DISCUSSION

DEPOSITIONAL FACIES AND AQUEOUS–SOLID GEOCHEMISTRY OF TRAVERTINE-DEPOSITING HOT SPRINGS (ANGEL TERRACE, MAMMOTH HOT SPRINGS, YELLOWSTONE NATIONAL PARK, U.S.A.)—DISCUSSION

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INTRODUCTION

Terrestrial CaCO3 precipitates, including travertines, tufas, and speleothems, are currently of great interest because of their potential as archives of environmental, climatic, and biologic information (e.g., Andrews et al. 1997; Bar-Matthews et al. 1997; Walter and Des Marais 1993). Detailed studies of examples of these terrestrial carbonates therefore provide valuable information and aid interpretation of their records of surface processes, environments, and associated organic influences. The recent paper by Fouke et al. (2000) is a useful contribution in this area, however, some of their comparisons with earlier studies are not wholly accurate and require clarification. More generally, we wish to debate further the issue of whether travertines such as those at Mammoth Hot Springs could record isotopic evidence of microbial activity.

COMPARISONS BETWEEN ANGEL TERRACE AND OTHER THERMAL TRAVERTINES

Fouke et al. (2000) draw the general conclusion, as have others before, including the classic work of Gonfiantini et al. (1968), that large shifts in δ13C of the dissolved inorganic carbon, and ultimately of the precipitating carbonate, are mainly controlled by rapid degassing of 12C-enriched CO2 rather than microbial activity. They proceed to compare data from Angel Terrace with a number of other sites (Fouke et al. 2000, figs. 13, 14), making the general point that the overall covariant trends between δ13C and δ18O are similar in each case. They regret, however, that detailed comparisons between sites in some previous studies cannot be made because distances from the feeder springs and details of microenvironments sampled were not recorded. As we were involved in one of these studies (Guo et al. 1996) we point out that this statement is not entirely true. The microenvironments of the Recent travertines sampled at Rapolano Terme in Italy are shown very clearly in Guo et al. (1996, table 1 and fig. 4A).

It is true that Guo et al. (1996) did not list the distance of each sample relative to the springs at the Terme San Giovanni locality. They did, however, show precisely the location of each set of samples (Guo et al. 1996, fig. 3). This figure shows, for example, that samples 21–25 and 39–40 are immediately adjacent to fissure ridge springs, whereas samples 41–51 are located 200 m away from the springs. It is a pity that these details were not noticed by Fouke et al. (2000), because they have a bearing on the interpretation of the isotope data at this site and their use as a comparator with Angel Terrace.

Guo et al. (1996) emphasized that cursory examination of the Rapolano Terme travertine data, without consideration of sample sites and fabrics, invites an interpretation similar to that of Gonfiantini et al. (1968), i.e., that increasing carbon isotope values are merely a result of progressive CO2 degassing with distance from the spring. However, they went on to stress that at Rapolano such an interpretation cannot be wholly correct because samples (21–25 and 39–40), collected on the fissure ridge immediately adjacent to the springs, have the largest δ13C values. In this case, the authors state that CO2 degassing produces large δ13C compositions, this process cannot account for the values around +7‰ to +8‰ at the fissure ridge springs, because the same water then flowed down the valley slopes precipitating travertine (samples 1–11, Guo et al. 1996, fig. 4A) with δ13C values around +1‰. If CO2 degassing were the only process involved, the downstream precipitates should be isotopically larger, not smaller, than +7‰ to +8‰. Guo et al. (1996) could find no obvious abiotic mechanism to account for the δ13C values observed, but noted that the calcites sampled near the springs were cyanobacterial and shrub microfacies that have clear microbial influence. Because these calcites formed in relatively closed microenvironments (stagnant pools with little or no water flushing), Guo et al. (1996) suggested that the effects of photosynthetic microbes preferentially extracting 12CO2 would cause the water of the calcite-precipitating microenvironment to be strongly enriched in 13CO2. Thus, the biotically mediated calcite close to the springs would have the anomalously large δ13C values observed, whilst the bulk of spring water would be capable of precipitating calcites downstream with smaller δ13C values.

