OXYGEN ISOTOPE GEOCHEMISTRY OF A QUARTZ-AGATE GEODE FROM NORTH-WESTERN NAMIBIA

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ABSTRACT

A geode from Sarusas, Namibia, consisting of zones of quartz and agate has δ^{18} O values (20,4‰-27,0‰) which indicate that it crystallized at a temperature of <200°C and possibly < 100°C. Differences between δ^{18} O of quartz and agate in the geode may be explained if the quartz crystallized from H₂O vapour and the agate crystallized from H₂O liquid in equilibrium at about 102°C. This model can explain how quartz and agate bands are formed in such geodes.

1. INTRODUCTION

This paper describes the oxygen isotope variations through a section of a geode collected 10 km from the coast at Sarusas ($12^{\circ}25$ 'E, $18^{\circ}45$ 'S) in the Skeleton Coast Park of north-western Namibia. Fig. 1 shows a fragment of the geode which has five distinct zones, two of agate and three of quartz. The term agate is used to describe microcrystalline silica. The agate zones form planar layers which appear to have been produced by gravity controlled deposition and thus were probably horizontal in the geode. The coarsely crystalline quartz occurs as layers which line the cavity wall and follow its uneven surface. The two types of layer were designated -h (horizontal) and -w (wall) by Florke *et al.* (1982). The outer zone (AM5) is separated from the



Fig. 1: The fragment of geode from which the five zones were taken for analysis in this study. This fragment is 6 cm in height. The inner amethyst zone projects into the cavity in the centre of the geode. Although it cannot be seen in this photograph, the quartz zones are wall-layered in that they are deposited parallel to the original cavity wall. The agate layers are horizontal and terminate against the wall-layered quartz.

wall of the geode by a very thin agate wall layer (1 mm thick) which is present around the entire wall of the geode. This material has not been analysed. Material from each of the five zones of the fragment shown in Fig. 1 was separated from the geode and analysed for its oxygen isotopic composition. Analytical methods are given in Harris *et al.* (in press) and all analyses were run in duplicate. Precision was better than 0,2 ‰ and results are expressed in δ notation relative to the V-SMOW standard, where $\delta x = ({}^{18}O/{}^{16}O$ sample/ ${}^{18}O/{}^{16}O$ standard -1) x 10³ ‰. During this work, quartz standard NBS-28 gave a δ ${}^{18}O$ of 9,64 ‰.

2. RESULTS

Table 1 gives the 1)180 values obtained and Fig. 2 the location of the analysed material within the geode. The δ^{18} O values for quartz and agate range from 20,4‰ to

TABLE 1 : Geode zone δ^{18} O values

Zone	Material	$\delta^{18}O$	
AM1	Amethyst	27,04	
AM2	Colourless quartz	23,52	
AM3	Agate	24,85	
AM4	Colourless quartz	20,41	
AM5	Agate	22,09	
AM2 AM3 AM4 AM5	Colourless quartz Agate Colourless quartz Agate	23,52 24,85 20,41 22,09	



Fig. 2: Oxygen isotope profile through the geode showing the location of each piece analysed.

27,0‰. These data are similar to the values obtained by Fallick *et al.* (1985) for Scottish agates and indicate low temperatures of crystallization.

3. TEMPERATURE OF FORMATION

In order to estimate the temperature of formation of each mineral zone in the geode, it is necessary to know the δ^{18} O value of the fluid from which the mineral was deposited and the variation with temperature of the oxygen isotope fractionation factor between mineral and fluid. The composition of the fluid depositing the geode is assumed to be close to pure H₂O, as low temperaturelow pressure fluids such as these are unlikely to contain significant quantities of dissolved CO₂ (see phase diagrams, Roedder, 1984, p. 238). The isotopic fractionation curve for quartz-H₂O of Clayton et al. (1972) has, therefore, been used to estimate its temperature of deposition. Table 2 shows the deposition temperature for the maximum and minimum δ^{18} O values observed in the geode (AM1 and AM4, Table 1) calculated for a range of δ^{18} O values of the fluid. The only δ^{18} O values available for meteoric water from Namibia are from areas much further inland than Sarusas. These values, averaging about -6 ‰ (NPRL, 1984), are lighter than those from coastal areas of southern Africa which average about -3 ‰ (NPRL, 1984). Regardless of the exact δ^{18} O value of the meteoric water at Sarusas, low-temperature deposition would have been required to give the δ^{18} O values of the geode. However, if the fluid was enriched in ¹⁸O as a result of isotopic exchange with the host quartz latite, the geode material could have crystallized at higher temperatures (Table 2).

