

Moganite and water content as a function of age in agate: an XRD and thermogravimetric study

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Abstract: The crystallite size, moganite, molecular surface water and internal water content of agates from volcanic host rocks ranging in age from 38 → 1 100 Ma have been measured. Molecular water was found to be independent of age but maturation produced a general decrease in both the moganite and internal water. Water is shown to be involved on the transformation of moganite into chalcedony and this change is responsible for an internal growth in chalcedony crystallites. The maximum content of moganite found in agate was 14 % but after ~ 410 Ma it is only present in trace amounts. Moganite has not been found in agates from any pre Silurian hosts. After the moganite transformation, the internal water in agate has been found to be constant at ~ 0.4 %. The change in composition of internal water is proposed as a method for approximate dating of agates that are from hosts younger than 410 Ma.

Changes in the degree of crystallinity of agates from 10 host rocks < 412 Ma have been determined. The growth in the crystallites from 8 regions suggests that agate genesis would be typically penecontemporaneous with the formation of the host rock. Evidence is offered for hydrothermal activity from a late second volcanic event to account for the formation of agates in the other 2 regions. It is proposed that hydrothermal solutions are the source of the silica in all cases of agate genesis in an igneous environment. With minimal moganite in hosts ≥ 412 Ma, crystallites from these older regions are shown to have achieved their maximum size. Furthermore, measurement of crystallite size, density, internal water and moganite can provide evidence of a later palaeoactivity.

Key-words: agate, moganite, water, age, genesis.

Introduction

Moganite was first found within the ignimbrite lava flows of the Mogan formation on Gran Canaria (Flörke *et al.*, 1976). The mineral is formed as a late in-filling of cavities and cooling cracks. Although moganite has only been observed in a near pure form from Gran Canaria, it has been detected as a common intergrowth within the microcrystalline quartz minerals. An extensive search was made for moganite in 150 examples of chert, chalcedony and agate. Apart from Arkansas novaculite, moganite was found in all the examined samples with chert and agate each registering up to 40 % and 20 % by weight respectively (Heaney & Post, 1992).

The crystal structure of moganite has been described as the alternate stacking of layers of left and right handed quartz on the unit-cell scale: Brazil law twinning (Miehe & Graetsch, 1992). Since 1976, detailed descriptions of the physical properties and structure of moganite have been given (Graetsch *et al.*, 1987; Miehe & Graetsch, 1992; Graetsch *et al.*, 1994; Petrovic *et al.*, 1996; Götze *et al.*, 1998; Heaney & Post, 2001). However, the mineral was not

acknowledged as an independent polymorph of silica until 1999 (IMA No 99-035).

Microcrystalline quartz is usually classified by its petrographic characteristics. Chert generally shows a granular microstructure while chalcedony is the fibrous variety of α -quartz; banded chalcedony is known as agate. Analyses of the non-volatile impurities in agate (Flörke *et al.*, 1982) and moganite (Miehe & Graetsch, 1992) are often < 1 %; both minerals are nearly pure silica with water the major impurity. The total water content (H₂O and silanol groups) is ~ 1.5 % in chalcedony and in moganite 2-3 % (Miehe & Graetsch, 1992) and ~ 5 % (Petrovic *et al.*, 1996). Recent studies have shown that the presence of water can result in the depletion of moganite from microcrystalline silica minerals: the change has been recognised as a moganite → quartz transformation (Heaney & Post, 1992). Heaney (1995) observed the scarcity of moganite in altered rocks older than 150 Ma. New Zealand sinters, 20 000 to 200 000 y old, contain up to 13 % moganite but moganite could not be detected in the older Tertiary sinters (Rodgers & Cressey, 2001).

A recent study of agate investigated changes in crystallite size, density and used scanning electron microscopy techniques (SEM) to measure the size of surface globulites.

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Table 1. Agate samples used for: a- XRD, b-TGA.

Region	Site and sample number
1. Chihuahua, Mexico.	Laguna: 3ab, 5ab, 7ab, 9ab, 10ab, 11ab, 12ab, 15b.
2. Khur, Iran.	Khur: 2b, 7b, 10a, 17a, 23ab, 24ab, 33ab, 49b, 50ab, 54ab.
3. BTVP, Scotland.	Mull: 1ab, 2b, 5ab, 11ab. Rhum: 12b, 15ab, 17ab, 19ab.
4. Rio do Sul, Brazil.	Soledado mines: 9ab, 20ab, 21ab, 25ab, 26ab, 37ab, 53ab, 58b, 59b.
5. Lune Valley, Tasmania Australia.	Lune: 1ab, 2ab, 3ab, 4ab, 5ab, 6b, 7ab.
6. Agate Creek, Queensland Australia.	Agate Creek: 1ab, 2b, 4ab, 5ab, 6b, 7ab, 9a, 12a, 14b, 15b, 17b.
7. Rotliegend deposits, Germany.	Thuringia Forest: 5ab, 9ab, 10ab, 11a, 14ab, Idar Q 1b, 3a, Saxony: 1b, 2b, 3b. Juchem Q 1b.
8. Derbyshire, England.	Waterswallows Quarry: 1a, 2a, 3a, 4a, 5a, 8a.
9. Northumbria, England	Cheviots: 1b, 3a, 4b, 5a, 12a, 18a, 19ab, 22ab, 24b, 25b, 26b, 30b.
10. East Midland Valley, Scotland.	Ethiebeaton Q 11b, 17ab, 13b, 37b. Ardownie Q 1b, 7a. Barras Q 3b, 4ab, 5b, 11a. Montrose 4b, 6b, 9a, 10b. Carphin Tay 71a, Scurdie Ness 1a. Luthrie 4b, Glenfarg 1b, 3b, 7b Strathern 1ab. Brown Carrick 2ab, 5ab, 7a. Maidens 1ab.
11. West Midland Valley, Scotland.	Dunure 3b, 14b, 20b. Carrick Hills 1ab. Burn Anne 1a.
12. Northern Territory Australia.	Antrim basalts: 1a, 2a, 3a, 4a, 5a, 6a.
13. Maydena, Tasmania Australia.	1ab, 2ab, 3ab, 4ab, 5ab, 7ab.
14. Lake Superior, USA.	Lincoln, Nebraska: 1ab, 3ab, 4ab, 6ab, 8b. Minneapolis-St. Paul. 11b, 13ab, 14 ab. Grey Cloud Island, Minnesota: 15b.

