

Dissected hydrologic system at the Grand Canyon: Interaction between deeply derived fluids and plateau aquifer waters in modern springs and travertine

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ABSTRACT

Geochemical study of water and gas discharging from the deeply incised aquifer system at the Grand Canyon, Arizona, provides a paradigm for understanding complex groundwater mixing phenomena, and Quaternary travertines deposited from cool springs provide a paleohydrologic record of this mixing. Geochemical data show that springs have marked compositional variability: those associated with active travertine accumulations (deeply derived endogenic waters) are more saline, richer in CO₂, and elevated in ⁸⁷Sr/⁸⁶Sr relative to springs derived dominantly from surface recharge of plateau aquifers (epigenic waters). Endogenic waters and associated travertine are preferentially located along basement-penetrating faults. We propose a model whereby deeply derived fluids are conveyed upward via both magmatism and seismicity. Our model is supported by: (1) gas analyses from spring waters with high He/Ar and He/N₂ and ³He/⁴He ratios indicating the presence of mantle-derived He; (2) large volumes of travertine and CO₂-rich gases in springs recording high CO₂ fluxes; and (3) ⁸⁷Sr/⁸⁶Sr in these springs that indicate circulation of waters through Precambrian basement. Geochemical trends are explained by mixing of epigenic waters of the Colorado Plateau aquifers with different endogenic end-member waters in different tectonic sub-provinces. Endogenic waters are volumetrically minor but have significant effects on water chemistry. They are an important and largely unrecognized component of the hydrogeochemistry and neotectonics of the southwestern United States.

Keywords: travertine, endogenic waters, helium isotopes, Grand Canyon, xenowhiffs.

INTRODUCTION

The Grand Canyon (Arizona, United States) provides a unique view of a deeply dissected aquifer system (~1.5 km deep). Grand Canyon springs exhibit physical and chemical variability, and large volumes of Quaternary travertine are associated with a distinct subset. Our hypothesis is that travertine-depositing springs of the Grand Canyon require a deep source of CO₂-rich fluid that mixes with larger volume surface and groundwaters, and these deeply sourced fluids influence water quality in the Colorado Plateau region. We test this hypothesis with: (1) field studies to show the location of springs and travertines relative to faults; (2) water and gas chemistry to identify end members and quantify mixing parameters; and (3) Sr isotope tracers to show deep circulation of waters through basement. Prior studies have developed models explaining geochemical variability in plateau

aquifers (Huntoon, 1996; Monroe et al., 2004) by water-rock interaction of surface recharge with diverse aquifer materials, fracture flow, and dual porosity systems (Huntoon, 2000). Existing models do not address the unique chemistry of the travertine-depositing springs, the chemical conditions required for extensive travertine deposition, or the variable chemical composition observed among springs issuing from the same stratigraphic unit. This paper examines both travertines and hydrochemistry, presents the first gas chemistries from springs of the region, and is the first attempt to integrate gas and water chemistry to identify a link between deeply derived components and regional groundwater chemistry.

GEOLOGIC SETTING OF SPRINGS AND TRAVERTINE IN GRAND CANYON

Springs

The Grand Canyon hydrologic system has several components (Figs. 1 and 2A). The Colorado River contains water that originates as runoff in the Rocky Mountains and interacts minimally with local aquifers. Springs issuing from Paleozoic layered rocks in the Grand Canyon are fed from surface recharge of Colorado Plateau aquifers that emerge into the canyon near the top of regional aquicludes (Huntoon, 2000). High-discharge springs emerge from karstic aquifers in the Muav and Redwall Limestones. Small-volume springs emerge along faults, in the Proterozoic basement, and at the Great Unconformity.

The term epigenic refers to groundwater components derived from surface recharge and includes recent recharge as well as older, chemically evolved, sedimentary basin groundwaters. Previous studies concluded that residence time through this aquifer system is long, probably thousands of years (Monroe et al., 2004; O'Brien, 2002). Epigenic waters are characterized by cool temperature (<20 °C), high discharge, low conductivity, neutral to slightly alkaline pH, and low CO₂ content.

