Oxygen, hydrogen, and helium isotopes for investigating groundwater systems of the Cape Verde Islands, West Africa

Victor M. Heilweil · D. Kip Solomon · Stephen B. Gingerich · Ingrid M. Verstraeten

Abstract Stable isotopes ($\delta^{18}O$, $\delta^{2}H$), tritium (^{3}H), and helium isotopes (^{3}He, ^{4}He) were used for evaluating groundwater recharge sources, flow paths, and residence times of three watersheds in the Cape Verde Islands (West Africa). Stable isotopes indicate the predominance of high-elevation precipitation that undergoes little evaporation prior to groundwater recharge. In contrast to other active oceanic hotspots, environmental tracers show that deep geothermal circulation does not strongly affect groundwater. Low tritium concentrations at seven groundwater sites indicate groundwater residence times of more than 50 years. Higher tritium values at other sites suggest some recent recharge. High ^{4}He and $^{3}He/^{4}He$ ratios precluded $^{3}H/^{3}He$ dating at six sites. These high $^{3}He/^{4}He$ ratios (R/R_a values of up to 8.3) are consistent with reported mantle derived helium of oceanic island basalts in Cape Verde and provided end-member constraints for improved dating at seven other locations. Tritium and $^{3}H/^{3}He$ dating shows that São Nicolau Island's Ribeira Fajã Basin has groundwater residence times of more than 50 years, whereas Fogo Island's Mosteiros Basin and Santo Antão Island's Ribeira Paul Basin contain a mixture of young and old groundwater. Young ages at selected sites within these two basins indicate local recharge and potential groundwater susceptibility to surface contamination and/or salt-water intrusion.

Keywords Cape Verde Islands · Groundwater age · Ocean island basalts (OIBs) · Mantle helium · Stable isotopes

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Introduction

The Republic of Cape Verde is an island archipelago located about 500 km west of Senegal, Africa (Fig. 1). Because of its proximity to the equator (about 15–17°N) and the thermal mass of the surrounding ocean, seasonal average daily temperatures vary by only 5°C throughout the year (22–27°C at Praia on the Island of Santiago; Irwin and Wilson 1998). The majority of the population resides in rural areas and derives its livelihood from rainfed agriculture. Farming is challenging in the Sahelian climate, dominated by the dry northeast trade winds. Total annual precipitation ranges from 0–50 mm along the populated coastal areas to 400–1,000 mm in the highlands (Vailleux and Bourguet 1974; Langworthy and Finan 1997) and is extremely variable from year to year. Total annual precipitation on the Island of São Nicolau (Posto Cachaço in Ribeira Fajã; 715 m elevation) varied from as little as 19 to as much as 677 mm during 1961–2005 (Vailleux and Bourguet 1974; Langworthy and Finan 1997; Heilweil et al. 2006). About 80% of this precipitation is associated with the equatorial monsoon from August to October (Vailleux and Bourguet 1974) and comes only a few days each year. The majority of the precipitation is lost to evapotranspiration and runoff to the sea, caused by a combination of warm climate, thin soil cover, and steep topographic gradients (Langworthy and Finan 1997). Surface-water resources on the islands are virtually non-existent; there are no lakes and only a few small perennial streams. Nearly all of the water for consumption comes either from rainfall catchment structures or groundwater. Because of the lack of rainfall and sparse water resources, Cape Verde currently imports

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Fig. 1 Location of study basins within the Republic of Cape Verde, West Africa

about 70% of its food (Instituto Nacional de Gestão dos Recursos Hídricos, personal communication, 2005).

To decrease this dependence on imported food, agricultural development projects funded by the US Millennium Challenge Corporation (MCC) are being considered for watersheds on three islands: Mosteiros on Fogo, Ribeira Paul on Santo Antão, and Ribeira Fajã on São Nicolau. These potential projects depend on enhanced availability of water resources through additional rainfall catchment infrastructure and/or groundwater development. Artificial recharge of groundwater is also being considered in order to increase available groundwater resources and as a mitigation strategy to offset the potential of declining aquifer water levels and/or deteriorating water quality associated with increased use.

The primary goal of this study is to improve the conceptual understanding of groundwater systems within three Cape Verde watersheds using geochemical and environmental tracers and establishing baseline data for evaluating future natural and anthropogenic changes. The objectives of this paper are to describe how natural tracers were utilized for evaluating:

1. Groundwater recharge sources
2. Groundwater flow paths and residence times
3. Potential aquifer susceptibility to contamination and potential enhancement through artificial recharge

Conceptual hydrogeologic model

Cape Verde consists of a chain of volcanic islands believed to have been recently formed over an oceanic hot spot (Lodge and Helffrich 2006). The islands are predominantly basaltic lava flows interspersed with pyroclastics and breccias and intruded by near-vertical mafic dikes (Barmen et al. 1990). Santo Antão and Fogo are young islands where magmatism has occurred within the last 10 Ma (Christensen et al. 2001). Young volcanic

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islands typically have high topographic relief, shallow soils, and rapid runoff or infiltration. As with many oceanic volcanic islands, rainfall distribution and infiltration is dependent upon topography and morphology, orientation with respect to the tropical trade winds, strength of monsoonal patterns, basalt permeability, and the thickness and type of soil cover (Peterson 1972). Also, the islands of Cape Verde typically have wet and dry sides as a result of these atmospheric circulation patterns and local topographic relief (Langworthy and Finan 1997). In general, most infiltration and recharge is thought to occur in the higher-altitude parts of the islands where precipitation rates are highest (Barmen et al. 1990).

