Agates: a literature review

and Electron Backscatter Diffraction study of Lake Superior agates

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Table of Contents

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AGATES: A LITERATURE REVEW

Introduction

Agates, valued as semiprecious gemstones for their colorful, intricate banding, (Fig.1) are microcrystalline quartz nodules found in veins and cavities in host rocks. They have been observed in sedimentary, metamorphic, and igneous environments, and can be found on every continent (Moxon, 2002). The commonly accepted theory is that they crystallize in the vugs found in flood basalts and usually consist of fibrous chalcedony and coarse quartz crystals surrounding a central void (Bryxina et al., 2002). More resistant to erosion than their surroundings, agates often survive long after their host rock has weathered away, leaving them to be found by enthusiasts.

Agates present one of the more spectacular examples of autonomous pattern generation in nature, but despite world-wide agate occurrences and numerous investigations, the process of formation of agate is not yet completely understood (Götze et al., 1999). Discussions involving the origin of agate are controversial due to the fact that no one has unambiguously documented agate formation in real time and agates have never been successfully replicated in the laboratory (Götze et al., 2001b). The mechanisms that produce agate in an igneous environment are especially enigmatic, and although it can be safely stated that agates form within cavities of volcanic host rocks when microcrystalline silica fibers nucleate on vug walls and grow inward, the silica sources, method of deposition, temperature, transportation, and final mechanism of crystallization are all unknowns that have added to the difficulties in determining the origin of agate (Moxon, 2002).

Figure 1: An example of the colorful, concentric banded chalcedony known as agate. www.opalcutter.com/laguna_agates.htm.

Structural and compositional description of agates

Agates from flood basalts commonly display repetitive textures and trace element compositions (Merino et al., 1995). From rim to core, agates typically consist of three parts: concentric layers of length-fast fibrous chalcedony, an inner layer of coarse length-slow quartz crystals (quartzine), and a central void (Wang and Merino, 1995). However, many agates lack a central void and instead are filled in completely with silica, while others consist only of banded fibrous chalcedony. Agates vary widely in shape, size, and color, but surprisingly their structural and compositional characteristics are relatively constant.

The feature that most agates have in common at the least is the region of banded chalcedony. To the naked eye, the width of the bands varies randomly in the mm range (Fig. 2). However, with SEM, visual banding is resolved into a concentric succession of zones on a micron to sub-micron scale (Frondel, 1985). An interesting characteristic that is almost universal within agates is a distinct band of first-generation chalcedony. This band is in immediate wall contact and varies from $1 - 2$ mm thick. Crystallite size of this outer band is larger than the comparable inner regions of agates (Moxon, 2002).

The banded region itself consists of layers made of fine-crystalline and untwisted quartz fibers that alternate with layers made of even finer and twisted fibers. The twisting can easily be observed under a microscope by the changing birefringence along any one fiber (Merino et al., 1995). The fibers are elongated along the [1 1 -2 0] face, and range in thickness up to about .5 microns and in length up to a few cm (Frondel, 1985). The fibrous chalcedony crystals are polysynthetically twinned according to the

Figure 2: the width of the bands in agates usually varies randomly in the mm range.

Brazil-law, with the c-axis twisted about the fiber axis (Götze et al., 1998). These brazil-twins are the dominant micro-structural feature of the fibers (Wahl et al., 2002).

The periodic Brazil-law twinning seen in agates is widely accepted to be a consequence of the presence of relatively large amounts of the silica polymorph moganite (Götze et al., 1998). The presence of moganite, which rarely occurs as a pure mineral, is confirmed by powder x-ray diffraction within agate samples (Heaney and Davis, 1995). The moganite:quartz ratio is often not uniform, but shows a cyclic pattern that correlates with the observed cathodoluminescence (color and intensity) pattern (Götze et al., 1998). The transitions from quartz to moganite within the fabric differ in a characteristic way. Whereas in the coarse quartz crystals the gradient between the structures is steep, the transition is more continuous in chalcedony (Wahl et al., 2002). Agate structure can probably be interpreted as alternating formation of fine-grained, highly defective chalcedony intergrown with moganite, and coarse-grained low defect quartz (Götze et al., 2001b). It has been hypothesized that cyclic variations in the moganite content must be a general feature that is connected to the mechanism of agate genesis (Götze et al., 1998).

In addition to the larger-scale cyclicity, some compositional cyclicity on the scale of ~200 nm was observed by Heaney and Davis (1995). These bands comprise layers with distinctly different grain sizes and defect concentrations. The coarse-grained zones contain nearly perfect quartz crystals that measure 10 – 100 nm in diameter, while the fine-grained lamellae consist primarily of crystals with diameters of 5 – 10 nm. Agates exhibit self-similarity over three length scales, each separated by roughly two orders of magnitude (Heaney and Davis, 1995). Virtually all of the compositional zoning in agates is systematic and is not due to chance. The coarse visual color banding is an independent

feature imposed on the compositional zonation by relatively long-term variations in the deposition of pigmenting impurities (Frondel, 1985).

Although agates are valued for their rhythmic colored banding, it is the non-pigmented iris banding that is most remarkable for its rhythmic uniformity. Iris bands appear as striations parallel to the cavity wall and perpendicular to the fiber axes. These bands oscillate with respect to refractive index, and the oscillations may cycle 8000 times or more within a given sector of an agate. Chalcedony fibers maintain crystallographic continuity as they traverse the iris striations. Zones with this particular type of banding are present in virtually all agates (Heaney and Davis, 1995).