We use the term endogenic to refer to a deeply derived groundwater component. Endogenic is preferred to thermogenic or magmatic because the waters are no longer hot, are distal to volcanic fields, and can have undergone deep crustal circulation and mixing in addition to mantle inputs. Springs rich in the endogenic component are associated with faults and typically exhibit warmer temperatures (20–35 °C), low discharge, high salinity, lower pH, high CO₂, mantle-derived He, and are associated with travertine deposition (e.g., endogene carbonates of Liu et al., 2003).

Travertine

Both travertine deposits and modern travertine-depositing springs are commonly located along faults that offset basement and form Lar-

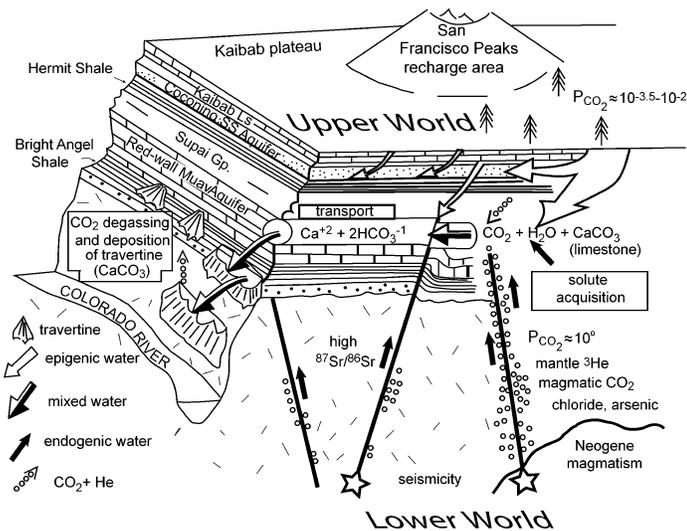
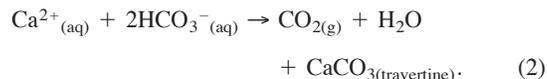
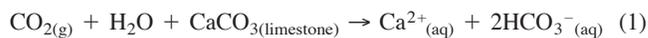


Figure 1. Model of Grand Canyon hydrologic system showing interaction of epigenic and endogenic water components during acquisition, transport, and deposition phases of travertine genesis. Depicted are major aquifer units and schematic flow lines indicating surface recharge and chemical evolution of epigenic waters (white arrows) and input of endogenic waters along faults (black arrows). Small circles depict upward transport of mantle-derived He and its carrier gas, CO₂. Inferred input of arsenic is from Monroe et al. (2004).

amide monoclines (Fig. 2). These faults have a long history of movement: first as Precambrian normal faults, then as high-angle reverse faults (e.g., Timmons et al., 2001), and finally as Cenozoic (and still active) normal faults. Large volumes (>10⁶ m³) of travertine are concentrated in several areas where fault zones intersect the Muav Limestone aquifer on the south and east sides of the eastern Grand Canyon and on both sides of the western Grand Canyon (Fig. 2). Quaternary ages have been obtained for many of these deposits (Szabo, 1990).

Travertine genesis is a three-stage process (Fig. 1): the *acquisition* of solute in groundwater, the aqueous *transport* of dissolved constituents, and the *deposition* of travertine (calcium carbonate). Equations are:



In equation 1, CO₂-charged groundwaters dissolve carbonate minerals from limestone, neutralizing acidic pH and increasing the calcium, magnesium, and alkalinity content of the groundwater. In equation 2, degassing of CO₂ at Earth's surface favors the precipitation of carbonate; when degassing is rapid (e.g., in turbulent streams and waterfalls), spring waters deposit travertine dams, coatings on vegetation and debris, and drapes (e.g., Chafetz and Folk, 1984). Evaporation is not a significant factor in Grand Canyon travertine precipitation (O'Brien, 2002). Our study focuses on determining the origin of the CO₂ required for travertine formation (equation 1). Past workers have considered the source of CO₂ for Grand Canyon travertines to be entirely surficial (atmospheric plus soil gas) (Giegengack et al., 1979; Szabo, 1990), but other possible CO₂ sources are crustal metamorphism, hydrocarbons, or mantle degassing.