The current conceptual understanding of volcanic oceanic island hydrogeology is based primarily on Hawaiian studies (Peterson 1972, Macdonald et al. 1983, Oki et al. 1999) and summarized by Hildenbrand et al. (2005) as consisting of a regional (basal) low-gradient water table aquifer with overlying perched and dike-confined groundwater. The vertical and steeply dipping intrusive feeder dikes form as magma moves upward through both the central caldera and along fissures along the volcano's flank through pre-existing lava flows. These dense, low-permeability intrusive feeder dikes often act as horizontal flow barriers, impounding large groundwater reservoirs (Mink 1963; Peterson 1972; Jackson and Lenat 1989). Similarly, low-permeability clay layers intercalated with and formed by the weathering of the upper surfaces of lava flows may also act as hydraulic barriers (Barmen et al. 1990). Such horizontal and vertical flow barriers may cause perched groundwater, high-altitude springs, and/or groundwater compartmentalization resulting in a stepped and discontinuous water table (Fig. 2). Based on the combination of more precipitation at high elevation (many times greater than along the coastal areas), high-permeability basalts, and closed-basin calderas, previous hydrogeologic investigations of Cape Verde (Barmen et al. 1984, 1990; Kallrén and Schreiber 1988) have suggested that the majority of infiltration and groundwater recharge occurs in the higher areas of the islands. Environmental tracers used in this study have tested this hypothesis.

Oceanic islands typically have a low-density freshwater lens of groundwater overlying higher-density brackish and saltwater. Under steady-state conditions, the Ghyben-Herzberg principle indicates that the freshwater hydraulic head above sea level should be balanced by an approximately 40-fold thickness of fresh water beneath sea level. The fresh water/brackish water boundary is generally not fixed or sharp; rather it is controlled by pressure and density and is dependent on the balance between groundwater recharge and groundwater discharge (Peterson 1972). Aquifer drawdown associated with excessive pumping, therefore, may lower water levels in the aquifer and move the fresh/brackish water boundary upward and inland, causing salt-water intrusion (Gingerich and Oki 2000). Increasing groundwater specific conductance values associated with pumping (up to 16,000 µS/cm) have been reported for coastal groundwater from both the northeastern (Mosteiros Basin) and western sides (Praia Ladrao) of Fogo (Kallrén and Schreiber 1988; Heilweil et

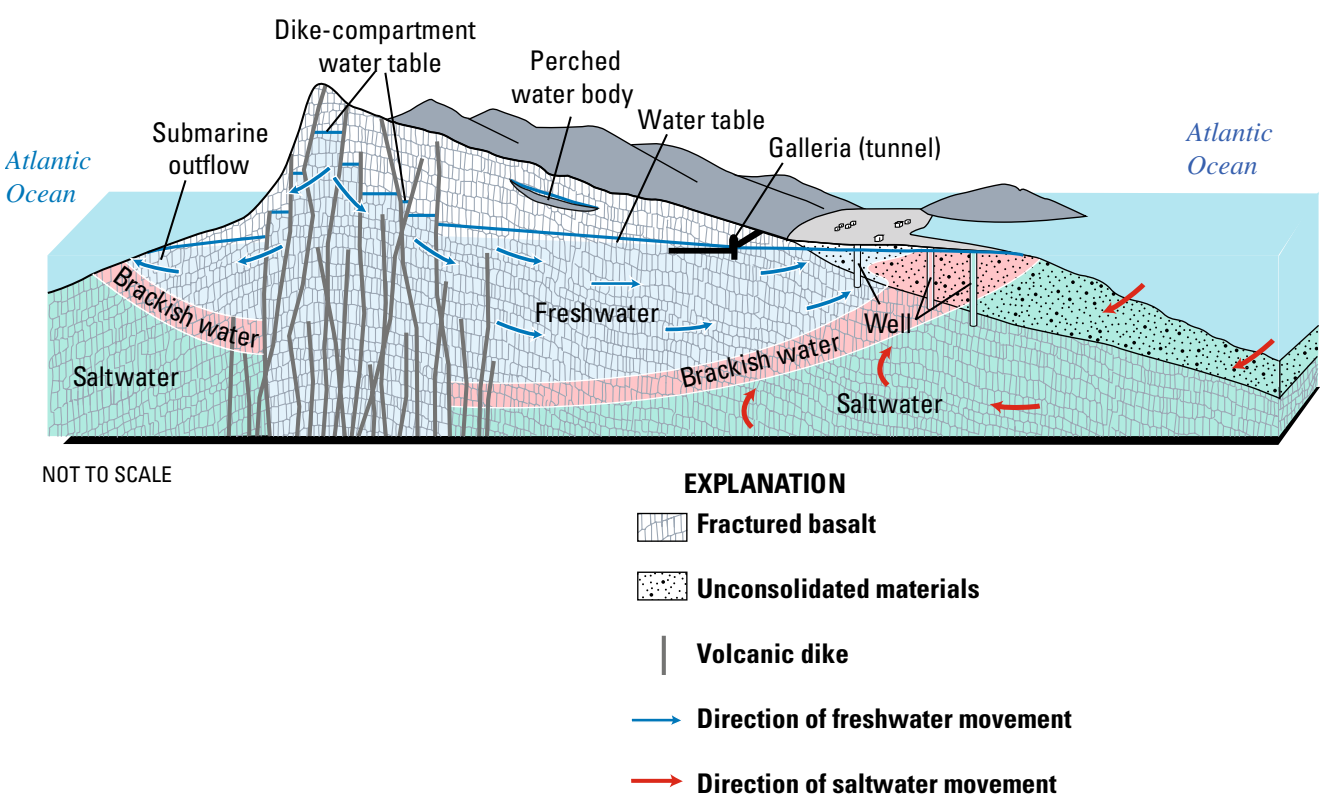

Fig. 2 Generalized conceptual model of volcanic island hydrogeology (modified from Macdonald et al. 1983)

