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THERMAL CHARACTERISTICS OF AUSTRALIAN SEDIMENTARY OPALS

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Abstract

Naturally occurring opals from three different regions in Australia were studied for their thermal characteristics. All the opals showed initial expansion followed by contraction in thermomechanical analysis (TMA) although the temperature at which the change from expansion to contraction occurred depended on their provenance. Thermogravimetric analysis (TG) revealed different rates and temperatures of dehydration for these opals. A general correlation between the temperature at which there was a zero thermal expansion and that of the maximum rate of dehydration was observed. A dehydration–sintering mechanism is proposed with the effect of sintering being more pronounced following total dehydration.

Keywords: amorphous silica, opal, TG, TMA

Introduction

Opals are naturally occurring hydrous silica with a chemical formula $SiO_2 \cdot nH_2O$. The water content ranges from 1 to 21% and is generally expressed as a percentage by mass of the opal [1]. Opals exhibit a range of morphologies from well-ordered crystalline to highly disordered, amorphous structures. They are commonly classified into three groups based on crystallinity and mineralogy – opal-A, opal-C and opal-CT [2]. Opal-A is regarded as having a highly disordered, amorphous structure; opal-C, a well-ordered, α-cristobalite type and opal-CT a disordered, α-cristobalite/α-tridymite type.

Australia is the largest producer of gem quality opal in the world, and opal is ‘Australia’s National Gemstone’. A major concern for the Australian opal industry is that a small proportion (less than 1%) of the naturally occurring opal is known to undergo cracking or crazing after cutting and polishing, which renders it worthless as a gem [3]. The mechanism of the cracking is not clear and is complicated by opal’s varied provenance. There are two distinct geological environments associated with opal formation. In Australia, commercial precious opals are formed almost exclusively in sedimentary environments in a number of localities including Coober Pedy and

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Andamooka in South Australia, and Lightning Ridge in New South Wales. While each individual opal field has its own characteristics, they all have similar stratigraphic sequences of sandstones, siltstones and claystones. The sedimentary opals typically belong to the amorphous opal-A group. This paper presents information on thermal characteristics of sedimentary opals from three of the principle opal fields in Australia – Coober Pedy, Andamooka and Lightning Ridge. The thermal analytical methods used for their characterisation are TG and TMA.

Experimental

The opals studied in this project were from three different Australian regions: Andamooka and Coober Pedy in South Australia, and Lightning Ridge in New South Wales. A total of 19 specimens were analysed, 8 of which were from Coober Pedy, 4 from Lightning Ridge and 7 from Andamooka.

The experiments were carried out using a TA Instruments TMA 2940 Thermomechanical Analyser and using the instrument as a dilatometer. The heating rate was set at 1.5°C per minute. For the opals from Coober Pedy, eight specimens were tested to check the precision of the experimental method. This was done by testing two specimens cut from the same opal sample (or piece), and then comparing those results to those acquired from other opal pieces.

Thermogravimetric experiments were performed with a TA Instruments 2960 Simultaneous DTA-TG. Where possible, the proportions of TG specimens were kept similar to those of the TMA specimens. In most cases, the opal cut-offs from TMA sample preparation were used for TG specimens. This ensured that the opal used for the TG was from the same piece as that used for the TMA.

Results and discussion

TMA

For all specimens, TMA curves showed a characteristic appearance. The opals initially expanded up to a certain temperature, beyond which they contracted. The temperature at which the opals changed from a positive to negative thermal expansion coefficient will be referred to in this paper as the transition temperature (Fig. 1).