Although agates are composed almost entirely of SiO_2, it is the trace quantities of various other elements that give agates their color and lead to their characteristic banding. Trace element compositions of agates vary widely from location to location, but Götze, Tichomirowa, et al. (2001) point out many trends that are common to almost all agates of igneous origin. Surprisingly, trace element data are similar for agates from both acidic and basic volcanic hosts. Ge and B are the only elements beside Si which are enriched in almost all agates compared to the Clarke values of the lithosphere (1.4 ppm for Ge, 12 ppm for B). The trace element signature of most agates is characterized by rare earth element (REE) distribution patterns with predominantly high light REE contents, low heavy REE and the presence of positive Eu anomalies in some samples. Unusually high concentrations of uranium are also sometimes detected in agates.

Agates contain impurities less than ppm level for most of the elements except Na, K, and Fe (Tanaka and Kamioka, 1994). Nonetheless, even red chalcedony bands often have relatively low concentrations of substitutional Fe, indicating that the color is caused

by fine dispersed iron oxides not incorporated into the structure of the fibers (Götze et al., 2001b). It has been stated that trace element impurities outside the fibrous agate structure cause the pigmenting qualities of agates, while the incorporation of trace elements lead to the small-scale, structural banding seen in agates. These impurities may promote Brazil-twinning, since cations can occupy the sites of bridging tetrahedra (Götze et al., 1998).

Another characteristic feature of agates is their ^{18}O values, which are higher than associated quartz incrustations. In general, oxygen isotope compositions become heavier as volcanic host rocks grow more acidic (Götze et al., 2001b). Also in contrast to macrocrystalline quartz, agates often contain water in the range of 1-2 weight % (Götze et al., 1998). Successive zones within agates involve variation in the amount of (OH^-) in structural sites in the quartz itself. Individual fibers in agates may show a succession of hundreds of thousands of such zones or compositional units (Frondel, 1985). Generally, the abundance of inherent defects (silicon and oxygen vacancies, silanol groups, etc.) in agate is noticeably higher than in macrocrystalline quartz (Götze et al., 1999).

Given the structural and compositional similarities between agates of all regions, it has been hypothesized that agate formation occurs independently of outside influences, and that the banding, as well as the pigmenting, is largely chemically controlled. In other words, the oscillating textures and compositions must result from the internal dynamics of the growth itself, not from oscillating conditions outside the agate (Wang and Merino, 1995). It is clear that the crystallization behavior that governs this compositionally simple mineral system is universally complex (Heaney and Davis, 1995). So complex, in fact, that in spite of the many investigations into the process, factors such as silica source,

method of deposition, and temperature of formation (among others) are still largely

unknown.

Some problems concerning agate genesis

Silica sources

One of the most obvious uncertainties workers have involving agate genesis

is the source of the silica from which agates are formed. Among others, it has been

proposed that the silica source could be from the surroundings, hydrothermal activity, late

magma deposition, or a silica glass within the magma (Moxon, 2002). However,

interested workers are basically divided into two camps, with ample evidence supporting

both. The first represents the hypothesis that the silica originated in the host rock or

surroundings, and was deposited in a gas vesicle by hydrothermal activity. The second

believes that agates are formed from a silica lump or gel within the magma that contains

trace elements and water (Merino et al., 1995). Although most believe that agate genesis

is contemporaneous with the formation of the host rock, some have argued that agate

formation occurs up to tens of millions of years after the formation of the host rock

(Ingerson, 1953).

A widely-held belief regarding the silica source for agate genesis is that the SiO_2

necessary for agate formation is mobilized during the alteration of the volcanic wall rocks

by hydrothermal action (Götze et al., 2001b). In fact, Moxon (2002) argues that the direct

deposition of crystalline chalcedony is the only viable alternative to an amorphous (silica

lump) origin. He reasons that since crystallization from an amorphous origin results in a contraction and loss of volume, an initial amorphous silica deposit would eventually require an extra ~20% of silica in order to maintain a full amygdale of chalcedony. Therefore, agate amygdales would rely upon percolating silica-saturated solutions for any late input of silica, since they exist in a closed environment.

Additionally, the similarity in the shape of the REE patterns between agates and the parent volcanic rocks suggests that the elements are mobilized by circulating fluids during syn- and postvolcanic alteration of the host rocks (Götze et al., 2001b). Based on oscillatory structures, Heaney and Davis (1995) suggest crystallization from fluids with fluctuating degrees of polymerization. Similarly, it has been hypothesized that observed alternating crystallization of quartz and chalcedony may be caused by variations in the degree of silica saturation of the mineral-forming SiO_2-bearing fluids (Götze et al., 2001b). Despite the evidence in support of this theory, there is enough evidence to the contrary and in support of other theories to keep many workers doubtful.

Crystallization of agates from hydrous silica gel or glass lumps has been championed in the literature by Wang (1995) and Merino (1995), as well as Bryxina and Sheplev (1999). They theorize that agates probably crystallize not from aqueous solutions but from lumps of polymerized silica containing trace elements and water. Amorphous silica is the first deposit from solutions with a high silica concentration and is found in hot springs (Moxon, 2002), suggesting that a similar process takes place with agate genesis. One of the most problematic aspects of the hydrothermal fluid-based theory of agate deposition is that initial crystalline deposits of chalcedony would be expected to block incoming silica solutions (Moxon, 2002). This would not present a problem with a

lump of polymerized silica within the magma – all the silica needed for the formation of the agate would already be there.

In a related idea, it has also been postulated that agates in volcanics are xenoliths of marine chert because of the similarity of $\delta^{18}O$ values between the two. These chert xenoliths are not resorbed by the magma, but are carried within it as melt drops and thus transformed to agate (Fallick et al., 1985).