It was shown that the crystallites developed with age and this resulted in an increase in the diameter of surface globulites. This development caused an increase in density (Moxon, 2002).

This present study was established to try and find the cause of the changes in the crystallite size in agate. In addition, changes in moganite and water content in agate were measured with the intention that any variation was to be linked to the age of the host rock.

Experimental Methods

Agate samples

The agates used in this study were entirely of the wall lining type and were formed in gas vesicles of igneous hosts (Table 1). X-ray diffraction (XRD) was used to determine the moganite content (at least two samples/region) and the degree of crystallinity (at least six samples/region). A minimum of eight samples/region was also used for thermogravimetric analysis (TGA).

X-ray diffraction

The diffractometer used for this study has an in-house design, and for a detailed description the reader is referred to Locherer *et al.* (1996). The diffractometer, in reflection geometry, uses $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54 \text{ \AA}$). X-rays are produced by a fixed-anode generator, proceeding through a slit onto a focusing monochromator. A further pair of slits defines the incident beam profile that is typically of $0.2 \times 3 \text{ mm}^2$. Samples are mounted on a silicon wafer in order to minimize the background signal. The angle of inci-

dence was fixed at 8° and the sample was continuously rotated in its own plane in order to improve particle statistics.

The detector is an INEL position-sensitive detector (CPS120) covering 120° in 2θ simultaneously. A delay line that enables the electronics to determine the exact location of the incident photon connects all 8192 sections of the detector. This is achieved by measuring the difference in arrival time between the two ends of the detector leading to an angular resolution of approximately 0.015° . Such a device allows for rapid data collection with a high signal-to-noise ratio. It is important to point out that curved detectors do have some inherent problems, such as linearity (Evain *et al.*, 1993). Data were thus scaled using an external standard (silicon + quartz mixture).

For this XRD study, agate samples were prepared in three different ways: i) As ground powders using a ball mill grinder and, after a SEM examination, these powders were found to be in the $4\text{-}10 \mu\text{m}$ range. ii) Powders were crushed and sieved at $< 52 \mu\text{m}$. iii) Small agate slabs were cut and polished prior to examination. The grinding process contributed to the formation of amorphous silica shown by the increase of the background signal (Fig. 1). This change was not evident in either the crushed samples or the slabs and both produced identical diffraction patterns. Nevertheless, and in order to avoid any preferred orientation within the slabs, the quantification of the moganite content was obtained from ball mill powders ground to $4\text{-}10 \mu\text{m}$.

Thermogravimetric analysis

Three previous studies have collectively investigated chalcedony dehydration over the 20 to 1400°C temperature range; these investigations produced similar TGA dehydration curves of agate and chalcedony (Graetsch *et al.*, 1985;

