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Very-high-temperature, closed-system
origin of agates in basalts:
A new model, new and old evidence

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Crystallization of the self-organized, *repetitive* chalcedony textures (Fig 1) and trace-element compositions typical of many agates theoretically requires that the growth be from a phase with huge silica concentration and very low silica self-diffusivity. Both requirements point toward agate crystallization from a blob of silica gel (Wang & Merino, GCA 1990, AJS 1995), and precludes crystallization of agate (one with repetitive textures) from aqueous silica solutions at any T,P.

We have come up with the following picture to form blobs of hydrous silica gel within a basalt. All the predictions following from this picture are confirmed by observations of many kinds – isotopic, mineralogical, textural, microstructural, trace-element, dynamic, etc – collected by others and by us.

Blobs of silica gel must form instantaneously if a hot basalt (1200 °C) flowing on the ground happens to trap water puddles: the water goes instantly supercritical, enters the flow from below, reacts with silica polymers in the melt, and forms silanol-ended silica polymer chains that via hydrogen bonds should attach to each other at T junctions – this *is* a hydrous silica-rich gel. There is independent experimental evidence (Doremus, 2002) that above 450 °C that reaction does take place. (First prediction: If gel blobs form by puddle trapping, agates

should occur near the bottom of the basalt flow. Agates do occur only in the bottom 3 meters of a 14-meter-thick basalt flow/agate quarry that I visited in 1991 in the Parana Basalt at Rio Jacui, NW of Porto Alegre, Brazil, whereas the basalt vesicles, which occur only in the top meter, are still today all empty.)

The basalt flow stops moving and starts cooling down. As the 1000-degree isotherm sweeps inward through the flow, the basalt crystallizes fast. Each glob of silica gel, as a closed system, quickly crystallizes into an agate too, just as fast as the surrounding basalt, and at a similar, very high temperature. (The high growth rate predicted independently from the self-organizational crystallization model of Wang & Merino, 1990, coincides with the high rate predicted now similar to that of the surrounding basalt.)

Because this is a silica gel, the basic condition for it to develop repetitive textures is satisfied. Trace elements and silanols in the gel get mostly (not completely) segregated into the residual gel as the repetitive layers of chalcedony grow. Repetitive layering, fibrosity, alternate trace-element content, alternate $\delta^{18}\text{O}$, and alternate-band fiber twisting all are predicted to follow, as often observed, and must eventually give way inward to non-banded quartz, also as observed. (It's because the silanol and the trace elements do not get completely segregated to the residual gel that a) agates show an unusually high silanol content, as analyzed by Florke et al in 1971; and that b) agate chalcedony contains a little nickel in solid solution.) Predicted see-saw $\delta^{18}\text{O}$ values were indeed measured by Savin, Case Western Reserve Univ., unpublished.

The last quartz (often coarse amethyst) grows when trace iron has been forced to become both concentrated and oxidized (through the awesome reaction $\text{Fe}^{++} + \text{H}_2\text{O} = \text{Fe}^{3+} + \text{OH}^- + 0.5\text{H}_2$). This explains both why the last

quartz is darker and darker amethyst (Fig 2) and why it may contain coprecipitated fibrous goethite (Fig 3). All this should happen at very high temp. Indeed, we have measured the ^{18}O fractionation between the amethyst and the goethite; the two minerals differ by only about 1.5 ‰, confirming that the crystallization of both was at several hundred degrees C, say, 800 °C plus/minus 100 °C. The silanol water of the initial gel blob collects as H_2O water in the agate's central void, itself resulting from the density difference between gel and quartz.

The chalcedony layers *should* be high in $\delta^{18}\text{O}$ – as they indeed are – but it is not because they have crystallized from low-temperature water as Fallick (1985) assumed and then isotopically recovered.

Eventually, when the cooling of the agate (and the basalt it is in) proceeds down to 350-400 °C and crosses the boiling curve of water, the Fe- and Ni-bearing, fairly heavy ^{18}O water accumulated in the center of the agate leaks or flashes out, and should isotopically alter a shell of basalt around the agate in a declining gradient. Indeed, in a sample of fresh Deccan basalt + agate we have measured $\delta^{18}\text{O}$ values of: 16.6 ‰ at the edge of the agate, 9.5 ‰ in basalt at 2 mm from the agate, 9.2 ‰ at 1 cm, and 6.7 ‰ at 1.9 cm from the agate - that is, down to fresh basalt. Each agate produces its own small “centrifugal” aureole of isotopic alteration, even in a fresh basalt.

