A review of:

Agates from Western Atlas (Morocco)—Constraints from Mineralogical and Microtextural Characteristics
By: Jaroslav Pršek, Magdalena Dumanska-Słowik , Tomasz Powolny, Lucyna Natkaniec-Nowak, Tomasz Toboła, Damian Zych, and Dominika Skrepnicka (2020) Minerals, MDPI.com, Vol. 10. No. 198, 15 Pgs.

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Review by: Donald Kasper, 11/23/2022

Overview: The authors study a Moroccan agate locale and discover how agates really form, that is, with sulfates, carbonates, iron oxides, and clays. A little bit of progress was made in this paper, now all they must do is connect the dots linking the minerals to inclusion structures instead of random stuff, and they will start to complete the story of agate genesis.

Donald Kasper

Items as encountered are:

1. Pg. 1. "Agate can be considered as a rock that consists mainly of low-quartz, with admixture of other mineral phases such as moganite, opal-C, and coloring agents including hematite, goethite, calcite, barite, zeolite…" There you go; they are beginning to comprehend that agates are complex rocks of variable composition that has nothing to do with being a variety of chalcedony. Chert is a variety of chalcedony, but agate is not. Then there is some zeolite around in the matrix and then conclude it is in the agate because it is nearby in the matrix. Okay, the author has reflectance infrared, a massive agate collection, can roam around taking spot samples of agate slices, and with that the number of zeolite specimens in agates stand at zero. So, this was a bad mistake. It doesn't matter how really, really close to the agate the zeolite gets, it is not in the agate. The closest so far is ferrierite from Kamloops, BC, Canada that lines the voids before the agate formed. The basalt is even folded with the vein agate producing the appearance the zeolite is in the agate. Only the highest silica content zeolites are near the agates. For Fallen Tree Claim, Oregon, the heulandite and mesolite zeolites fill the agate central voids, dumped into geodes after the silica formation stopped, which slams the idea of successive silica deposition. Gels form slow while silicates crystallize fast, so if a silicate is around, it steals all the silica and agates do not form.
2. Pg. 1. "That agates could originate either from the direct precipitation of silica minerals from hydrothermal fluids or the deposition of an amorphous silica gel that subsequently crystallizes or matures by diagenetic processes is still a topic of controversy…" This confuses several topics. Hydrothermal formation of agate is in ore body systems on faults all the time. Generally, hydrothermal signature is an opal shell around the agate, which is the case for one of the author's Moroccan agate nodules. The author identifies several additional opal species in infrared, such as opal-beta-cristobalite. The transition temperature is variable depending if the system is heating or cooling, over a range of 198C to 275C, and with that, the author sees opal-BC in the Moroccan agate shell, indicating hydrothermal formation. This is different than saying if it starts as a gel as there can be hydrothermal gels. In infrared, opal-C the author finds only in the waterlines of continental geodes, so far, which are agates with rhyolite shells. This site is in basalt, with no agate lava shells

formed in basalts. Rhyolite has high enough silica content to attach to the agate cores, but basalt does not.