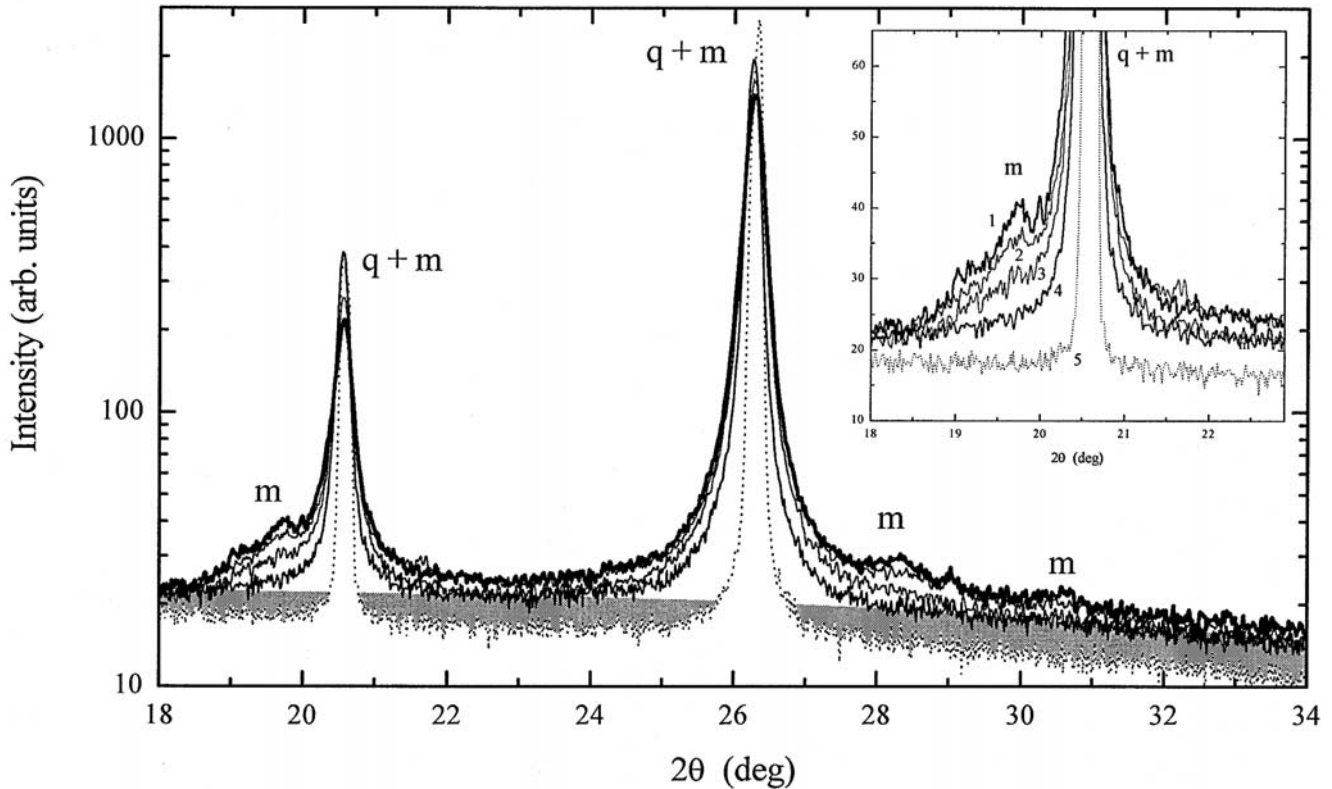


Fig. 1. Diffractograms from various samples with moganite and quartz peaks labelled as *m* and *q* respectively. The diffractograms shown, and enlarged in the inset for clarity, are: 1) Hunstanton flint (12-17 %, Heaney & Post (1992)), 2) Brazil (14 %), 3) Mexico (8 %), 4) Lake Superior (0 %) and 5) macrocrystalline quartz. Note the decrease in the moganite peaks, and the simultaneous increase in the quartz peaks. The shaded background is due to the presence of amorphous silica. The dotted line corresponds to a macrocrystalline quartz sample.

Petrovic *et al.*, 1996; Yamagishi *et al.*, 1997). Yamagishi *et al.*, (1997) also used infrared spectroscopy (IR) to study the dehydration process. Initially, there was the loss of loosely bound water and their TGA plots show that this is complete at $\sim 120^{\circ}\text{C}$ with no further water loss up to $\sim 200^{\circ}\text{C}$. Tightly bound water and some silanol water (SiOH) is slowly removed between 200 and $\sim 350^{\circ}\text{C}$; this is followed by a rapid rate of water loss up to $\sim 600^{\circ}\text{C}$. Dehydration was completed with the loss of the remaining silanol water at temperatures up to $\sim 1000^{\circ}\text{C}$.

In this study, agate powders were examined by XRD to establish the purity of the samples. Only silica pure agates were used in the dehydration experiments. The agate samples were crushed and sieved to $< 52\ \mu\text{m}$. Here, free molecular water was found by heating the powders in a box oven at 170°C for 4 hours. Total water was determined by furnace heating at 1200°C for 2 hours. These heating times were sufficient to produce a constant mass loss. At least eight agates were selected from each region and each run was carried out in triplicate. Post 170°C dehydration will be referred to as internal water loss throughout this paper.

Sample suitability

It has been previously suggested that the alteration in microtexture in agate from fibrous chalcedony to the occasional formation of granular quartz in the geode centre is due to a change from polymeric to monomeric silicic acid

and an increase in free water (Moxon, 1991; Heaney, 1993). Brazilian agates show the greatest range of size of all agates and two smaller samples were selected to investigate the variation of water from area to area and band to band within the same agate using near infrared spectroscopy (nIR). The first agate consisted of a lower third with weak white horizontal banding and the upper two thirds were of the wall lining type. The sample was examined using nIR at 10 positions along the 48 mm height of the agate, with special focus on the H_2O combination absorption mode at $5210\ \text{cm}^{-1}$, and the broad combination mode due to OH and SiOH at $4500\ \text{cm}^{-1}$. The 10 spectra were found to be identical. A second agate was totally of the wall lining type and 5 bands were investigated along the 40 mm height. Again, it was not possible to differentiate between bands using the $4500\ \text{cm}^{-1}$ mode but there was a 5 % decrease in free water from the outer half to the inner half of the agate.

One large Brazilian agate was selected to investigate the variation of water within a single agate using TGA. This 12 cm diameter round agate had repetitive circular banding. The outer edge to centre of this agate conveniently produced four differently coloured circular areas of banding. The agate was cut in 4 directions: N \rightarrow S and W \rightarrow E. The 4 slab sections were cut further into 4 blocks of the same coloured banding type in order to compare water within groups of similar bands along the 4 directions. The 16 blocks of agate were separately crushed and samples

Table 2. Variation in water loss (wt %) and moganite content (wt %) with the age of the host rock.

Agate & age of host / Ma (sample no)	Molecular water lost at 170 °C *	Total water lost at 1200 °C *	Moganite content
Mexico / 38 (5)	0.24	1.18	11
Mexico / 38 (10)	0.57	1.29	11
Iran / 50 (2)	0.15	1.22	9
Iran / 50 (23)	0.51	1.35	12
Rhum /60 (17)	0.20	1.00	9
Mull / 60 (1)	0.20	0.85	12
Brazil / 133 (20)	0.20	1.19	13
Brazil / 133 (26)	0.25	1.38	14
Lune, Tasmania / 145			
7 samples tested for water	0.16(10)	0.75(09)	
6 samples tested for moganite			0
Agate Cr' Aust' / 275 (1)	0.15	0.83	5
Agate Cr', Aust' / 275 (5)	0.33	0.92	11
Germany / 285 (Thuring' 9)	0.48	0.99	5
Germany / 285 (Juchem 1)	0.41	0.68	1
Derbyshire, England. / 311	NA	NA ^{*1}	
6 samples tested for moganite			0-2 ^{*2}
North', England. / 391 (19)	0.29	0.65	5
North', England. / 391 (22)	0.30	0.91	7
West MV, Scotland / 412			
8 samples tested for water	0.21(04)	0.58(18)	
6 samples tested for moganite			0
East MV, Scotland / 412			
16 samples tested for water	0.22(11)	0.68(32)	
8 samples tested for moganite			0-2 ^{*2}
North' Terr', Australia / 513	NA	NA ^{*1}	
6 samples tested for moganite			0
Maydena, Tasmania / 540			
6 samples tested for water	0.22(08)	NA ^{*3}	
6 samples tested for moganite			0
Lake S' USA / 1100			
8 samples tested for water	0.21(10)	0.66(27)	
6 samples tested for moganite			0

* A larger number of agates from hosts older than 412 Ma were examined for moganite. The bulk water data shows the mean (st. dev.) for the given number of samples.
^{*1} Water content experiments were not carried out on these agates. The samples were limited in size.
^{*2} Only one sample from each of these regions showed any moganite content.
^{*3} All Maydena agates contain additional calcite that invalidates any water data at 1200°C.

removed to find the free and total water by heating at 170°C and 1200°C; each run was carried out in triplicate. The free water showed no particular trend and the 16 blocks produced a mean free water content of 0.24(4)%. However the internal water showed a decrease as the centre was approached. The outer 8 blocks (~40% of the agate) produced a mean internal water of 0.92(8)% while the inner 8 blocks contained a mean internal water content of 0.75(11)%. This is contrary to expectation. If the occasional growth of macrocrystalline quartz at the centre of the agate is due to the changing conditions of polymeric to monomeric silicic acid, then the water content should increase as the centre of the agate is approached (Moxon, 1991; Heaney, 1993). Further work is underway to investigate this trend.

