

Review of:

Mineralogy, Geochemistry and Genesis of Agate—A Review

By: Jens Goetze, Robert Moekel, Yuanming Pan (2020), Minerals, MDPI.com, Vol. 10, No. 1037, 51 pgs.

MDPI.com is an open-source, likely B-class journal company meaning it takes your money and posts your article online. They appear now to have some form of peer-review. A number of agate papers from Europeans have been posted to this site recently.

Review by Donald Kasper, 11/28/2020, rev4

Overview: This may be the first European science paper that recognizes that the myth agates are 99% quartz is disinformation and not science. Beyond that, it promotes a number of urban myths about agates, some lingering for over 200 years. In general, European science agate models are weak models. These are models that pick-and-choose specimens and data to cobble a narrative. They are not strong models that account for all the specimens and data we have. They are a class of shallow studies using a few rocks, massively under sampled for the some 700 structures and inclusions agates have.

When they have two populations of agates and two temperature populations (supercritical and subcritical) and all the structures of historical interest are mainly in the volcanic supercritical candidates, trying to make a unifying model of genesis does not work.

I will go through the paper in order of occurrence of items that I comment on. The paper is typical of agate genesis works that use clichés, magic, and shallow thinking to cobble an agate genesis model combined with clear fallacies.

Detailed errors and problems in this study:

1. In the abstract, it is mentioned that agates have opal-A. Based on 10 years infrared spectroscopy study and armed with a classification key of opals that I generated from hundreds of specimens, I know conclusively what an opal-A is in infrared, and I can also see mixed opal species in rocks. Infrared is the clearly superior method of spectroscopy to study glasses, clays, opals, and length-slow silica minerals. Agates have zero opal-A using infrared study. Also, it is strange they did not mention agates have opal-C.
2. In the abstract, this is the first paper to show that agates contain mineral inclusions beyond silica. Bravo. So how much? They won't say. The dogma of Moxon is that agates are 99% quartz, but the reality is that specimens we collect have as little as about 30% silica. A good example is the Laguna, Mexico agates that are flooded with carbonates, usually calcite and aragonite.
3. In the abstract, agates are said to form from diagenesis (internal alteration over time) of sedimentary rocks. Yes, this is true. If you get out a microscope and zoom in at 200x you can see micron banding in silcrete (ash) soils. But this is not what we call an agate. Can an agate an inch in size form in soils? Never. If I am wrong, prove it. Show me a soil profile with bigger agates at depth since the deeper you go in soil, the older it is. You cannot. Here in Southern California, we have 300 miles of the San Gabriel mountains, it is granite and schist, a third is quartz, voids are everywhere, and the agate count is zero. Quartz and voids and

weathering produces no agates there. If you believe agates are diagenesis of quartz source rocks, go to any beach in the world with silica sand, and dig for agates. There aren't any. The reason is that quartz rocks break down into smaller quartz rocks, but they do not dissolve in surface waters.

