

Optical Features, Microstructure and Microanalysis of Botswana Agates

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Abstract

In Botswana agates are found in the north-eastern region of the Central District in the basalt from the 180 Ma Karoo volcanic rocks. Predominantly they are wall-lining agates but some vein agates can also be found. There is another form of microcrystalline quartz with green streaks of impurity, locally known as green-moss agate or gorgonzola, found in the same area. Both the wall-lining agates and the gorgonzola are coated with a green-clay which is easily eroded on weathering. In this paper the optical features of polished Botswana agates and gorgonzola are presented, and their microstructure is studied using a scanning electron microscope. From the microstructure it is revealed that gorgonzola is not an agate, as it is commonly known, but it is microcrystalline quartz. Compositions of the green-earth coating on the agates and the green impurity in gorgonzola are determined from Energy Dispersive Spectrum (EDS) analysis. Both the green-earth coating on agates and the green impurity in gorgonzola are characterized by x-ray diffraction (XRD), and both are found to be a loosely bound clay mineral, Celadonite-1M, aluminian.

Introduction

Agates are microcrystalline quartz mineral which have a fibrous structure when viewed under a polarizing microscope (Moxon 1996:1-10; Webster 1994:236-239; Woodward 1987:26-27). Sectioned agates display a variety of banded colour patterns of varying translucency. Except for the opposite halves of a sectioned agate, no two agates have an identical pattern (Macpherson 1989:3-5). Because of their relative scarcity, colours, unique patterns, and beauty in general, agates are regarded as semiprecious gem stones. They are used in the manufacture of jewellery and artefacts, collected by hobbyists, and used as charms by mystics. Agates are ~98 wt% silica with up to ~2 wt% water being the major impurity. A variety of trace impurities are primarily responsible for the colouration of bands (Möckel et al 2009:123-138; Götze et al 2001:523-541; Heaney & Davis 1995:1562-1565). Unweathered agates have a characteristic green-earth coating of a weakly structured clay mineral (Moxon 1996:81). Weathering may abrade the green coating, but the agate nodule itself is resistant to abrasion (Macpherson 1989:3-5).

Agates are most commonly found associated with volcanic rocks, in particular andesites and basalts, which are low in silica. Globally the age of the host rocks ranges from 13 Ma volcanic tuffs, Yucca Mountain, USA to 3480 Ma rhyolite in Australia (Moxon and Reed 2006:485-498). Agates can also be found in sedimentary and metamorphic rocks (Götze et al 2009:673-690), and less commonly as vein agate in cracks and fissures of various rock types (Macpherson 1989:3-5). Less commonly, agates can also be found as loose nodules when set free from the host rock through weathering (Macpherson 1989:3-5), such as erosion by the sea, wind, rain, and flood waters.

Substantial literature exists on optical and polarizing microscope, and x-ray diffraction studies of agates, but only a few electron-microscope (EM) investigations on unpolished fractured samples of agates are reported (Moxon 2002:1109-1118). Here, the optical features, and microstructure of agates and microcrystalline quartz known as green-moss agate, found in Botswana, are presented. Chemical

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composition of the green-clay coating on these agates, and the green impurity streaks in the green-moss agate is determined using EDS analysis, and characterized using XRD analysis.

Agate Genesis

Agate genesis is poorly understood, and has been an on-going enigma. Only a few answers have conclusively been given. The main processes in the formation of agate are the temperature of formation, silica source, silica deposition, crystallization and band formation. Chalcedony can precipitate from slightly saturated aqueous solutions at relatively low temperatures of 100°C (Heaney 1993:66-74), however, a temperature of 120°C is the most widely accepted temperature of agate formation (Möckel et al 2009:123-138; Götze et al 2009:673-690). Proposed silica sources include immiscible silica within the molten magma, weathering of host rocks, silica bearing colloidal solutions from localized hydrothermal activity, and reconstituted chert xenoliths within the magma. Most likely forms of silica deposition seem to be either silica gel or powder which evolves into chalcedony or direct crystallization of fibrous chalcedony from a silica solution (Moxon 1996:54-59). Table 1 gives the proposed stages in the formation of wall lining agates (Moxon 1996:60-92; Moxon 2002:1109-1118; Webster 1994:236-239).

