A review of:

Copper-Containing Agates of the Avacha Bay (Eastern Kamchatka, Russia)
By: Galina Palyanova, Evgeny Sidorov, Andrey Borovikov, and Yurii Seryotkin (2020) Minerals, MDPI.com, Vol. 10. No. 1124, 24 Pgs.

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Review by: Donald Kasper, 11/26/2022

Overview: The authors study mineral inclusions of a Kamchatka Peninsula agate locale, with notably native copper in the banding, and copper sulfides in the shell, some aggregate intrusions, and in later brecciation and cross-veining. They find colloform (botryoidal aggregate) coronas around intrusion minerals, identifying the coronas as cristobalite but ignore the cores of clay, often celadonite these form around, or why ooid streams off walls to an agate interior form at all, namely, dewatering during silica gel syneresis.

Donald Kasper

Items as encountered are:

1. Pg. 1. Abstract. The authors study native copper in agate banding and copper sulfide in the shells and crosscut postgenetic veining. From all the sulfides, they conclude how these agates formed, although they clearly formed from late intrusion and weathering oxidation of the original native copper emplacement. Formation occurs from the outside to the center. Studying quartz crystal centers conclude from the fluid inclusions formed well under 110-50C. However, this tells us the last stage of formation of quartz crystals not agate banding conditions of formation.
2. Pg 1. "Agate is a banded chalcedony". This is gibberish. Chalcedony is granular quartz. Agate banding has fiber and quartz crystal layers. Crystal quartz is chalcedony like diamond is a variety of graphite.
3. Pg. 1. "calcite would be regarded as an impurity'. They have no idea what the presence of calcite in agate means. For the pH, it means alkaline conditions.
4. Pg. 1. Native copper means reducing conditions. With air exposure, cuprite is produced. This is found in agate veining, presumably from weathering.
5. Pg. 6, Figure 4. The key observation are the white opal reaction rims around all copper and aggregate wall accumulations. This is omitted by the authors. This is a gel interface reaction as water was released into the agate from the inclusions.
6. Pg. 7. The "white shell" of these agates is the dewatering of the host lava into the agate interior. The actual shell is celadonite, which the authors ignore as unimportant.
7. Pg. 7. The authors continue from other papers to call any granular debris in an agate a moss structure, but the term comes literally from the appearance of branching microtubes in agates, like an actual moss plant has, and, comprised of celadonite typically, is also green. The term "moss" for agate is a very literal term that does not apply to these agates.
8. Pg. 10. The aggregate botryoidal (colloform) coronas around inclusions are cristobalite. This is perhaps the most important observation in this paper.

9. Pg. 10. Figure 9d. Cryolite, a salt, was found in a void in a quartz area. This site is on a sea shore in marine rocks and looks fractured. What this means is not clear. It could be erosional intrusion of sea salt.

10. Pg. 10. The colloform cristobalite structures are called pseudomorphs because their existence to the authors is what, impossible? The lining forms first and at the highest temperature. The center forms last and at the coolest temperature. Then they study fluid inclusions of the core and determine what, the temperature the agate formed at was likely under 50 C? Well, maybe the last quartz was. But the first quartz in the wall was and is still, cristobalite. So, is that alpha (low temperature) or beta (high temperature) cristobalite? The transition varies with how you study it in raising or cooling conditions but is anywhere from 198 to 275 C. Why do we just see cristobalite in Raman and maybe infer it is alpha? Because Raman cannot distinguish alpha from beta anything at least in the silica group. Not beta-quartz. Not beta-moganite. Not hex-tridymite. Not beta-cristobalite. None of them. They conclude later a tiny XRD band shift means it is alpha-cristobalite. Yet, they use search software to study the peaks and it does not identify alpha- from beta-cristobalite. It just says cristobalite.

11. Pg. 10. Study of mica (fluorphlogopite) that intruded as a granular hash the authors call "moss". This is wall mineralization dragged into the void as the gel hardened and contracted. This also happens when the wall lining is celadonite, which is another mica. It can be argued their fluorophlogopite is celadonite. Mica names keep changing. Fluorophlogopite is a biotite. The chemical difference with celadonite is fluorophlogopite has more magnesium, celadonite has iron. Phlogopites are stated to have some aluminum substituted for silicon. Curls of celadonite are pulled into agates in many locales, this intrusion was granular clusters.