3. Pg. 2. “Agate mineralization is pervasively accompanied by other products of hydrothermal activity in this area such as ore deposits of manganese, iron, copper, gold, and lead-zinc…” Iron, manganese, copper, gold, yes, lead and zinc no. There are no crystals of lead and zinc in any agate. Notice the barite in this locale. Carbonate and acid make sulfate, and barite is a sulfate. This reaction neutralizes the acid. We don’t care exclusively what the regional geology is; agates form on the millimeter scale of what the pH and temperature was. When Goetze found banded vein agate with galena (lead sulfide) in Germany and declared agates form in acid systems with galena, he didn’t bother to notice the banded barite separating them. When there is a sudden pH drop with alkaline-silica fluid encountering an acid, the acid is neutralized and the silica comes out of solution. There are no agates in strong acid systems, such as pH 4 or less systems. This paper conflates they form in any conditions, a sort of outcome of agates formed from weathering, but this is quite untrue.
4. Pg. 4. “Many polycentric agates have irregular shapes…” Polycentric agates are formed at lower temperatures (under supercritical, <374C) by replacement infill, often of organic structures, and with calcite and sulfate replacement. Calcite behaves from its carbon dioxide component that has reverse solubility in that it is less soluble at higher temperature so in hot systems, the calcite comes out first.
5. Pg.6. “Agate nodules are accompanied by secondary hydrothermal phases including celadonite, Fe-oxides/hydroxides, and calcite…” Hydrothermal intrusions often leave their marker of calcite hash, which appears to occur in some of these agates, but iron oxides/hydroxides occur in any system. Celadonite is a supercritical fluid marker (>374C) which is hotter than general hydrothermal systems.
6. Pg. 6. “The numerous goethite pseudomorphs after quartz/barite crystals were also observed. They were surrounded by lepidocrocite-forming characteristic halo effects around the goethite pseudomorphs…” The white halos or reaction rims around inclusions are certainly not lepidocrocite because they are white. They turn out to be opal and are formed by inclusion dewatering into the silica gel during syneresis (hardening). That involves the water pushing out included agate mineralization, bleaching it.
7. Pg. 6. Sulfides found in agates. The authors describe pyrite, but there is a polymorph more likely found in oceanic, reducing conditions, low temperature formation, which is marcasite. Its pH is different than pyrite, and can range to neutral pH. It is more likely they found marcasite.
8. Pg. 8, Figure 5. Because you see a cube in an agate does not prove it is sylvite. There is no information this came from Raman spectroscopy observation. Well, what else can be cubic? The most common is melanophlogite, and yes, the author has specimens with this from Southern California. The Romanian blue agate also has this.
9. Pg. 9. There is a propensity by the authors to say this Raman band means this is present, and that one means something else, etc. From an infrared standpoint, previous Polish authors of Moroccan agates made preposterous claims of feldspars in agate by picking out single bands they consider unique identifiers. This is not how infrared works. You must match EVERY BAND, NOT JUST ONE to identify a mineral. From Raman infrared, this likely applies as well. For example, it is not a 502 cm band that proves moganite in Raman. It is an overall quartz set of bands, the quartz 463 cm band and a 502 cm band that identifies moganite. Moganite is only found in quartz.
10. Pg. 10. The authors may call the carbon a bituminous matter, but it just may be humic acid, which means weathering. Can petroleum be found in agates? Yes.

11. Pg. 11. "The abundance of growth lines (so-called Bambauer quartz)…" This is also called chevron quartz for individual crystals. Do quartz growth lines correlate to hydrothermal conditions of formation? Yes, the author sees this in hydrothermal geodes from Oregon. These are also called feather agates, from Brazil. However, these are in torn wall banding "feathers" flung into the interior of the specimen original void and represent a type of banding the authors ignore. They also ignore that the wall banding can lead directly into these quartz crystal "growth lines" instead of the banding going around the crystal points.
12. Pg. 11. "alkaline/sulfur-rich solutions…" Sulfur systems are very acid, not very alkaline, so this is gibberish. Their presumed link is optical-slow moganites with sulfur-rich systems but only sulfides that can form in neutral pH conditions are found in agates, often neutralized in pH by carbonate presence. Sulfur-rich solutions produces melanophlogite, a cubic quartz, which along with petroleum is found in Santa Monica Mountains, CA agates the author has studied. How is this possible? Because the agates are also rich in calcite and barite. It is not that nearby is a pyrite deposit in terms of regional geology, it is what is the host rock in actual contact with the agate that matters. Regional geology we use to hunt for sites, but the actual host rock tells us what precisely happened. Volcanoes can erupt through any host rock such as carbonates and sea sediments, but agates will only form in volcanic rocks under specific conditions.
13. Pg. 11. "The development of this fabric could be induced by boiling-related conditions…" Is there evidence of boiling or incipient boiling in some agates? Yes, definitely. This can be induced by fracturing of volcanic country rock in an eruption that depressurizes suddenly.
14. Pg. 11. "The presence of celadonite, found in the outer parts of agate nodules, reflects oxidizing near-surface conditions.." Oxidizing solution is called ground water. Hydrothermal water as circulating heated ground water is going to be loaded in opal-A and caliche (mainly carbonate). Opal-A has never been found in any agate the author has scanned in infrared, by many thousands of specimens, and caliche is found post-genetic by geode fracturing and ground water intrusion. It is not found or at least recognized as a geode inclusion. Since calcite is thousands of times more soluble that quartz in ground water, all agates must be all calcite with trace quartz to be formed from ground water. Caliche can be a mix of quartz and carbonate, and with that agates of quartz will not form. No quartz crystals in any form, and in any agate, form from ground water circulation without hydrothermal temperatures (>150 C). Celadonite is found in lava flows not soil formation, so is not formed in oxidizing conditions.
15. Pg. 11. "low-hydrothermal activity of SiO_2-bearing fluids (i.e., meteoric waters)" If these authors are really serious that groundwater circulation of quartz moves to and fro and makes agates then show us a single agate in granite voids on this planet. Tick, tock, their time is up and the answer is no, never. So, this model has been disproven. Since you must go to volcanic flows to find agates, generic weathering is not the answer, and as stated before, when you find agates in sandstones, scan the matrix in infrared for celadonite. If you do that for the Union Road, Missouri sedimentary agates chert shells, for example, you will find an infrared celadonite water signature and note the locale is on a specific fault structure that introduced the hydrothermal fluid. You need quality IR spectroscopy in the 4500 cm-1 region to see it so if your machine is old or you read old literature of the first generation spectrometers that run at 4000 to 400 cm-1, you won't find it. In trace concentration you only find clays by their water signature in near-infrared.
16. Pg. 12. Opal-A to opal-CT to opal-C to chalcedony. Opal-A means amorphous to X-ray spectroscopy and so there is no mineral opal-amorphous. Opal-CT has no cristobalite seen by any method of