Table 1: Proposed stages in Formation of Wall-lining Agnates

Stage	Explanation
1	Trapped gas bubbles form vesicles in the lava
2	Inflow of silica solution or silica gel fills the vesicles
3	As silica gel gets denser it reaches crystallization state
4	Crystallization begins only after the vesicle is completely filled
5	Trace impurities are responsible for coloration
6	During crystalization gel separates into fibrous chalcedony and water rich front, and layers of hydrous and anhydrous silica are formed. Each layer has its own composition of silica, water and pigment impurity which crystalizes forming the banded pattern
7	Alternatively, bands are formed ether by natural rhythmic external processes such as alternate deposits of pure and impurity containing silica or from separation of impurity during crystalization
8	Quartz crystals are frequently observed at the centre of the agate nodule. These are believed to develop from a more dilute solution
9	On crystallization and aging, the density of agate increases resulting in shrinkage. This leaves a gap between the agate and the cavity
10	A weakly structured clay mineral fills the gap between the vesicle wall and the agate which is responsible for the characteristic green coating found on unweathered agates.

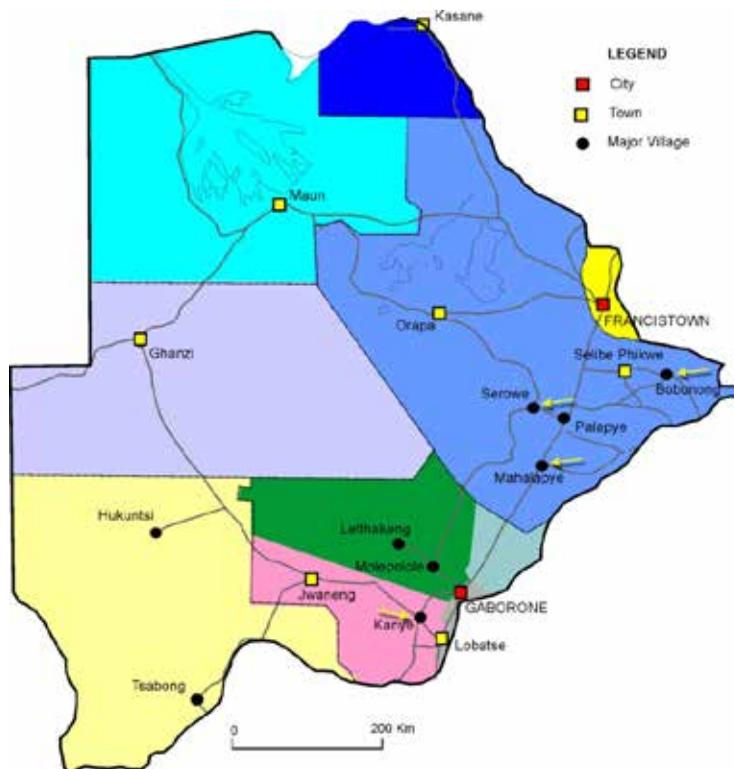
The Botswana Agates

Agates not only contribute as a mineral resource, though at a small scale, to the mineral based economy of Botswana, but also through the creation of employment opportunities in the mining, processing, and application sectors. About 48 tonnes of polished agates are exported annually from Botswana (Newman 2010:51-55) for use in the jewellery and artifact industry worldwide. Agate-embedded basalt fields can also be developed into potential tourist attractions to create job opportunities among the local communities, and as an additional source of income to the nation from the tourism sector.

Agates in Botswana are predominantly found in the Central District in the Bobonong area, in north-east along the Motloutse River, and in the Serowe area south-west of Bobonong (Figure 1). The host rock is the basalt from the 180 Ma Karoo volcanics (Paya 1996:9-11). After the rainy season, fields along the river are littered with agates that have been pried loose from the host rocks. The bulk of agates are wall-lining agates, which are small-sized nodules covered with the usual green clay. Vein-agates in the cracks and fissures in the rocks, though not common, are also found in the same areas. Agates in lesser quantities are also found in Mahalapye and Kanye areas (Figure 1) that are deeply embedded in the rocks, and not as loose pebbles (Jain 2007:24-26).

A microcrystalline quartz mineral, locally known as “Green Moss Agate”, is also found in the same area of Bobonong as the agate containing basalt. It is a white marble like quartz, and draws its name from the streaks of green clay impurity that were thought to be fossilized moss. It is also known as Gorgonzola because of its resemblance to the rich creamy white cheese with streaks of green from Gorgonzola in Italy. Having eroded from the basalt, it is found in blocks of a few kg up to 70 kg. Occasionally, gorgonzola can also be found embedded in the host rock (Jain 2007:24-26).