12. Pg. 17. "Gas-filled two-phase inclusions with a large bubble are homogenized at high temperatures of 250 C and more, but such temperatures are unrealistic, since sulphide mineralization is confined to amorphous SiO2 modifications." The authors conclude there is amorphous something or opal or it is unbelievable that the fluid inclusions would be showing formation at 250 C so they just throw it out and put in the abstract under 50 C, which is weathering. Okay, show formation of cristobalite with weathering. No one has. This would match if the wall banding colloform structures are beta-cristobalite. The copper was intruded under hydrothermal conditions, which is why the shells are celadonite. Then they start speculating about the fluid inclusion data being corrupted by harsh winters with freeze-thaw, and so it all formed by weathering. On to page 18, XRD data they indicate shows alpha-cristobalite, but XRD is not distinguishing alpha- from beta-moganite.

13. Pg. 19. Figure 19. These XRD spectra purport to identify moganite as weak shoulders on the sides of quartz peaks. Realistically, no, the author sees noise and that is all. This is defined by Raman, and is easy to cross-correlate to infrared spectroscopy. Those methods show moganite clearly.

14. Pg. 20. They quote stability diagram data for two sulfides indicating conditions under 93 C, but forget these are probably weathering byproducts of the original native copper, and have nothing to do with agate formation temperature. This contracts cristobalite and quartz presence, neither of which form crystal structures from weathering. Eroded quartz as silicic acid in solution and calcite makes caliche, not agate. Silica is mobilized in solution with submicron volcanic ash, not massive quartz. The ash is hyperalkaline, increasing greatly the silica solubility and mobilizes it into solution. Otherwise, the quartz is mechanically broken down into sand and washed to the ocean making our beaches, a testament to the near total insolubility of quartz at surface water pH.

15. One trap they seem to fall into is they have a cut of an agate, they find and study a round glob of something. Socially, they construct the notion it is a round or oval glob with no evidence. They do no serial sectioning to prove it is a glob. It can also be a pendant that points up into the cut and they see crosscuts. This would make them shell pendant intrusions, of which they saw and document others when they were parallel to the cut.

16. There is a general consensus that agates in basic igneous hosts form at <100 _C." There is no such consensus. This is more weathering ranting. This is trivial to disprove. Three examples of this are: Granite is 30% quartz, so you have a source of quartz. Granite rocks in mountains have lots of voids. Show us an agate locale anywhere on earth in a granite. You cannot. Therefore, quartz, voids, and weathering don't make agates. If agates form from weathering, show them in a soil profile, with more and bigger agates at depth. Neither of these two exist. Celadonite is not formed from weathering. It lines vesicles filled with agate because that is part of the geochemistry. Agates to not erode to make celadonite. The source for celadonite is biotite, which cannot form from weathering.

17. Notice how none of these agates, nor others in this series from Russia in 2020 and 2021, have wall dilation structures sometimes called tubes-of-entry or alternatively tubes-of-escape. This is a major part of the weathering model and silica intrusion theory for agates. These agates don't have any shown. The reason is that most of these are vein agates, and there are no dilations in that entire class of agate that have ever been observed. The authors claim weathering makes agates, but everyone else calls the dilations proof of silica entry points. These authors ignore the issue and their lack of dilations.

18. Pg. 20. "Rosemeyer [19,21] shows the Kearsarge copper-bearing agate photos confirming a partial or almost complete replacement of the chalcedony banding by native copper." This is false. Nothing etches out quartz in agate except supercritical fluid breaches that eat through the agate making tunneling structures and dumping a calcite hash as their calling card. These authors don't understand that the fiber bands are very porous and the copper intrudes into the bands between the fibers, sometimes around all the fibers in an area, looking "solid" to a nondiscerning observer.

Conclusion:

The authors don't grasp the obvious—the copper is a monodispersion and disseminated throughout the agates. The copper is not in a clump in a spot and agate around that. This is called ionic repulsion in a silica gel. The particles of copper are all microscopic. They cannot see it, don't acknowledge gel behavior when found, and just throw all that data away.

The copper sulfides are in the agate shells, some intruded into outer agate wall margins, and later tectonic brecciation and fracturing brought in more, or exposed copper in the basalt to weathering. The sulfides aren't in agate banding. The reason would be that the sulfides are negatively charged, so is the quartz gel in alkaline conditions, so is repelled from the silica gel precursor. Only the native copper, positively charged, gets in. Native copper is only found in reducing conditions, or it readily oxidizes. This is all the same for the native silver found in these agates.