Despite many in-depth studies and improving technologies and investigative methods, the source of the silica required for the growth of agate is still largely unknown. Agate deposition, which is a complex, multi-step process, presents an even greater problem for scientists however.

Method of Deposition

Agates have not been successfully recreated in laboratory experiments to date, leaving workers baffled as to the method of agate deposition. Most believe that agate genesis would be typically penecontemporaneous with the formation of the host rock (Moxon and Ríos, 2004), but solely knowing the relative time and exterior conditions present during deposition is not enough to answer all the questions scientists have regarding agate deposition. As with the other unresolved issues concerning agate genesis, there have been many studies designed to unearth the mystery behind the method of agate deposition.

Much of the depositional ambiguity lies with the formation of the small-scale quartzine-chalcedony bands, not the colored banding that can be seen with the naked eye.

According to Frondel (1985), this oscillatory zonation is the result of a cyclic interplay between growth rate and diffusion rates at the crystal/solution interface. Textural transformation from chalcedony to quartzine could also be caused by variations in the degree of silica saturation of the mineral-forming, SiO_2-bearing fluids (Götze et al., 2001b). The high defect (Brazil twin) density found, as well as impurities in agates point to a rapid growth of silica from a strongly supersaturated solution probably with a non-crystalline precursor (Götze et al., 1999). This depositional process is thought to be self-organizational, and not dependent on exterior conditions (Götze et al., 1998).

Merino, Wang, and others (1995) and Wang and Merino (1995) extensively modeled a chemically controlled method of agate deposition. Their model attempts to explain both the twisted nature of the quartz fibers and how that process causes the banding in agates. Unfortunately, the model assumes the less popular theory that agates form from an amorphous lump of silica within the magma.

According to the model, silica lumps can crystallize in an oscillatory fashion, acquiring repetitive features through self-organization (Merino et al., 1995). Two mechanisms cooperate and interact during agate genesis: morphologically unstable crystallization fronts (i.e. growth rate >0), and cation-enhanced quartz growth. Cations at the crystallization front can accelerate quartz growth, and the fibrous texture characteristic of agates is produced by a morphological instability of the crystallization front, with each fiber growing by adding conical sleeves. They contend that the crystallization of agate is self-organizational and because self-organization requires non-linearity, the growth rate of quartz is assumed to be non-linear.

Fiber twisting is caused by trace-element substitution for Si^{+4} (Wang and Merino, 1995). Al^{+3} and Fe^{+3} (and other trace elements) oscillatorily enter the quartz fibers, some substituting for Si^{+4} and some balancing the charge loss incurred by the substitution (Merino et al., 1995). The need for the fiber to maintain its structural continuity while simultaneously making room for the larger Al^{+3} and Fe^{+3} ions along its periphery requires that it grow twisted. The banding of agates is produced by quartz growth that is accelerated by the accumulation of these cations at the growth front (Wang and Merino, 1995). The model predicts that fiber size changes periodically, as observed in agates.

Alternatively, Harris (1989) analyzed differences in the ^{18}O values of quartzine and chalcedony layers. He concluded that the differences are best explained by the quartzine layers forming from water vapor and the chalcedony layers crystallizing from liquid water. With this model, agate deposition is initiated not from a silica lump, but from hydrothermal fluids. The chemical composition of these fluids is assumed to be close to pure H_20.

Heaney and Davis (1995) also suggest crystallization from fluids. In their model, cavity fluids that are partly polymerized rapidly precipitate spherulitic chalcedony, creating bands with a relatively high (OH^-) content. If depletion of silica near the fiber tips outpaces diffusion toward the tips, then the activity of silica in solution decreases and polymerization is no longer sustained. The resulting monomeric solution precipitates defect-free quartz, generating iris bands with a low OH^- content. Because this crystallization rate is slow, silica loss near the growing crystal face is eventually overrun by diffusion of silica toward the fiber tips, and the local activity of silica in solution

increases. When polymerization is tenable again, the spiral growth mechanism is reactivated and rapid crystallization of defective chalcedony continues.

Each of these models appears to explain agate deposition adequately, but unfortunately none have resulted in the replication of agate-like pattern generation in the laboratory. Determining factors such as temperature of formation or the time frame required for deposition may possibly provide workers with the information needed to construct a truly workable model of agate deposition.

Temperature of Formation

The temperature of formation for agates in igneous environments is not at all known, and is a key point of the controversy over the origins of agate. Studies undertaken on the topic have concluded with temperatures from <50° C to >400° C (Götze et al., 2001a). This wide range suggests one of two things: either agates form under a wide range of temperature, or the conclusions of such studies are largely inaccurate.

Fallick, Jocelyn, and others (1985) presented evidence that suggested agates are formed at low temperatures (~50°C) from fluids having at least a component of meteoric origin. Moxon (2002), conducted isotopic studies of agates that suggested agate formation temperatures in the range of 50 – 120 °C. By analyzing the ^{18}O values of both the quartzine and chalcedony zones, Harris (1989) concluded that the magnitude of the difference between the two zones suggests that the temperature was above 100 °C, with a maximum temperature of 169 °C indicated by the data. Based on calculations for different fluid compositions, a temperature range of 50-250 °C was reached by Götze and Tichomirowa (2001).

Additionally, agate formation temperatures >375 °C were proposed on the basis of a crystallite size geothermometer, and there exist theories of formation at even higher temperatures, up to >400 °C (Moxon, 1996). According to Götze, Plötze and others (2001), experiments investigating the formation of chalcedony went well at elevated temperatures. Finally, aluminum concentrations in quartz were measured (Götze et al., 2001a), and a formation temperature range of 50 – 200 °C was estimated based on that data.