Figure 1: Locations around where agates are found in Botswana



Equipment and Experimental Techniques

Six Botswana agate samples: banded red carnelian, red carnelian, pink agate, grey agate, concentrically banded brown agate, and gorgonzola from Bobonong area were studied. Sectioned agate samples were mounted in an epoxy resin, and polished to 1 μm finish on a Buehler polisher. Optical features of the polished samples were examined at magnifications of up to 5x using a Nikon stereo microscope model SMZ 1000 with Fiberoptic-Heim model LQ 1000 light source for illumination. The polished samples were given a thin carbon coating to prepare them for microstructure and microanalysis investigations using a Philips XL30 ESEM (environmental scanning electron microscope) in high vacuum mode equipped with EDAX-EDS system with ultra-thin wafer sapphire window for microanalysis, and a Centaurus cathodoluminescence detector. The green-earth coating and intrusions were characterized by x-ray diffraction using a Philips PW3710 XRD system with copper anode, PW1752 graphite monochromator, PW3011 Xe detector, and X'PERT 2000 data collection and analysis software. Powdered scrapings from the green earth coating and the streaks in the gorgonzola were used. The generator voltage and current were set at 40 kV and 30 mA respectively. A continuous scan with step size of $0.02^\circ\theta$ and measurement angle of $20\text{--}90^\circ\theta$ was done at a controlled temperature of 25°C .

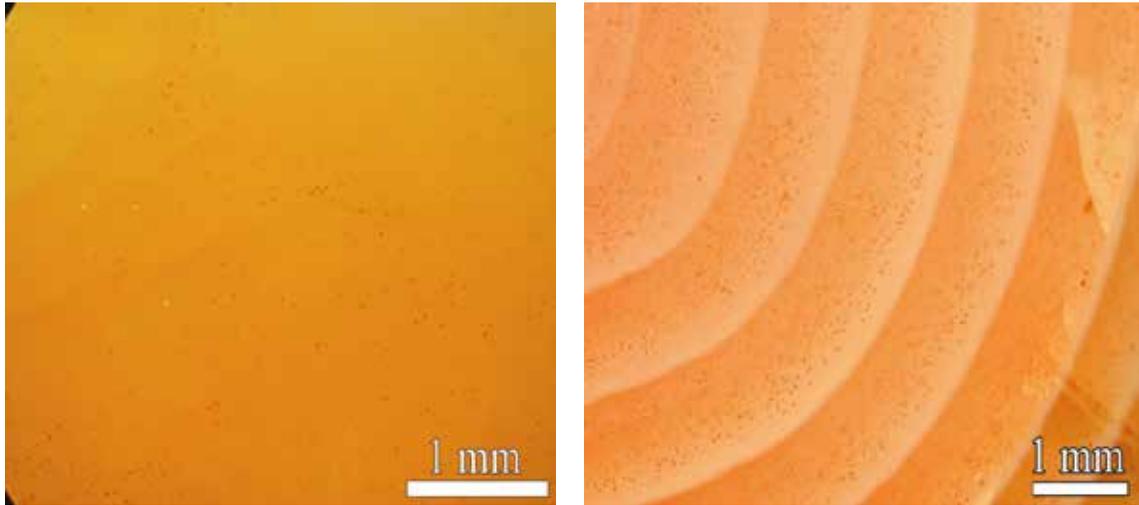
Optical Features

Optical images of the six polished agate samples that were investigated are shown in Figure 2. These are, clockwise from top left, banded red carnelian, red carnelian, grey agate, gorgonzola, brown agate, and red agate. Both the carnelian samples are examples of translucent chalcedony which may or may not be banded. In fact, the difference between an agate and a banded carnelian is marginal, and sometimes the terms are used interchangeably. Colour bands in the wall-lining agates are nearly concentric with band pattern almost following the shape of the vesicle boundary in which they are formed. The band pattern points to rhythmic deposition of impurities with silica inflow in the vesicle. There is an uneven rate of band growth from the outer edge to the centre. The bands tend to get wider towards the centre. The shift in the centre of the band pattern from the centre of the vesicle is due to the effect of gravity. In some cases, the centre of the agate is filled with quartz crystallites, as can be seen along the right edge of the pink agate. The polished sample of gorgonzola has a pure white marble like appearance with uneven, random streaks, mainly of green and some rusty impurity throughout the sample. Under high magnification, the green streaks appear to have a tube like porous structure. Figures 3(a) and 3(b) are optical stereo microscope images of carnelians with uniform colouration and with banded colouration respectively. The band formation in Figure 3(b) is seen to be due to non-uniform, rhythmic distribution of red spheric globules of impurity which impart red-orange colour to the carnelian. The impurity is identified to be 3 to 9 wt% of iron from EDS analysis. Distribution of impurity in the banded carnelian from high concentration at inner to low at the outer edge of a band is a characteristic feature of diffusion and a process of self-internal purification.

Figure 2: Polished Samples of Botswana Agates. Clockwise from top left, banded red carnelian, red carnelian, grey agate, gorgonzola, brown agate, and red agate.



