A review of:

Agate Genesis: A Continuing Enigma
By: Terry Moxon, Galina Palyanova, (2020) Minerals, MDPI.com, Vol. 10. No. 953, 26 Pgs.

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Review by: Donald Kasper, 12/10/2020, updated 11/18/2022

Overview: The refusal of Moxon and Palyanova to study agate inclusions leave them repeatedly lost about agate genesis. As one example, are agates filled once or in succession with silica-rich fluids? It turns out, when water intrudes it reacts with the silica gel in the interior to form opal or granular microquartz structures. Quartz and microquartz produce different spectra in infrared spectroscopy. In addition, they only are found attached to or based from the outer void host rock wall that was originally present. If silica intrudes established banding, geologic common sense of many other studies such as vein ore deposits shows that the intruded rock is brecciated, etched, altered, and new deposits in it occur. Since none of this exists in agate banding, there is no intrusion into established wall bands unless the outer silica layer is fractured or an implosion event occurs.

The refusal of the authors to study rhyolitic agates (geodes/thundereggs) drops out a major class of specimen study. The refusal of the authors to study vein agates until their first paper in 2020 that involve one, drops out a major class of specimen study. It is not how an agate in basalt formed, it is a model of how they all form that is relevant.

The proposal that fluid goes in and out of the same host rock is called nonsense physics. The net flow would be zero. If a dominant flow comes from one direction through a void and out the other end, this would be the candidate model for chevron agates whose banding meets at right angles to the void walls and whose specimens don't appear to ever have void relicts in the center. They don't recognize this banding type exists in European science so far.

Silica entering voids at points with a little fluid makes vent cones and chalcedony buttons attached to the walls, not agate wall banding. If the structures all combine, we get hurricane agate/feather agate, as in the Ochos Brazil amygdules. Look them up. That is how they formed. The banding is all torn up hydrothermally. That class of banding is not in European science.

If the temperature is hot enough, miarolites form which are voids filled with crystals and no agate. It is not how agate fills voids, it is how a void is filled with either celadonite, celadonite and agate, or zeolite, but never agate and zeolite because as these authors do not understand, there are no zeolites in agates. Left over voids when the agates stopped forming, filled with hydrothermal zeolite along fissures later is not agate genesis and related to post-agate formation of caliche, calcite, gypsum, or mud intrusion.

Void entry of any mineral makes ONE structural type, not two or ten or twenty. Each morphology forms based on conditions not chance and another morphology means something else occurred that the scientist is ignoring due to laziness or refusal to study morphologies (shape-types) and recognize their importance. Dana years ago, wrote A System of Mineralogy. The book A System of Morphologies has not yet been written, so understand that our mineralogy is limited and primitive and agates form from a combination of morphologies and crystallography.

Their refusal to study enough specimens, Western US agates, vein agates, comparison to nodules (formed by accretion) and none of the silica gel structures all over agates is typical of European scientists and popular agate book writers. In fact, since quartzine, beta-moganite, beta-quartz, opal-beta-cristobalite (opal-BC), opal-Q (a microgranular quartz), opal-beta-quartz (opal-BQ), silhydrite, mono- ortho- and hex-tridymite, magadiite, and melanophlogite all exist in agates and can typically be identified with infrared spectroscopy using modern

equipment, modern analysis and statistical study, the ability of this class of authors to come up with anything we can call real is difficult and subject to chance. To study the host rocks with no resolution to the identification of all the feldspars with spectroscopy means that the lavas are not competently studied, and the discussion will substitute clichés, slang, and urban myths masquerading as science.

They use the oceanic mud metamorphism with burial model of radiolarians (opal-A and biosilica) to opal-CT to quartz with depth of burial, and use that for volcanic rocks where the process is rhyolite micro shards of silica gel glass or basalt sideromelane silica gel glass to quartz having nothing to do with the marine process. That is what forms the outer, primary silica layer (PSL) in 100% of all volcanic agates. It is vapor phase silica gel deposition. If you want to study this glass before it is altered, get Hawaii, Fissure #8 Pele's hair and study the vent clumps of that. This has not been studied other than by me using modern spectroscopy. It is labradorite glass, augite glass, and silica gel glass. Don't obsess over trace iron and titanium. Stay focused. The silica gel glass coats the voids as it does for, say, Klamath, CA basaltic volcanics.

