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

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ABSTRACT

Oxygen-isotope profiles through six agates from Sarusas, in the Skeleton Coast Park, Namibia, show that $\delta^{18}O$ varies from 20.4‰ to 28.9‰. These values are consistent with low temperatures of formation. Systematic differences in $\delta^{18}O$ exist between coarsely crystalline quartz (Q) bands and microcrystalline quartz (MQ) zones within the same agate, with the Q zones being, on average, 3‰ lighter than MQ zones. This difference is consistent with the crystallization of Q zones from H_2O vapor and MQ zones from H_2O liquid at about 120 °C. Boiling hydrous fluids at pressures just higher than 1 atm should be expected at shallow levels in a cooling lava pile. A temperature of formation of 120 °C requires that the depositing fluids were enriched in ^{18}O relative to present-day meteoric waters. Enrichment of meteoric fluid in ^{18}O probably occurred as the result of prolonged boiling and loss of vapor rather than exchange with the host Karoo volcanics.

INTRODUCTION

The term "agate" is usually taken to mean silica infillings of cavities in volcanic rocks (e.g., Flörke et al., 1982). The variety of silica types in such infilling may include quartz, microcrystalline quartz (including chalcedony), and opal. The present paper described the oxygen-isotope variations through a variety of agates collected at Sarusas (lat 12°25′E, long 18°25′S) in the Skeleton Coast Park, Namibia. These agates have formed in cavities in quartz latite volcanics. The host rock is the silicic variety of the bimodal Etendeka Formation volcanics that were described by Erlank et al. (1984) and Milner (1988). These quartz latites, which are chemically similar to rhyodacites, are considered by Milner (1988) to have been erupted as high-temperature ash flows. The Etendeka Formation volcanics show considerable oxygen-isotope disequilibrium between whole rocks and phenocrysts. Harris et al. (1988) attributed this disequilibrium to secondary alteration. The aim of this paper is to use the agate oxygen-isotope data to determine the temperature of formation and, by inference, the temperature of alteration of the host volcanic rocks. The oxygen-isotope composition of quartz crystallizing from an aqueous fluid depends on both temperature and the oxygen-isotope composition of the fluid. Temperature of formation of silica minerals cannot be determined from their $\delta^{18}O$ values without some knowledge of the isotope composition of the fluid. In these agates, differences in the $\delta^{18}O$ values of quartz and microcrystalline quartz layers are best explained by the quartz layers' forming from water vapor and the microcrystalline quartz layers' crystallizing from water liquid. The oxygen-isotope fractionation curve between liquid and vapor for water can therefore be used to estimate temperature from the difference in $\delta^{18}O$ value between quartz and microcrystalline quartz.

SAMPLE DESCRIPTION

Samples were collected from quarried material, and no information is available on the in situ orientation of the samples. Figure 1 shows the morphology of the six agates analyzed, and Appendix 1 describes the salient features of each agate. The nomenclature of Flörke et al. (1982) is adopted for the material described here. These authors distinguished three different types of silica, namely quartz (Q), microcrystalline quartz (MQ), and opal, which is not present in the six agates that are the subject of this paper. MQ is divided into fine quartz, quartzine, and length-fast chalcedony by Flörke et al. (1982); in these agates, MQ is either fine quartz or length-fast chalcedony.

Flörke et al. (1982) also considered the nature of the banding, i.e., horizontal or wall-layered. Horizontal layering consists of distinct layers and is apparently produced by gravity-controlled deposition. Wall-layering occurs as continuous zones that line the cavity wall, covering uneven surfaces and predeposited horizontal layers. In the samples studied in this paper, the Q layers are always wall-layered, and the MQ layers are generally horizontal (see Fig. 1). Agates 1–4 are surrounded by a thin zone of wall-layered MQ as in the examples described by Flörke et al. (1982). Agates 5 and 6 have much thicker wall-layered MQ on the outside.