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al. 2006). High chloride concentrations (up to 5,000 mg/L) associated with saltwater intrusion have also been documented along the northeastern coast of the nearby island of Santiago (Santos et al. 2006).

Measurable groundwater discharge from volcanic island aquifers typically includes discharge to springs, well withdrawals, seepage to streams, and evapotranspiration in areas having a shallow water table. Like many other volcanic islands (Peterson 1972; Cabrera and Custodio 2004; Prada et al. 2005), horizontal tunnels, alternatively referred to as galleries or extended springs, have been constructed in Cape Verde to capture groundwater as an additional water-supply source (Kallrén and Schreiber 1988). Groundwater discharge also includes sub-surface outflow to the ocean, which is difficult to quantify. Such submarine discharge has been documented in other volcanic island sites (Izuka and Gingerich 2003; Hildenbrand et al. 2005; Prada et al. 2005) and estimated in other settings (Bokuniewicz 1980; Cable 1997; Cambereri and Eichner 1998; Michael et al. 2003; Cross et al. 2006) and may be a substantial fraction of total groundwater discharge from the aquifer.

Previous studies

Previous studies of Cape Verde provide hydrogeologic data and conceptual understandings pertinent to the watersheds on the three islands investigated during this study (Fogo, Santo Antão, and São Nicolau). Langworthy and Finan (1997) present information on precipitation and groundwater availability for each of these three islands. An overview of the climate, generalized groundwater conditions, traditional surface-water impoundment structures, and water management on Santo Antão is provided by Haagsma (1995). Reports by Kallrén and Schrieber (1988), Barmen et al. (1990), and Descloitres et al. (2000) include both detailed geologic descriptions of Fogo and results of reconnaissance groundwater studies using environmental tracers. Similarly, Barmen et al. (1984), Akiti (1985), and Santos et al. (2006) describe hydrogeology, conceptual models, and environmental tracer studies on the nearby island of Santiago. Detailed precipitation records for São Nicolau are reported by Olivry (1981). Vailleux and Bourguet (1974) present an empirical relation for estimating the amount of infiltration from precipitation and develop recharge estimates for various Cape Verde watersheds. Heilweil et al. (2006) provide detailed hydrogeologic data and interpretations for each of the three watersheds evaluated during this study.

On the basis of International Atomic Energy Agency (IAEA) records from network stations at similar latitudes (Barbados, Ascension Island, St. Helena), Barmen et al. (1990) estimated that the natural background concentration of ^{3}H in precipitation in Cape Verde was less than or equal to about 3 tritium units (TU) prior to 1953 and after 1990. Relatively large amounts of anthropogenic ^{3}H were introduced into the atmosphere by thermonuclear testing in the 1950s and 1960s, with estimated peak precipitation ^{3}H concentrations in Cape Verde reaching about 175 TU in 1964 (Kallrén and Schreiber 1988). Tritium measured in precipitation at Bamato, Mali (the nearest IAEA station to Cape Verde) ranged from 15.6 to 67.0 TU (mean = 43 TU) between 1975 and 1979 (Barmen et al. 1984). Atmospheric ^{3}H concentrations decreased rapidly to less than about 5 TU during the 1980s, as indicated by five precipitation samples collected on Santiago Island during 1984 with ^{3}H concentrations ranging from 2.3±0.1 to 4.4±0.2 TU (Akiti 1985) and one sample collected on Fogo Island in 1987 with a ^{3}H concentration of 3.0±1 TU (Barmen et al. 1990).

The atmospheric ^{3}He/^{4}He ratio, referred to as R_a, is assumed to be 1.384×10^{-6} (Clarke et al. 1976). The presence of high ^{3}He/^{4}He ratios in groundwater has been shown to indicate interaction with mantle-derived rocks (Andrews 1985). Crustal rocks typically have ^{3}He/^{4}He ratios of 10^{-7}–10^{-8} (0.1–0.01 R_a) because of ^{4}He production from U/Th radioactive decay (Mamyrin and Tolstikhin 1984; Castro 2004). In contrast, fluids in contact with upper-mantle rocks typically have ratios of about 10^{-5} (9 R_a; Ozima and Podosek 1983). While mid-ocean ridge basalts (MORBs) show little variation and have a mean ^{3}He/^{4}He ratio of 8±1 R_a, ocean island basalts (OIBs), including Cape Verde, have much more variability and range from 3 to over 40 R_a (Graham 2002). 'High-^{3}He hotspot' ratios have been defined as being above the mean MORB value of 8 R_a (Craig and Lupton 1976; Moreira et al. 1999). Values of over 30 R_a were found in basalts from Hawaii (Kurz et al. 1983) and Iceland (Breddam and Kurz 2001), indicating lower mantle source rocks and fluids. Other 'high-^{3}He hotspot' OIBs include Samoa (up to 24 R_a, Farley et al. 1992), the Galapagos (up to 23 R_a, Graham et al. 1993), the Juan Fernandez and Heard Islands (up to 18 R_a, Farley et al. 1993; Hilton et al. 1995), and Easter Island (up to 12 R_a, Poreda et al. 1993).