Figures 3: Red carnelian with Uniform Colouration, and with Banded Colouration



Microstructure

Figure 4 is a cathodoluminescence (CL) micrograph of the grey agate sample. We note that crystallization in the white bands produces cathodoluminescence. The band width increases towards the centre from (a) to (b) to (c), and the centre at (d) is filled with quartz crystallites. Cathodoluminescence from white bands can also be seen in another sample of grey agate (Figure 5), and the quartz crystallites at the center of an agate are seen in yet another sample (Figure 6).

Figure 4: Cathodoluminescence (CL) Image of the Grey Agate

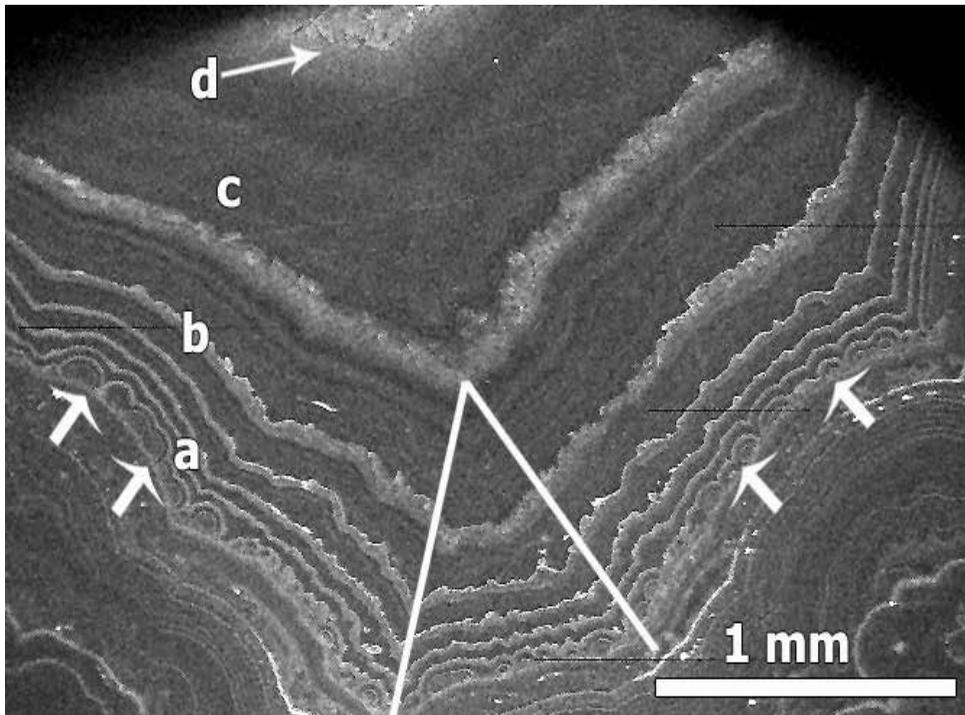


Figure 5: CL By White Bands in an Agate

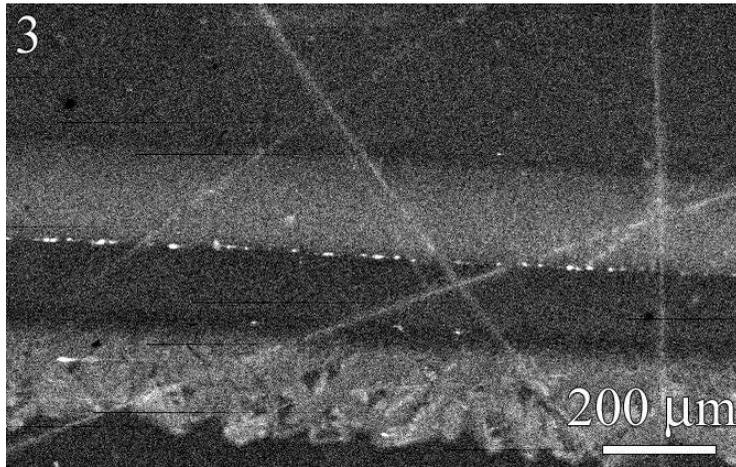
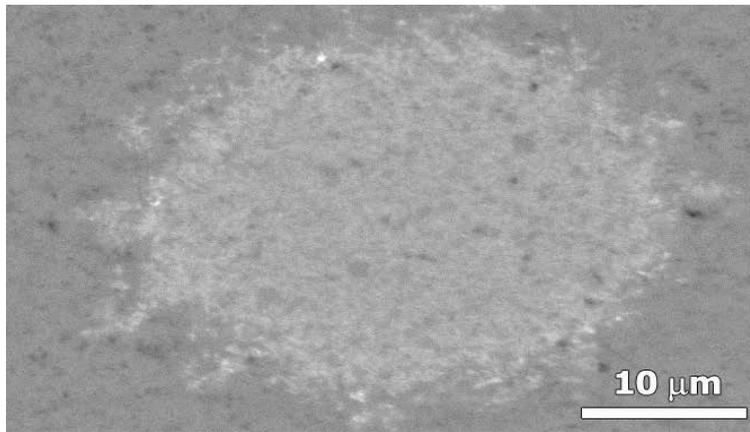