ANALYTICAL METHODS

Material was removed from all observed zones of the agates shown in Figure 1 and was washed in acetone. The quantity of material varied but was always >40 mg, and

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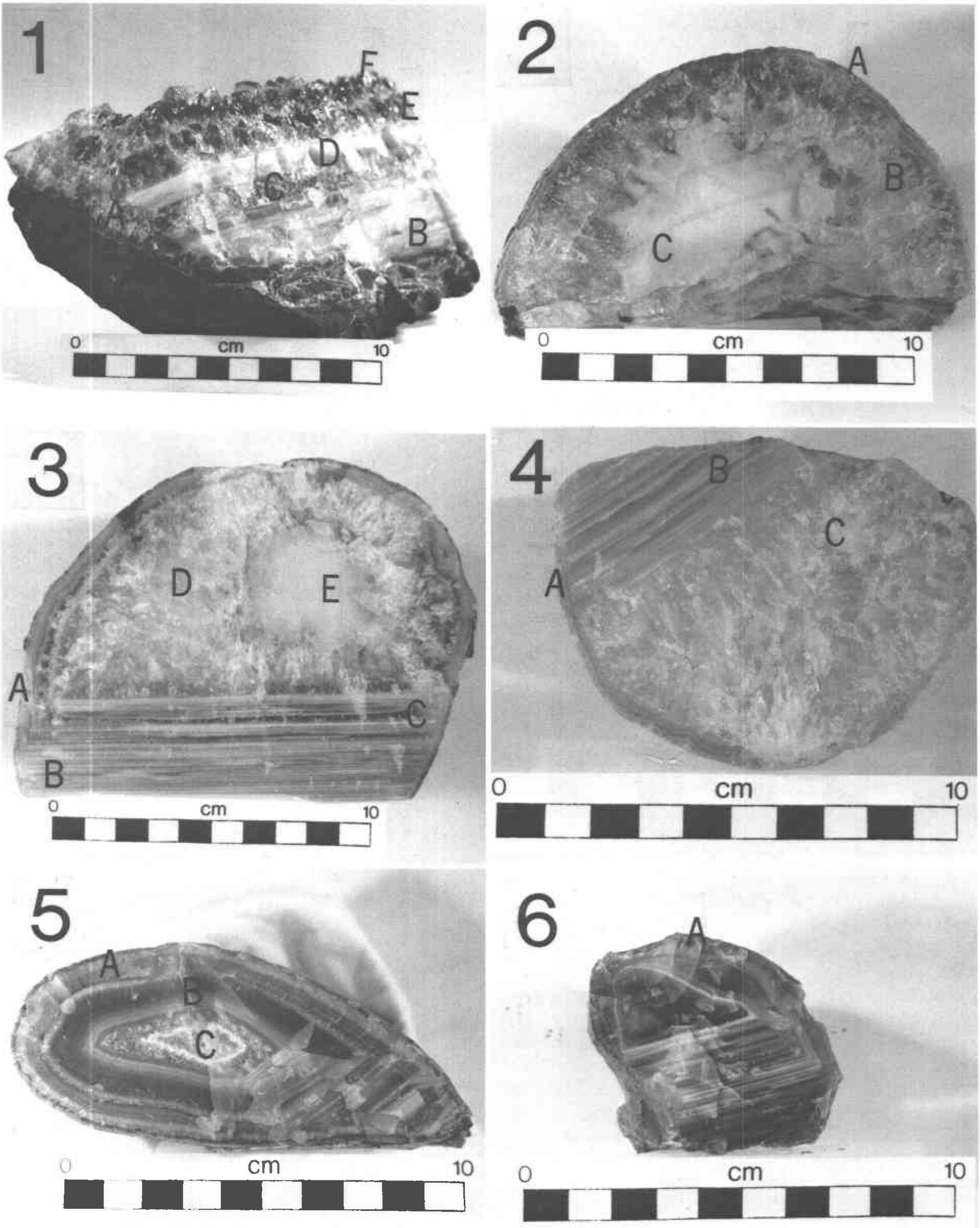

Fig. 1. The agates analyzed in this study. Agate numbers and zone letters correspond to those of Table 1. The photograph of agate 1 shows only the portion that was collected.

