

Oxygen-isotope zonation of agates from Karoo volcanics of the Skeleton Coast, Namibia: Discussion

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Harris (1989) presented O-isotope data from siliceous nodules (agate) in Jurassic ash-flow tuffs from Namibia and used the data to place constraints on the origin of these nodules. Harris recognized two principal silica textural types: (1) Q variety, consisting of relatively coarse-grained quartz that typically forms concentric layers (wall-layered) in the nodules; and (2) MQ variety, consisting of microcrystalline quartz and chalcedony that is present both as wall layers that typically alternate with Q layers and as horizontal bands that presumably formed at the bottom of the open cavity, "apparently produced by gravity-controlled deposition" (Harris, 1989). The study showed that there are differences in $\delta^{18}\text{O}$ for the MQ- and Q-silica textural varieties, with the Q zones 3‰ lighter on average, and that the observed range of $\delta^{18}\text{O}$ values for the agate was consistent with a relatively low temperature of formation. Harris concluded that the differences in $\delta^{18}\text{O}$ values between Q and MQ silica are best explained by a model that incorporates solution boiling. In the model, the isotopically lighter Q bands precipitate from the $\delta^{18}\text{O}$ -depleted H_2O vapor phase, and the MQ layers precipitate from the residual liquid. The effects of boiling solutions in volcanic environments have been extensively studied in geothermal and epithermal systems (e.g., White, 1981; Henley et al., 1984; Drummond and Ohmoto, 1985; Henley, 1986; and Cline et al., 1987) and the results provide the framework for evaluating Harris's conclusion of the role of boiling in agate formation. Whereas boiling is a very plausible mechanism for causing silica saturation in solutions of elevated temperature (e.g., Holland and Malinin, 1979; Fournier, 1985; and Fournier, 1986), several features of the agate nodules suggest that boiling was not directly responsible for their formation:

1. Temperature of formation: Because of the uncertainty of the $\delta^{18}\text{O}$ value for Jurassic meteoric H_2O , the use of the O-isotope data to determine temperature is ambiguous, as discussed by Harris (1989). Using a range of assumed values of $\delta^{18}\text{O}$ for Jurassic meteoric H_2O in the region, Harris showed that the agate depositional temperature was in the range of 26–169 °C. Clearly, if the actual temperature of formation was at the low end of this range, boiling did not occur. Harris (1989) reported that present-day meteoric H_2O in the Karoo region has a $\delta^{18}\text{O}$ content of -3‰ and that the latitude of this part of Africa, and presumably its proximity to the coast, has not changed significantly since the breakup of Gondwanaland at about 120 Ma. If this value is used, a temper-

ature of formation of 39–85 °C is implied for the agate based on isotopic composition reported for the various stages of silica deposition. This temperature range is consistent with a temperature of deposition as low as 50 °C, which was interpreted for agates from Scotland (Fallick et al., 1985).

2. Pressure considerations: Harris (1989) presented no geologic evidence that indicates a very shallow origin for the agate nodules, and if they did not form at very shallow depths, then the ambient hydrostatic pressure is an important variable in the proposed boiling model.

3. Physical effects of boiling: Much of the textural information on the agate presented by Harris (1989) indicates deposition in a quiescent environment, where silica probably precipitates as semicolloidal gels and crystalline quartz that form crustifications along the cavity walls or occur as finely-laminated sediment at the floor of the cavity. It seems likely that a solution that boiled enough to generate 95 wt% vapor, as proposed by Harris, would have certainly been recorded in some brecciation of the previously deposited silica, as is commonly seen in shallow epithermal quartz veins and breccias deposited from boiling solutions.

4. Chemical and mass-balance considerations: That silica is concentrated in the residual liquid during boiling argues against substantial H_2O vapor-phase transport of silica. In fact the solubility of quartz in low-density H_2O vapor is very small (Kennedy, 1950). In addition, the tremendous increase in volume of the vapor over the liquid phase argues that if boiling had occurred, the vapor would have rapidly escaped from the cavity, leaving little mass of H_2O to precipitate quartz. It seems likely that the amount of MQ silica would be much greater than that of Q silica because of this. However, photographs presented by Harris indicate subequal amounts of Q and MQ quartz in the agate.

5. Textural evidence: There is no indication from photographs published by Harris (1989) that any horizontally deposited MQ bands formed at the same time as any wall-layered Q band. For example, from his sample 3 (Harris, 1989, Fig. 1), the following order of events is evident: (1) deposition of thin MQ layer A as both horizontal and wall layers, (2) deposition of MQ layer B as a thick horizontal layer and possibly a thin wall layer, (3) deposition of Q layer C as both a wall and a horizontal layer (actually one continuous concentric band), (4) deposition of another thin MQ band (not labeled or analyzed) as both wall and horizontal layers, (5) deposition

of a thick filling of a coarse Q zone D, and (6) deposition of the inner MQ zone. Clearly, in this case the bulk of the Q silica postdates deposition of most MQ silica. Possibly even more significant, is that some Q bands grew upward from a horizontal substrate, which is difficult to envision if MQ were being deposited below, and Q above, a boiling liquid-vapor interface.

From these considerations, it seems that the evaluation of other mechanisms for the deposition of silica bands is warranted. One possibility is that the solutions that deposited MQ silica reached supersaturation with respect to silica at a deeper level, resulting in the nucleation of colloidal silica particles, which were transported to the agate-forming cavities. This supersaturation could have occurred in response to solution boiling, rapid cooling, reaction of the hot H₂O with fresh volcanic glass (Fournier, 1985), or some combination of these processes. In the cavities, colloidal silica could either be deposited as a sediment or adhere to cavity walls. Q-layer quartz could have precipitated more slowly (on top of or encrusting MQ layers) from the remaining solution, which could have mixed locally with silica-saturated meteoric H₂O. Truesdell and Fournier (1977) and Fournier (1985) have shown that mixing of two solutions of different temperatures, both saturated with respect to quartz, can produce supersaturation in the resulting mixture. In addition, Fournier (1985) proposed that some amethystine quartz, such as is present in one of the agate nodules in Harris's study, forms by the mixing of deeper thermal waters with cold, shallow, oxygenated ground water, where oxidation produces the Fe³⁺ that gives amethyst its characteristic color.

The upward transport of colloidal silica precipitated at deeper levels has been described by Fournier (1985; and written communication, 1989) at a new spring at Sylvan Springs, Yellowstone Park, that formed after the 1959 Hebgen Lake earthquake. In this spring, colloidal silica is present in the active discharge, as opposed to the more typical case where it develops in pools after significant H₂O has evaporated. In addition, Saunders (1989) proposed that colloidal silica (and Au) were transported by the hydrothermal solutions that repeatedly deposited silica bands of submillimeter thickness in shallow bonanza Au veins at the Sleeper deposit, Humboldt County, Nevada. The transport of colloidal silica into the agate-forming cavities at Karoo is consistent with the agate microstratigraphy and differences in silica textures between Q and MQ layers and provides an alternative process capable of explaining differences in isotopic signa-

tures. MQ and Q layers may have precipitated from fluids of different physical and chemical characteristics (including isotopic composition) at different times during the agate-forming history of the Karoo volcanics.

On the basis of the large volume of data generated on silica textures and hydrothermal processes in geothermal and epithermal systems, Harris's (1989) conclusion that the Karoo agates formed as a direct consequence of boiling in the agate-forming cavities appears to be largely unsubstantiated by the data presented.

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