p_c=22064 kPa, a_1=–7.85951783, a_2=1.84408259, a_3=–11.7866497, a_4=22.6807411, a_5=–15.9618719, a_6=1.80122502. Pressures are calculated in kPa.

Experimental

A sun flash crystal opal specimen, soured from Lightning Ridge in New South Wales, Australia, was selected for this study as a large volume of relatively homogenous specimen was available and will be retained as a standard specimen. The opal was first fractured into small pieces. Pieces weighing approximately 15 mg (approximately 2×3×1 mm in dimension) were collected as 'bulk' specimens. The remaining material was hand ground 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 powder derived from this hand grinding process provided the specimen for thermal analysis, nominally, containing no bulk.

Thermal analysis was carried out on a TA Instruments SDT 2960 simultaneous TG-DTA instrument by placing either 1 lump or approximately 15 mg of powder into a platinum crucible before heating at a rate of 0.25°C min^{-1} to 1200°C in an air atmosphere with a purge gas flow rate of 20 mL min^{-1}.

Results and discussion

The TG and DTG curves for the powdered and bulk specimens of the opal are shown in Figs 1 and 2, respectively. The TG data show single step mass loss over the range studied. The total mass loss for the bulk samples was consistently observed to be greater (0.1 to 0.5 mass%) than for the powdered samples. This difference may be due to the grinding process which is likely to impart some heat to the specimen resulting in water loss (although the creation of surface may result in water gain) or may be due to the loss of molecular pore water liberated during particle size reduction. The

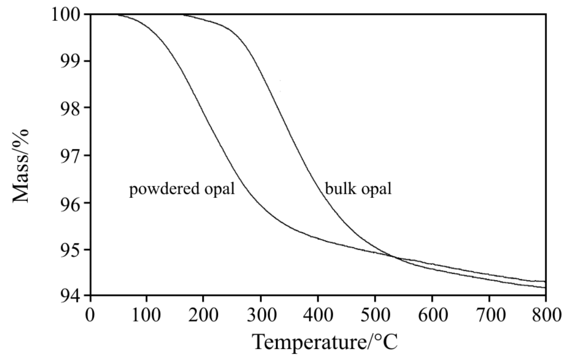

Fig. 1 TG curves for the powdered and bulk samples of opal heated at a rate of 0.25°C min^{-1} in a flowing air atmosphere

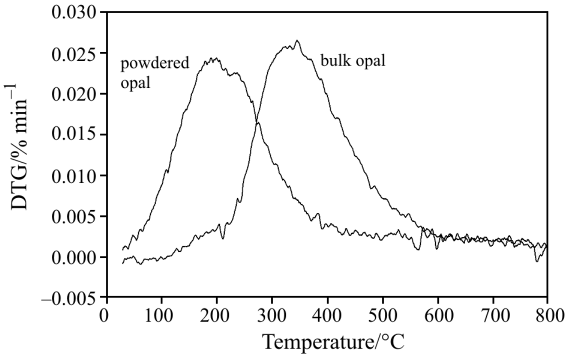

Fig. 2 DTG curves for the powdered and bulk samples of opal heated at a rate of 0.25°C min^{-1} in a flowing air atmosphere

data in Fig. 1 shows a 0.1 mass% difference between the powdered and bulk samples. For the purpose of the model, the excess water in the bulk sample prior to dehydration is counted as free water.

The effect of grinding the opal to a powder is also reflected in the positions of the DTG peaks which are at 203 and 340°C for the powder and bulk specimens, respectively. The delay in mass loss in the bulk specimen, based on the proposed model, is attributed to the diffusion step (Eq. (3)). Other factors may also be at work in the inhibition of the dehydration reaction such as the reversibility of Eq. (3). These factors have not been considered here, but will be considered in the further development of the model.

Based on the model, the mass of bound, liberated and free water were determined from Eqs (9), (11) and (13) and are plotted in Fig. 3. The maximum in the free water peak is at 276°C which, as might be expected, is close to the mean of the peak positions of the DTG peaks of the powder and bulk specimens. From the calculated proportion of free water, w_f, present in the silica, the diffusion coefficient can be determined from Eq. (19) using Eq. (20) to estimate the pressure. The value of the diffusion length, δ, was estimated as 0.001 m in the calculation of the diffusion coefficient.