TABLE 1. Oxygen-isotope analyses of agates

Agate	Zone	$\delta^{18}O$	Type of material
1	A	27.08	MQ; wall-layered outer rim
	B	22.09	MQ; horizontal
	C	20.41	Q; wall-layered
	D	24.85	MQ; horizontal
	E	23.52	Q; wall-layered
	F	27.03	Q; wall-layered
2	A	27.34	MQ; wall-layered outer rim
	B	24.29	Q; wall-layered
	C	27.41	MQ; horizontal
3	A	28.69	MQ; wall-layered outer rim
	B	28.37	MQ; lower horizontal layer
	C	25.80	Q; wall-layered
	D	24.30	Q; wall-layered
	E	27.16	MQ; center zone
4	A	28.46	MQ; wall-layered outer zone
	B	28.51	MQ; horizontal
	C	25.05	Q; center zone
5	A	25.22	MQ; wall-layered outer zone
	B	24.38	MQ; wall-layered part of inner zone
	C	21.07	Q; inner zone
6	A	28.51	MQ; wall-layered outer zone
	B	28.87	MQ; wall-layered inner zone

Note: All samples run in duplicate. The average difference between runs = 0.25‰ ($n = 22$).

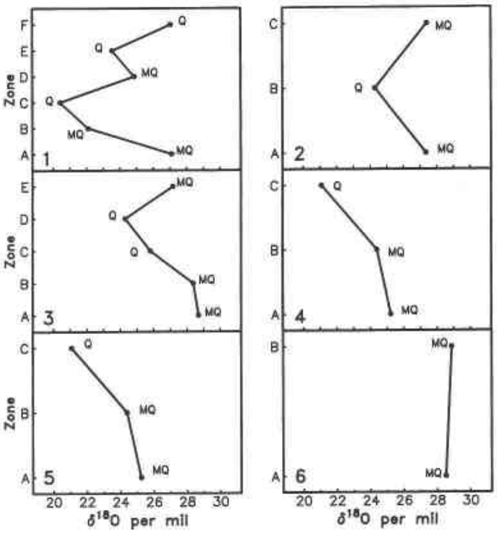

Fig. 2. Oxygen-isotope profiles through the agates of Fig. 1. The Y axis in each case is not to scale.

it was ground in an agate mortar to <90 mesh. The material was not ground to finer grain size in order to minimize possible contamination by the agate mortar. In any case the effect of contamination during grinding is not likely to have been significant as the agate mortar has a $\delta^{18}O$ in the same range as the samples (28.9‰, Smith, pers. comm., 1987). Samples were dried at 50 °C for a minimum of 48 h, before loading into the reaction vessels. All samples were degassed at 200 °C for 2 h in order to remove adsorbed moisture before reacting with ClF_3 at 550 °C overnight. The extracted oxygen was converted to CO_2 via a heated C rod and analyzed for $^{18}O/^{16}O$ using a VG 602E mass spectrometer at the University of Cape Town. All analyses were run in duplicate, and results are expressed in δ notation relative to the V-SMOW standard, where $\delta x = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 10^3$ and $R = {}^{18}O/{}^{16}O$. During this work, 14 analyses of the quartz standard NBS-28 gave a $\delta^{18}O$ of 9.64‰ with a standard deviation of 0.09‰. The average difference between duplicate analyses given in Table 1 was 0.25‰. This is marginally worse than the expected 2σ based on the NBS-28 data and may be due to some sample heterogeneity.

Within the structure, MQ can contain up to 2 wt% H_2O that is not driven off by heating to 200 °C (e.g., Graetch et al., 1985, 1987). This water exists both as molecular H_2O and silanole (SiOH) groups. At the time of formation, MQ will consist of SiO_2 and isotopically lighter H_2O. The difference in $\delta^{18}O$ between the SiO_2 and the H_2O will depend on temperature; the lower the temperature, the greater the difference. The present-day measured $\delta^{18}O$ for MQ will therefore be lighter than the actual $\delta^{18}O$ of the SiO_2 alone. The difference can be estimated using the equation for α of Clayton et al. (1972) ($10^3 \ln \alpha = (3.38 \times 10^6)T^{-2} - 2.90$; where T is in kelvins). MQ formed at 120 °C with 1 wt% H_2O will be 0.3‰ lighter than MQ containing no H_2O. At 50 °C, this difference is 0.5‰. These estimates assume that all the water is present as molecular H_2O. The oxygen-isotope fractionation factor between silanole groups and water is unknown.