4. In the abstract, clays and zeolites are said to be found in agates. Yes, clays are. The count of zeolite inclusions in agates is zero. After they form, zeolites can intrude agate voids and the host rock can have zeolites, but zeolites are pigs and steal all the quartz so where zeolites set up, agates do not form. It should be noted only the highest silica content zeolites are found around agates. Not any zeolite will do. So that is ferrierite, stilbite, clinoptilolite, erionite.
5. In the abstract, it says oxygen isotope studies show agates form to 230 C. These isotopes are referenced to standard mean ocean water (SMOW). Someone took a bucket of sea water from the equator, took it back to Europe and declared it SMOW. Oh, oh, 15 years ago they ran out. No problem, now everyone develops their own standard and from that tells us what the oxygen isotope ratio is in our rocks. However, this is not SMOW, this is personal mean ocean water (PMOW). Second, it means anything you like depending on your assumptions of what the water is and where it came from. This is a standard by which you get to confirm your model assumptions and prove yourself right, every time. From this type of analysis, we know, for example, the earth formed at 50 C. The oceanographers tell us so. This is the oxygen isotope study results of oceanic basalt. Why 50C? Well, if you get to 100 C you blow off your ocean as water vapor, and this is bad. 50 C it is. But, Goetze hesitates, and goes to 230 C for continental volcanics. He has to study continental volcanics because zero agates form in oceanic lavas (mostly basalt) whether it is now continental or still in the ocean. Weathering apparently doesn't work in oceanic lavas of any type.
6. Page 1. Liesegang is alleged to have proved diffusion can make agate banding. The problem is these experiments are discontinuous ion accumulation by diffusion, did not involve gels, and is not silica banding by diffusion. Also, agates, don't have discontinuous banding unless exposed to acid systems, which is quite rare, but Liesegang bands always do. Now, we get iron staining in volcanic tuff is proof of agate genesis physics, or as we will see in figure 2f later, Dulcote, England chert nodules with iron staining is evidence of agate genesis. That banding alternates between granular quartz, and quartz crystal bands in some cases from that locale, but agates don't do this. This chert is dominated by sponge spicule debris for those that look, so these are accumulations of siliceous sponges.
7. They indicate that Daubree, a German, who published in German showed agate formation at 400 C and 1 Kbar. This is a supercritical fluid. This proves agates can form in a supercritical system. But agates form over a wide range of temperature. As they do, their structures change. These structural changes are ignored in this paper. From two sets of supercritical experiments that made agates (and another the authors missed), the authors complain this was done to make the experiments run fast. True, but how long is an experiment chemical reaction supposed to take? Millions of years? Prove they take millions of years. Second, they do prove agates can form in supercritical fluids. The only question that remains is—how common is this in nature?
8. Page 4, Figure 1. Note no oceanic basalt in the world is linked to agates. They do not list trachyte and trachyandesite, which also have geodes/thundereggs. Part of those two lava compositional types are under the continental/oceanic basalt compositional line that separates continental from oceanic lavas in a Total Alkali Silica (TAS) lava diagram. Only lavas under this salinity line can have agates.
9. Page 6, agates are found in river gravels and marine sediments. So what. It is called erosion but the strange inference is that this occurrence relates to genesis, which is false. No, it is childishly false. The attempt to say agates form where there is water is false. Most agates are found in modern deserts. They are not related to rivers, lakes, swamps, water tables, springs, etc. They are found on faults. Is there supposed to

be just weathering on faults? There is no agate correlation to surface water accumulation whatsoever for volcanic agates, which means they are not related to weathering. Volcanic ash nodules of jasper-agate occur at the caliche horizon in deserts due to water entrapment, but these form by accretion at low temperatures. Accretion is triggered by wetting/drying cyclone. How can minute agate veining occur in these nodules? 800 sq meters/gram surface area silica shard in the ash is the trigger. Which is why no soil horizon without ash won't form them. Gel systems are driven by surface area, concentration, and ionic charge, all missing from the understanding of gels in this class of works. When they start talking about Point of Zero Charge (PZC) related to pH (acidity) then I will know they have a clue what gels do, but that won't be found here.