spectroscopy. This is the series take from oceanic sediments studies the authors use without understanding that fossil diatomite is not even opal-A. Infrared spectroscopy clearly shows it is its own species of opal, the author and others call biogenic silica because of this difference. The diatoms precipitate it with enzymes in their shells. Infrared shows mostly biogenic silica, and one can argue the spectra shows some opal-A present. Chalcedony is granular quartz, a chert, and agates are not cherts so from any study of this alleged mineral sequence, it is meaningless garbage. Based on infrared study, the opal-A is monoclinic tridymite, the opal-CT is orthorhombic tridymite. Opal-C in infrared matches infrared literature exactly so that sequence is opal-MT to opal-OT to opal-C to quartz. In continental rocks, the author has never found opal-C anywhere except in the waterlines (horizontal banding) of volcanic geodes, which means geodes with lava shells.

17. Pg. 12. The agates have moganite of Triassic age. That is 200 to 250 million years old. That is enough time to disprove the notion it inverts to quartz.

Conclusion:

The authors can see inclusions in the agates, but connecting them to specifics of silica gel chemistry has not been accomplished in their scientific circle of colleagues. Specific details of basic gel chemistry and geochemistry is lost on these authors. They can see the rudimentary observations of agates containing many minerals, primarily carbonates, but agate geochemistry is beyond their study so far. As long as the geomyth continues that agates are a variety of quartz, this lack of understanding will continue, and for them the enigma of agate genesis will remain.

At this point, these authors and their European compatriots don’t have the interest to study agates of the world, and therefore cannot see the diversity of amygdules shells of celadonite, goethite, and opal, they don’t study the Brazil feather agates to see what hydrothermal intrusions look like (silica “feather” structures), don’t see Southwestern US conical silica intrusions with central vent holes in geodes. They don’t even study hydrothermal quartz clusters with central vent holes from sites like Pakistan. They show a remarkable lack of curiosity and depth in their study. Geodes in rhyolite from Germany to France to the Western US all drop out. Amygdules of Scotland all drop out. Everything just goes away and they learn a few crumbs of their locale cluster in Central Morocco, and from that make sweeping generalities of agates of the world. However, agates are not a thing formed in a system to be discovered. They form in a suite of interrelated conditions, and when their structures beyond composition become a point of study, they will find that those structural morphologies matter, and they have entered into study of a system at least three orders of magnitude more complex than they presumed. Dana wrote A System of Mineralogy, but the book A System of Morphologies has yet to be written.

How does moganite form? It forms from sodium silicate, magadiite. Therefore, it is linked by some to evaporites, but for the Gran Canaria type locality where it is dug on the 60-degree volcanic ash slope of the southwest end of a caldera in the Atlantic Ocean, its sodium came from basalt eruption through sea water. Magadiite may also form silhydrite, which the author has found in Namibia agate. The author links rocks over about 5% moganite to erionite volcanic tuffs, found only in Magadii-type (snakeskin) cherts. The authors here don’t care about any of the geology, geophysics, and geochemistry of moganite and what it indicates for agate genesis.