RESULTS

Table 1 gives the $\delta^{18}O$ values obtained and Figure 1 the location of the analyzed material within each agate. The total range in $\delta^{18}O$ values for Q and MQ is from 20.41‰ to 28.87‰. These data are similar to the values obtained by Fallick et al. (1985) for Scottish agates and indicate low temperatures of crystallization. The average value for Q zones is 23.93‰, whereas for MQ zones it is 26.92‰. The Q zones are therefore on average 3‰ lighter in $\delta^{18}O$ than the MQ zones. Table 1 also shows that in general the outer rim of MQ has the highest $\delta^{18}O$ values in each agate.

These differences are well illustrated by a profile through individual agates (Fig. 2). Agate 1 has a MQ rim of $\delta^{18}O = 27.08‰$ followed by a horizontally banded MQ (zone B) 5‰ lighter. Apart from the outer MQ zone, the remaining zones show a "saw-toothed" profile towards the center. The three Q zones and the two MQ zones become heavier toward the center with two Q zones, E and C, being about 2‰ lighter than the immediately preceding MQ zone. This agate is unlike the others as it is not completely filled. The innermost Q zone is purple amethyst, and euhedral crystals project into the cavity at the center of the sample. This Q zone is the heaviest of all the Q zones analyzed in the six agates. The lack of any similarities between the $\delta^{18}O$ profiles for each agate is perhaps to be expected, as the agates are not likely to be from the same stratigraphic horizons. Agate 6 consists only of MQ, and its inner and outer zones are very similar in $\delta^{18}O$.

TEMPERATURE OF FORMATION

It is not possible to determine both temperature and $\delta^{18}O$ of the depositing fluid from the silica $\delta^{18}O$ data alone. The $\delta^{18}O$ of each zone analyzed is dependent on the $\delta^{18}O$ of the fluid from which it was deposited, the temperature of deposition and the oxygen-isotope fractionation factor between quartz and water. In addition, there may have been secondary exchange resulting from the continued passage of fluids through each zone after deposition. As a first approximation, the temperature of formation of each mineral zone has been estimated for a range of plausible $\delta^{18}O$ values for the fluid responsible for its deposition. The chemical composition of the fluid depositing the agate is assumed to be close to pure H_2O, as low-temperature–low-pressure fluids such as these are unlikely to contain significant quantities of dissolved CO_2 (see phase diagrams, Roedder, 1984, p. 238). The presence of dissolved silica is not likely to have much effect on the critical temperature, as the solubility of silica in H_2O at low temperatures is small. The isotopic fractionation curve for quartz-H_2O of Clayton et al. (1972) has, therefore, been used to estimate the temperature of deposition for the range of $\delta^{18}O$ values observed in each agate.

Table 2 gives the range of calculated temperatures for a range of putative $\delta^{18}O$ values for the depositing fluid. The only $\delta^{18}O$ values available for meteoric water from Namibia are from areas much further inland than Sarusas, which is about 10 km from the coast. These values, averaging about −6‰, are lighter than those from coastal areas of southern Africa, which average about −3‰ (National Physical Research Laboratory, 1984). The Etendeka volcanics have been dated at 121 Ma. The latitude of this part of Africa has not changed significantly since the break-up of Gondwanaland at about 120 Ma (e.g., Martin and Hartnady, 1986), so meteoric waters have probably maintained a fairly constant $\delta^{18}O$ value throughout the history of the Etendeka volcanics. Regardless of the exact $\delta^{18}O$ value of the meteoric water at Sarusas, low temperatures of deposition are required to have given the $\delta^{18}O$ values of the agates. For a fluid that was enriched in ^{18}O relative to SMOW as a result of isotopic exchange with the host quartz latite, higher temperatures of deposition are possible (Table 2), but even for a fluid of $\delta^{18}O$ of +6‰, the maximum temperature indicated by the data is 169 °C, which is well below the critical temperature of pure water (374 °C).