METHODS

Springs and spring-fed side streams were sampled at base flow conditions. Field temperature, pH, and conductivity were recorded. Water samples were analyzed using standard methods (see Data Repository Table DR1 and Methods¹). Both dissolved and exsolved gases were collected and analyzed for major, trace, and He isotope composition (Giggenbach et al., 1993; Hilton et al., 2002; Table DR2). Stron-

¹GSA Data Repository item 2006005, Tables DR1–DR3 and methods, is available online at <http://www.geosociety.org/pubs/ft2006.htm>, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

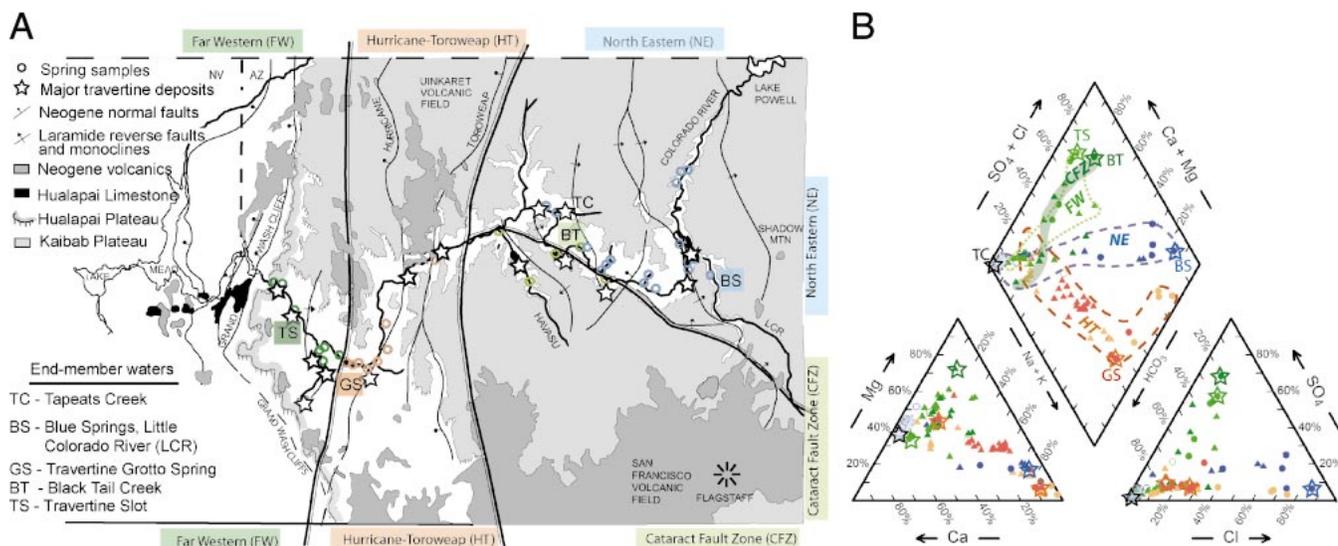


Figure 2. Study area and chemical characteristics of Grand Canyon springs and spring-fed side streams (Table DR1; see footnote 1). A: Map of Grand Canyon region showing sample locations (dots; color coded by region), major travertine accumulations, Hualapai Limestone, Neogene volcanic fields, and selected faults. B: Piper diagram showing regional mixing trends. Regions are color coded: blue—northeastern region (NE); dark green—Cataract fault zone (CFZ); red and orange—Hurricane-Toroweap (HT); light green—far-western region (FW). Red points represent Travertine Grotto. Symbol shapes denote variations in total dissolved solids (TDS): open circles—TDS < 350; triangle—TDS = 350–1250; closed circle—TDS > 1250 (in ppm). End members (stars) include: epigenic water composition [black; Tapeats Creek (TC)] and three different endogenic end members represented by colored stars: blue—Blue Spring, dark green—Black Tail Creek, red—Travertine Grotto Spring, and light green—Travertine Slot. TDS increases within each trend toward endogenic end-member composition.

tium isotope composition of waters and carbonates was measured to provide a sensitive tracer for mixing between Sr derived from Paleozoic limestones ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7090$) versus Proterozoic basement ($^{87}\text{Sr}/^{86}\text{Sr} \gg 0.714$; Patchett and Spencer, 2002; Table DR3).