A helium isotope study of basalts on the Cape Verde Islands of Santo Antão and Fogo reported ^{3}He/^{4}He ratios of 3.2–13.8 R_a (Christensen et al. 2001), similar to those of other nearby Atlantic OIBs: 6.3–8.9 R_a for the Canary Islands (Hilton et al. 2000), 3.5–11.3 R_a for the Azores (Kurz et al. 1990; Tolstikhin et al. 1991; Moreira et al. 1999), and 5–6 R_a for Tristan da Cunhã and Gough (Kurz et al. 1990). Studies of volcanically active areas often show elevated ^{4}He and ^{3}He/^{4}He ratios in groundwater. This indicates significant magmatic helium contributions either through mantle degassing (Perez et al. 1996) or diffusion from phenocrysts in the basaltic aquifer matrix, similar to the ^{3}He diffusive loss from deep-sea basalts to surrounding ocean water proposed by Craig and Luptin (1976). ^{3}He/^{4}He ratios of 9.5–9.7 R_a are reported for springs in volcanic calderas of the Canary Islands (Perez et al. 1994, 1996) and up to 5.3 R_a for springs in eastern Oregon, USA (Saar et al. 2005).

Hydrogeologic settings

Mosteiros Basin (42 km^2), the southernmost of the three study basins, is located on the island of Fogo (Fig. 1),

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which has the only active volcano in the archipelago. Its peak at 2,900 m above sea level (m asl) is the second highest point of land in the Atlantic Ocean. Mosteiros Basin itself has a maximum altitude of 2,400 m (about 1,000 m higher than the other two basins) with an average topographic slope of 27°. Because of the island's conical shape, Mosteiros Basin is composed of eight smaller watersheds on the flank of the volcano that each drain directly to the ocean (Fig. 3). In contrast, the other two basins each consist of a single watershed draining to the ocean. Average annual precipitation is estimated to range from about 200 mm to more than 1,000 mm and follows the expected trend of higher precipitation rates at higher altitudes (Langworthy and Finan 1997; Descloitres et al. 2000; Heilweil et al. 2006). This precipitation supplies sporadic runoff and flow to gullies, but there are no perennial streams in the basin. The geology of Mosteiros Basin (Fig. 3) is dominated by basaltic lava flows with intercalated pyroclastic deposits (Barmen et al. 1990). The basin is also dotted with numerous cinder cones made of coarse volcanic fragments (lapilli). The lava flows form fairly continuous layers that dip steeply from the island's central caldera complex (Cha das Caldeiras) towards the ocean; these flows are likely important conduits for groundwater flow. Because of the recent lava flows and topographic steepness, soil layers are generally very thin or non-existent. The southern border of Mosteiros Basin is defined by the 1,000-m vertical wall of the island's 8 km-wide caldera. Water falling on the north-facing slope of the caldera wall runs off toward the coastal areas of Mosteiros Basin; water falling on the south-facing slope drains into the closed basin of the caldera. Because the caldera bottom is covered by highly permeable volcanic deposits (lapilli, scoria, and basalt flows) and receives relatively large amounts of precipitation, this area likely provides a substantial amount of recharge to the island's groundwater system (Barmen et al. 1990). Measurable groundwater discharge in Mosteiros Basin includes the