10. Page 7, quartzine. Quartzine is mentioned repeatedly in terms of polarizing microscopy but its distinction in terms of any method of spectroscopy for modern science and whether it is distinct from moganite identified by spectroscopy, is missing. The 1800's definition of quartzine is what we get here. The literature tells us nothing but the reviewer models they are distinct with infrared spectroscopy. Quartzine and moganite are unique in the silica mineral group in that they cause peak suppression in infrared. The more that is found, the more suppressed their key marker bands becomes. More of any length-fast mineral causes infrared peak enlargement. These two cause different bands to be suppressed. Start there in your quest for them.
11. Page 7, Figure 4. This shows alternating bands of length-fast, regular chalcedony and length-slow quartzine with and without polarizing microscopy. Left out is moganite. Also left out is that the zig-zag fiber bundles are chalcedony, and the straight bands are quartzine and that impurities in the agates are preferentially pushed into the straight quartzine layers. No impurities are going to be found in the quartz crystal (stockade quartz) band layers, which are omitted in this paper as a banding type of silica. All of the moganite found as microdiscs in some banding plane regions consisting of a world within a world, is all missing. Banding planes have their own internal geochemistry! It may be that the quartzine accommodates the moganite structures, which themselves can be concentrically zoned such as for moganite ellipsoids. There are no opal ellipsoids in agates. They are moganites. Shadow agates are bands of moganite that block light and make shadows.
12. Page 7 discusses opal-CT as lepispheres and says they can have opal-A in them as well, then refers to Figure 5 on the next page. That figure is just opal-CT. Opal-A cannot be found in agates. Its indicated temperature of formation is at or under 45 C, while opal-CT formation is indicated at or above 160 C. Infrared by far, and bar none, is the superior spectroscopy method to identify opals, and with that no opal-A has been found by the reviewer in any agate, anywhere in the world. Furthermore, opal-CT has no cristobalite identifiable with infrared, and is a tridymite opal with that method. The authors ignore that opal-A means opal-amorphous, which has no meaning other than to say an X-ray spectrometer produces no identifiable return signal, just a broad, noisy roll. There is no opal or mineral species called "amorphous". Opal-A is a tridymite opal in infrared.
13. Page 8 they mention opal-CT is found in an Oregon geode. This is not the issue. The issue is that opals are found in specific structures of agates and therefore their proposed genesis and that of Moxon they cite frequently that opal-CT forms chalcedony then forms quartz is untrue and opal still remains in these agate structures regardless of how many tens or hundreds of millions years old the agates are. The Moxon agate transformation myth is just illogical and nonsensical thinking not based on comprehensive observation. Moxon thinks that way a lot in his papers. Find one agate. Study it with 20 instruments. Conclude how all agates of the world form. That kind of dogmatic thinking.
14. Page 9, that is correct, as they cite Florke stating, there is no opal-A in agates. Yes, opal-A is common in sinters, which means hydrothermal deposits, vents, geysers, and it does occur with opal-CT, and also the reviewer finds a mixed opal-CTA, however, these sites have no macroscopic agates. The main reasons are

the temperature is too low and visible agates don't form at the surface. They go on to cite Moxon who claims moganite inverts to quartz over time because 9 of their old agates have 6% moganite. Well, they never have over 6% anyway. Moganite is still found in a Kentucky agate of Mississippian age (360 Ma.) by the reviewer, and quite distinctly, and within pendant structures only, which is one structure where beta-moganite as the reviewer classifies it, is found. For this paper the concept of beta-moganite does not exist. This is high temperature moganite formed at 354 C and with that, is a supercritical fluid marker. This is why the authors see agates forming lower as they have no technology to see agates formed at higher temperatures. For example, zeolites will decompose above 300 C into other silicates, but zeolites are not found in agates, so this is not a limiting mineral feature.