In conclusion, a direct estimate of the formation temperature of agates is difficult, and the plethora of results on the topic does not clarify the situation. Nevertheless, the majority view of interested workers is that genesis starts with polymerization of siliceous fluids at temperatures ~100 °C (Moxon, 2002).

Age of Agates

Studies have shown (Moxon, 2002; Moxon and Ríos, 2004) that ageing gradually alters agates at known rates. Moxon and Ríos (2004) have shown that maturation produces a general decrease in both the moganite and internal water content of agates studied. In fact, moganite has not been found in agates from any pre-Silurian hosts. Water is involved in the transformation of moganite into chalcedony and this change is responsible for an internal growth in chalcedony crystallites. The mobilization of water during the geologic time scale allows some of the silica in agate to dissolve and re-crystallize. The growth of the crystallites and contraction in volume causes an increase in density, with an increase in density from the youngest agate to the oldest agate of about 2% (Moxon, 2002).

Crystallites from agates ~400 Ma old have achieved their maximum size, indicating that the dynamic crystal growth is restricted to the first ~400 Ma. It would be expected that the continued crystallite growth would result in a slow deterioration in the banding and the eventual destruction of fibrous chalcedony in agates, but this is not the case (Moxon, 2002). This change in agate crystallites is proposed as a method for approximate dating of agates that are from hosts younger than 400 Ma, as well as finding the disparity, if any, between the relative ages of agates and their host rocks. Additionally, the measurement of crystallite size, density, internal water content and moganite can provide evidence of a later palaeoactivity in the region (Moxon and Ríos, 2004). Further work is underway to see if the agatization process can be used in the dating of siliceous deposits and fossils (Moxon, 2002).

LAKE SUPERIOR AGATES: AN ELECTRON BACKSCATTER DIFFRACTION (EBSD) ANALYSIS

Abstract

Despite many studies, the mechanism of agate deposition is still unknown. EBSD analysis of agates could give quantitative data on the crystallographic orientation of fibers. This could add to our understanding of the complex structure of agates, and perhaps give insight into the mechanisms of agate growth. It is believed that Lake Superior agates crystallized within gas vesicles 1.1 G.y.a. EBSD, which is a relatively new technique, was carried out on one Lake Superior agate in hopes of obtaining quantitative data on the crystallographic orientation of silica fibers throughout the specimen. An attempt was made to obtain Kikuchi patterns, as well as pattern quality maps, and pole figures. The results of this study were indeterminate at best. Further EBSD study will have to be carried out to determine whether or not the procedure will work on agates.

Introduction

As explained above, the mechanism of agate growth is still a mystery to scientists. Not only has agate deposition not been recorded in real time, workers also haven't been able to recreate agates in the laboratory. As far as this author can tell from the literature, EBSD has never been done with an agate sample before. It was hoped that EBSD analysis of agates could give quantitative data on the crystallographic orientation of individual silica fibers, and how that orientation changes from rim to core.

This process would add to our understanding of the complex structure of agates, and perhaps give insight into the mechanisms of agate growth. Agates represent one of the most impressive examples of spontaneous pattern generation in the world, and studying agate crystal growth could help explain how natural patterns like these are generated without an external template. Agates are a noteworthy case of self-

organization, both texturally and compositionally, and their origin has far-reaching geochemical, crystal-growth, and petrologic implications.

Geologic setting

Lake Superior agates formed mostly within basalt flows in a mid-continental rift setting. Assuming that their formation was contemporaneous with the formation of their host rock, these agates are ~1.1 billion years old (Davis and Paces, 1990). It is believed that Lake Superior agates crystallized within gas vesicles. These vesicles formed when the basalt, which contained water and dissolved gases, erupted to the surface. Quartz has a hardness of seven on the Mohs scale, above those of the minerals commonly found in basalt (Klein, 2002). This means that after 1.1 Ga, Lake Superior agates have resisted erosion much better than their host rock, leaving them to be deposited by wave action on the beaches of Lake Superior.

Methods

Agate samples were collected in Minnesota, U.S.A., on several different beaches on the North Shore of Lake Superior. The agate used in this study was collected from A beach close to Judge Magney State Park, near Hovland, Minnesota. Samples ranged in size from 1 – 5 cm in diameter (Fig. 3). The agate used in this study was the largest one collected, and consisted of horizontal, gravity-driven depositional banding as well as wall lining, concentric banding (Fig. 4). To prepare for EBSD analysis, a fine polish was put on the agate. Using a Buehler Minimet Polisher, the sample was abraded with successively finer diamond grit, eventually reaching a .05 micron polish.