Water differences within a single agate could be significant with larger agates. However, all agates used, apart from a few found in Scotland and Brazil, were smaller than 6 cm. For the present study, over 90% of the agates were from whole or half nodules and the rest were fractured samples but with outer edges. A small proportion of the agates had macrocrystalline quartz centres. In all cases, ~8 g was

removed from the outer third of the agate and crushed. This material was used for TGA and all XRD examination.

Results

X-ray diffraction

Figure 1 shows an interval of the diffraction pattern obtained in one flint, three agate specimens and one macrocrystalline quartz: moganite reflections are labelled as *m*, and the quartz reflections as *q*. As the age of the specimen increases the intensity of the moganite peaks was found to decrease in agate. As previously mentioned, the diffraction pattern also showed the presence of some amorphous silica formed during the grinding process. This is evident when comparing agate patterns with the one obtained from the macrocrystalline quartz.

For comparison two flint specimens were also used for this study. Nodular flint occurs in Western European chalk formed during the Upper Cretaceous Period. Heaney & Post (1992) investigated the moganite content of flint from

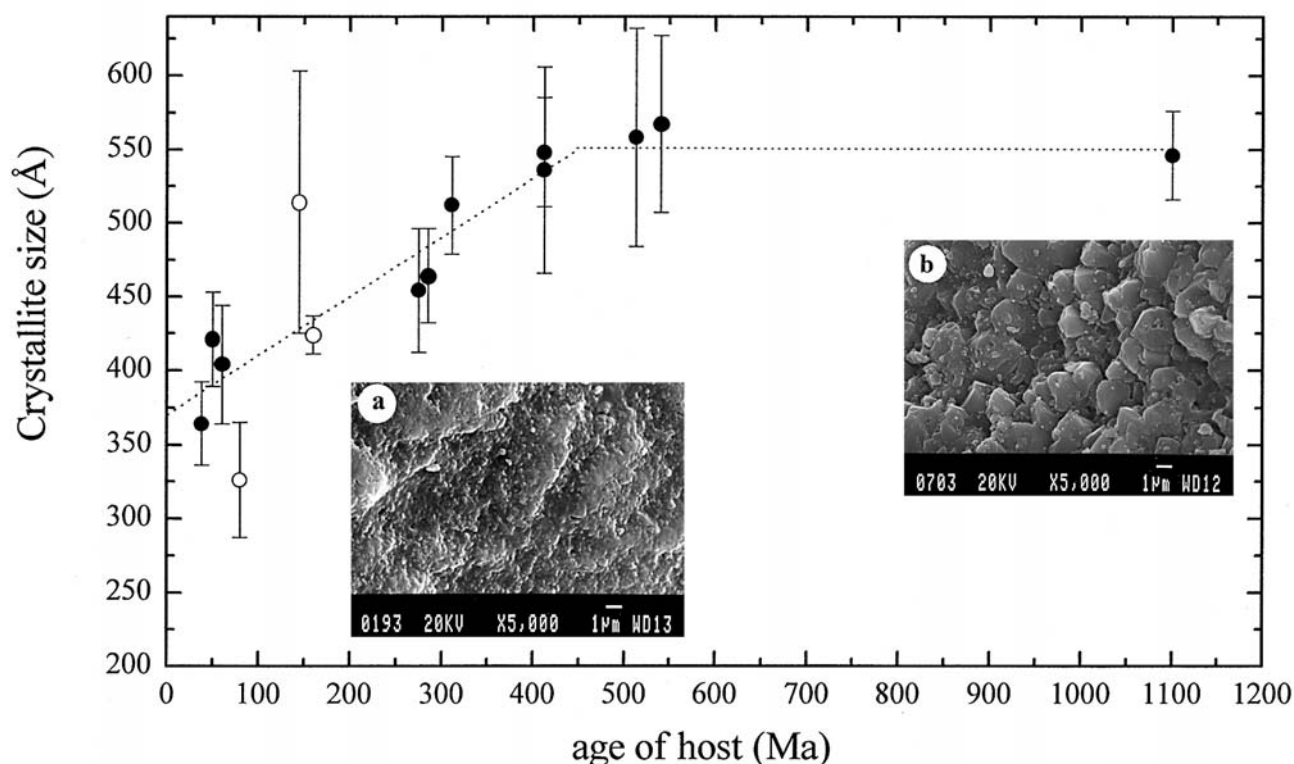


Fig. 2. Growth of crystallites in agate. The micrographs show the effect of the growth on the globulites: a) in young agates (38 Ma) and b) old agates (1100 Ma). (Age of host rock / Ma) 1. Mexico (38), 2. Iran (50), 3. BTVP (60), 4. Brazil (133), 5. Lune, Australia (145), 6. Agate Creek, Australia (275), 7. Germany (285), 8. Derbyshire, England (311), 9. Northumbria, England (391), 10. East M V, Scotland (412), 11. West M V, Scotland (412), 12. Northern Territory, Australia, (513), 13. Maydena, Australia (540), 14. Lake Superior, USA (1100). The solid and open circles are the mean of at least 6 agates for that region. Open circles representing Brazil and Northumbria have been adjusted to show the predicted age of deposition (see text). Error bars show the \pm one standard deviation for that region.

several European countries. They found that the percentage of moganite was approximately constant between 13-17%. In this study, two English flints from Hunstanton, Norfolk and White Nothe, Dorset were selected for purposes of evaluation. From Fig. 1, a qualitative comparison shows that all the agates considered in this study contain less than the moganite content present in flints.