These transitions occurred at various temperatures depending on the type of opal (Table 1). For instance, the Andamooka opals showed the highest transition temperature followed by the Lightning Ridge specimens with the Coober Pedy specimens displaying the lowest transition temperature. In general, the Coober Pedy opals showed a relatively sharp transition from expansion to contraction making the estimation of their transition temperature relatively simple in contrast with the Andamooka opals, which exhibited gradual transitions from expansion to contraction. (One of the Andamooka specimens showed a second transition from contraction to expansion.) These results are generally consistent with those reported elsewhere [2, 4–6]. For the Coober Pedy samples, the transition temperature was estimated to be

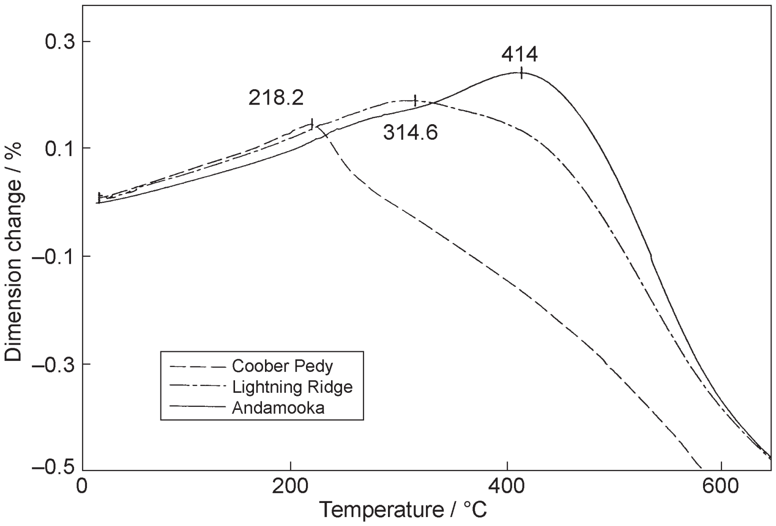

Fig. 1 Thermal expansion curves of three sedimentary opals

between ±5°C of the value stated. For all others, the transition temperature was estimated to be within ±10°C of the reported value.

Table 1 Transition temperatures and thermal expansion coefficients of various opals

Type of opal	TMA transition temperature/°C	TMA coefficient of thermal expansion/μm m°C^{-1}
Coober Pedy	212	6.22
	213	6.42
	218	6.87
	205	7.05
	222	5.75
	217	6.55
	195	7.95
	211	5.78
Lightning Ridge	303	6.76
	315	7.38
	347	6.44
	284	6.66
Andamooka	406	9.59
	377	4.83
	404	6.24
	407	6.22
	385	6.24
	414	5.83
	402	3.92

The total amount of expansion up until the transition temperature also varied depending on the opals' origins. Specimens exhibiting high transition temperatures expanded more than those showing low transition temperatures. The *total* amount of contraction at the completion of the experiment also displayed variation; generally it was less in the Andamooka samples and more in the Coober Pedy samples. (These effects may be due to the variable proportion of water in the different types of opal.)

The thermal expansion coefficient was measured from the lowest temperature possible up to the point that the slope became noticeably non-linear or until a step was encountered. The thermal expansion coefficient values showed considerable variation even among specimens from the same region and therefore, cannot be used to distinguish between opals from different regions.

The cooling curves were typically featureless with no detectable expansion-contraction transitions. Once heated, all specimens changed in appearance to an opaque white colour and lost almost all of their play of colour.

For all opal samples analysed in this study, a change from positive to negative thermal expansion coefficient was observed. The reason for this characteristic is unclear. A possible explanation for this behaviour is presented below. It is envisaged that there are two competing processes operating – initially, the opals show expansion because the water that is trapped within the mesopores expands during heating (in addition to the hydroxylated water that is bound to the silica network). Once all the water has been expelled, the expansion ceases and the opals behave like pure silica. These 'anhydrous' opals will have a tendency to collapse or shrink because of their semiporous void structure. Upon further heating, the structure becomes more pliable, and it will progressively contract. The degree of contraction will depend on experimental factors including temperature and time, and on intrinsic factors such as size, shape and packing of spheres in individual opals. This theory adequately explains why the cooling curve in all cases is almost a straight line, because once all the water has been lost, what remains is a pure silica product with an inherently low thermal expansion coefficient.

Essentially, above the transition temperature, solid state sintering is a likely event. While the initial stage of neck formation between individual spheres in the opal structure might have reached completion when it originally formed, a second stage of sintering in the solid state is conceivable during the heating cycle of the thermal analysis.