One set of microbially influenced travertines (samples 13–20, Guo et al. 1996, fig. 4A) was not discussed adequately by Guo et al. (1996), and may have led Fouke et al. (2000) to infer that these samples were heavily influenced by microbial activity, leading to larger δ13C values downstream. This might explain their statement that “Because the abundance of photosynthetic microbes increases downstream, a downstream increase in δ13C and δ18O would be expected” (Fouke et al. 2000, p. 581, referencing Guo et al. 1996 in support). However, Guo et al. (1996) did not make this interpretation. Instead, they stated that the rest of their Recent data (i.e., all the data excepting samples 21–25 and 39–40 close to the spring) “. . .is adequately explained by progressive degassing of CO2, leading to larger δ13C values with increasing distance from the spring.” We concede that Guo et al. (1996) should have gone on to say that δ13C values in the valley floor of Borro Canatoppa near Terme San Giovanni are again lower, presumably caused by mixing of spring waters with the river water.

BIOTIC EFFECTS ON TRAVERTINE δ13C VALUES?

As Fouke et al. (2000) point out, there is currently debate about whether biotic effects are recorded in travertine δ13C values. In our view, there is now strong evidence that biotic effects are recorded in ambient temperature tufas and microbial carbonates (e.g., Andrews et al. 1997). It is less clear that biotic effects are recorded in most thermal travertines, although the Rapolano Terme fissure ridge deposits discussed above suggest that they are in some cases. Guo et al. (1996) also showed that Recent and Quaternary Tuscan travertines with microbial fabrics have δ13C values about 0.5‰ larger than the closely associated abiotic crystalline crusts, and that the microbial (shrub) travertines generally have slightly larger δ13C values relative to abiotic crust values (excluding one datum). These differences are small but they could be records of microbial activity in thermal spring waters (Guo et al. 1996).

The sites sampled by Fouke et al. (2000, fig. 3) range over a short distance (< 5 m). Ambient flow rates at Angel Terrace Spring are not quantified, but the samples appear to be mainly from sites where actively flowing spring waters move in relatively large volumes and with depths of...
We would not expect carbonate precipitates at such well-flushed sites to clearly reflect microbial influence because of the efficient mixing in the flowing water. We would instead expect such sites to reflect rapid CO$_2$ degassing as the principal control on $\delta^{13}$C values of the carbonate; this is consistent with the data and conclusions that Fouke et al. (2000) present. In contrast, flow rates at Rapolano are much lower (Guo and Riding 1999). Furthermore, precipitates at the Angel Terrace sites include aragonite needle shrubs (Fouke et al. 2000, fig. 4B, fig. 8, table 4). These distinctive precipitates have been interpreted as essentially abiotic (Pentecost 1990). In contrast, Recent shrubs with isotopic values in excess of $+6\%$e (samples 21–25, Guo et al. 1996) at Rapolano are quite different. They are stubby, arborescent masses, formed by apparently random associations of micrite aggregates and rhombic spar crystals, and show petrographic evidence of microbial influence (Guo and Riding 1994).

We suggest that studies at other Mammoth sites characterized by lower and/or variable flow rates and volumes might reveal microbial effects on $\delta^{13}$C composition that are not apparent at sites adjacent to active vents, such as the one that Fouke et al. (2000) have examined. One broad implication that can be drawn from this comparison of the Angel Terrace and Rapolano Terme samples is that studies exploring for isotopic evidence of microbial life in thermal springs should specifically include examination of poorly flushed sites where flow rates and volumes are, or have been, relatively low.
flows laterally from this vent point source to precipitate terraced travertine accumulations along the spring drainage flow path (Fig. 1). Conversely, the Terme San Giovanni travertine deposit is a fissure ridge where hot-spring water emerges from a long and narrow fracture (Guo et al. 1996). Spring water flows away from the fissure line source along opposite drainage flow paths to form an elongate travertine mound several meters in height (Fig. 1). A detailed depositional facies model has not yet been established for fissure-ridge travertine.

My reconnaissance observations of the Terme San Giovanni fissure ridge in July 2000 indicate that the environmental conditions at this locality are significantly different from those at Angel Terrace. These differences range from natural spring water temperature and chemical composition to human manipulation of the spring drainage hydrology. It is important to emphasize that Guo et al. (1996) analyzed modern travertine deposits but not the spring water from which they precipitated. Guo et al. (1996) quote Bar-azzuoli et al. (1988) to suggest that spring water emerges from the Terme San Giovanni fissure ridge at 29 to 34°C. These temperatures are consistent with my measurements of 30 to 32°C and are almost 40°C cooler than the 71 to 73°C spring water emerging from the vent at Angel Terrace (Fouke et al. 2000). This indicates that the entire Terme San Giovanni system is analogous to the low-temperature proximal-slope and distal-slope facies of the Angel Terrace system.