ORIGIN OF Q AND MQ ZONES

It was shown above that Q zones have systematically lower $\delta^{18}O$ values than MQ zones by an average of about 3‰, or, in the case of agate 1, the Q zones are about 2‰ lighter than the preceding MQ zone. This difference cannot be related to the presence of H_2O in MQ because, as discussed above, the effect on $\delta^{18}O$ is small and in the opposite sense in that the measured $\delta^{18}O$ for MQ is lighter than the actual value for the SiO_2 alone. Three possible explanations could account for the differences in $\delta^{18}O$ between Q and MQ.

TABLE 2. Calculated deposition temperatures

$(\delta^{18}O)_{fluid}$	T_{max}	T_{min}
−6‰	67 °C	26 °C
−3‰	85 °C	39 °C
0‰	108 °C	53 °C
+6‰	169 °C	89 °C

Note: T_{max} and T_{min} are temperatures calculated for the range of $\delta^{18}O$ shown in all the agates (20.41‰ to 28.87‰) calculated using the equation of Clayton et al. (1972) $\delta s - \delta w = (3.38 \times 10^6)T^{-2} - 2.90$ where T is in kelvins.

1. Differences in oxygen-isotope fractionation factors for Q-H_2O and MQ-H_2O. The formation of MQ is poorly understood and may involve intermediate stages such as opal. However, oxygen-isotope studies of cherts and diatoms (e.g., Labeyrie, 1974; Knauth and Epstein, 1975; Murata et al., 1977) do not suggest that different oxygen-isotope fractionation factors should apply to different silica types over the same temperature range. O'Neil (1986, p. 19) considered that "crystal structure or even the presence of structural water is not important to the oxygen isotope properties of silica species."

2. The MQ zones were deposited at lower temperatures than the quartz zones, the agates having irregular cooling histories. This explanation does not account for the differences in silica type and the presence of Q only as wall-layered zones and MQ as horizontal layers as well as wall layers. Declining temperature is presumably the cause of the overall increase in $\delta^{18}O$ toward the center of the agate, but temperature changes alone are not likely to have produced the pattern shown in Figure 2.

3. The MQ zones crystallized from H_2O liquid, whereas the Q zones crystallized from H_2O vapor. H_2O liquid is isotopically heavier than H_2O vapor when the two are in equilibrium (i.e., during condensation or boiling) by an amount that is dependent on temperature. It has been shown previously that the $\delta^{18}O$ of Q zones is about 3‰ lighter than that of MQ zones. A fractionation factor of 3‰ between H_2O liquid and H_2O vapor occurs at about 120 °C, and the existence of two fluid phases just above 100 °C is consistent with boiling at just greater than atmospheric pressure. This third explanation is preferred because it not only explains the isotopic differences between Q and MQ in a single agate but also the tendency for agate to form as horizontal layers together with wall-layered coarsely crystalline quartz.

ORIGIN OF AGATE

Three recent papers have proposed rather different mechanisms for the origin of agate. Flörke et al. (1982) studied the chemistry, mineralogy, and the water content (using infrared spectroscopy) of various agates, mainly from Brazil, which are very similar to those described in this paper. They suggested that mixed Q and MQ agates result from a protracted cooling history. Their interpretation was that agate precipitated from supercritical fluids (i.e., >374 °C), whereas coarsely crystalline quartz formed from a low-temperature (<100 °C) H_2O liquid. In a later paper, Graetch et al. (1985), using similar methods, suggested that chalcedony in Brazilian agate formed at <250 °C. Fallick et al. (1985) studied the oxygen- and hydrogen-isotope composition of agates from Scotland and concluded that the agates formed at temperatures as low as 50 °C, with no initial precipitation from supercritical fluids.

The present work supports the conclusion of Fallick et al. (1985) in that low temperatures of deposition are implied. The observed differences between Q and MQ zones is consistent with deposition at just above 100 °C. The deposition of MQ layers from supercritical fluids is not supported by the data presented in this paper. Furthermore, the range in $\delta^{18}O$ observed in the Sarusas agates does not indicate a protracted cooling history of these agates from supercritical to room temperature, as suggested by Flörke et al. (1982). The coexistence of H_2O liquid and H_2O vapor during the evolution of the agates indicates that the *P-T* conditions were close to the two-phase curve for H_2O. The dominance of agate (precipitated from H_2O in the liquid phase) or quartz (precipitated from H_2O in the vapor phase) in a particular zone is most probably due to changes in pressure and/or temperature during the growth of the agate. These changes could result from changes in the hydrothermal plumbing or from cycles of eruption followed by erosion above the zone of agate formation.