In order to quantify the moganite content in a series of agate samples (described in Table 2), the corresponding diffractograms were systematically analysed using the program Fullprof for Rietveld refinement (Rodríguez-Carvajal, 1990). Data up to 100° in 2θ were included in the refinement. Structural parameters at room temperature were taken for moganite and quartz from Heaney & Post (2001) and Le Page & Donnay (1976) respectively. Refined parameters included scale factor, sample displacement, background and a Gaussian component for size effects and a Lorentzian component for isotropic strain effects. Parameters defining the peak shape were kept constant for all the samples, and equal to those obtained from the external standard.

Rietveld refinement showed poor sensitivity to the presence of moganite in our samples due to the low moganite content. This refinement is further complicated by the peak broadening due to varying crystallite size, and the similarity between the moganite and the quartz structures. The final $\chi^2 = M/(N_{\text{obs}} - N_{\text{ref}})$ of the refinement, with $M = \sum w(I_{\text{obs}} - I_{\text{cal}})^2$ and, using only the quartz phase, was

for the 14 moganite containing samples below 1.5 (w = the standard deviation, N_{obs} = the total number of points used, N_{ref} = the number of refined parameters). The improvement in the final χ^2 was insignificant when the moganite phase was also included. Hunstanton and White Nothe flints confirmed that the moganite content calculated in this way appeared to be greatly underestimated at $< 10\%$.

An alternative method was chosen for quantification of the moganite content. The moganite doublet (011)/(200) (at $\sim 20^\circ$ in 2θ) is the strongest moganite peak that only partially overlaps with neighbouring quartz peaks (Heaney & Post, 2001). The interval between $17-23^\circ$ in 2θ was thus fitted by means of two Lorentzian functions and a constant background, with the moganite content being estimated in each of the agate specimens from the ratio: peak area (moganite)/peak area (total) (Table 2). This method is potentially less quantitative, as it does not take into account possible preferential orientation effects between the moganite and the quartz grains. However, the linear absorption coefficient for both crystalline phases is very similar due to the similarity in chemical composition and structure. Moreover, although quartz and moganite are known to intergrow *via* twin planes, this is not likely to lead to texture effects as twin domains are much smaller than powder grains. Therefore, we consider that the present method, although semi-quantitative, is sufficiently valid to be used as a calibration tool in the case of samples with low

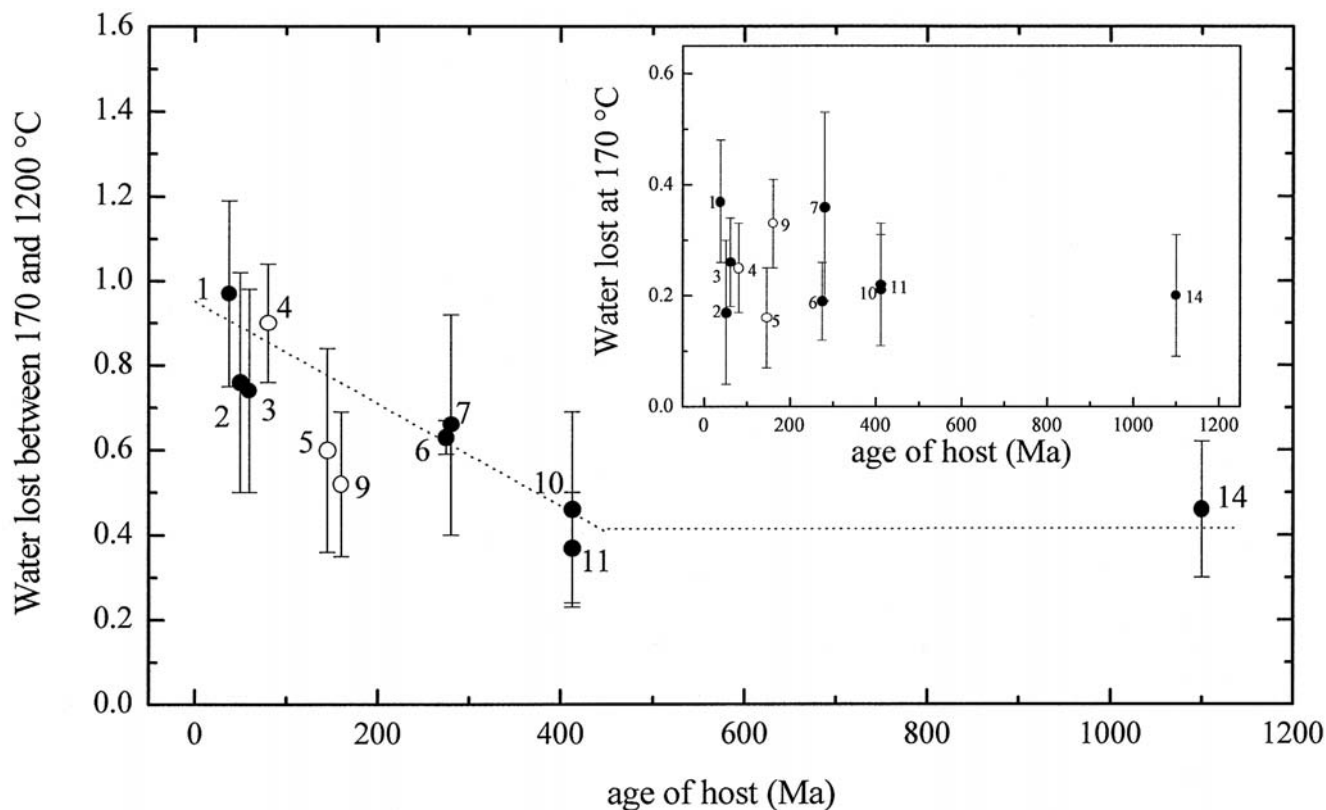


Fig. 3. Water as a function of age. The solid and open circles are the mean of at least 8 agates for that region. Open circles representing Brazil and Northumbria have been adjusted to show the predicted age of deposition (see text). Error bars for both plots show the \pm one standard deviation for that region. Numbers correspond to those given in Table 1.

moganite content. The error in moganite quantification was estimated to be $\pm 2\%$. The imposition of all diffractograms over the 18 to $23^\circ 2\theta$ range shows either identical moganite patterns or allows differentiation as shown with the sample diffractograms of the insert in Fig. 1.