Figure 6: Quartz Crystallite at the Centre of an Agate Sample Revealed by CL



From Figure 4, the process of nucleation and growth of bands can also be inferred. Nucleation generally starts from the outside edge with spherulitic growth as at (a). Initially the crystallites have the freedom to grow as separate entities as spherulites until they meet other crystallites. Subsequently, the growth is distorted because of the restriction of space, and as per Grigorev's geometrical selection principle the lower nucleated spherulites are prevented from further growth (Moxon 1996:24-29). From more and more suppression of uneven growth as the centre is approached, the bands become smoother as at (c) in the figure. From here on fibrous crystallization takes over and continuous crystal fronts are formed.

Figure 4 suggests a link between the crystallization and band formation processes because only the white bands produce cathodoluminescence. It is proposed that as crystallization proceeds, the bands in this case are formed through a chemical differentiation and diffusion process. As gel separates into fibrous chalcedony and water rich front, layers of hydrous and anhydrous silica are formed. These layers have distinct composition of silica, water and pigmentation impurities and are responsible for bands in the agate.

Not all agates produce cathodoluminescence, and neither do all agates have quartz crystallites at the centre. For example, the bands in banded carnelian do not produce cathodoluminescence. This shows that crystallization in banded carnelian differs from the process of spherulitic crystallization as seen in the case of the grey agate.

The iron impurity inclusions in carnelian are seen as lighter spots in the BSE image (Figure 7). This is consistent with the higher atomic mass of the iron impurity. The iron impurity inclusions are not always uniform spheroids in shape. Some have an uneven surface, characteristic of diffusion. This is further evidence of diffusion being the underlying process for band formation in carnelian as concluded from the optical micrograph, (Figure 3 (b)).

Figure 7: Back Scatter Electron (BSE) Image of a Banded Carnelian

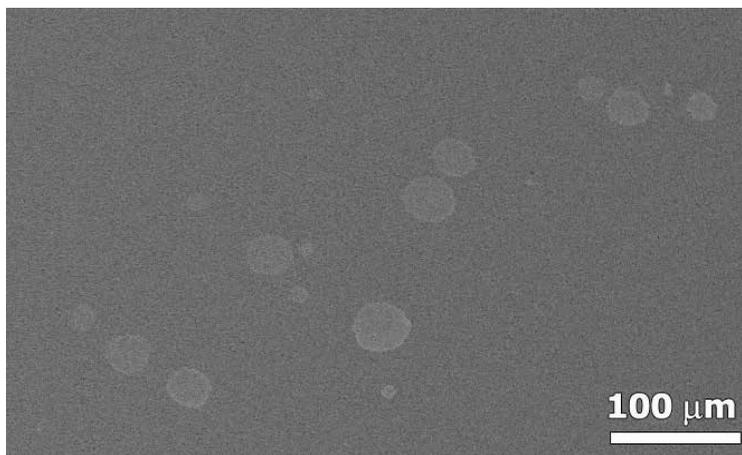
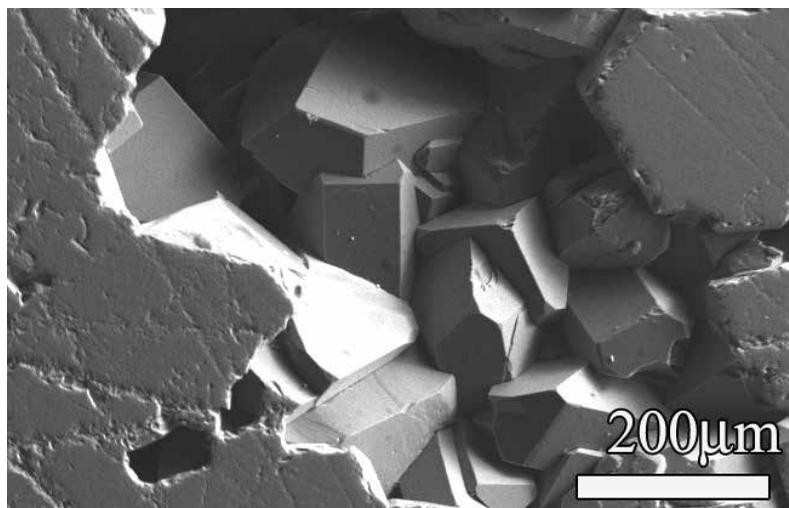