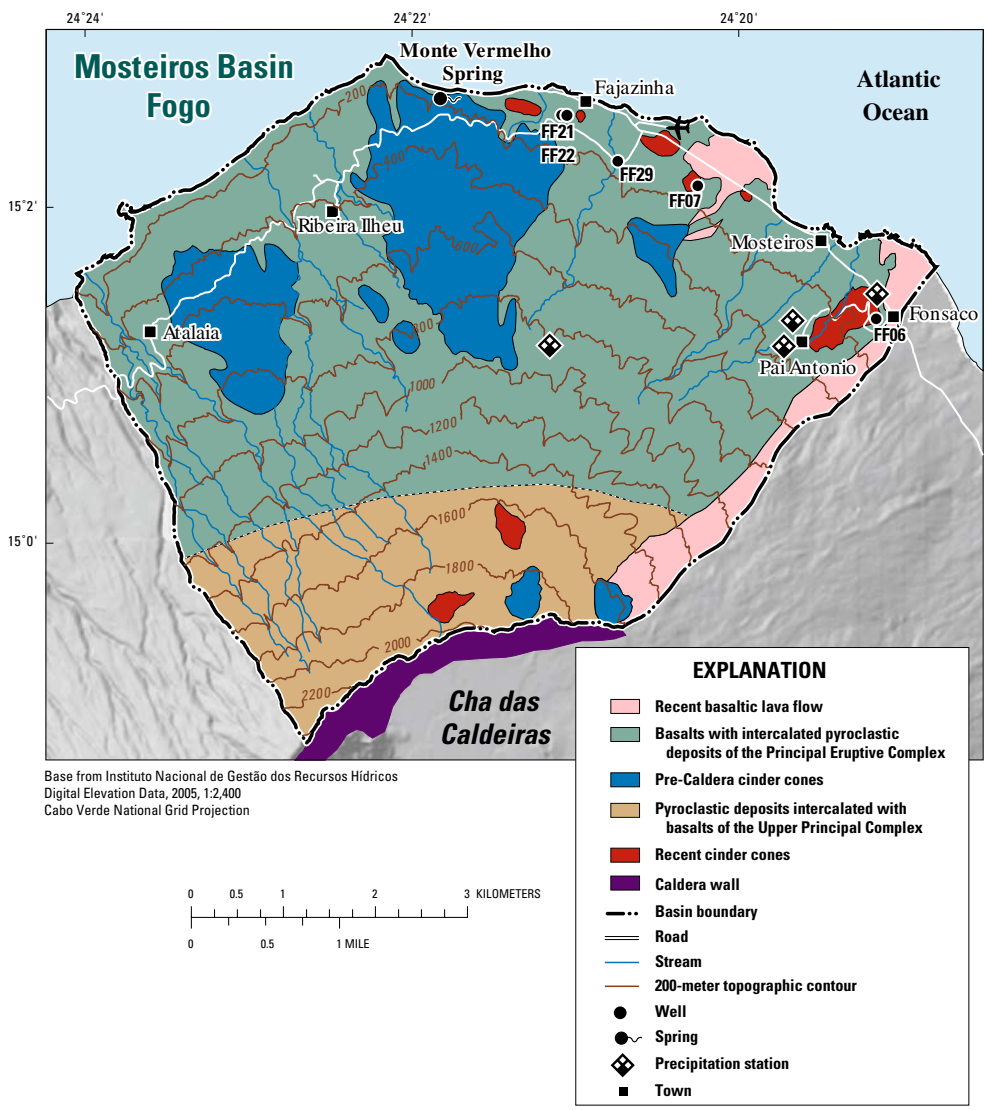

Fig. 3 Geology and location of wells, springs, and precipitation stations in the Mosteiros Basin, Fogo, Cape Verde (geologic data modified from Barmen et al. 1990)

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Monte Vermelho spring (500 m^3/day) and two pumping wells (about 100 m^3/day; Heilweil et al. 2006). Submarine discharge near the Monte Vermelho spring off the northwest coast of Fogo has been observed but not quantified (Institut Géographique National de France 1981). Groundwater levels measured at five wells (FF 06, 07, 21, 22, and 29) located along the coastal plain all had water depths of 18–64 m below land surface during 2005–2006. There are no wells located in the upland part of the basin to evaluate groundwater levels or hydraulic gradients in these areas.

Ribeira Paul Basin (15 km^2) is located on the northeastern coast of Santo Antão, the northwestern-most island of Cape Verde (Fig. 1). The basin's vertical relief of 1,500 m (Fig. 4) is less than Mosteiros Basin. Annual precipitation in the Ribeira Paul Basin is estimated to range from 500 to 800 mm, generally higher than the other two study basins even though the average basin altitude is lower than Mosteiros. This difference is caused by the orientation of the basin, the steep topographic relief (38°), and its ability to trap the moisture of ascending air masses associated with the northeastern trade winds and the equatorial monsoon winds (Haagsma 1995). Like Mosteiros, Ribeira Paul Basin has been recently formed (<10 Ma) and its geology is dominated by exposed volcanic rocks including basaltic lava flows and pyroclastic deposits (Fig. 4), with many near-vertical igneous dikes exposed along the upper canyon headwalls. Most of the steeply sloping terrain within the basin has only a veneer of soils; thicker alluvial deposits are only present along the wash at the lower end of Ribeira Paul Basin. Ribeira Paul is unique among the three study basins in its abundance of springs and spring-fed streams. The basins on the northeast side of Santo Antão, including Ribeira Paul, are the only ones in all of Cape Verde containing perennial streams. In addition to the larger amount of annual precipitation, low-permeability mafic dikes, tuffs, and breccias may impede lateral flow and cause groundwater discharge to springs and streams. Total estimated discharge from springs and spring-fed streams is 4,000 m^3/day and occurs predominantly near the base of the canyon walls at altitudes between 600 to 900 m (Heilweil et al. 2006). The only production well in the basin (FA 57) has a small average discharge of about