15. Pages 9 and 10 they mention the existence of an outer wall lining of silica, then say nothing about why it is there or what it might be other than it can be quartzine. This primary silica layer or PSL is in 100% of all agates in volcanic rocks with no exception, and therefore weathering cannot make it because the weather and hence rainfall is not 100% certain on time to fill a lava flow void system. Second, they don't mention until much later in their paper that at or about 0% of sedimentary agates have this PSL structure. So, these two temperature classes of agates are totally different in terms of internal structure. All the major inclusions of agates such as tubes, moss, plumes, included carbonates, waterlines, the PSL, etc. are only found in volcanic agates. The reviewer models all these as evidence of supercritical fluid formation (over 374 C). The lower temperature, sedimentary agates, form with ash dumped onto carbonate rocks. If the ash isn't dumped onto carbonates, we get silcrete soil instead, a silicified tuff with microchannels, cracks, fissures of microscopic agate that is then called isopachous quartz. Cherts only form from ash fallen onto carbonates, but in sea water where the salt prevents agate formation. No chert forms without volcanic ash. Eruptions into sea water cause radiolarian and sponge blooms, whose fossils are then found in these rocks.
16. Page 10 discusses horizontal banding as a coincidence of silica gel settling. However, there is no wall-to-wall horizontal (waterline) banding in existence in any agate, 100% are contained within a PSL. Note settling is a coincidence of timing, implied to justify horizontal bands 100% of the time in an exact geologic setting, so the enforcer of that is something else. As a supercritical fluid (one vapor gas) goes subcritical, the physics is that two phases form—water vapor and liquid water. From that, agates in volcanic rocks have banded or quartz crystal tops and waterline bottoms. The banding occurs in the vapor and the waterlines form in the water with silica. The PSL is vapor phase amorphous silica gel glass deposition which explains its occurrence and the waterlines and other agate structures contained within it. No other physics exists that can explain all this. No sticky physics for water with silica coating surfaces uniformly, exists. However, vapor deposition of silica gel glass does explain it. You want to find silica gel glass you need to visit the Hawaiian East Rift Zone and collect Pele's hair. It comes in strands and mats. I suggest Fissure 9 Pele's hair. That is where mine came from. That glass alters, or rather is well documented that basaltic glass alters, to celadonite clay and zeolites. Celadonite clay coats all of these volcanic agates unless it is hematite or its weathering oxide goethite, which probably has celadonite also in it. Silica glass also alters to zeolites, which can line the outside of an agate.
17. Page 11, Figure 10a. It is unclear how they proved a layer is opal-C, but the reviewer only finds opal-C in waterlines and one vein opal site in a basaltic mound in Boron, CA.
18. Pages and pages about cathodoluminescence and trace elements and oxygen-18. Okay.
19. Page 23, I don't see how you get reliable anything when studying supercritical fluids including atomic element ratios go to hell from diffusion, their oxygen-18 data is all over the place, and they complain about variable temperatures from fluid inclusion study. A supercritical fluid is called medium grade metamorphism, fluid-rock interaction, and metasomatism. This means your rock to this fluid doesn't really

exist and the fluid goes right through. So, explain to me all about your atomic ratios and how they just went to hell and how this proves how unstable agates form. There was a paper I read some years ago about the uranium atomic ratios to tell the age of micas, but if the micas after formation were exposed to a temperature over 374 C (supercritical) the clock to report rock age is reset from metasomatism (ionic transfer). If you don't study the behavior of supercritical fluids, you won't ever figure out what is going on in volcanic systems and their agates.