That same flashing water may – thanks to its high pH – alter a film of surrounding basalt to zeolite, as often observed. (Zeolites stuck to agates were the only zeolites known prior to 1955, when sedimentary zeolites and zeolitites were discovered.)

Back to the fibrous and twisted chalcedony layers: soon after growing, twisted quartz fibers start to anneal – that is, they start to resolve their strain into twins, defects, and dislocations. This is when the huge submicroscopic dislocation density

characteristic of agates (including the highly Brazil-twinned moganite) is generated, with the fibers and the twisting remaining observable on an optical scale.

When the puddle of water that gets initially trapped by the basalt flow is large then a huge lump of low-silica-concentration gel forms. Because this gel is low-density, both the lump will stretch itself vertically and it will generate only very few repetitive bands before passing to nonbanded, non-fibrous coarse amethyst, and the agate's central hollow will be large relative to the whole agate. This is exactly what the large “geodes” that one can walk into look like: bottle-shaped, having very few chalcedony bands, and lined with big amethyst crystals.

The same 1995 theoretical quantitative model that accounts for the self-organizational textures and compositions of agates and for their fibrous, length-fast quartz also accounts for a score of geochemical, mineralogical, microstructural, isotopic, and chromatic features of agates.

Summary. Agates probably crystallize from lumps of gel formed at very high temperature within a basalt flow, as the flow traps a puddle, or water soaking the ground. The crystallization of the gel lump to form an agate takes place at roughly the same high temperature, fast rate, and time as those for the surrounding basalt. As each agate crystallizes one predicts that it will form a directional sequence of textures (alternate chalcedony bands, non-banded non-fibrous quartz with increasingly darker amethyst, and a center void); all this is exactly as seen. Coprecipitated amethyst and goethite show little fractionation, confirming the very-high-temp of crystallization predicted by the geological model. Predicted flashing of water accumulated at an agate's center should isotopically alter surrounding basalt in a declining pattern of $\delta^{18}\text{O}$ values; this is nicely confirmed by measured values.

References

- Doremus RH, 2002, Diffusion of reactive molecules in solids and melts, New York, Wiley, 293 p.
- Fallick A.E., Jocelyn J., Donnelly T., Guy M., and Behan C. (1985) Origin of agates in volcanic rocks from Scotland. *Nature* 313, 672-674.
- Merino E., Wang Y., and Deloule E. (1995) Genesis of agates in flood basalts: Twisting of chalcedony fibers and trace-element geochemistry. *Amer. J. Science* 295, 1156-1176.
- Wang Y. and Merino E. (1990) Self-organizational origin of agates: banding, fiber twisting, composition, and dynamic crystallization model. *Geochim. Cosmochim. Acta* 54, 1627-1638
- Wang Y. and Merino E. (1995) Origin of fibrosity and banding in agates from flood basalts. *Amer. J. Science* 295, 49-77
- Merino E. and Wang Y. (2001) Self-organization in rocks: Occurrences, observations, modeling, testing – with emphasis on agate genesis. In: Hans-Jürgen Krug & Jörn H. Kruhl, eds., *Non-Equilibrium Processes and Dissipative Structures in Geoscience, Yearbook “Self-Organization”* vol 11, pp.13-45, Berlin, Duncker & Humblot, 380 p.

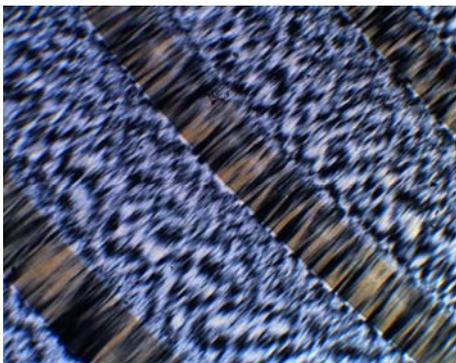


Fig 1: Repetitive alternating chalcedony bands, with fibers twisted and untwisted: a case of self-organization; diagonal =2 mm.



Fig 2: Increasingly darker purple of amethyst: best single evidence of closed-system growth



Fig 3: Ferric iron segregated to the residual gel/aq soln during crystallization of an agate makes the coarse quartz increasingly darker purple as in Fig. 2 and also coprecipitates with quartz as brown bundles of goethite needles. ^{18}O fractionation between goethite and amethyst is only 1.5‰, evidence that both crystallized at many hundreds of degrees.