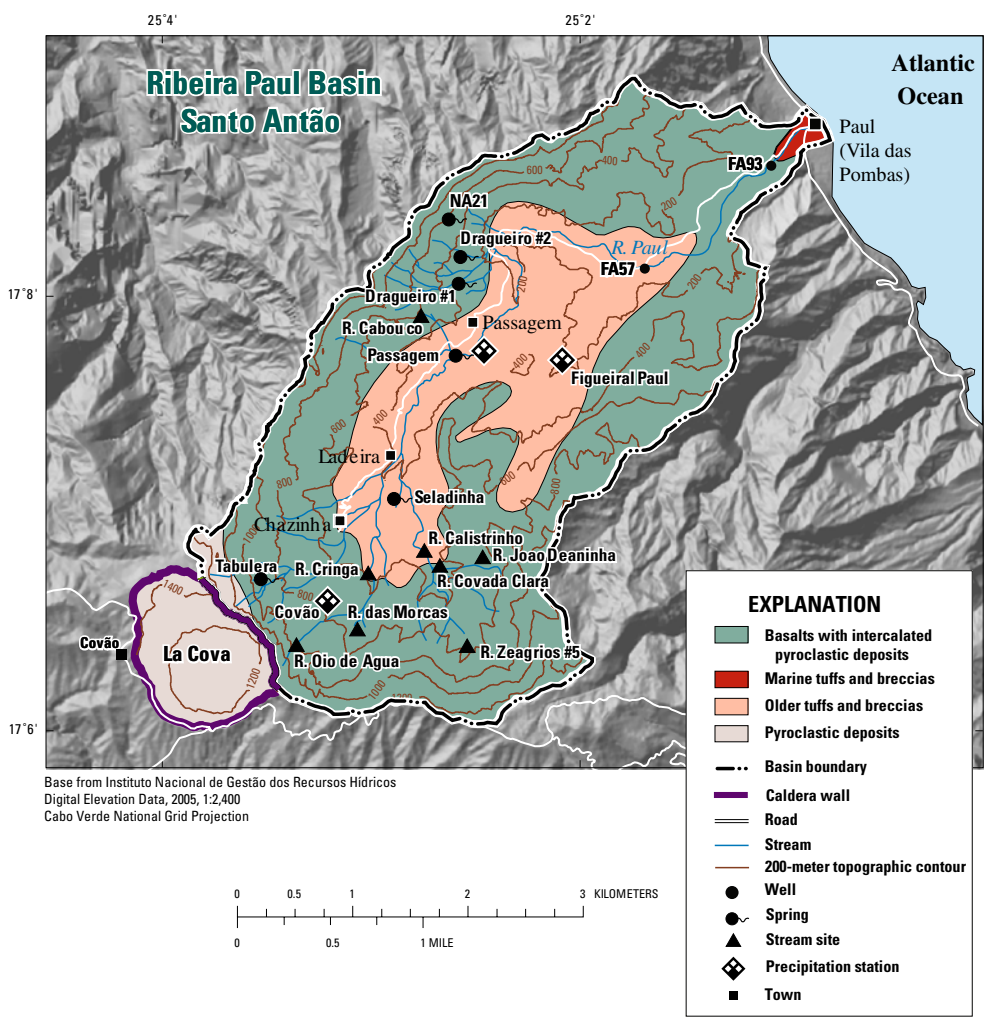

Fig. 4 Geology and location of wells, springs, stream sites, and precipitation stations in the Ribeira Paul Basin, Santo Antão, Cape Verde (geologic data modified from Vailleux and Bourguet 1974)

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30 m^3/day. Subsurface inflow from the adjacent La Cova volcanic caldera likely provides additional recharge to the groundwater system. Similar to Cha das Caldieras on Fogo, La Cova receives substantial precipitation and is a closed basin; none of its rainfall leaves the basin as surface water.

Ribeira Fajã Basin (16 km^2) is located on São Nicolau Island, near the center of the Cape Verde archipelago (Figs. 1 and 5). In contrast to Fogo and Santo Antão, São Nicolau is geologically much older and has been more highly eroded. While Ribeira Fajã basin has similar overall vertical relief as Ribeira Paul, it has a smaller average topographic slope (23°). Average annual precipitation (1996–2002) in Ribeira Fajã is much less than that in the other two basins, ranging from about 300 to 400 mm depending on elevation (Heilweil et al. 2006). Like the other two basins, Ribeira Fajã Basin is volcanic with exposures of basalt, mafic dikes, and pyroclastic deposits (Fig. 5; Hidroprojecto Engenharia Gestão 2000). No natural springs or groundwater evapotranspiration occurs within the basin and there is currently no well production. The main source of groundwater discharge in Ribeira Fajã Basin is from the Galleria Fajã tunnel. This 1,800-m tunnel was constructed during the 1980s to intercept the deep water table and provide a steady supply for agriculture and culinary needs. Water enters the upper end of the tunnel at the Lombo Pelado, Cruz Roque, and Monte Gordo springs, with altitudes between 265 and 270 m (compared with land surface altitudes above the tunnel of 500–600 m). As in the other basins, submarine discharge is likely an important form of groundwater discharge from Ribeira Fajã.

Sampling and methods

Stable isotopes

Precipitation falling at higher altitudes generally is more isotopically depleted in ^2H and ^{18}O than is precipitation at lower altitudes; thus stable isotopes are helpful for evaluating precipitation source altitudes and recharge areas (Mazor 1991). Stable isotope studies of other volcanic islands with steep topographic gradients and latitudes similar to Cape Verde have documented this altitude effect, along with seasonal/isotope amount effects in precipitation (Gonfiantini et al. 2001). This relationship