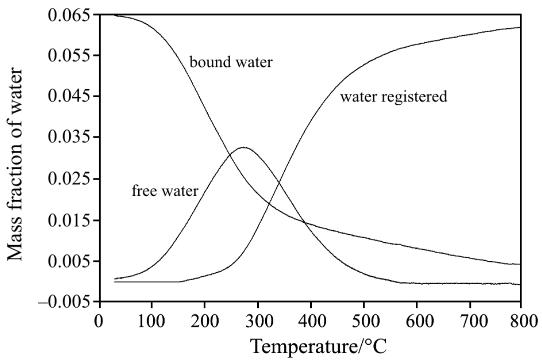

Fig. 3 Plot of the calculated values of bound, w_b, liberated, w_l, and free, w_f, water as a function of temperature

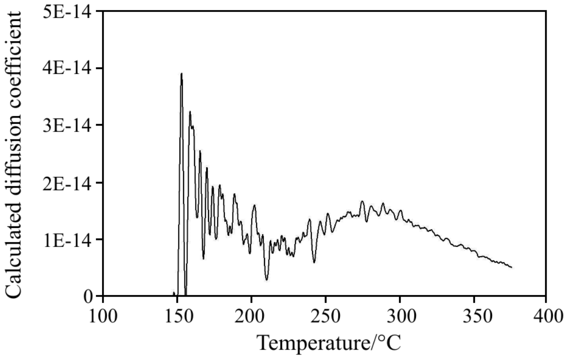

Fig. 4 Plot of the calculated diffusion coefficient as a function of temperature

The calculated diffusion coefficient was observed to be fairly independent of the temperature with an estimated value of $1\cdot10^{-14}$ mol m N^{-1} min^{-1} (Fig. 4). This is unusual, as the diffusion coefficient is typically expected to be an exponential function of temperature. The temperature independence is indicative of a changing system where diffusion is inhibited by contraction of the available pore volume. TMA analysis of the coefficient of expansion of opal has shown that opal typically expands by 0.1 to 0.3% before contraction (circa 0.5 to 0.8% up to 600°C) is observed [3]. A peak temperature is observed in the TMA expansion curve which, for Lightning Ridge opal, has been observed at approximately 300°C. These variations in dimensions affect the available pore volume for diffusion and, hence, influence the magnitude of the diffusion coefficient resulting in the apparent observation of a temperature independent diffusion coefficient.

In determining the diffusion coefficient, the pore pressure in the opal was estimated using the assumption that water vapour saturation was achieved. It is likely that saturation has been reached and can be justified by estimating the pressures required for expansion during initial heating. If it is assumed that the expansion is predominantly due to the pressure developed by the evolved water and given that the modulus of opal is approximately 50 GPa (determined from indentation measurements on opal), the internal stresses required to produce such an expansion are of the order of 50 MPa which is significantly higher than the saturation vapour pressures estimated from Eq. (20). As the saturation pressure is not great enough to cause the expansion, it is likely that the expansion is due to the hydraulic action of the condensed phase suggesting that saturation pressure is a good approximation for the vapour pressure in opal. A consequence of the effect of hydraulic action of the condensed phase is that if the rate of heating is too high (of the order of 2 to 5°C $\min^{-1}$), the opal specimen will spontaneously fracture due to the high stresses developed.

Conclusions

Based on the relative rate of dehydration of powdered and bulk opal specimens, a model has been developed and applied to the dehydration of bulk opal. Although a number of assumptions have been made in the development of the model, the model represents a first step in the understanding of the processes involved in the dehydration of opal and helps to explain the rate of dehydration of opal through a diffusion limiting process. In order to further test the viability of the assumptions made, the model will be tested through the characterisation of graded specimens of opal samples with differing particle size ranges and, thence, applied to the characterisation of a range of opal specimens. As the dehydration of opal is known to be sensitive to the origin of opal and as thermal methods are known to be sensitive to morphology, the analysis proposed will aid the further understanding of the character of opal and will aid the further understanding of the mechanisms of formation as well as giving an insight into the potential problems such as cracking and crazing of precious opal gem stones.

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