RESULTS AND DISCUSSION

Water Chemistry

We report 93 analyses from springs and side streams (Table DR1, see footnote 1). Chemical composition is graphically depicted in Figure 2B. Epigenic waters from the large-volume springs on the North Rim of the canyon have low total dissolved solids (TDS; <350 mg/L), are cold (13–17 °C), exhibit pH values >8 , and have a narrow compositional range. This suite of waters is considered as one end member (a Ca-Mg- HCO_3 freshwater typical of limestone aquifers); Tapeats Creek is an example (TC; Fig. 2).

In contrast, endogenic waters are highly variable in composition. All are warm (22–31 °C), have neutral to slightly acid pH (pH 6–7.5), higher salinity (TDS $\gg 350$ mg/L), and high alkalinity (up to 2276 mg/L as HCO_3). Geochemical modeling of these waters (Parkhurst, 1995) indicates equilibration at high P_{CO_2} values (up to $10^{0.1}$), more than two orders of magnitude above atmospheric or soil gas values (Table DR1). Endogenic waters exhibit several end members (Fig. 2): Cl-rich Blue Springs; SO_4 -rich Travertine Slot and Black Tail Creek; and HCO_3 -rich Travertine Grotto Spring.

The Piper diagram shows mixing trends between the epigenic and endogenic end members (Fig. 2B). Even at the scale of a single side canyon (Travertine Grotto; 25 red circles in Fig. 2B), there is a simple mixing trend between markedly different spring compositions. One spring (Travertine Grotto) has gas and water chemistry comprising a regional deeply derived endogenic end member; the other is closer to the epigenic end member. The regional data set shows mixing trends where different endogenic water end members mix with the narrowly defined epigenic end member (TC in Fig. 2B). The trends correspond to regional subprovinces: (1) northeastern Grand Canyon (characterized by Blue Spring), (2) southeastern Grand Canyon (Cataract fault zone, characterized by Havasu Creek and Black Tail Creek), (3) western Grand Canyon (Hurricane-Toroweap trend, characterized by Lava Warm Spring, Pumpkin Spring, and Travertine Grotto Spring), and (4) far western Grand Canyon (characterized by Travertine Slot near the Grand Wash cliffs). The northeastern trend is Na-Cl rich, and the Hurricane-Toroweap trend is also saline, but Ca-Mg-, HCO_3 -dominated waters indicate reaction of the NaCl end member with carbonate strata. The far western Grand Canyon and Cataract fault zone trends are SO_4 rich, perhaps due to the oxidation of reduced sulfur gases from magmatic sources. Along each trend, TDS increases from the epigenic end member (Tapeats Creek) to the endogenic end members (Fig. 2B). Blue Springs, Tapeats Creek, and Havasu Creek all issue from the Redwall Limestone aquifer, yet differ widely in chemical composition, indicating that the observed compositional variability of waters cannot be explained by aquifer host-rock lithology.