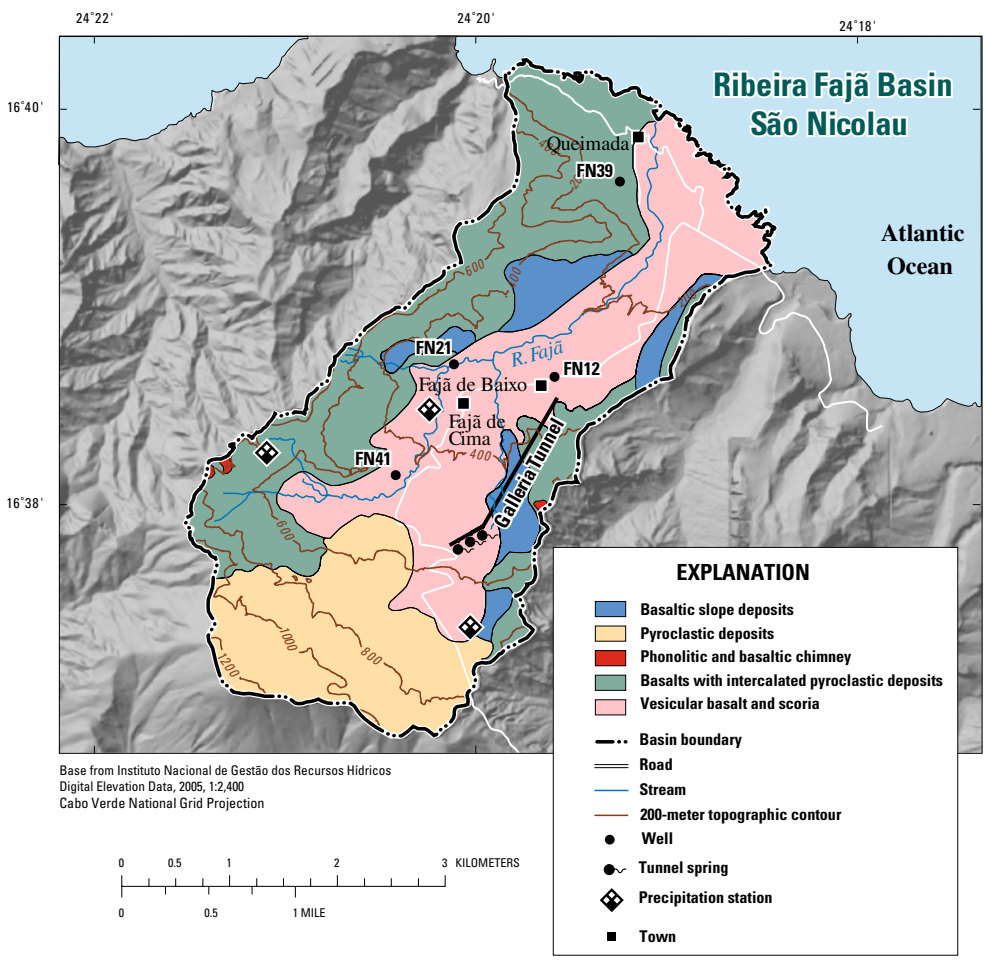

Fig. 5 Geology and location of wells, springs, and precipitation stations in the Ribeira Fajã Basin, São Nicolau, Cape Verde (geologic data modified from Hidroprojecto Engenharia E Gestão 2000)

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has been utilized for interpreting groundwater recharge sources and flow paths (Scholl et al. 2002, Hildenbrand et al. 2005). Stable isotope studies of precipitation in other tropical volcanic areas show altitude effects on $\delta^{18}O$ ranging from −0.7 to 1.6‰/km (Gonfiantini et al. 2001; Hildenbrand et al. 2005). This increase in isotopic depletion is generally attributed to a Rayleigh adiabatic condensation process. Stable isotope samples of precipitation, streams, springs, and wells were collected according to procedures described by Révész and Coplen (2008) and analyzed by the US Geological Survey (USGS) Stable Isotope Laboratory in Reston, Virginia using isotope ratio mass spectrometers. Results are expressed in ‰ versus VSMOW (Vienna Standard Mean Ocean Water). Analytical uncertainties (2σ) for these techniques are 2‰ and 0.2‰ for δ^2H and $\delta^{18}O$, respectively.

$^3H/^3He$

Tritium (^3H) is produced both naturally and during thermonuclear weapons testing. As a radioactive isotope of hydrogen, tritium decays to helium (^3He) with a half-life of about 12.3 years and, therefore, can be used for evaluating the relative age of younger groundwater in Cape Verde. Tritium concentrations in this study are reported in tritium units (TU), where one TU equals one molecule of $^3H^1HO$ in 10^{18} ^1H_2O molecules (Solomon and Cook 2000). Natural tritium production occurs in the earth's upper atmosphere through cosmic-ray neutron bombardment of nitrogen. Tritium in groundwater samples was analyzed with the in-growth method (Clarke et al. 1976) at the University of Utah's Dissolved Gas Service Center. Analytical uncertainty (2σ) for this technique is estimated to be up to 0.2 TU. Based on its 12.3-year half-life, decay-corrected ^3H concentrations can be calculated by the equation:

$$C = C_o e^{-t\lambda} \quad (1)$$

where C is the measured ^3H concentration in water, C_o is the initial ^3H concentration, t is the number of years since the precipitation occurred, and λ is the decay constant (0.0562/year for ^3H).