Early work in this study showed that agates formed in the 38 to 133 Ma time scale had the highest moganite content and low moganite was found in agates from hosts greater than 133 to 285 Ma. A larger number of agates were examined for moganite from hosts over 300 Ma in order to establish whether moganite could be found in any agates from these older hosts.

Following a previous work, the crystallite size of a series of agates was also determined, see Fig. 2. For details of the method, data collection and analysis the reader is referred to Moxon (2002). The mean full-width at half maximum (FWHM) of diffraction maxima within the $15^\circ < 2\theta < 65^\circ$ range was converted into a mean particle size (\AA), based upon the Scherrer equation, for a total of 86 samples.

Thermogravimetry

Several studies have investigated and clarified the nature of water in chalcedony using IR and TGA techniques. Molecular water from the surface and near surface positions is lost by heating up to 200°C ; this water loss has varied from $\sim 0.6\%$ with Brazilian agates (Graetsch *et al.*, 1985) to 0.15% in a Japanese agate (Yamagishi *et al.*, 1997);

these studies used a limited number of agates. In the present work, 104 agates from around the world were heated to 170°C and produced a mean molecular water value of $0.25(13)\%$ with a range from 0.06 to 0.57% (Fig. 3). The mean molecular water was found to be independent of age.

Tightly bound water is lost at temperatures $> 350^\circ\text{C}$. Further heating results in more dehydration due to the loss of water from SiOH at structural defects and water loss from close SiOH groups. A final dehydration of surface SiOH continues up to 1000°C (Yamagishi *et al.*, 1997). In this study, the same 104 agates were heated at 1200°C and produced a variable total water content ranging from 0.23 to 1.78% ; the internal water decreases with increasing age. Changes in internal water as a function of age are shown in Fig. 3.

Discussion

Wall lining agates were shown to have been formed around the same time of the supporting host rock (Moxon, 2002). Reference to the age of the agate is regarded as synonymous with the age of the agate host throughout the discussion.

Amorphous silica in agate

During the course of this work, ball mill grinding was found to produce an amorphous coating on the crystallites (see Fig. 1). The production of amorphous silica has a

Table 3. Variation of agate crystallite size with the age of the host rock.

Region (no of samples Analysed) / collector	Mean particle size (st dev) (Å)	Host rock	Age (Ma)	Age* ¹ - reference
Chihuahua, Mexico (7) / BC.	364 (30)	Basaltic andesite	38	*
Khur, Iran. (7) / MN.	421 (34)	Andesite	50	*
British Tertiary Volcanic Province, Scotland* ¹ (6) / NC, BT, RL.	404 (43)	Mugearite	60	*
Rio Grande do Sul Brazil. (6) / * ²	326 (42)	Basalt	133	*
Lune, Tasmania (6) / J Ri	514 (98)	Basalt	145	Tidwell <i>et al.</i> (1987)
Agate Creek, Australia (6) / AMS, BL.	454 (47)	Andesite	275* ³	*
Rotliegend Deposits Germany.(6) / GH.	464 (35)	Rhyolite	285	*
Derbyshire, England. (6) / TM.	512 (36)	Dolerite	311	*
Northumbria, England. (6) / TM.	424 (14)	Basalt	391	*
West Midland Valley, Scotland. * ⁴ (6) / TM, JR.	536 (37)	Basalt	412	*
East Midland Valley, Scotland. * ⁴ (6) / TM, BL, BW.	548 (77)	Basalt	412	*
Northern Terr', Austr' (6) / J Ri	558 (81)	Basalt	513	Hanley & Wingate (2000)
Maydena, Tasmania (6) / J Ri	567 (65)	Basalt	540* ⁵	
Lake Superior, USA. (6) / BC, SW, TH	546 (32)	Basalt	1100	*

* References are given in Moxon (2002).
¹ Unless stated otherwise, radiometric dated ages of the host rock have been used
² The Brazilian agates were purchased from the Brazilian agate importing company of Gunther Bohrer in Idar-Oberstein, Germany
³ Agates from Agate Creek, Australia are from a trapped andesite that is between fossil dated shales with an age of 260 and 290 Ma. A mean value for the agate host has been used.
⁴ The agate hosts in the Western and Eastern Midland Valley, Scotland are from different lava flows some 190 km apart. These hosts have been treated as two separate regions.
⁵ Tasmanian Geological Survey, Maydena, Sheet 4626 lists the basalt agate host as Cambrian. The mid point has been used: 540 Ma

bearing on recent comments by Moxon (2002). Here, the diffuse signal caused by amorphous silica over the 15 to 33° 2θ range was shown to decrease with the increasing age of the agate. It is suggested that the amorphous silica content increases as the surface area of the globulites increases. Since younger agates have the smallest globulites, a greater proportion of amorphous silica would be produced in these specimens. A similar trend was observed in this study, see Fig. 1, although the effect was less pronounced.

Water in agate

Agate that has been previously dehydrated at low temperatures will readily re-hydrate with molecular water at room temperature over a 24 hr period (Graetsch *et al.*, 1985). It is not surprising, given the ease with which water can be lost and regained in agate, that molecular water in agate should be able to make a full adjustment to a position of water equilibrium over the geological time scale. Fig. 3 shows that there is no age link with the molecular water: the mean molecular water value of Iranian agate (50 Ma) being comparable with molecular water in Lake Superior

agate (1 100 Ma). Therefore, the concentration of molecular water is independent of age and the environment.