4. ORIGIN OF QUARTZ AND AGATE ZONES

Fig. 2 shows that the two agate zones have higher δ^{18} O values than the adjacent coarsely crystalline quartz zones, thus giving the δ^{18} O profile through the geode a saw-toothed appearance. This cannot be due to differences in isotopic fractionation factors for quartz-H₂O and agate-H₂O as these are the same for all silica minerals (Knauth and Epstein, 1975). One possible explanation is that the agate zones were deposited at lower temperatures than the quartz zones, reflecting an

TABLE 2: Calculated deposition temperatures

δ ¹⁸ fluid	TempAM1	TempAM4
-6 ‰	31°C	67°C
-3 ‰	47°C	85°C
0 ‰	63°C	108°C
+ 6 ‰	103°C	169°C

Temperatures calculated from the equation $\delta s \cdot \delta w = 3,38(10^6T^2) - 2,90$ (Clayton *et al.* 1972) where $\delta s \cdot \delta w$ is the difference between the $\delta^{18}O$ value of the quartz and the fluid and T is the temperature in Kelvin.

undulating cooling history of the geode. A more satisfactory explanation is that the agate zones crystallized from H₂O liquid while the coarsely-crystalline quartz crystallized from H₂O vapour, H₂O liquid being isotopically heavier than H₂O vapour when the two are in equilibrium (i.e. during condensation or boiling). AM3 is displaced about +3 ‰ from a line joining AM2 and AM4 (Fig. 2) which is consistent with the liquid being 3 ‰ heavier than the vapour. A fractionation factor of 3 ‰ between H₂O-liquid and H₂O-vapour occurs at about 120°C (Friedman and O'Neil, 1977) which would be consistent with boiling at just above atmospheric pressure. Harris (in press) has shown that a difference in δ^{18} O value of 3 ‰ between quartz and agate in the same geode occurs in other geodes from this locality.

The second explanation is preferred because it not only explains the isotopic differences between quartz and agate in a single geode but also the presence of agate as horizontal layers together with wall-layered coarsely crystalline quartz.

The crystallization of agate from H_2O liquid is consistent with the fact that in many aqueous environments, silica is precipitated in cryptocrystalline form. In their study of similar geodes, mainly from Brazil, Florke *et al.* (1982) suggested that quartz and agate in the same geode result from a protracted cooling history. Agate is said to precipitate from supercritical fluids while the coarsely crystalline quartz crystallizes from low-temperature (<100°C) H₂O liquid. The Sarusas geode agate could not have precipitated from supercritical H₂O as this implies temperatures above the critical point of H₂O (374°C). The data presented in this paper support the conclusion of Fallick *et al.* (1985) that agates form at low temperature of 50°C.

The δ^{18} O values of the quartz zones decrease towards the centre of the geode and this presumably reflects decreasing temperature during infilling of the original cavity. The coexistence of H₂O liquid and H₂O vapour during the evolution of the geode indicates that the P,T conditions were close to the two phase curve for H₂O. The dominance of agate (precipitated from H₂O in the liquid phase) or quartz (precipitated from H₂O in the vapour phase) in a particular zone is most probably due to changes in pressure and/or temperature during the growth of the geode. This could result from changes in the hydrothermal plumbing or from cycles of eruption followed by erosion above the zone of geode formation.

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