American Mineralogist, Volume 75, pages 1207–1208, 1990

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

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I am grateful to Saunders for comments concerning my interpretation of systematic differences between the O-isotope ratios of quartz and microcrystalline quartz in Karoo agates (Harris, 1989). Although much of the criticism of my model is pertinent, Saunders did not provide an alternative explanation of the O-isotope zonation. In this reply I will first consider some of the features of these agates that Saunders argued, "suggest that boiling was not directly responsible for their [the agate nodules'] origin," and then consider the implications of his model for the O-isotope variation in the Sarusas agates.

In point two, Saunders considered that I presented "no geologic evidence that indicates a very shallow origin for the agate nodules." I am not sure what Saunders considers to be a shallow origin, but the general geology of the area allows constraints to be placed on the range of possible depths. The shallowest possible depth of origin is the depth of the agates from the top of the quartz latite flow in which they are contained, if one assumes that the agates were completely formed before extrusion of the next flow. The greatest possible depth of origin is that of the largest thickness of cover material that has existed over this area. The Karoo volcanics were extruded during a period of regional uplift and rifting caused by mantle plume activity (White and Mackenzie, 1989), and the result of this is that there appears to have been little or no sedimentation on top of the lava pile since eruptions ceased (e.g., Miller, 1988; Ward, 1987, p. 53). The maximum preserved thickness of Etendeka Formation volcanics is at Tafelberg and is of the order of 900 m (Milner, 1988). How much has been lost because of erosion is unknown. The volcanic stratigraphy in the Sarusas region is complicated by faulting (Milner, 1988) and consists of volcanics that are chemically distinct from those at Tafelberg (Milner, 1988; Harris et al., 1989). The best estimate of the original thickness of volcanics at Sarusas is that it is probably less than 1000 m. The maximum depth of formation of the Sarusas agates is therefore probably less than 1000 m.

In point three, Saunders commented on the lack of textural evidence for boiling, specifically a lack of brecciation of early deposited material in the agates. Figure 1 of Harris (1989) shows some brecciation of the volcanic material adhering to sample 1; in the other samples the wall rock is not present. It should be noted that I did not suggest that 95% loss of vapor occurred from within the agate, rather that "high $\delta^{18}O$ values in the fluid would have been achieved before each new layer of the agate was deposited."

In his conclusions, Saunders stated that "the transport of colloidal silica into the agate-forming cavities at [the] 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 signatures." This is the only mention of O isotopes in Saunders's discussion of my paper, and I shall therefore discuss the consequence of his model on possible $\delta^{18}O$ variations within the agates.

As I understand it, Saunders proposed that MQ silica is deposited from solutions which "reached supersaturation with respect to silica at a deeper level," and the Q-layer quartz "could have precipitated more slowly . . . from the remaining solution, which could have mixed locally with silica-saturated meteoric H_2O." The question Saunders did not address is what are the consequences of this model for the $\delta^{18}O$ values of the precipitating silica.

Let us first consider the MQ solutions. If these reached supersaturation with respect to silica at deeper levels, the amount of exchange between fluid and volcanics would be greater. I pointed out in Harris (1989) that alteration shifts $\delta^{18}O$ values in the Etendeka volcanics to higher values (see also Harris et al., 1989). This means that the fluid responsible for the alteration will have lower $\delta^{18}O$ values than its initial value (presumably that of meteoric H_2O) as a result of the exchange, though not necessarily significantly lower if the water/rock ratio was high. The MQ-forming layers of Saunders's model would therefore be expected to have lower $\delta^{18}O$ values than that of meteoric H_2O, if it is assumed that the MQ-forming fluid was the alteration fluid. If Q layers precipitated from solutions formed from mixing of meteoric H_2O with the supernatant fluid after MQ deposition, then the $\delta^{18}O$ values of Q layers ought to be slightly greater than those of MQ layers. This clearly is not the case, as $\delta^{18}O$ values of MQ are on average 3‰ heavier than those of Q layers (Harris, 1989). Some mechanism is therefore needed to increase the $\delta^{18}O$ value of the MQ-forming fluid. Saunders suggested that supersaturation in the MQ-forming fluids may have occurred as a response to solution boiling (among other processes). In order to raise $\delta^{18}O$ by 3‰, 44% boiling at 100 °C is required (calculated from the Rayleigh equation using a value of α of 1.005 from Friedman and O'Neil, 1977, Fig. 7). This is the minimum amount of vapor loss necessary to generate a liquid that is 3‰ heavier, because the temperature must have been above 100 °C.

To conclude, Saunders's model is consistent with many of the features found in the Sarusas, and I suspect in most other agates. Saunders did not, however, make much of an attempt to account for the O-isotope zoning patterns described in my original paper. A compromise model whereby the MQ-forming fluids become enriched in ^{18}O as a result of considerable (>50%) boiling and the Q-forming fluids are dominated by meteoric H_2O would account for the O-isotope zonation. As stated in Harris (1989), the influx of fluid into the cavities may have been continuous or episodic. The main drawback of this model is that it requires the amount of boiling in successive MQ-forming fluids to be similar (e.g., in zones B–F in agate 1 and in agate 2). The reason why I preferred a model in which MQ and Q precipitate from coexisting H_2O liquid and vapor is that it explains the differences in isotopic composition of MQ and Q without resort to separate fluid sources.

References cited

Friedman, I., and O'Neil, J.R. (1977) Compilation of stable isotope fractionation factors of geochemical interests. Geological Survey Professional Paper 440-KK.

Harris, C. (1989) Oxygen-isotope zonation of agates from Karoo volcanics of the Skeleton Coast, Namibia. American Mineralogist, 74, 476–481.

Harris, C., Smith, H.S., Milner, S.C., Erlank, A.J., Marsh, J.S., and Ikin, N.P. (1989) Oxygen isotope geochemistry of the Mesozoic volcanics of the Etendeka Formation, Namibia. Contributions to Mineralogy and Petrology, 102, 454–461.

Miller, R.McG. (1988) Compiler; Geological map 2013 Cape Cross, 1:250,000 Geological Series, Geological Survey, Windhoek, Namibia.

Milner, S.C. (1988) The geochemistry and petrogenesis of the quartz latites of the Etendeka Formation of S.W.A./Namibia. Ph.D. thesis, University of Cape Town, Cape Town, South Africa.

Ward, J.D. (1987) The Cenozoic succession in the Kuiseb Valley, central Namib Desert. Memoir 9, Geological Survey S.W.A./Namibia, 124 p.

White, R., and Mackenzie, D. (1989) Magmatism at rift zones: The generation of volcanic continental margins and flood basalts. Journal of Geophysical Research, 94, B6, 7685–7729.

Manuscript received June 10, 1989
Manuscript accepted June 15, 1990