Later stage dehydration, > 170 to 1200°C, results in the removal of the remaining molecular water that is hydrogen bonded to silanol groups together with pore water. In addition, all silanol groups are eventually removed by a condensation reaction. The water lost over this temperature range decreases with increasing age and produces the regression line with agates from hosts ≤ 412 Ma: mean internal water = -1.1×10^{-3} age (Ma) + 0.95 (Fig. 3). There was a strong negative correlation found between internal water and age: $r_{67} = -0.60$, $p < 0.01$. Agates from Brazil, Northumbria, Lune and all agates older than 412 Ma are excluded; this is discussed later. The independence of molecular water with age demonstrates that it is the internal water that is involved in the moganite transformation. The mean internal water for the Lune and Brazil agate regions produce results suggesting values respectively older and younger ages than would be predicted and values for these agates have been ignored. This point will be discussed later.

In this study, 104 agate samples have shown that the mean internal water is 76 % of the total water that ranges

from 1.78 % to 0.23 % . This change from high to low internal water during ageing shows that some of the internal water must leave the agate amygdale, presumably as molecular water, after completion of any moganite → chalcedony transformation.

Moganite in agate

Gíslason *et al.* (1997) showed that moganite had a greater solubility than quartz: 44 and 6 mg/kg of silica respectively at 25°C and 1 bar. This increased solubility of moganite was used to account for the lack of moganite in rocks from non-arid environments older than 100 Ma. In this present study, all the ≤ 133 Ma agate hosts have a moganite content of ~ 9-14 %. The moganite content in the Permian (275, 285 Ma) agates of Australia and Germany has, apart from one sample at 11 %, decreased with age to ~ 5-7 %. However, moganite in trace amounts ~ 2 % has been detected in only 1 of 14 agates from the Midland Valley, Scotland (412 Ma). When the moganite content is less than 5 %, then the moganite peaks are too weak to be fully resolved from the tails of the quartz peaks. This renders the quantification of moganite at low concentrations difficult. Moganite has not been found in any pre Silurian agates: Northern Territory Australia (513 Ma), Maydena, Tasmania (Cambrian), and Lake Superior, USA (1 100 Ma) (Table 2). After the completion of the moganite transformation, the internal water in agate is constant at ~ 0.44 (20) % (Fig. 3).

Crystallite growth in agate

A recent study proposed a relationship between crystallite size and age of the host rock: the increasing crystallite size caused agate shrinkage that was demonstrated by an increase in density with age. SEM evidence was used to show that the size of the chalcedony surface globulites was also age related. The globulite size ranged from 0.2 µm with the youngest agates (38 Ma) to ~ 2 µm with the oldest agates (≥ 412 Ma). On the basis of similar crystallite sizes in agates from the Midland Valley, Scotland (412 Ma) and Lake Superior (1 100 Ma), it was proposed that growth probably ceased after ~ 412 Ma (Moxon, 2002). This present study has extended the previous work of Moxon 2002 by allowing for further comments on three points.

1) Figure 2 shows a strong correlation between the age of the host and the crystallite size for 8 of 10 regions from hosts ≤ 412 Ma. The plot is for the mean of at least 6 samples/region and produces the regression line: mean crystallite size (Å) = 0.39 age (Ma) + 373 ($r = 0.95$ or 0.79 for the mean crystallite size or the 58 values respectively). This high correlation for these 8 regions suggests a penecontemporaneous deposition of agate and the host rock.

One standard deviation for individual regions varies from the mean of each region between ± 3 to ± 19 %. In 7 of the 14 agate regions the standard deviation as a % of the mean was < ± 10 %. In general, the wider the collection area, then the greater is the spread of the crystallite size from the mean value. This is shown with the 412 Ma agate hosts from the West and East Midland Valley, Scotland. The

WMV agates (± 7 % deviation from the mean) are only to be found in Ayrshire whereas the EMV agates (± 14 % deviation from the mean) are from several counties and cover an area approximately 4 times larger. Conversely, the agates from Lake Superior (± 6 % deviation from the mean) have been obtained from 3 sources 600 km apart. The largest deviation from the mean of ± 19 % was with the heated Lune agates and is discussed later.

2) The agates from Brazil (133 Ma host) and Northumbria (391 Ma host) are outliers with a lower crystallinity than expected from their respective ages. The possibility that the agates were formed by later hydrothermal activity is discussed next.

The region of the Rio do Sul, Brazil has the world's largest and most productive deposit of agate. The agate basalt hosts are highly altered and the agates are found in streams and fields (Macpherson, 1989). The host rock is part of the massive Paraná Continental Flood Basalt system formed during the Early Cretaceous Period. The host basalt has been dated at 133 ± 1 Ma and lava analysis from the upper and lower flows show essentially the same date. It has been proposed that the complete flow was synchronous and spanned, at the most, 1 Ma (Renne *et al.*, 1992).

Innocent *et al.* (1997) have demonstrated a later deposition of secondary minerals in the 133 Ma Paraná basalts. They determined the ages for the vesicular deposition of celadonite using Rb/Sr isotopes and concluded that the celadonite could be the result of one prolonged hydrothermal event lasting from 107 to 80 Ma. Alternatively, they propose that the hydrothermal activity could be diachronous with the older event lasting ~ 10 Ma (from 110 to 100 Ma) and a second activity lasting 85 to 80 Ma. A second study investigated the formation of amethyst geodes in the Rio do Sul region. Some geodes were agate rimmed and it was demonstrated that amethyst formation was the result of a late low temperature infill some 40 to 60 Ma after the Paraná basalt host formation. This study used evidence from REE, O and Sr isotopes found in the amethyst (Gilg *et al.*, 2002).

The data found in this study would also support the view that the Rio do Sul agates were formed as the result of a late deposition. The present study has found that the moganite content of Brazilian agate is ~ 14 % and a mean internal water content of 1.1(1) %. This high moganite content is comparable with that of the youngest agate host: 38 Ma Mexico (11 %). The internal water also closely matches that of the 38 Ma Mexican agates. The mean crystallite size of Brazilian and Mexican agate was found in this study to be 326 (42), 364 (30) Å respectively. The mean respective densities have been found to be 2.582 (10), 2.576 (11) g/cm³ (Moxon, 2002). Overall, this data suggests an agate formation much later than the 133 Ma of the host lava.