Figure 8 is a secondary electron (SE) image of the white matrix of gorgonzola in which individual quartz crystallites at various orientations are distinctly visible. Figure 9 is the CL image of the same area of the white matrix. Here one can see the crystal growth planes of individual cross-sectioned crystallites. This suggests that gorgonzola has a granular, microcrystalline structure, as opposed to the fibrous structure of an agate resulting from spherulitic growth (Figure 4). We, therefore, conclude that gorgonzola is not an agate as is commonly referred to, rather it is microcrystalline quartz. Figure 10 is the BSE image of a typical green intrusion in gorgonzola. It has a varying grey density corresponding to the back scatter yield that is directly related to the average atomic density of the constituents of the green impurity. The streaks of the green impurity do not produce cathodoluminescence.

Figure 8: Secondary Electron (SE) Image of the White Region of Gorgonzola



Microanalysis of the Green Earth

Chemical compositions of the white matrix of gorgonzola, the green earth coating on Botswana agates, and the green impurity streaks in gorgonzola were determined by EDS analysis. The white matrix of gorgonzola was predominantly quartz (98 wt% SiO₂) with traces of Mg and Al impurities. This is consistent with the microcrystalline structure observed in the SE and CL images of the white regions of gorgonzola (Figures 8 and 9). On the other hand, the green impurity in gorgonzola and the green earth coating on agates were found to be low in silica and rich in Fe, K, Al and Mg impurities. Their compositions are given in Table 2:

Figure 9: CL Image of the Same White Region of Gorgonzola as in Figure 8

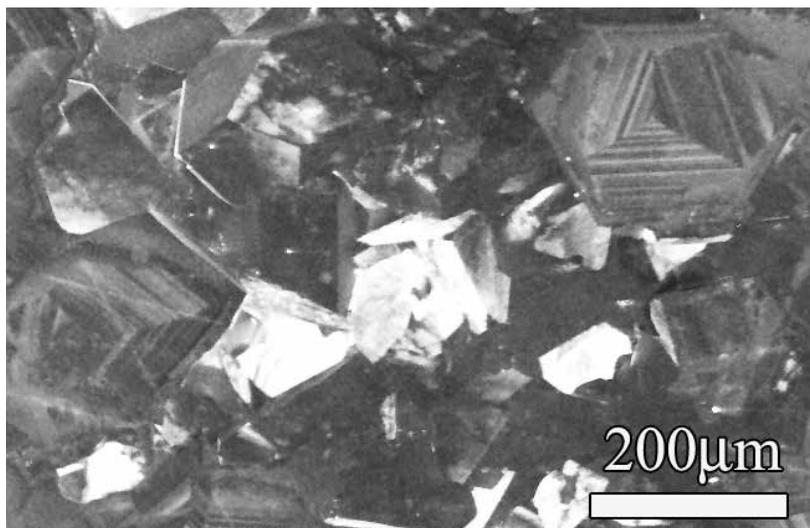


Figure 10: BSE Image of a Typical Green Inclusion in Gorgonzola

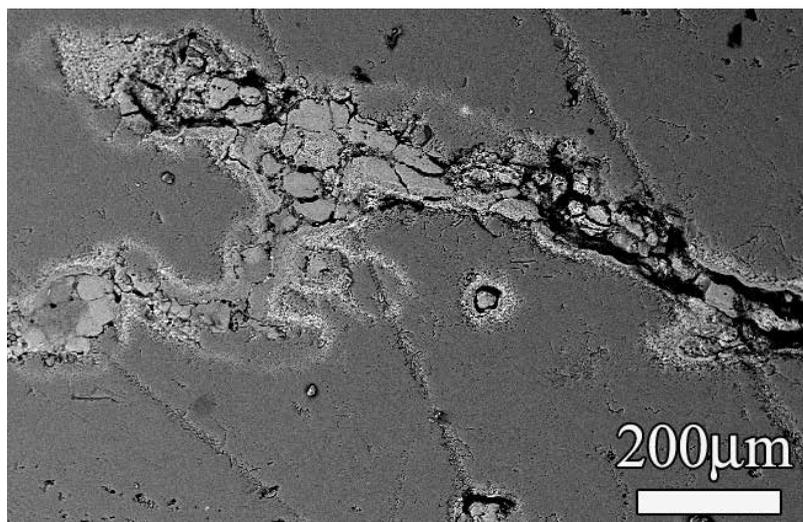


Table 2: Compositions (wt %) of green impurity streaks in gorgonzola, and green coating on wall-lining agates from Botswana