Figure 3: agate samples collected from Lake Superior beaches.
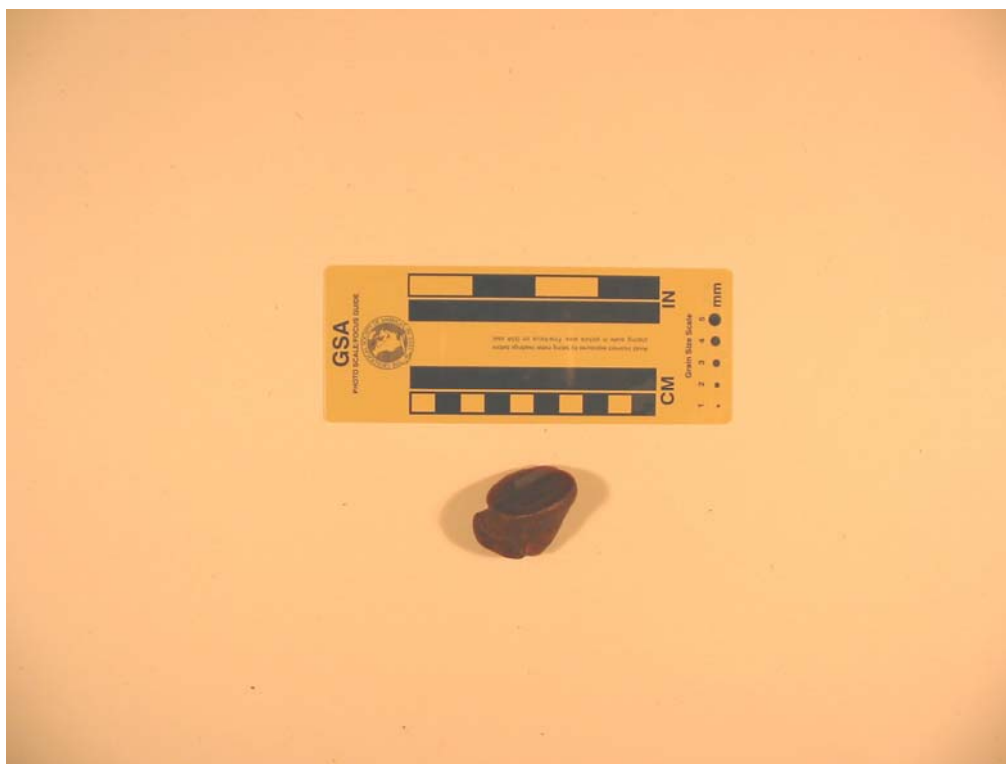

Figure 4: agate used in EBSD study. Specimen was adhered to a glass slide, cut into a thin section, and polished.

EBSD is a relatively new technique for petrologists. Also called electron backscatter patterns (EBSP) and backscatter kikuchi diffraction, EBSD is an SEM-based tool. The basic process behind it is rather simple. In an SEM, an electron beam is aimed at the specimen at a 70° angle. Diffraction of these electrons will occur simultaneously on all lattice planes in the sample, and the backscattered electrons, which escape from the specimen, will form a diffraction pattern that can be imaged on a phosphor screen (Fig. 5) (Prior et al., 1999). EBSD enables measurement of the crystallographic orientation of individual rock-forming minerals as small as one micron, as well as the calculation of misorientation axes and angles between any two data points on a sample.

Using the scanning electron microscope in Hulings Hall, Carleton College, EBSD analysis was carried out on one Lake Superior agate in hopes of obtaining quantitative data on the crystallographic orientation of silica fibers throughout the specimen. An attempt was made to obtain Kikuchi patterns from various points throughout an area on the sample (Fig. 6). A map was also acquired of the same area, plotting the quality of the diffraction pattern for every point in the area.

Results

The results of this study were indeterminate at best. The attempt to obtain a Kikuchi pattern failed (Fig. 7). Additionally, the map of pattern quality did not reveal positive results (Fig. 8). The associated points were then plotted on a histogram (Figure 9). Pole figures produced from plotting the crystallographic axes of points seemed to show a slight favored orientation (Fig. 10).
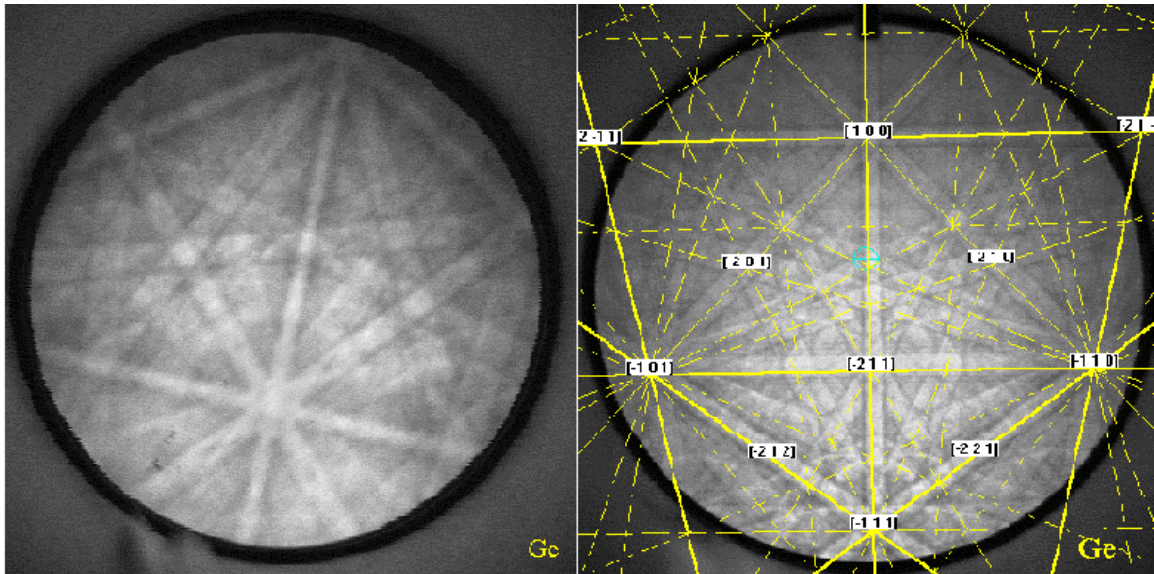
Figure 5: Left: an example of the diffraction pattern that can be imaged on a phosphor screen. Image was created with a Germanium crystal. Right: that same image with crystallographic axes shown.
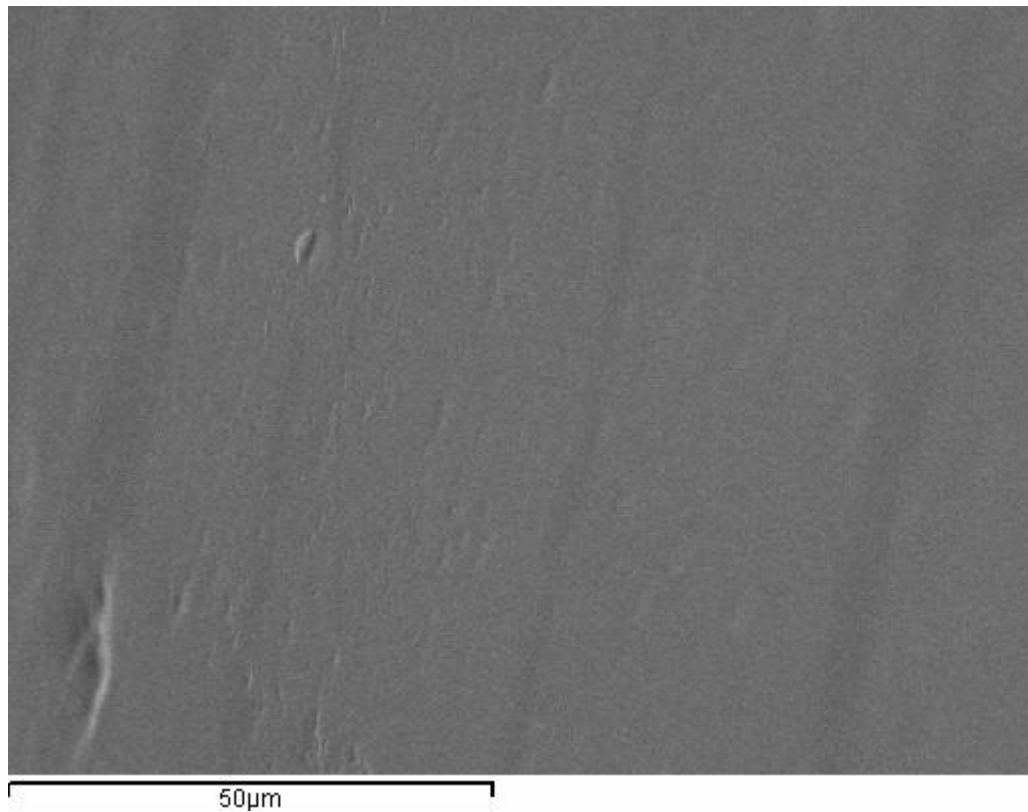