20. Page 23. "Different degrees of filling in the inclusions...provide indications for fluid trapping under heterogeneous conditions". No, it shows supercritical-subcritical fluid transition change or it shows deposition with internal diffusion whose silica/fluid ratio is cycling. This comment is unclear and may be conflating several reports of different homogenation temperatures of agates formed under different regimes. Agates don't form at a temperature, they form over a wide range of temperature, slower and smaller at lower temperatures. A hydrothermal vein agate at 80C? As the system shut down, yes. But the macro structures would not form that cool. Or, the vein breached an opening and decompressed.
21. Page 24. It is unlikely an agate has 30% salinity. In calcite spectra for agate inclusions where there isn't silica band interference, the presence of salt can be read in infrared. It is found in host rocks with agates in former marine rocks in a few locales by the reviewer. No halite or other group halides claimed to be found as agate inclusions and due to their solubility in water, are not expected to remain. The cubes of Keokuk quartz geodes are probably melanophlogite, not fluorite pseudomorphs.
22. Page 24. All mineral classes occur in agates? Totally false. The list is extremely restricted. Zeolites are common in agates? Certainly not. There are zero zeolites in agates. No amphiboles. No pyroxenes. No broad spectrum of sulfides and then only in trace amounts. The reason sulfates are found in agates is that when calcite encounters acid it forms sulfate and neutralizes the acid. When Goetze in other works cites German vein galena occurrences with quartz agate banding, he ignores the presence of barite. It is there for a reason and he needs to learn why. He also ignores that the galena came in after the agate formed.
23. Page 25 mineral list would have to be posted as a separate table but the table is generally incorrect. Carbonates are found in agates, yes, and can be the dominant mineral in an agate specimen. Finely disseminated calcite in Santa Monica Mtns., CA agates in volcanics and marine sediments can be milky white, opaque from the calcite. Manganese minerals in general, intrude with groundwater with weathering intrusion along agate fractures.
24. Page 26. "Geochemical investigations of calcite in agates sometimes showed several carbonate generations". The solubility of calcite means it is less soluble at high temperatures, so comes out of solution first. It then deposits last. Not multiple generations. Two generations. If there is a pause in deposition as the CO₂ load in a hydrothermal system changes such as the Big Diggin's [sic] site out of Deming, New Mexico, you get internal agate layers with calcite. Since calcite is thousands of times more soluble than silica and since the silica has to come from a melt, hydrothermal decomposition, or volcanic ash, external water is carbonate water not silica water. This is the biggest problem promoting weathering models which literally say the insoluble minerals make agates, and the highly soluble minerals don't infiltrate ground water and no one has caliche in mineral specimens of the deserts of the world. Apparently, they cannot recognize caliche. When they can, they won't find caliche as an agate inclusion. This is bad, and shows the harm caused by science writers that apparently don't collect for themselves.
25. Page 26. It is not that iron oxides are unique in agates, they are necessary since they indicate reducing conditions. Agates cannot form under oxygenated, surface conditions. This means they cannot form with ground water, as that is also oxygenated. No, their inclusions especially as microspheres does not prove high concentrations in intruding fluids. It can also indicate weathering intrusion into agate and into

microsphere gas voids. We don't know at what stage the iron intruded, but in many cases, fracturing is the entry point with weathering. Not only is there iron oxide, but the cores can be hematite. As such, the original mineralization may have been magnetite, which the reviewer finds in certain Mexican thundereggs as acicular needle bundles. All the other iron minerals could then be weathering oxidation byproducts of the original magnetite. Magnetite represents extreme reducing (oxygen depleted) conditions. You have magnetite, you don't have weathering.

26. Page 27, Figure 22a. No, this is not hematite in an agate. This is analysis based on a look, which can even be close a third of the time, but infrared study by the reviewer shows that all muddy structures of this type are calcite. Not siderite, they are calcite. Siderite is very rare geologically.
27. Page 27, Figure 22c. This striping of iron oxide microspheres is seen using DIC microscopy for the St. Egidien thundereggs. The cores are hematite, and the outer zonation is iron oxide.
28. Page 27. "On one hand, laminated and lenticular agglomerations of very small hematite particles (<10 microns) occur". No, the hematite only forms as microspheres due to immiscibility, but as the banding sets up, they get squashed into microdiscs on banding planes showing banding compression during setup.
29. Page 27. Cathodoluminescence is not reliable for mineral identification. Kaolinite in Germany geodes is from weathering infiltration since Permian when they formed. Very old agates are kaolinite included. The kaolinite is from geode shell feldspar decomposition.
30. Page 29. To get large accumulations of agates in sites like the photographed trachyandesite site in China, and the site in Germany, the silica, water, gas has to come from the melt, otherwise the rock alteration from fluid migration has to be shown. For example, fluid migration causes illitization of the host rock wall around the fractures, faults, breaches of hydrothermal fluid intrusion making the rock white, and brecciation and other hydrothermal structures in the host rock will be evident. Since none of this is seen in this Chinese site, German site, or any other, we know there was no fluid migration on a large scale, or over travel distances more than centimeters in scale.
31. Page 29. "Cavity formation is assumed to be the result of transient tensional stress in the melt", in discussing rhyolite geode formation. This would be false as expansion can produce silica glass stringers that alters to moss structures as they are called for collectors. Accordion structures of split and expanded wedges occur (box core structures). There are several classes of geodes formed in slightly different ways, which is not identified or discussed here. If they scanned the Figure 25b thunderegg, the green floor will be quartz and beta-moganite which collectors identify as jasper. 4 meter megaspherulites cited are sandstone concretions, not volcanic thundereggs. That statement is just wrong. The largest volcanic megaspherulites are about a meter across.
32. Page 30, Figures 26b and c of a cauliflower or lumpy agate from Iraq is reported as an anhydrite replacement specimen. However, the reviewer only knows of anhydrite replacement making quartz crystal and quartz geode nodules, not agates, so there is something wrong with the reporting of this locale where the description is not specific enough to investigate.
33. Page 30, states sedimentary agates are typified by cauliflower structures as anhydrite replacements. This is false. Quartz nodules and geodes replace anhydrite nodules but banded agates do not. The geodes are quartz crystal hashes and fine quartz with kaolinite group clay, celadonite showing volcanic ash, and radiolarians.
34. Page 31 cites two papers showing agates formed in supercritical fluids then cite Oehler who they state formed agate at 100 to 300 C. The latter citation association is false. Oehler earlier in 1971 was testing silica replacement of algae with a specific manufacturer silica gel chemical and made, in his own words, granular chert in which the algae were encapsulated. He did not make agate.