Elements	Green impurity in gorgonzola	Green coating on wall-lining agates
	wt%	wt%
Si	52 – 61%	35 – 48%
Fe	16 – 18%	29 – 50%
K	2 – 13%	4 – 15%
Al	6 – 9%	2 – 4%
Mg	4.5%	3 – 6%
Trace elements	Ca and P	Zn, Mn, Ca, P, V., and Cr

Characterization of the Green Earth

The green coating on wall-lining agates and the green impurity in gorgonzola were characterized using x-ray diffraction (XRD). Figure 11 is the XRD spectrum of the green earth coating on the wall-lining agate, and Figure 12 is that of the green impurity in gorgonzola. From the X'PERT 2000 analysis software data base the coating on agates and the streaks of impurity in gorgonzola were both identified to be Celadonite-1M, aluminian (Potassium Magnesium Aluminium Iron Silicate Hydroxide). This is consistent with the elements detected in the composition of the green clay for both cases from EDS analysis, and suggests that the green coating of wall-lining agates and the green impurity in gorgonzola are of the same origin. In fact, celadonite frequently forms the green cover that surrounds agates from worldwide sources (Heaney 1963:66-74; Iancu et al 2009:37-41; Harder 1993:31-48; Jain et al 2008:15). The white matrix of gorgonzola is confirmed to be predominantly quartz as was determined from EDS analysis. The celadonite XRD-peak positions in 2θ for the green earth coating on agates are given in Table 3, and those for the green impurity in gorgonzola are given in Table 4:

Figure 11: XRD Spectrum of the Green-earth Coating on Botswana Agates Showing the Celadonite Peaks

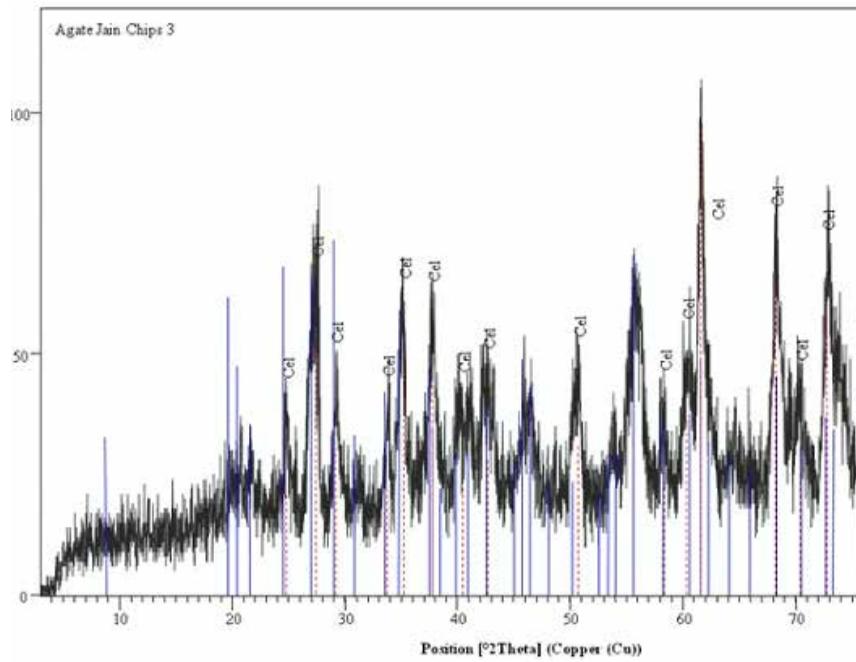


Figure 12: XRD Spectrum of the Green Inclusions in Gorgonzola Showing the Celadonite Peaks