I rebut this paper's logic and those of others in full detail in my new book An Intermediate Guide to Agate Formation, their Structures, and Inclusions, about 210 pgs., to be released on Amazon soon (spiral bound, full color, laser printed). The book covers all the structures and inclusions related to agate genesis these authors such as Moxon and Goetze don't know exist, and don't care. They therefore remain confused, and always will be. We can leave them there and move on with a better understanding of volcanology, vesiculation, quartz/feldspar immiscibility, and gel point-of-zero-charge, thixotropy, and ionic charge behavior they cannot understand is part of the agate genesis story.

Donald Kasper

Article items as encountered are:

1. Abstract. The claim is that all agates form under 100C. They then set about showing clear evidence agates form to 250 C. 4 sets of lab experiments have produced agate in supercritical fluid (>364 C) so this conclusion is false on the face of it.
2. Introduction. Fibrous chalcedony is a structural morphology key to the term agate and is therefore not a variety of anything else in the silica group. A variety is a gem term for a color variant of the same bulk composition as the host mineral. A structural morphology is not a variety.
3. Introduction. Agate banding does not replicate the supporting void wall. Agates form on surfaces, including all inclusion structures.
4. Introduction. Basalt and andesite are not the most common agate host rock unless you are in Scotland, or you are Moxon and drive up from England. Basalt and rhyolite are, but agates form in all continental lavas, not marine lavas with higher alkali content and pyroxenes. The pyroxenes in higher concentration in marine basalt form faster than agate, and steal all the quartz, leaving nothing for agate genesis. Augite and olivine rich basalts do not contain agates for this reason.
5. Page 3. "A simulated wall lining agate pattern develops…" referring to a Liesegang band experiment where you have to drag a knife across a plate of gel with iron oxide. First, the banding is erratic and discontinuous but agate banding is not. Second, the knife part has nothing to do with how ions start moving in agates. An example is 2b shows banding with mixed color resin in a dish with an obstruction, but the banding around the obstruction does not merge. This is gibberish.
6. Page 5. For one historical model the authors comment "Solution inflow equals outflow." How does a pressure gradient surrounding a void self-oppose its own flow direction? This is gibberish.
7. Keep in mind, you don't just go from amorphous silica such as opal or silicic acid and then get quartz. In all lab experiments you run at or above 300C, and convert the silica gel to cristobalite then to keatite then to quartz. What is the discussion in the literature anywhere on how the transformation really occurs? Zero. What are the detailed properties of keatite? No one has a clue beyond density and refractive index. So how are they going to figure out how volcanic agates form? Claim it is all weathering. Things transform by magic. What does mindat.org, the mineralogy database, say about keatite? Nothing. The measured refractive index and density of keatite means it has a marker band the author can find in infrared spectroscopy. The keatite band is only found with cristobalite and cristobalite opals, just like the lab transformation series has keatite formed from cristobalite. It is there in quartz when you know how to look for it.
8. Page 6. Keatite has never been identified in an agate if you don't know what it is or how to find it, but it occurs with cristobalite and cristobalite opals in waterlines and shells. It is not found without them.
9. Page 6. Silica-X is called kenyaite. No, it is not found in agates. The magadiite and kenyaite will alter to silhydrite, which is in agate of at least one African locale. The author has specimens from this site and has the IR data on its silhydrite presence in quartz agate banding. Geochemical systems are not absolute things meaning they don't provably always run to completion and when they commonly don't we get to see the precursor relicts to study.
10. Page 8. "Unfortunately, the silica glass starting material discounts any direct link with agate genesis." Prove it. Prove there must be a precursor void and that the void if any is not an artifact of formation.
11. Page 8. "Any question of agate genesis occurring at temperatures higher than 200 C has to be totally discounted. Agates when heated produce irreversible property changes." Yeah, and just after they cited a paper and missed a Russian paper where agates where made in supercritical fluid. Good going. Who said the agate formation process was reversible? Terry never heated an agate in a supercritical fluid to see what it does. No one has done this. Heating an agate is more syneresis dewatering of the gel, not re-watering.
12. Page 9. "Raman spectroscopy is also a common technique for determining the moganite content." No, Moxon, Raman is how moganite is defined and the Gran Canaria type locality discovery was discovered with Raman.

