## A review of:

Gemological Characteristics and Origin of the Zhanguohong Agate from Beipiao, Liaoning Province, China: A Combined Microscopic, X-ray Diffraction, and Raman Spectroscopic Study By: Xuemei Zhang, Lei Ji, and Xuemei He (2020) Minerals, MDPI.com, Vol. 10. No. 401 20 Pgs.

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## Review by: Donald Kasper, 11/21/2022

Overview: The authors study a Chinese locale of agates and conclude high Fe oxide content and geologic age are the controls for moganite in agates of the world. They find variable moganite content in their hydrothermal vein agates, and struggle to explain why.

## Donald Kasper

Items as encountered are:

- 1. Pg 1 citation that agates contain opal-A. This is totally false. Opal-A can form from weathering, but agates do not so rather than all agates contain opal-A, zero do applies to refute this theory. Of course, the claim would be it alters to something else, but then saying opal-A is found in agates refutes this excuse.
- 2. Pg 1. Agates occur with Fe compounds, carbonates, and sulfates. Quite true. In fact, the author models that they form not from silica gels, but from calcium-silica-hydroxyl (CSH) gels, with hardening (syneresis) activate by the presence of iron.
- 3. Pg 1 citation that agates form in igneous, metamorphic, and sedimentary rocks around the world. False. Sites with agates in granite and pegmatite stands at zero. Sites with agates in coal stands at zero. Sites with agates in slate stands at zero. Sites with agates in schist stands at zero. Sites with agates in sandstone and no volcanic ash stands at zero. Stating that a volcanic ash cemented sandstone is sedimentary is poor geologic reporting.
- 4. Pg 2. Rocks are early Cretaceous, up to 145 million years old. Moganite in those rocks at 17-54% refutes the moganite alteration to something else theory.
- 5. Pg 8. Quartz spherical silica structures. In the literature historically the Maltese cross polarizing microscopy orbs are called cristobalite. They show up a couple of times in this paper photography.
- 6. Pg 11. Cited that ferric iron aids in the formation of moganite. Well, 94% Gran Canaria, Spain, and the similar author's Carlin, Nevada locale are translucent Magadii-type cherts with no detectable iron inclusions. This proposition is not supported by the highest concentration sites. What Fe oxides do is aide in the syneresis (hardening) of silica gels. Since the iron occur in the fiber banding only (it is extruded from the quartz crystals in the crystal banding layers) and since the quartz fibers penetrate right through the iron orb concentrations and since banding does not go around them like with any other inclusions, then it is clear the iron is post-genetic, intruding due to weathering. This mistake is typical and consists of over extending observations into broad theory from undersampling.
- 7. Pg 11, Figure 11 showing Fe oxide concentration to moganite content shows to the author a small amount of Fe oxides is correlated to any amount of moganite, and therefore shows no correlation.
- 8. Pg 12 conclusions. The authors state that variable moganite composition proves successive fluid intrusions. However, even within banding planes this varies, which would be one intrusion event. What they confused is that there is alpha-moganite and beta-moganite. Background alpha-moganite is in banding widely, and betamoganite is in specific structures, and so varies with where the structures are based on the author's infrared spectroscopy study of moganites. This wide moganite content variation also invalidate the age versus moganite content model of Moxon that the authors revive and extend here.

- 9. Pg 13, Figure 13 is not a correlation of geologic age to moganite content, it is a maxima trend of moganite to geologic age. Low moganite content rocks occur in all ages. That is a much weaker correlation. The author finds high moganite content rocks only in erionite zeolitic tuffs and only as cherts. The moderate moganite content rocks are siliceous tuffs like Australian mookaite. There are no high content moganite agates over 5% the author sees in his huge infrared spectroscopy archive, calibrated in samples back to a Raman comparison by Caltech University, CA.
- 10. Pg 14 description of iron only in certain bands from "self-purification". Rather the reality is the iron occurs in the fiber layers but all mineralization is extruded from the quartz crystal banding layers, and gets pushed to the interior tops of the crystals.
- 11. Pg 14 spherical inclusions attributed to a gelatinous precursor. However, larger sampling shows them also elliptical perpendicular to banding planes and contracted along banding planes, that leads the author to infer they are from incipient boiling.
- 12. Pg 14 iron inclusions. Weathering alters iron. The authors did not consider that they were originally magnetite or iron, later oxidized from weathering to iron oxides. The author has microphotography of zone iron orbicular inclusions with iron cores and oxidized shells.
- 13. Pg 14 conclusion that lack of nontronite and Fe-saponite means the ore fluids were oxidizing. No, the typical green shells in volcanic amygdules comes from celadonite formed in supercritical conditions and the lack of it means celadonite does not form from weathering, and that therefore these agates formed in subcritical conditions (<374C).
- 14. Pg 14 model is that veining of more agate across the original agates proves that the agates were formed by multiple silica intrusions. Actually, if silica was intruding repeatedly, then the rocks would be brecciated repeatedly with cross veining. Since there is just one set of cross veining, there were two episodes of silica migration, one for the agates and one for the veining. The silicification is not a benign event, it is linked to brecciation tectonics and a silica source mobilization. If the brecciation had surface water intrude, the veining would all be calcite which is vastly more soluble in water than silica.
- 15. Pg 15 states that intruding silica solutions alternated between acidic and alkaline. From a silica gel standpoint this is gibberish as it changes the ionic charge and hence behavior of the gel system. The silica is negatively charged only in alkaline conditions, which then attracts positively charged ions like iron, copper, manganese, and clays. These minerals have a zero charge (PZC) pH point where they precipitate out of solution in a gel.
- 16. Pg 16 conclusion is that quartz crystal defects as well as Fe oxides precipitate moganite. However, the author has a substantial quartz crystal collection of specimens from around the world, and not one has moganite. Moganite in low concentrations is strongly linked to evaporite systems with alkaline conditions. The high concentration sites are strongly linked to erionite tuffs and their IR spectra indicate erionite present. The author's Carlin, NV site stratum has opal-CT, nontronite, goethite, with indicated magadiite (sodium silicate). The Lake Magadii, Kenya cherts with moganite are strongly linked to magadiite bearing rocks.

## **Conclusion:**

The authors don't collect for themselves, they use the literature, which causes errors. High moganite content rocks are linked to cherts in erionite tuffs not Fe oxide content or geologic age. The lobate "snakeskin agates" (chalcedonies/cherts as granular silica rocks) have much lower moganite while the tabular ones are the high content cherts, so morphology also matters, indicating that the cherts might themselves be magadiite replacements. The lack of erionite and magadiite geologically would then be the constraint on finding high moganite content in older rocks. Essentially, the authors did not study high moganite content cherts from well-known sites worldwide such as Lake Magadii, Kenya, and Rome, Oregon, and Gran Canaria, Spain, so they don't get a good handle on where moganites occur in the first place. People sitting around in offices defining how the agates and cherts of the world form without collecting them, reach false generalizations easily. The authors have no concept of the geologic conditions for moganite formation around the world.

For any study, the conclusions are not just anything the researchers find, it is what they find and conclude at a certain scale. In terms of moganite, the paper confuses resolution with content where they aimed at micron inclusions, found high moganite concentration, and then report the agates have high concentration, implying this is an overall concentration. The fact they got to 54% moganite means that their beam was too wide and they got background quartz, and aiming the Raman microscope with a higher magnification optical eyepiece will increase the moganite concentration found. This is not overall concentration, which is under 5% for all agates except shadow agates where the opaque beta-moganite formed on banding planes as stellate plates, merged in high enough silica concentration, and block light.