The presence of a thin MQ zone around all mixed Q and MQ agates was noted by Flörke et al. (1982). Agates 1–4 (App. 1) have a thin outer MQ zone, and, in each case, this zone is isotopically the heaviest. It is not clear whether this zone was deposited from H_2O vapor (it is wall-layered) or from H_2O liquid (it is isotopically heavy MQ). The high $\delta^{18}O$ values indicate low temperature of deposition relative to the other zones in each individual agate. Agates from other localities have a thin rim of opal around the outside rather than MQ (Flörke et al., 1982). It is possible that the wall-layered MQ rims on the Sarusas agates were originally opal that later transformed to MQ. Opal can contain up to 5 wt% H_2O (Graetch et al., 1987) and formation of MQ in this way will result in $\delta^{18}O$ values that are heavier than those of "primary" MQ if the transformation takes place at low temperatures. The bulk $\delta^{18}O$ of opal containing 5 wt% H_2O formed at 120 °C will be 1.5‰ lighter than coprecipitating water-free SiO_2. If 4 wt% H_2O is lost at 30 °C during transformation to MQ, the new bulk $\delta^{18}O$ will be 2‰ heavier (i.e., 0.5‰ heavier than the water-free SiO_2 formed at 120 °C). This calculation assumes that isotopic equilibrium is maintained between water and silica at the time of water loss. It seems, therefore, that formation of opal followed by transformation to MQ will not result in MQ with significantly higher $\delta^{18}O$ values than "primary" MQ. The most plausible explanation for the high $\delta^{18}O$ values in the outer MQ zones is that these zones were able to exchange with fluids (liquid or vapor) via the outer surface of the geode over the entire temperature range of infilling. The high $\delta^{18}O$ values, therefore, reflect the low temperatures of final isotopic equilibration. It may be that this material is transformed opal, but this cannot explain the high $\delta^{18}O$ values of these outer MQ zones.

DEPOSITION OF AGATES AND ALTERATION OF THE KAROO VOLCANICS

The model presented above suggests that at times during the formation of the agates H_2O liquid and H_2O vapor coexisted, and the magnitude of the difference between Q and MQ zones suggests that the temperature was above 100 °C. If these agates formed at a constant temperature of about 120 °C, the value implied by the 3‰ difference between MQ and Q zones, then the range in observed $\delta^{18}O$ values (Table 1) require fluid $\delta^{18}O$ values between +1.4‰ and +9.9‰. It is obviously unlikely that the temperature remained constant during formation of the agates, and fluctuations in temperature must, in part, be the cause of the range in observed $\delta^{18}O$ values. Nevertheless, formation above 100 °C requires that the $(\delta^{18}O)_{fluid}$ was greater than $(\delta^{18}O)_{SMOW}$. Meteoric water could have achieved the appropriate $\delta^{18}O$ values by (1) concentration of ^{18}O during prolonged boiling and loss of the vapor phase or (2) exchange with the surrounding rocks.

During boiling, ^{18}O is preferentially partitioned into the liquid, and it is possible that meteoric water became ^{18}O-enriched in this way. Using the Rayleigh equation, it can be shown that at 120 °C, the required 13‰ increase in $\delta^{18}O$ value from meteoric water (−3‰) to the inferred upper limit of 9.9‰ could have been generated by >95 wt% loss of vapor. This may also be the mechanism by which silica saturation in the liquid is achieved. Influx of water into the cavities within the volcanics may have been continuous or episodic. If boiling is required to produce silica saturation, high $\delta^{18}O$ values in the fluid would have been achieved before each new layer of the agate was deposited.