13. Page 9. Moxon picked up old rocks with less moganite than some young rocks with more moganite and concluded the moganite changes to quartz over time instead of that he just happened to find some rocks with less and some rocks with more moganite having nothing to do with age. Various sites of various ages and moganite doesn't prove a process; a decrease in moganite in one stratum site does. Moxon has not done this. High moganite content is restricted to erionite tuffs, and if you don't find old erionite tuffs, you aren't going to find old moganite. Maybe the issue is what happens to erionite over time. But for agates, the amount of moganite is always small. High moganite content is only found in cherts, called erroneously "snakeskin agates" and geologically called Magadii-type cherts.
14. Page 10. Not only does citing borehole silica in basalt in Kauai, Hawaii mean nothing, there are no agates in any oceanic basalts of the world. This is a study of how agates don't form. You must go to the West Indies on continental plates erupting continental dacite from a subduction system to find agates.
15. Page 11. Lot of discussion about metal ions and what it may mean but the model is silica gel and the controlling factors for a gel are: particle size, ionic charge, pH, salinity, and point of zero charge (PZC) for any foreign mineral or ion. Essentially, Moxon has no concept of the parameters of silica gel systems and won't study gel chemistry (even though his PhD is in chemistry, not geology). That chemistry is very specific, and inferring its occurrence means certain types of rock structures will be found.
16. Page 12. Moxon is big on XRD to identify everything including opals. Okay, differentiate between opal-C and cristobalite and show me opal-beta-cristobalite (opal-BC) and beta-moganite in XRD, then get back to me.
17. Page 12. Discussing Yucca Mtn the claim is made that the agates are a different age than the rock. However, I have a drill core sample from Yucca Mtn and the voids are miarolites. These are vugs filled with amphibole minerals. No agate. I have looked at many dozens of Yucca Mtn reports, and none discuss agate (banded chalcedony).
18. Page 13. Discussion promotes again moganite to quartz, but the shadow agates consist of plates and oolites that scan as beta-moganite in infrared, in quartz banding. They are contemporaneous structures and have their own concentric banding. This ghastly mistake is based on the problem Moxon cannot and will not study any structure or inclusion in an agate, so he doesn't know what is going on.
19. Page 14. Some Scottish agates don't have dilations (tubes-of-entry/escape)? That is because they were missed in the cut. These are not serial sections slicing up the whole agate because if you do, some are folds. Be careful interpreting one slice for a 3-D structure, Moxon. No, Moxon never did this so he does not know.
20. Page 14. Correct. Horizontal banding in proposed tubes-of-entry doesn't work for inflow very well. He showed pictures, but made no comment, so I will. BTW, they are not infiltration canals. Objects should not be given derivative model names. They are dilations. What they are doing is something else, and is speculation.
21. Page 14-15. In volcanic agates the outer silica layer may appear to be absent? This is disinformation. The answer is never absent, unless they are stream agates where the exterior was stripped off. Never study river agates from Brazil and Paraguay and talk about the absence of wall lining silica, please. The only agates without outer silica banding are the sedimentary cherty agates (agates formed in chert). These formed in subcritical conditions (<374C) and therefore are typically silica precipitated in contact with organics subjected to decay, that is, acid conditions.
22. Page 16. They found cristobalite in some waterlines of agates and conclude a whole silica series based on speculation. However, if they use IR spectroscopy instead of XRD, the cristobalite is in opal-C. Cristobalite is distinct in infrared from opal-C.
23. Page 16. In their silica to quartz model does it take millions of years to get granular quartz in agates? No, current agate specimens have granular quartz structures on some banding planes but this is not common. All sorts of mineral systems exist on banding planes which have their own chemistry that Moxon ignores because he doesn't study agate inclusions.
24. Page 16. The entire issue of the outer silica layer being different that the rest of the agate just got dropped and went away. No wait, he has a specimen with a thicker top and bottom outer silica layer and proposes shrinkage and outer fill, and therefore the outer layer came last. Okay, this works for his one agate, how

about all the others where the lining is uniform? The agate shrank and fell to the bottom of the void. How is uniform outer lining going to form now? One case and hyper-extrapolation is not justified. Can you see the problem with shrinkage and outer wall lining growth? Right, show me an agate with 20 bands of outer growth. Right, no such specimen. Well, they must just shrink a tad, but the bigger the void the more shrinkage and the more outer wall lining, correct? No.