35. Page 31 they cite the White and Corwin paper briefly about making an agate from cristobalite glass in supercritical conditions then left out that at 100 C all they got was opal and could not get agate to form below 300C.
36. Page 32, "There is no indication for participation of supercritical fluids" after citing three papers that did just that and he forgot the Russian research that also did that.
37. Page 32, "SiO₂ in volcanic agates represents a product of late- or post-volcanic alteration/weathering of the volcanic host rocks". The authors wrote that with a straight face after just saying "volcanic host rocks" as though that is the only place where weathering occurs. What about agates in granites of the world? Zero, because weathering does not occur with granite rock regions of the whole world? The fact that they occur in volcanic rocks means what, lowest possible temperatures of formation? Then they won't occur in volcanic rocks, will they. Shale is quartz. Schist is mostly quartz. Show an agate in a shale or schist locale anywhere in the world. You won't be able to.
38. Page 32 they state "Additionally, a formation of agate directly from igneous melt is unlikely" then show on page 33, Table 5 of geodes formed in pitchstone (obsidian with feldspar inclusions) in Germany comprised of 64% silica glass after debating where the silica comes from and conclude it must be weathering and cannot come from the host rock. In the reviewer's study, geodes form preferentially in the highest silica content portion of rhyolite lavas for a reason—the geodes get their silica directly from the melt, and since the shells of the geodes of many locales are pure potassium feldspar, we see the melt cooled where the silica and feldspar separated in a process of exsolution extensively documented in geochemical literature. Silica and feldspar types is how you define a lava as they are the main components. This is called solvus immiscibility of a lava upon cooling where the silica will not stay dissolved with the feldspar. This discussion is ignoring basic volcanic geochemistry and physics.
39. Page 33, "In mafic volcanic rocks a greenish layer of sheet silicates (celadonite) can be observed at the interface between the agate geode and host rock." Mafic refers to basalt, and therefore this is false. All rocks in all volcanic lavas including vein agates commonly have an outer layer of celadonite. It is just that the rhyolite geodes/thundereggs are found with an outer crust of mixed opal-Q (microquartz opal), feldspar, beta-cristobalite (yes, this can be identified in infrared if you do your homework), quartz, and celadonite. The celadonite may be in low concentration, so the alteration shell is white and the celadonite is only seen with near-infrared spectroscopy. No, geodes/thundereggs are not formed in perlite (hydrated obsidian). On this one, Colburn got it wrong.
40. Pages 33-34 describes how silicic acid now magically makes agate with all the problems tossed out such as how does the second layer form after the first layer PSL seals the void? How does that second layer get beyond the primary silica layer? How do solutions coat the void and always completely flood the agate to line it all with agate bands instead of just the bottom in drought years? How does outflow work and how does it work against the inflow? How does silica flow through a silica membrane and not alter it at all, ever? Figure 28 shows a solidified collection of silica particles falling to the bottom, but this is not how agates look. The silica coats the void walls. Then when the story gets interesting to explain a miracle happens and it is all just self-organization. The largest void we have is the surface of the earth and with rain water and 250 ppm silica in an example, we should be walking about on a crust of opal slowly burying all that we know. Thank goodness this whole system is bogus and does not exist.
41. Page 35. It is not that spherulitic growth merges and leads to banded growth. It is that any time there is a pause in deposition indicated by internal spherulite layers inside agate banding, the process starts over again, telling us there was a pause. But the authors don't mention there can be many generations of spherulite growth. About as often as spherulites start on the outer void wall, the PSL forms on top of it,