Northumbrian agate (391 Ma host) would also appear to be the result of later activity. One agate sample from the East and West Midland Valley regions contained ~ 2 % moganite but the remaining 13 samples had 0 % moganite and yet were formed only 20 Ma earlier than the nearby Northumbrian agates. Agates that are 80 Ma younger (Derbyshire 311 Ma host) contain, apart from one sample 0 % moganite. Northumbrian agates have ~ 6 % moganite

and a low mean crystallite size of 424 (14) Å. This is evidence that the agates formed much later than the host.

In 1970, BP discovered a new pre-Cretaceous volcanic province while drilling the North Sea Forties oil field some 150 km off Aberdeen, Scotland. The age of the province has been estimated from the Bathonian to Bajocian sediments at 160 to 174 Ma (Fall *et al.*, 1982). A measure of the wide scale volcanic activity during the Jurassic Period is shown by the altered volcanic material found in Bathonian sediments of Eastern England (Bradshaw, 1975) and Southern England (Jeans *et al.*, 1977).

We propose that the hydrothermal events from the Jurassic volcanic activity in the North Sea could be responsible for the Northumbrian agates. A shift of data from the 391 Ma Northumbrian host to a mid point of 160-174 Ma results in an excellent fit on the regression line (Fig. 2). A similar shift of the Brazilian data from the 133 Ma host to the 80 Ma as proposed by Innocent *et al.* (1997) and Gilg *et al.* (2002) produces a closer fit for the Brazilian data (Fig. 2).

3) Agates from 5 regions formed at and after the Devonian Period (412 Ma) have a similar mean crystallite size ~ 550 Å. This demonstrates that the growth of the crystallites has ceased at ~ 412 Ma. As this cessation also coincides with the near total loss of moganite, it supports the view that the crystallite growth is due to the conversion of moganite into α -quartz. While the crystallites are developing, the internal water shows a decrease of a mean value from 0.97(27) % (Mexico, 38 Ma) to 0.66(27) % (Germany, 275 Ma). After growth has ceased at 412 Ma, the internal water is approximately constant: mean value 0.44(20) %.

Agates as palaeoindicators

The Lune agate host basalt is ~ 4 km inland from Ida Bay in southern Tasmania. The area is known as the Lune River and is famous for its preserved silicified ferns. The agate host basalt has not been radiodated but fossils have been found interbedded with and just beneath the basalt. The fossil genera and species suggest Late Jurassic or more likely Early Cretaceous: 160 to 130 Ma (Tidwell *et al.*, 1987). The physical properties of the agates from this region suggest an age of at least 400 Ma. Seven Lune agates were examined using XRD and they were all found to be free from moganite. Although the molecular water is not age dependent, the Lune agates do have the lowest percentage of mean molecular water found in this study.

The internal water content of the individual Lune agates shows the greatest regional diversity and produces a weighting towards the older group: more than twice their chronological age. The mean density of six Lune agates was found to be 2.617(8) g/cm³ and the mean crystallite size of these agates was 514 (98) Å. These values compare with the 1 100 Ma Lake Superior agates that had a mean density of 2.619(6) g/cm³ and a mean crystallite size of 546 (33) Å. Sharples & Klootwijk (1981) carried out an investigation of the Ida Bay limestones and, using a conodont colour indicator, estimated that the limestones had been heated to temperatures < 100°C over a period of

~ 10 Ma. The source of the heat had been previously recognised in other rocks as the geothermal heatflow from the initial rift forming processes preceding the formation of the Tasmanian Sea during the Late Cretaceous Period. Any extended heating of this nature would result in an increasing crystallinity of the agates within their basalt host. It is proposed that these Lune agates have retained an imprint of extended heating demonstrated by the advanced crystallinity, increased density, zero moganite, low molecular and low internal water.

Conclusion

Internal water and moganite in wall lining agate show a general decrease in concentration with increasing age; the internal water is involved in the transformation of moganite → chalcedony. The slow maturation process in agate is shown by the survival of moganite, to a mean ~ 7 %, in the Permian agates of Germany and Agate Creek, Australia. Moganite has only been found in trace amounts (~ 2 %) in 2 of 48 agates older than 311 Ma (Derbyshire).

Free water was found to be independent of age in all 11 agate regions studied, but the internal water was shown to decrease with time. Given the geological time scale, internal water becomes sufficiently mobile to leave the defective sites to allow for further re-crystallization of chalcedony. This offers an explanation for the growth of surface globulites. The approximate constancy of free water and the decrease in internal water with age shows that some of this internal water has been converted to free water and eventually becomes lost. This crystallite growth and banding development ceases when all the moganite has been transformed. After the cessation of growth, the internal water is approximately constant with a mean at 0.44(20) %.

Provided there is an awareness for the late entry of silica, the growth of the chalcedony crystallites can allow a possible identification of agate or a host rock that is younger than ~ 412 Ma. Agates from 2 out of 10 of the regions that are ≤ 412 Ma are formed many millions of years after the host. Late agate formation must be limited to those regions where there has been a further volcanic event followed by hydrothermal activity. The silica source for agate has been an enigma for over two hundred years. Propositions have suggested that the silica could be due to immiscible silica drops within the magma, hydrothermal activity, weathering of the host rock and the direct deposition of silica gel. As only hydrothermal activity can account for this separate late formation of Brazilian and Northumbrian agate, it is suggested that hydrothermal events are the silica source in all cases of agate genesis in an igneous environment.

Although the understanding of the microstructure of chalcedony has increased dramatically over the last 30 years, the in situ study of agate or chalcedony as a secondary mineral within igneous hosts has received only passing attention. This work demonstrates that agate can play a role as an indicator of geological events. A determination of moganite, internal water, crystallite size and

density in wall lining agates from agate hosts younger than ≤ 412 Ma can serve to identify ancient geoactivity.

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