25. Page 16. Yes, hydrocarbons in motion through the host rock do get captured in agates. They also dewater and all the streamers intruding are captured in agates, but the streamers all extend to the agate void walls. Every one. Nothing got in later. One silica fill did it.
26. Page 16. "The identification of hydrocarbons between horizontal agate layers is particularly interesting as the different formations in these horizontal layers is indicative of their long time-relation formations." First, I have studied petroleum agates and it occurs in streamers from the void walls, not typically on banding planes. Second, to form petroleum takes medium grade metamorphism of at least 150 C. Third, the agates are on faults where the oil came up.
27. Page 16. For alteration over time of agate to quartz, show me an agate that is half granular quartz. Such a specimen is not in his paper. Still waiting. This genesis to granular quartz needs to show at least one specimen from somewhere. So far, zero. If Moxon studied inclusions, he would know that plumes are opal-Q (microquartz) streamers in agate. This micron granular quartz is in specific structures that attached to the original vein agate wall. Moxon does not study vein agates to know this. So, this agate to granular quartz evolution model is dead. Apparently, he is trying to connect agates and cherts. Further, tubes and moss inclusions in agates are opal in quartz, so this cannot be a specimen evolution. Again, Moxon does not study inclusions, so he doesn't know. Most of his enigmas are of his own making--they are not geologic enigmas; they are sampling bias enigmas.
28. Page 16-17. Moxon finds microdiscs of moganite on banding planes and gets confused because XRD does not work finding moganite. It is found using Raman or Infrared spectroscopy. He concludes agates don't have opal, which is egregiously false, but is probably linking the moganite to an opal because that is all he knows. That is, he doesn't understand moganite in agates as beta-moganite is immiscible and not integrated in the banding as alpha-moganite does.
29. Page 18. "Agates are found mainly in basic igneous rocks." False. Vein agates in andesites and geodes/thundereggs in dacites and rhyolites. Well, in his last paper he said waterlines were coincidental and unimportant. At least he dropped that statement.
30. Page 18. Oxygen isotope data is anything you want depending on what water you assume is in the system. It proves what you model. You can prove that the whole earth formed at 25 C with this, and they do prove spreading centers with basalt erupting at 1250 C form minerals at 25 C there.
31. Page 18. "Any proposal of a higher formation temperature has to explain the conflict of evidence found by the various irreversible silanol water losses that are observed between 200 and 850 C." Okay, the silica was a gel and now it is not. Second, it was a supercritical fluid but isn't now, so the water is entrapped but wasn't before. Third, infrared 3585 cm^{-1} marker bands in agate can only form at 300 C. This is found in continental volcanic agates. Fourth, the agates contain celadonite, which does not form with weathering. It is linked to the supercritical transition of 354 to 374 C. Start there. In other words, there are minerals in agates that cannot form under 100 C. Moxon needs to stop constantly claiming that all the lab experiments published where agates were formed in supercritical fluids over 400 C don't exist.
32. Page 18. "All the observed changes would not be observed if agate formed at a temperature > 250 C." Yes they would. Second, opal-beta-cristobalite, formed anywhere between 198 and 270 C is common in the tube structures and waterlines of agates. Yes, there is opal-C and opal-BC, beyond Moxon's level of technical study.
33. Page 18. "However, these tuffs are not the typical agate host rocks." Referring to Yucca Mtn. Yeah, well, there may not be tuff left in Europe for half billion year old rocks, but the Western U.S. is full of tuffs with jaspers, jasper-agates, and agates. Come here and look some time.