Figure 6: image of the area on the sample that was analyzed. Agate banding can be seen as darker gray areas running roughly vertical on the image.
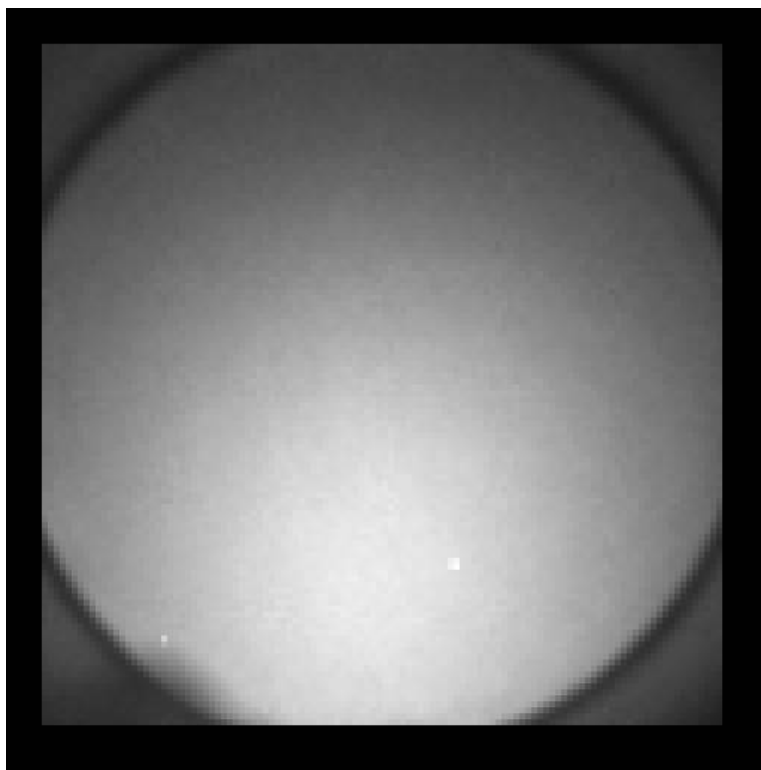
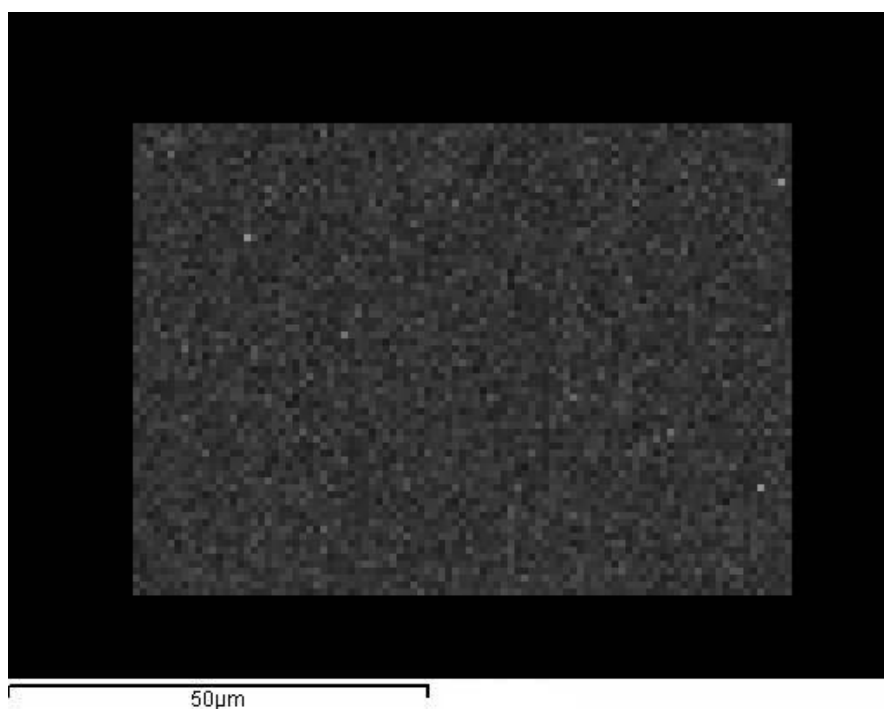Figure 7: the Kikuchi pattern obtained from the agate specimen. Note the total absence of Kikuchi lines, as opposed to Figure 5.