Gas Chemistry

Major and trace gas analyses are presented in Table DR2 (see footnote 1) as volume percent of dry gas. The main gas species are CO_2 , H_2S , N_2 , O_2 , and Ar. Noble gas chemistry (Fig. 3) shows mixing between end-member gases. Gases from epigenic waters are similar to air-saturated water (low He/Ar, high N_2/Ar , and N_2/He); gases from endogenic waters are distinctly non-air-like (high He/Ar and low N_2/Ar and N_2/He). The latter have $^3\text{He}/^4\text{He}$ ratios significantly different from air: $R_c/R_A = 0.07, 0.14$ for Travertine Grotto, 0.15 for Lava Falls Warm Springs, and 0.12 for Pumpkin Spring, where $R_A = ^3\text{He}/^4\text{He}$ of air (1.4×10^{-6}) and R_c represents our measured value corrected for atmospheric contamination using He/Ne measurements (Hilton et al., 2002). The He/Ne values for endogenic springs greatly exceed the atmospheric value (air correction factors in Table DR2) indicating a large addition of nonatmospheric He. These R_c/R_A values indicate a signif-

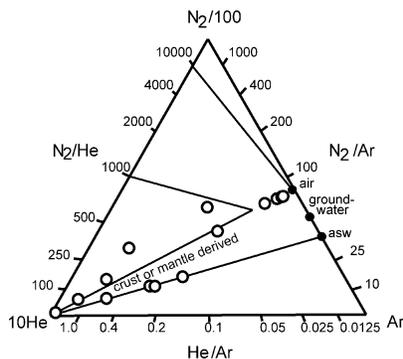


Figure 3. Trace gas compositions for gases with detectable noble gas content (Table DR2; see footnote 1). Fields for crustal and/or mantle-derived gases, air, groundwater, and air-saturated water are from Giggenbach et al. (1993).

icant contribution of mantle-derived helium, as they are higher than values characteristic of crustal lithologies (0.01–0.05 R_A ; Ballentine and Burnard, 2002). The ^3He contribution from possible tritium decay in the sample suite is considered negligible because of the long groundwater residence times (Monroe et al., 2004). The $\text{CO}_2/^3\text{He}$ ratios (Table DR2) from gas-phase samples (1.4×10^9 and 5.7×10^{10}) also suggest mixing between a mantle-derived end member ($\sim 2 \times 10^9$) and a crustal reservoir (up to 10^{13} ; Ballentine et al., 2001); values from water-phase samples differ slightly because of fractionation (Van Soest et al., 1998). The CO_2/N_2 ratios (Table DR2) show great variability and are used to distinguish samples that received CO_2 from a deep source rather than air or soil gas. The CO_2/N_2 ratio in soil gases is ~ 0.004 ; all samples are elevated relative to this value and range up to 320. Gases from epigenic waters exhibit the lowest CO_2/N_2 ratios (<1) compared to endogenic samples that show CO_2/N_2 ratios >4 . The combined data set of gas composition, helium isotope ratios, and $\text{CO}_2/^3\text{He}$ provides compelling evidence for a mantle contribution rather than a purely crustal origin for gases associated with endogenic springs. Although the percentage of mantle-derived versus crustally derived CO_2 remains unquantified, future carbon isotope work will help constrain inputs (Ballentine et al., 2001; Lollar et al., 1997).

Strontium Isotope Geochemistry

Strontium isotopic data for selected endogenic springs and travertines (Table DR3; see footnote 1) exhibit a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.711–0.734). A simple binary mixing model for reasonable end-member compositions for endogenic and epigenic waters (Fig. 4) shows an interpretation for the observed distribution. The solid line in Figure 4 fits all four points from the Travertine Grotto locale. The dashed lines illustrate the sensitivity of the model to heterogeneity of the Precambrian basement. The range observed is consistent with model endogenic contributions of as much as 10%. The spread in all values is explained through a combination of mixing of these waters with epigenic waters, as well as carbonate precipitation and/or dissolution (which affect Sr concentration, but not Sr isotopic composition). Additional tracers (including Cl/Br ratios and stable isotopes of C and O) will be required to further understand this complex system.