then the banding starts, or the PSL forms first, and spherulites form on top of (interior to) that. Opal-CT spherulite growth and agate banding in cherty agate formation in sedimentary systems with volcanic ash, and is conflated with a volcanic method of genesis where wall hemispheres form from efflorescence, the leaching out of minerals from the host rock as an external surface contact from decompression.

42. Page 35, agate does not form on void walls, it forms on surfaces, so that internal inclusions in an agate grows outward to the outer walls as wall banding forms to the interior. So, a diffusion model of outside-in is nonsense. There is an internal mass of sufficient silica formed by feldspar separation that crystallizes without fluid migration. If fluid does move in, it leaves a dump of calcite mud as its calling card as calcite is thousands of times more soluble in solution than silica. In fact, carbonate, barite, and silica in solution makes hard water scale everywhere, including in dead agate cores that fractured to allow groundwater in.
43. Page 35. If agates form at high temperature above supercritical the likely silica phase around is cristobalite glass, but the White and Corbin paper only formed agate from that glass on rods with hollow centers. The agate formed in the void cores, it did not convert in place.
44. Page 35. Silica moving into voids in tuff miarolites is where the interior is quartz crystals and sometimes other minerals like rutile on the void walls, no PSL and no agate banding. This is ignored.
45. Page 36. Making the claim that silicic acid leaches through agate banding without ever affecting the existing agate is just illiterate. Ions move in and out of agates after formation called color zoning, but those are cations. The migration is typically sideways along the quartzine bands. Kaolinization is only sideways and the incomplete sideways fill along bands by differing amounts is evident in specimens. Over time, the only thing that happens to an agate is kaolinization, and then we call it a chert.
46. Page 36 says that fiber and quartz crystal bands show silica migration through the agate. Okay the agate is 3-D and diffusion comes in from all angles. Now what? Where does the water go? Explain how in and out water flow simultaneously works because I don't get it. Second, diffusion from a mass of silica gel in the void center onto a wall front of agate banding causes depletion, depletion causes undersaturation, and undersaturation makes quartz crystal layers as it takes supersaturation to make agate fiber banding. Then after a pause the diffusion catches up and then fiber banding starts again. This does not involve external migration of silica. In addition to all that there is an intermediate banding where the quartz crystal layers have fine growth zoning on the same scale as the fiber banding. Both quartz crystals and fibers can make the same magnitude growth layer structures. I have microphotography of agates with quartz crystal layers showing easily 50 or more growth bands. Lastly, external supply of silica from weather introducing ground water cannot cycle anything as consistently as agate banding. A chaotic source cannot make a regular rock structure just as a common geologic process (weathering) does not rationally account for rare rock and mineral formation (agates).
47. Page 36. Given the high Aluminum content in agates and the silica, you get hydrothermal movement about you are going to make zeolites. The only zeolites seen are in the voids after the agates stopped forming, agate walls under the PSL, and the host rock including the geode shells. That void accumulation of zeolite could actually be fluid migration. As such, the agates would be filled with zeolite inclusions. This does not occur, so external silica arrival is not consistent with the agate structures in addition to the total lack of external channels present to bring in those fluids.
48. Page 36, the white plates on banding planes are called moganite when they get around to studying its composition. Wait, moganite forms in the agate fibers and now there is an immiscible moganite. Okay, this moganite in infrared is different and the reviewer calls it beta-moganite. It never graphs as alpha-moganite. Really, these authors sound like they don't have a Raman microscope or infrared microscope to know what is going on.