TG

The temperature at which a maximum rate of water loss was observed, varied over a broad range between 215 and 350°C, depending on the location of the opals (Table 2). Other workers [7, 8], report that opals generally lose water between 200 and 500°C. The Coober Pedy specimens were found to lose water over a narrower temperature range than the other opals. The water content was calculated from the amount of silica residue remaining after heating the opal to 1200°C. This value was subtracted from the initial mass of the specimen to determine the total water.

Table 2 Temperatures of dehydroxylation (maximum rate) and water contents of various opals

Type of Opal	TG temperature of maximum dehydroxylation/°C	Water content/%
Coober Pedy	215	7.82
	233	>5.5
	222	7.95
Lightning Ridge	325	7.19
	322	7.24
	317	9.05
	334	>4.5
Andamooka	344	6.64
	343	7.12
	352	6.64
	356	6.40

Due to the broad nature of the peaks and the microcracking of the opal specimens, it was often difficult to pinpoint the exact peak. The error in determining the exact position of the peaks where the maximum rate of water loss occurred, was estimated to be ±4°C for the Coober Pedy samples and ±15°C for all other opal samples.

The Andamooka opals showed the highest temperature at which there was a maximum rate of dehydroxylation; they were followed by those from Lightning Ridge with Coober Pedy specimens displaying the lowest dehydroxylation temperature. The Coober Pedy opals displayed greater dehydroxylation and at lower temperatures than the other types; furthermore, they exhibited a considerably faster rate of dehydroxylation. The opal from Coober Pedy correlates well with an amorphous Coober Pedy opal from reference [8]; the rate of water loss being greatest at around 230°C and most of the water having been lost by 500°C.

There seemed to be a general correlation between the transition temperature and the temperature of maximum dehydroxylation. The higher the transition temperature, the higher the temperature of maximum dehydroxylation seemed to be. This agrees with the assumption that at the transition temperature there is a contention between dehydroxylation and sintering. The accuracy of this relationship is affected by the variation in sample size and shape between TG and TMA. This is because a smaller specimen (as used in the TG) has a higher surface area to volume ratio, which makes the exodus of water somewhat easier. In addition, the samples used in the TG were not of uniform shape, they were rectangular prisms but occasionally small ‘chips’, while in TMA they were a regular rectangular prism shape.

It is possible that once the detailed chemistry of these opals is known, the noted difference in their thermal behaviour will be better understood. In this context, it is worth mentioning that Laser Ablation ICP-MS Analyses are being carried out to reveal the details of the minor and trace elements of these opals. A paper containing these chemical details will be reported elsewhere.

Conclusions

TMA revealed that the thermal expansion coefficient before the transition temperature could not be related to the location or type of the opal. This was partly because a dependable method of measuring the thermal expansion coefficients could not be found, and also because sample variance was quite high in some samples of opal.

The transition temperature of the opal was found to be dependent on the type of opal investigated, and its locality. They are as follows: Coober Pedy 212±8.5°C; Lightning Ridge 312±26°C; and Andamooka 400±13°C. The transition temperature itself was explained in terms of dehydroxylation and sintering. The differences observed in the transition temperatures are most likely influenced by the opal's porosity; the silica sphere size distribution; the ordering of the silica sphere array; and the water content. The transition temperature is most likely due to the combined effect of water loss and microstructural change, since these are the only attributes that alter once the opal has been heated. The various types of opals also exhibited different contraction rates, as well as total percentage of contraction and expansion.

TG revealed that the temperature of maximum rate of dehydroxylation was also related to the type of opal investigated. The magnitude of the dehydroxylation rate was also found to be dependent on the type of opal; types with a lower dehydroxylation temperature having higher overall rates. There was also a general correlation between the transition temperature and temperature of maximum dehydroxylation.

The ability for these results to correlate with precious opal of gem quality is not a certainty, because they are microstructurally different. The size of the silica spheres is much larger (up to 350 nm) for gem quality opals, and these spheres are much more ordered in their packing than lower quality precious opals.

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