The exchange mechanism for increasing $\delta^{18}O$ in meteoric fluids is not supported by the $\delta^{18}O$ data for the volcanics themselves. Harris et al. (1988) have shown that the Sarusas quartz latites contain pyroxene and plagioclase that have $\delta^{18}O$ values of 10.6‰ and 10.9‰, respectively. These values are interpreted as being similar to the original magmatic values and indicate a crustal source for the acid volcanics at Sarusas, in the north of the Etendeka area. The whole-rock $\delta^{18}O$ value for the Sarusas quartz latite is 17.9‰, and it is suggested that the 10‰ difference between whole-rock and phenocryst $\delta^{18}O$ is due to secondary alteration (Harris et al., 1988). This shift to higher $\delta^{18}O$ values is a feature of all the Etendeka volcanics of both basaltic and quartz latite compositions. The fluid responsible for raising the $\delta^{18}O$ of the volcanics must itself become isotopically lighter as a result of the exchange (though this lowering could have been very small if the water/rock ratio was large). Nevertheless, if meteoric water was responsible for the alteration, it would be shifted to lighter values.

CONCLUSIONS

The data presented in this paper confirm that agates form at low temperatures. Unambiguous determination of both temperature and the $\delta^{18}O$ value of the depositing fluid is not possible, but systematic differences between the $\delta^{18}O$ values of horizontally layered MQ and wall-layered Q are best explained if MQ is deposited from H_2O (liquid) and Q deposited from H_2O (vapor). The average difference between $\delta^{18}O$ of the Q and MQ is 3‰ which, if this model is correct, indicates temperatures around 120 °C. If this temperature remained constant, $\delta^{18}O$ values for the fluid between +1.4 and +9.9 are required to give the range in silica $\delta^{18}O$ values. Obviously, temperature did not remain constant, but values above 100 °C require that the $\delta^{18}O$ value of the depositing fluid be greater than modern meteoric water observed in the area. Boiling of water and removal of the vapor phase is one mechanism of producing a high $\delta^{18}O$ fluid. Greater than 95 wt% loss of vapor at 120 °C will increase the $\delta^{18}O$ value of a fluid by the 10‰, which seems to be required and may also have been the mechanism by which silica becomes saturated in the fluid. High $\delta^{18}O$ fluids cannot have been produced by exchange with the host volcanics because alteration of these rocks has resulted in increasing $\delta^{18}O$ values. Mass balance of ^{18}O therefore requires the fluid to have been isotopically lighter after such an exchange.

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APPENDIX 1. DESCRIPTION OF AGATES STUDIED

Agate 1 (silica types Q and MQ). Thin outer MQ zone with two horizontal MQ layers sandwiching wall-layered Q. Inner two layers are coarse Q with the innermost having euhedral Q projecting into empty cavity. Inner Q zone is purple amethyst. The MQ in this agate is granular fine quartz.

Agate 2 (silica types Q and MQ). Thin outer MQ zone, then wall-layered Q mantle to MQ inner zone.

Agate 3 (silica types Q and MQ). Thin outer MQ zone, then horizontal MQ. This is followed by a Q zone that also forms a thin wall-layered zone followed by a second MQ zone that has a horizontal part and a much thinner wall-layered part. Inside this is a coarsely crystalline Q zone with an inner MQ zone.

Agate 4 (silica types Q and MQ). Thin outer MQ zone with horizontally layered MQ. Inner zone is coarsely crystalline Q that makes up ⅔ of the geode. The thin outer MQ is spherulitic, length-fast chalcedony, and the horizontal MQ is dominantly granular fine quartz with minor patches of length-fast chalcedony.

Agate 5 (silica types Q and MQ). Outer zone of MQ much wider than agates 1–4. Inner MQ zone is horizontally layered (bottom right of photograph in Fig. 1), then wall-layered. The wall-layered MQ is dominantly length-fast chalcedony, whereas the horizontal MQ is mixed length-fast chalcedony and granular fine quartz. There are two inner wall-layered Q zones separated by a thin zone of length-fast chalcedony.

Agate 6 (silica type MQ only). Outer MQ zone with inner MQ zone showing both wall and horizontal layering. The wall-layered MQ is length-fast chalcedony; the horizontal layers mixed length-fast chalcedony and granular fine quartz. The center zone is length-fast chalcedony.