Figure 8: map of pattern quality for points across the sample area. Lighter pixels represent higher quality patterns. Note the near-absence of any lighter-colored pixels.
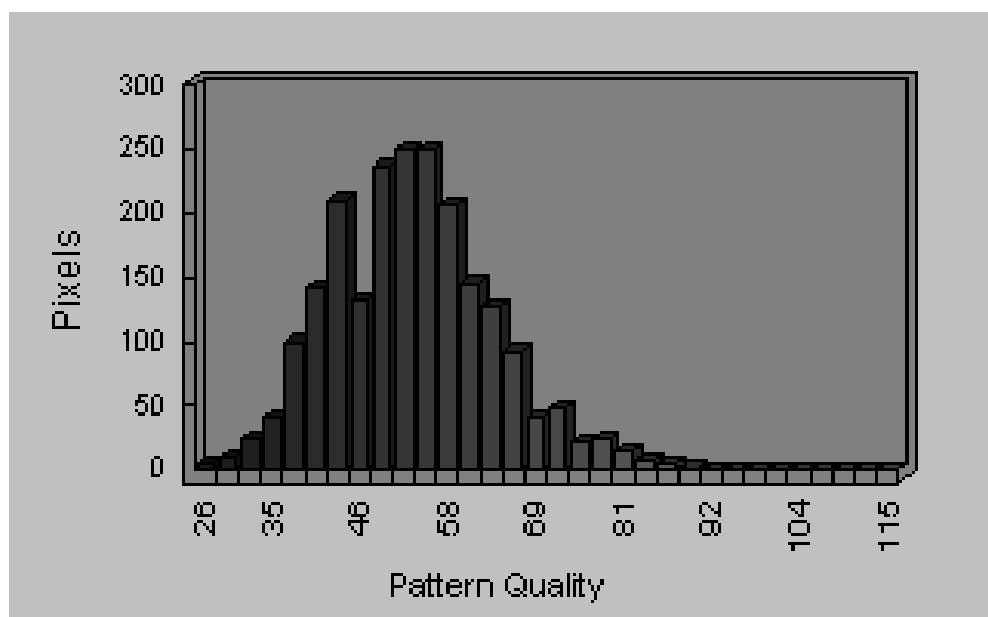
Figure 9: pattern quality points were plotted on a histogram. The majority of points lie to the left, with lower pattern qualities.
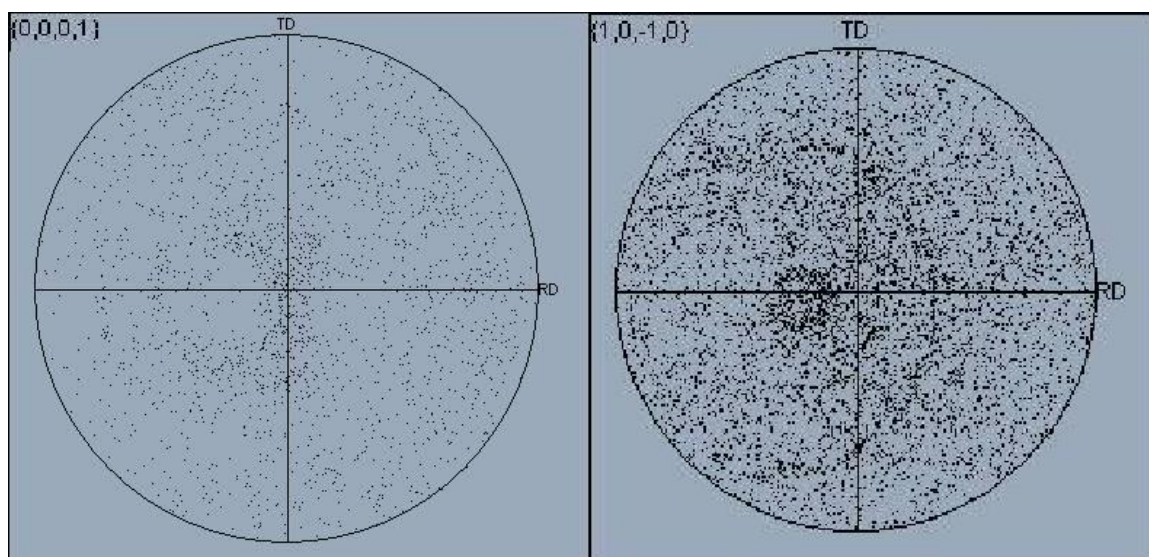

Figure 10: Pole figures produced from plotting the crystallographic axes of points showed a favored orientation. Note the opposite grouping of points between the two. Example: the right pole figure has a somewhat dense cluster to the left of center, while the left pole figure is sparsely populated in that same area. Crystallographic axis plotted is shown in the upper left corner.