49. Page 38 looks like a rebuttal to Moxon, acknowledging that other minerals stack up on banding planes, something Moxon won't consider possible.
50. Page 40. Now tubes and pendants occur so the science goes berserk, can't comprehend basic supercritical-subcritical transition consequences like boiling and in come the microbial bacteria to explain it and by God some claims they see chitin. Well, infrared spectroscopy is the standard for organic compounds and the author hasn't seen organic anything in an agate yet. To get stromatolites, you have to look at jaspers in very low temperature systems. However, the author does have some agates with apparent blue-green algae bloom structures captured. Those are segmented tubes and rods. These are exceptionally rare, and are found in formed hydrothermal locales with agates flooded with carbonates. For every biosignature of an organic tube that the authors want to cite, let me cite a paper on vermicular clays. Right, they have celadonite, and no, celadonite is not a biocompound. When the gel contracts, it can opportunistically pull the celadonite from the PSL shell into the interior because after all, it is a gel for some time. Goethite also makes tube streamers. Basically, they are talking about blue-green algae. What gets left out is that little problem called they are photosynthetic organisms require sunlight but agates don't form upon the surface of the earth, ever. If the bio organism doesn't use sunlight, then you have to explain what it eats. It is filled up in a silica gel and was eating what? Sulfur? Sulfur is not found in agates unless it is at the small ppm level. Iron? The cores of iron oxide microspheres of St. Egidien are hematite. Iron is in things like radiolarian nuclei (cores) in cherts.
51. Page 40. Acicular structures are a morphology that the reviewer models as only formed in supercritical fluids of the type related to the mineral. Acicular calcite in supercritical CO₂. Acicular silicates in supercritical fluid ("water"). You can get a supercritical fluid under 374 C by mixing it with CO₂, for example, as can mixtures occur. This may explain the so-called hydrothermal agates. How do acicular structures like this happen? Rapid nucleation? Ostwald ripening? Other clichés and fairy tales? No, just no surface tension in a supercritical fluid, unlike water, so they are stable. Morphologies matter, and so far, these authors are not on the ball because morphologies occur under exact geochemical conditions and are geochemical markers.
52. Page 40. More c-axis stacking. I just received flat m-face faden quartz crystal clusters from Pakistan up to an inch in size, stacked on their c-axis with hydrothermal vent tubes that run down the center, so don't get the impression that only 5 micron quartz crystals stack on their c-axis as the basis of agate fibers. This type of morphology gets truly huge and occurs in systems beyond agates. You just have to get the right specimens to know.
53. Page 41 conclusions. Agates form in rhyolites above the glass transition temperature. Agates form at up to 230 C. Okay, what is the rhyolite glass transition temperature? Say it. Supercritical above 374 C. Up to 575 C. Supercritical is not infinitely hot. Above 575 C is ultra-supercritical but the authors have not found that literature from chemical engineering yet. If you don't understand the systems of water, you won't ever understand the silica mineral group.

Conclusion:

Overgeneralization cobbled together by clichés and 1800's technology of observations without modern instrumentation defines most agate study compounded with undersampling. Agates are the most complex and diversely structured rocks on the surface of the earth and therefore huge specimen compilations are necessary to see patterns. Agates are calcite-silica (calcsilica) rocks, that virtually never reach 99% quartz for those that study the actual, whole specimen collected.