As acknowledged by Guo et al. (1996), the Terme San Giovanni spring water has been diverted for use in the local hotel and spa, causing a significant reduction in the volume and flow rate of spring water emerging from the fissure ridge. An additional aspect not described by Guo et al. (1996) is that the entire 150-m-long drainage channel in the middle of the Terme San Giovanni drainage system is a man-made conduit designed to route water into the nearby Borro Canatoppa stream valley. Therefore, many of the hydrologic and geochemical environmental conditions of the Terme San Giovanni hot-spring system are altered by human intervention and are no longer in their natural state. In contrast, protection by the U.S. National Park Service has allowed Angel Terrace to remain a pristine hot-spring environment, which is shown in figures 13 and 14 of Fouke et al. (2000). This contextual environmental information is shown on all aqueous and travertine geochemistry cross-plots (figs. 6, 7, 11, 12, and 13 in Fouke et al. 2000). This environmental context is also not clearly shown on the travertine isotope cross-plots (figs. 4 and 5 in Guo et al. 1996). Therefore, the coarse spatial constraints on sampling presented in Guo et al. (1996) are not sufficient to permit detailed correlation and comparison with Angel Terrace.

COMPARISON OF SYSTEM-Scale ISOTOPIC FRACTIONATION BETWEEN THE HOT SPRINGS

As indicated by Andrews and Riding (2001), the sampling strategy of Guo et al. (1996) is sufficient for a tens of meters system-scale comparison with Angel Terrace, which is shown in figures 13 and 14 of Fouke et al. (2000). Sample numbers and crystalline textures rather than explicit descriptions of the environment of travertine precipitation are shown in figure 4A of Guo et al. (1996). This style of sample labeling, in conjunction with the fact that all previously studied hot-spring travertine exhibits isotopic trends similar to those at Angel Terrace, lead to an incorrect interpretation of the Guo et al. (1996) data. As shown in Figure 2, the Terme San Giovanni travertine exhibits downflow trends in travertine δ18O and δ13C that are opposite in direction but similar in magnitude to those of the Angel Terrace spring water and travertine.

Andrews and Riding (2001) do not emphasize the significance of the correlation of systematic changes in Angel Terrace spring water δ18O and dissolved inorganic carbon (DIC) with modeled Rayleigh-type fractionation trajectories (fig. 7 in Fouke et al. 2000). This close fit indicates that CO2 degassing is the dominant control on Angel Terrace spring water δ13C (Usdowski et al. 1979; Michaelis et al. 1985). It should be recognized that the Usdowski et al. (1979) and Michaelis et al. (1985) fractionation equations were developed from measurements taken along a natural spring system rather than in a sterile laboratory experiment. Therefore, the final fitted

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**Fig. 1.**—Field photographs of: A) a terraced travertine deposit at Angel Terrace Spring AT-1, Mammoth Hot Springs, Yellowstone National Park, U.S.A.; and B) a fissure-ridge travertine deposit at Terme San Giovanni, Rapaleno, Tuscany, Italy.
equations may incorporate some isotopic byproducts of microbial respiration or photosynthesis. However, these equations are presently the standard references for calculating degassing fractionation, and it is therefore assumed that the effect of microbial activity is minimal.

Andrews and Riding (2001) discuss the possible influence of spring water flow rate and resulting hydrologic solute flux on travertine isotopic composition. Although they do not develop these concepts in detail, their argument suggests that the amount of $^{13}$C and $^{18}$O isotopes consumed or liberated by respiration and photosynthesis would be small in comparison to the flowing spring water reservoir. Therefore, travertine precipitated in low-flow and low-temperature spring systems are more likely to precipitate travertine containing biologically fractionated isotopes.