In order to test whether or not the indeterminate results of this study were due to the coarseness of the polish or the cryptocrystalline nature of the agate (EBSD does not work on grains much smaller than 10 microns), a test sample of a mylonite with quartz veins was polished using the same method employed on the agate. This sample was also analyzed with EBSD, and the results were the same as with the agate. The pole figures were almost identical between the two samples (Fig. 11), with the same favored orientation appearing. Kikuchi patterns were again impossible to obtain.

Discussion

The results of this EBSD study leave little to discuss. The similarity between the pole figures from the agate and the mylonite suggest that the detector was not noticing the crystallographic orientations of the samples, but rather some unknown geometric aspect of the microscope chamber (Davidson, 2005). The mylonite specimen did not have the polished sheen of the agate, suggesting that it was too coarse for the detector to pick up a pattern. The agate, on the other hand, was highly polished, so it is thought that the cryptocrystalline nature of the agate prevented the detector from obtaining a pattern. The map and histogram of pattern quality support this conclusion.

Conclusions

Further EBSD study will have to be carried out to determine whether or not the procedure will truly work on agates. More advanced polishing techniques certainly would help to eliminate that variable, leaving only the microcrystalline makeup of agates as the
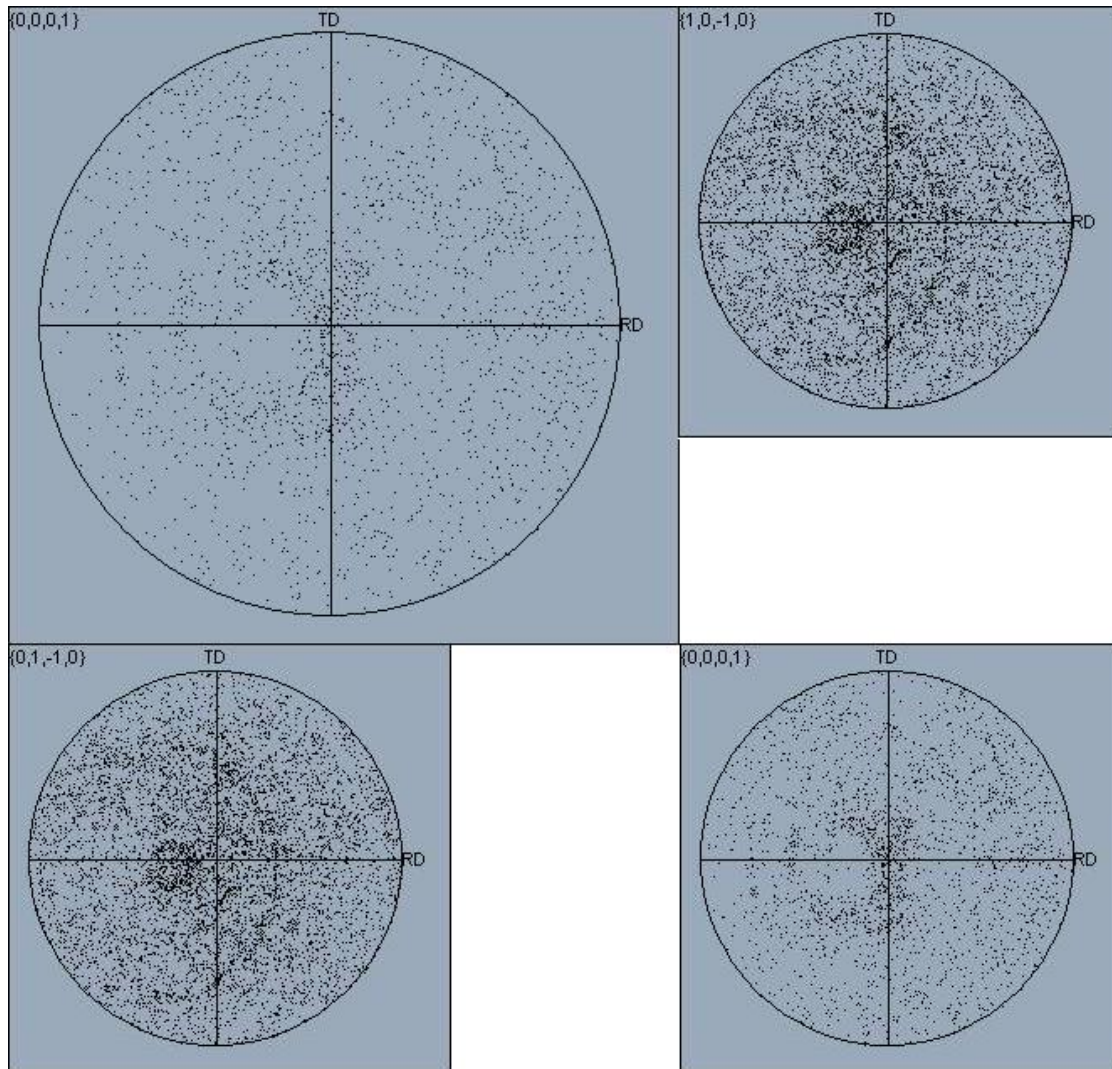
Figure 11: The top two pole figures are taken from the agate sample, while the bottom two are from the mylonite. Notice that the top-left and bottom-right figures are almost identical, as well as the bottom-left and top-right.

barrier to reliable EBSD data. The conclusion of this study is that the silica fibers in agates are probably too fine for EBSD analysis, but further study is required to prove this.

Acknowledgements

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