34. Page 18. “The link between agate age and agate crystallinity…” Stop. There is no standard for crystallinity of quartz and every paper says something different. This is slang garbage. Effectively, “crystallinity” has no quantifiable meaning. Writers have griped about this at length in the literature. You cannot compare crystallinity discussion of any two papers. If you want to say the term “crystallinity” first define your experiment exactly. Different spectra could be from scanning different crystal faces or from impurities, grain size, or from mixed crystal phases, not just crystallinity.
35. Page 18. Hot spring sinter is opal-A. Agates are not. No agate in the world has opal-A. Prove me wrong. Hot springs are main a source of microscopic veining of silica banding, usually a few bands and only at some sites. They are not agate structures (amygdules, geodes). This is also found on fault or body systems where hydrothermal water intruded. Some systems have alternating carbonate or silica deposition probably depending on the CO2 load that was in the system at that time. Hot spring deposits of banded carbonates filled with lenses of quartz and tiny agate lenses are a thing, Moxon.
36. Page 18. “Elsewhere, quartz crystals have been grown in the laboratory from a solution containing 4.4 ppm of silicic acid at 20 C.” That is bunk science. Quartz crystals we can see never form from weathering, and if so, go dig in your back yard and show us some. This is gibberish. The report cited shows 2 micron quartz. This work is talking about soil cementation or silcretes. First, agates don’t form at the surface. Second, silica, barite, and calcite combine to form hard water scale, not quartz crystals as we can see them. So yes, quartz can form films, but everything else more soluble in water like sulfates, carbonates, and salts will come out first because they are thousands of times more soluble. However, I will look at the hard water film on my glassware differently from now on, but extrapolating that to agates is absurd. Agates do not have caliche as an inclusion, when you bother to study inclusions, so you have a problem with weathering. They literally ground a quartz crystal to micron size, stirred it for two years and found micron quartz crystals. They did not use opal or silicic acid. Some nucleation on the quartz probably occurred. They got the silica to dissolve by using sea water, which has a pH of 8.1. In ground water, this will not occur at neutral pH of 7.
37. Page 19. “…chalcedony is presently being formed in the Tengchong geothermal area of China…” Yeah, and the report shows 5-micron quartz. In infrared this will produce a spectrum of what the author calls opal-Q, a microquartz with a partial opal, mostly quartz spectrum. This is not agate. And if there is some, it is silcrete, the silicification of rock with veinlets of silica. These are not agates and the system does not scale up to make them. Geologic scale matters, but the authors don’t recognize this issue. Think of it this way. Because astronomers can find quartz in the coronas around some stars does not prove how agates form in interstellar dust. There are more parameters than just one to make an agate.
38. Page 20. A lot more discussion of sinters and 100 C all the time, but agates don’t form with boiling. Hundreds of millions of years to diagenetically alter rock in a sedimentary basin has nothing to do with volcanoes and their agates. Agates in sedimentary hosts only occur with volcanic ash. Notice the authors don’t conceive of this relationship as they don’t study volcanic ash systems.
39. Page 20. They start confusing cristobalite/tridymite with opal-CT. Opal-C is not the same as cristobalite in infrared. Historically, all these temperature transitions are muddled because tridymite and cristobalite each have two sets of transitions—one for opal forms and one for structured forms. This gets back to Florke defining and opal-A as two types, an opal-AG (gel) and opal-AN (glass).
40. Page 20. Do the agates opals convert to quartz at ages over 60 million years? No, the fibrosity remains. Old agates are kaolinized, but Moxon does not see this in specimens from Germany, for example. If the rocks of Germany are generally Permian (450 million years old), then they have nontronite opal. Opals may invert to quartz, but they may also invert to moganite, which appears to be stable over extremely long time scales in opposition to Moxon’s view. He may be right on opals not hanging around. They may also alter to clays, particularly kaolinite.
41. Page 20. Yeah, Moxon found an opal-CT to opal-C indication using XRD, but opal-CT is opal-T, as confirmed by Raman and Infrared, and by naming the two peaks of XRD opal-CT that are both tridymite as one being

cristobalite (Wilson, 2014,The Structure of Opal-CT Revisited, Journal of Non-Crystalline Solids, Vol. 405, Pp. 68-75).