Fouke et al. (2000) also present and develop these hypotheses regarding the detection of biological fractionation in travertine isotopes. The sulfur isotopic system at Angel Terrace exhibits little downflow variation in water and travertine $\delta^{34}$S (figs. 6G and 11D in Fouke et al. 2000). Proposed mechanisms to generate this pattern include swamping by open-system solute mass flux by the flowing spring water, low rates of metabolic activity, and steady-state mass balancing of oxidizing or reduced solutes (p. 581 in Fouke et al. 2000). Conversely, the robust downflow trends in carbon- and oxygen-isotope composition at Angel Terrace (Fig. 2) indicate that open-system flushing is not enough to completely overwhelm biological $\delta^{13}$C and $\delta^{18}$O fractionation. Calculated $\delta^{13}$C values for travertine in equilibrium with the Angel Terrace spring water (fig. 11A in Fouke et al. 2000) indicate that: (1) the CO$_2$ degassing of the spring water is also the dominant control on $\delta^{13}$C for travertine precipitated in high-temperature facies, and (2) a decrease of up to 5% PDB below equilibrium $\delta^{13}$C values is observed in travertine precipitated in the low-temperature facies. These $\delta^{13}$C values are interpreted to represent fractionation by microbial aerobic respiration in addition to some downstream transport and mixing of travertine (p. 580–581 in Fouke et al. 2000). In an analogous manner, the Angel Terrace travertine $\delta^{18}$O values were compared with oxygen-isotope equilibrium values for aragonite and calcite calculated from the spring water compositions. Results indicate that the high-temperature travertine is near or slightly above equilibrium (fig. 15A in Fouke et al. 2000). Conversely, shifts of $-3\%$e in both $\delta^{18}$O and $\delta^{13}$C are observed in the middle to low-temperature travertine precipitated in the proximal-slope and distal-slope facies (Fig. 15A in Fouke et al. 2000). It is suggested that these trends in travertine $\delta^{13}$C and $\delta^{18}$O may be the result of microbial aerobic respiration (p. 581 in Fouke et al. 2000).

INTERPRETATION OF THE TERME SAN GIOVANNI TRAVERTINE $\delta^{13}$C AND $\delta^{18}$O COMPOSITIONS

Interpretation of the unique $\delta^{13}$C and $\delta^{18}$O composition of modern travertine at Terme San Giovanni (Fig. 2) remains speculative because of the absence of spring water geochemical analyses. Guo et al. (1996) suggest that removal of $^{13}$C from spring water by microbial photosynthesis could cause the observed downstream decrease of $7\%$e $\delta^{13}$C in travertine $\delta^{13}$C (Fig. 2; Hinga et al. 1994; Flanagan et al. 1996). Carbon-isotope fractionation driven by degassing at Angel Terrace is comparable in magnitude but opposite in direction to the negative trend observed at Terme San Giovanni (Fig. 2). This implies that: (1) Terme San Giovanni spring water experiences significantly less CO$_2$ degassing due to reduced concentrations of dissolved CO$_2$ or temperature effects, and (2) fractionation by degassing is masking the photosynthetic fractionation at Angel Terrace. However, without accompanying spring water temperature, pH, and isotopic analyses at Terme San Giovanni, it is not possible to calculate comparative equilibrium travertine compositions. Therefore environmental isotopic trends cannot be identified, nor can the responsible fractionation mechanisms be fully interpreted.

Guo et al. (1996) incorrectly state that oxygen-isotope variation in the Terme San Giovanni travertine can be explained by CO$_2$ degassing. Oxygen-isotope equilibrium is nearly instantaneous between atmospheric CO$_2$ and water (Truesdell and Hulston 1980; Usdowski and Hoefs 1990). Therefore, degassing will not fractionate oxygen isotopes. As a result, the nearly 7%e SMOW $\delta^{18}$O decrease observed in the Terme San Giovanni travertine (Fig. 2) must result from other processes, such as temperature change, evaporation, or biological fractionation.

A maximum spring water temperature drop from approximately 30° C across the Terme San Giovanni drainage system (Guo et al. 1996) would produce a positive 3%e SMOW travertine $\delta^{18}$O equilibrium fractionation (Kim and O’Neal 1997). Therefore, temperature change cannot by itself explain the large-magnitude decrease observed in travertine $\delta^{18}$O (Fig. 2). Mixing with water from other sources in the distal portions of the drainage flow path is suggested by Andrews and Riding (2001) to explain the non-sequential decrease in Terme San Giovanni travertine $\delta^{13}$C (Fig. 2). If this distal water was warm, then temperature fractionation effects during mixing might also explain, at least in part, the travertine $\delta^{13}$O. However, no evidence or discussion to support water mixing in the distal drainage system was presented by Guo et al. (1996) or Andrews and Riding (2001).

The evaporation of the spring water is expected to increasingly concentrate $^{18}$O along the drainage flow path (Gonfiantini 1986). The $\delta^{18}$O of
travertine precipitated from this spring water would therefore progressively increase down flow. However, this is opposite to the decreasing $\delta^{18}O$ trend observed in the Terme San Giovanni travertine (Fig. 2). Therefore, by the process of elimination, this implies that the decreasing trend in travertine $\delta^{18}O$ values (Fig. 2) may reflect fractionation due to microbial activity (Flanagan et al. 1996). This further accentuates the need for a future study that includes physical and chemical analyses of paired spring water and travertine samples at Terme San Giovanni.

REFERENCES


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Received 6 November 2000; accepted 7 November 2000.