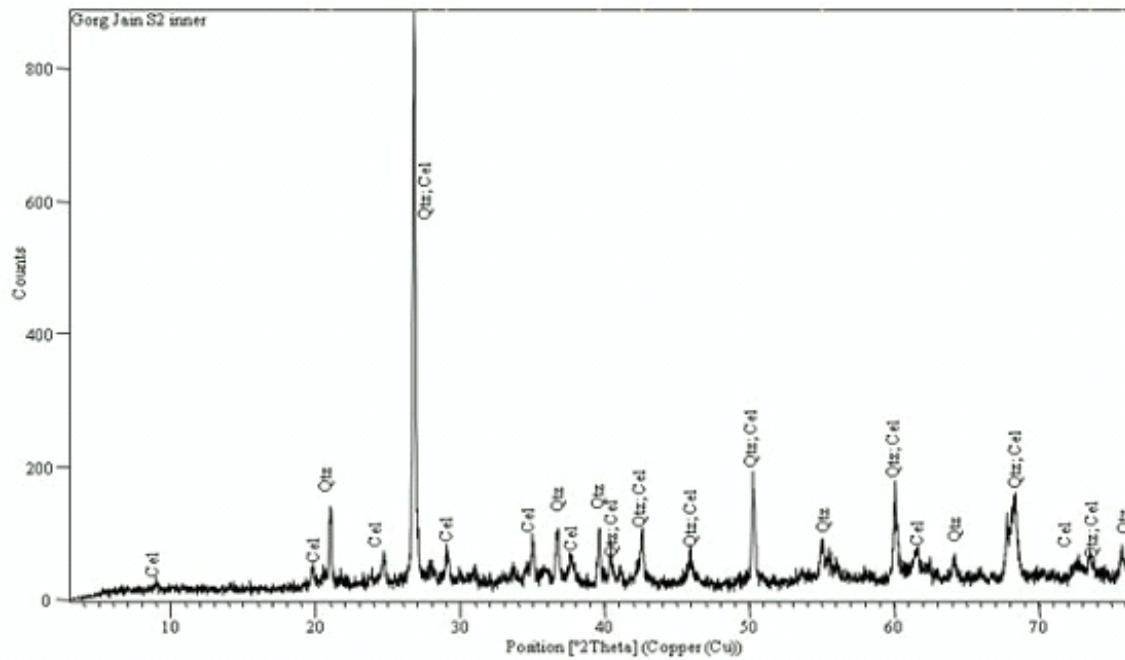


Table 3: XRD Peak Positions in 2θ for the Green Earth Coating on Botswana Agates.

Pos. [2θ .]	d-spacing [\AA]	Rel. Int. [%]
24.7789	3.59318	24.72
27.3850	3.25687	59.87
29.1956	3.05889	33.11
33.6906	2.66034	25.26
35.1581	2.55259	52.95
37.7609	2.38242	50.67
40.4757	2.22867	22.05
42.7127	2.11699	27.92
50.7160	1.80011	32.61
58.3044	1.58261	17.21
60.3890	1.53287	30.38
61.5788	1.50608	100.00
68.2392	1.37441	66.36
70.3555	1.33816	19.91
72.7712	1.29959	52.08
76.2189	1.24812	19.77

Table 4: XRD Peak Positions in 2 θ for the Green Earth Impurity in Gorgonzola

Pos. [$^{\circ}2\theta$.]	d-spacing [\AA]	Rel. Int. [%]
19.7356	4.49854	3.37
24.6829	3.60694	5.34
26.7999	3.32663	100.00
29.0147	3.07754	4.53
35.0006	2.56372	6.70
37.6659	2.38821	4.76
40.4406	2.23052	4.79
42.5784	2.12335	9.15
45.9384	1.97557	5.49
50.2537	1.81558	17.59
60.0481	1.54075	15.22
61.5600	1.50649	5.23
68.3369	1.37268	13.78
72.3864	1.30554	1.51
73.5369	1.28794	4.39

Conclusion

Insight into the formation, crystallization and band formation processes in agates, using Botswana agate samples is obtained from optical and electron microscopic studies, and from micro composition determined from EDS analysis. The optical micrographs reveal that the shape of the bands follows the shape of the vesicles in which the wall-lining agates are formed. Diffusion of the pigmentation-impurity resulting in the formation of bands in carnelian can also be seen, and the bands in this case do not produce cathodoluminescence. The electron microscope investigation of microstructure and the cathodoluminescence images show how spherulitic crystallization leads to fibrous crystal growth in wall-lining agates and to the formation of bands from chemical differentiation and diffusion by rhythmic deposition and crystallization of silica gel with and without the pigmentation impurity. Thus, from cathodoluminescence we could confirm that the band formation and crystallization processes are different in the carnelian and the agate. It is established that gorgonzola is not an agate as it is wrongly believed to be; rather it is a natural microcrystalline quartz mineral. The green coating on agates and the green impurity streaks in gorgonzola are found to be of the same origin from their EDS microanalysis, and both are characterized from XRD spectrum to be loosely bound clay mineral, celadonite.

Agates are formed as a result of geological processes in nature over a span of millions of years, a process which cannot be replicated in laboratory time. However, some basic aspects of their genesis can be revealed from their analysis using appropriate investigative tools in modern materials research laboratories as has been done in this study.

Acknowledgements

Authors are grateful to H Knuettel of Agate Botswana for providing samples of Botswana agates, and to T Moxon in the United Kingdom for useful discussions and suggestions.

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