42. Page 20. He flipped opal-C to cristobalite in this text, and opal-CT to cristobalite/tridymite when no method of spectroscopy shows cristobalite in opal-CT. The name comes from counting the plate spacing using transmission electron microscopy, and with that opal-CT is the only mineral in the world defined by microscopy. It is a name not based on what any method of spectroscopy sees.
43. Page 21. Again, if Moxon wants to claim data to show the Brazilian agates formed 100 million years after the lava flow formed, then he just said agates form anywhere. Okay, go to the Alps and show me an agate. All granite, etc., no lava. Oh right, no agates. Weathering is so blatantly false as a story of agate genesis, only Englishmen can keep saying it.
44. Page 21, conclusions. Moxon now proved agates from gels is false. Okay, he just said the word "gel" constantly with zero concept that "gel chemistry" exists and what its parameters are, and as he is a chemist, this is unacceptably poor science. Gel chemistry has thixotropy, point-of-zero-charge, surface charge effects, silanol bonding formation, surface area effects, diffusion effects, charge gradients, particle sizes, etc., and from all that Moxon considered nothing, refusing to even see the dewatering laminae in Kentucky agates that are perpendicular to the banding.
45. Page 21. There is nothing on Brazil law twinning in this text. Why don't ceramics engineers heat glass over supercritical to make optical glass? Because it forms Brazil twinning. What is in agates? Brazil twinning. Oh my. Nothing about moganite formation, nothing about volcanic glass to celadonite, nothing about agates can have Japan Law twinning. Nothing about all the clays in the agates. Clays point-of-zero-charge behavior as a gel. Hey Moxon, look that up. It is not stuff in agates, it is stuff in a silica gel in an ionic negatively charged system where agates form in alkaline pH conditions. pH matter in gel systems, Moxon. Oh, so that is why the agates have metals cations that are positively charged.
46. Page 21. Conclusions. Moxon thinks tridymite forms before cristobalite. Okay, take cristobalite and add sodium or calcium and make tridymite. Some argue tridymite is not a true mineral.
47. Page 21. Conclusions. Agates change over geologic time scales by releasing water? Okay, a gel releasing water is called hardening. Gels do that. But not over geologic time scales. Then they are subjected to weathering, where agates have most of their water in their shells, and typically none in the center. Infrared shows this. High water content shells and no water content cores of agates is a) genesis data, or b) just weathering. Take your pick. Infrared is the standard for studying mineral water.
48. Page 21. Conclusions. The "white bands" as Moxon understands them are the beta-moganite bands on banding planes. Alpha-moganite is mixed with the fibers. Despite Moxon's paper on moganite, he only understands alpha-moganite exists.
49. Page 21. Conclusions. "It would appear that agates from the young host rocks have the most to offer future investigations into agate genesis. In this category, the islands of Hawaii would be a prime source for agate study". Agates do not form in oceanic basalts. The silica makes pyroxenes instead like augite and olivine. Good luck on his agate hunting.

Conclusion:

The paper:

Francois Froelich (2020) The Opal-CT Nanostructure, Journal of Non-Crystalline Solids, 19 Pgs., Draft posted on HAL, a French open-source site, states:

Monoclinic tridymite (opal-A, really opal-MT) forms under 110C by some, under 65 C by others, in water.

Orthorhombic tridymite (opal-CT, really opal-OT as it has no cristobalite as the paper shows) forms at 110-380 C in steam conditions (hydrothermal).

Hex tridymite (tridymite) forms over 380 C in supercritical fluid.

These tridymite species can be identified in infrared spectroscopy, which the review uses.

From this classification for agates, we have no opal-A, so no formation with water. We have structures of opal-CT in agates all the time (commonly hydrothermal conditions of formation), and some with hex-tridymite such as some Patagonia, Argentina agates and the brown shells of Brazil polyhedral agates in supercritical fluids. Hex-tridymite is not found in the agates alone. It seems to occur with iron, so we use beta-moganite markers and other mineral markers for supercritical fluid identifiers. This disproves the Moxon and Palyanova thesis on the temperature of agate formation. Temperatures under 100 C don't form agates, they form silcretes, which is ash soils altered to hard rock by the leaching of opal-CT to quartz genesis on a microscopic scale.