CONCLUSIONS AND IMPLICATIONS

Geochemical data provide evidence that the Grand Canyon aquifer system involves mixing of different components. The previously unrecognized deeply derived waters, issuing along faults, contribute excess CO_2 and explain the volume and location of travertine deposits and the geochemical variability among springs. The traditional view of Grand Canyon travertine formation (Szabo, 1990) was that near-surface biological respiration and other microbial activity provide soil gas CO_2 in aquifer recharge zones, with values ranging from $10^{-3.5}$ to 10^{-2} atmospheres (Fig. 1; Drever, 1997). Our data show that travertine-depositing waters are too rich in dissolved CO_2 to be explained by derivation from near-surface processes alone. Of possible other CO_2 sources (e.g., crustal metamorphism, hydrocarbon derived, or mantle

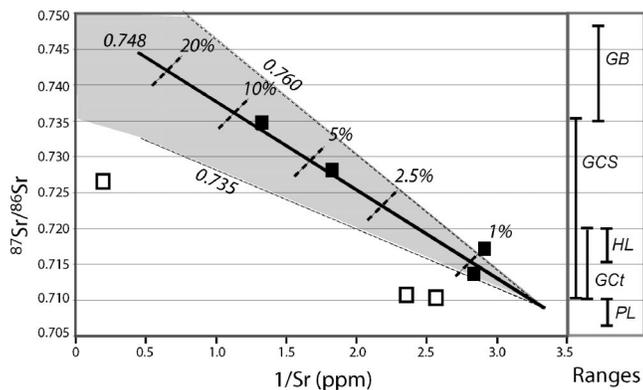


Figure 4. Simple two-component Sr isotope mixing model plotting $^{87}\text{Sr}/^{86}\text{Sr}$ ratio vs. $1/\text{Sr}$ for range of end-member compositions (Table DR3; see footnote 1). Solid line represents mixing model with end-member compositions of 0.3 ppm Sr and Sr isotope ratio of 0.709 with 5.0 ppm Sr and 0.748 Sr isotope ratio. End members were chosen to produce reasonable fit to Travertine Grotto data subset (closed squares) and are consistent with measured values (Tables DR1 and DR3). Shaded region depicts model spread for range of basement Sr isotope ratios (0.735–0.76). Sr isotopic ranges for local granitic basement (GB), range of Grand Canyon springs and travertines (GCS and GCt), Hualapai Limestone (HL), and typical Paleozoic limestone (PL) are indicated on right.

devolatilization), gas data indicate that significant volumes of CO_2 in Grand Canyon springs are mantle derived, in agreement with Ballentine et al. (2001) for the Permian Basin and Siegel et al. (2004) for Saratoga Springs, New York. We infer that CO_2 and He are released during mantle partial melting, are conveyed into the crust via magmatism, and travel with waters during seismogenic pulses, as also shown for Mammoth Springs, California, where $^3\text{He}/^4\text{He}$ pulses correlate with seismic events (Sorey et al., 1998). Our model also provides an explanation for variable groundwater composition, where the San Francisco, Uinkaret, and Basin and Range volcanic fields contribute different endogenic end-member compositions (Fig. 2).

Mixing of deeply derived components with groundwater also explains several neotectonic and hydrologic features of the Colorado Plateau. (1) Heat flow from the San Francisco volcanic field (Fig. 2A) is low despite the recent volcanism in the region; this has been explained by advective heat transport by groundwaters of the Colorado Plateau (Duffield et al., 2000; Sass et al., 1982). (2) $^{87}\text{Sr}/^{86}\text{Sr}$ values as high as 0.735 in springs indicate deep circulation through Precambrian basement, which helps explain the downstream increase in radiogenic Sr in the Colorado River and the radiogenic Sr of the 5.5 Ma spring-fed Hualapai Limestone (Fig. 4; Patchett and Spencer, 2002). (3) Trace element analysis reveals concentrations of arsenic and uranium exceeding allowable maximum contaminant levels in several Grand Canyon springs (Monroe et al., 2004). Also, the increased salinity and degradation of water quality downstream along the Colorado River, though traditionally attributed to evapotranspiration and anthropogenic effects, reflect endogenic inputs. Thus, the observed associations between CO_2 , salinity, sulfur, and mantle-derived He suggest that water quality is profoundly affected by endogenic waters and hence by active tectonism and magmatism.

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