The estimated initial and decay-corrected ^3H concentration of precipitation in Cape Verde from 1950 through 2005 is shown in Fig. 6. This is based on data from Barmen et al. (1990) and extended to 2005 based on sampling during this study indicating current atmospheric concentrations of about 1–3 TU. Assuming that precipitation recharging aquifers in Cape Verde prior to the early 1950s had an initial ^3H concentration of 3.0 TU, equivalent to a 2005 decay-corrected ^3H concentration of ≤0.3 TU. Recharge that occurred during above-ground nuclear testing in the late 1950s and 1960s, assuming initial ^3H concentrations in precipitation of 10-175 TU, would have 2005 ^3H concentrations of about 1–17 TU. Water recharging the aquifer during the 1970s and 1980s, assuming initial ^3H concentrations of 4-14 TU, would have 2005 ^3H concentrations between 0.6 and 2.0 TU. Finally, water recharging the aquifer during the 1990s to present, assuming an average ^3H concentration of about 1-3 TU, would have 2005 ^3H concentrations between 0.5 and 3 TU. These estimated ^3H concentrations are based on the assumption of piston flow (no mixing), which may be overly simplistic for springs or wells with large screened intervals where multiple flow paths likely coalesce and contain a mixture of water of various ages. Groundwater having a ^3H concentration less than 4 TU but greater than

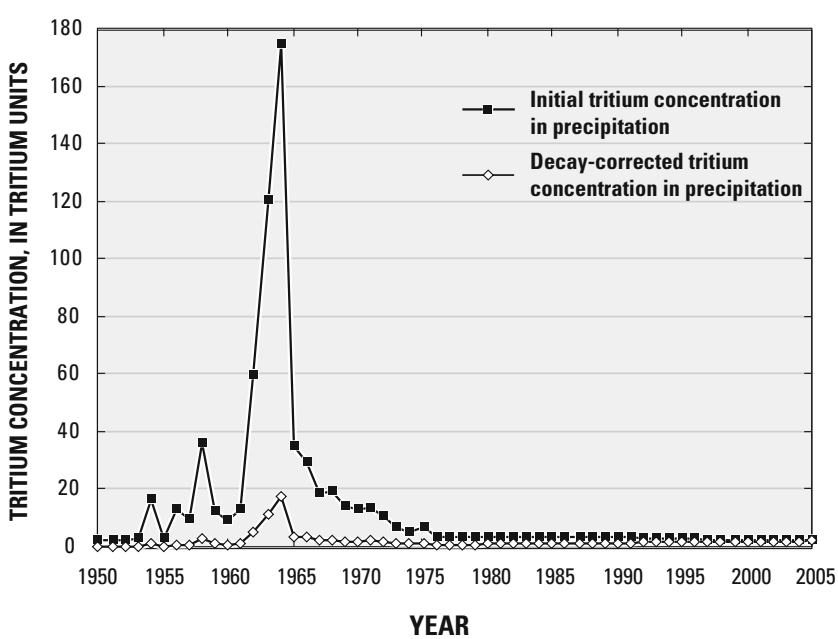

Fig. 6 Estimated initial and decay-corrected tritium concentration in precipitation in Cape Verde, 1950–2005 (modified from Barmen et al. 1990)

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0.3 TU may represent a mixture of both young and old waters rather than representing a discrete flow path and recharge year. Except for groundwater recharge occurring near the 1960s ^3H peak, it is generally not possible to uniquely determine modern (post-1950s) groundwater ages from tritium alone.

The tritium/tritiogenic helium ($^3H/^3He_{trit}$) method is a technique that can be used for dating relatively young groundwater recharged within the past 50 years. Tritium in the water molecule undergoes β-decay to $^3He_{trit}$, a gas which is readily lost to the atmosphere but is geochemically conservative (inert) when dissolved in groundwater. While other sources of ^3He besides tritium decay exist, it is possible to separate $^3He_{trit}$ from these other sources (Solomon and Cook 2000). The age-dating clock begins when recharge crosses the water table rather than when it infiltrates the subsurface. $^3H/^3He_{trit}$ can be used to determine the number of years (t) since the water entered the aquifer as recharge with the following equation (Solomon and Cook 2000):

$$t = \lambda^{-1} \ln\left({}^3He_{trit}/{}^3H + 1\right) \quad (2)$$

This apparent recharge age may underestimate the total time since infiltration of precipitation occurred because it does not include vadose-zone travel. Also, the apparent age of groundwater at sites with convergent flow such as at springs or wells with large screened intervals, will be a weighted average age of water traveling along various flow paths.

Total ^3He was determined from analytical measurements of ^4He and $^3He/^4He$ ratios dissolved in groundwater. Dissolved-gas samples were collected as water samples in copper tubes (Weiss 1968; Stute and Schlosser 2001) and as gas samples with in-situ diffusion samplers (Sheldon 2002). ^4He, ^{20}Ne, and $^3He/^4He$ ratios were analyzed by the University of Utah's (USA) Dissolved Gas Service Center using quadrapole and sector-field mass spectrometers. Analytical uncertainty (2σ) is estimated to be 1% for both ^4He and $^3He/^4He$ ratios and 2% for ^{20}Ne. For gas samples collected with in-situ diffusion samplers, mass-spectrometer analysis provided the relative mole fractions of ^4He and ^{20}Ne. Total ^4He and ^{20}Ne were then calculated based on Henry's Law relations by using field measurements of total dissolved-gas pressure and water temperature.

In addition to analytical precision, the uncertainty in $^3H/^3He_{trit}$ dating depends on how accurately the $^3He_{trit}$ component of total ^3He can be determined. The $^3He_{trit}$ component is estimated by subtracting the atmospheric and terrigenic (both crustal and mantle) components from total ^3He (Solomon and Cook 2000). The atmospheric component of ^3He was determined from ^{20}Ne measurements and $^4He/^{20}Ne$ ratios. The terrigenic helium concentration ($^3He_{terr}$) depends on the $^3He/^4He$ ratio of mantle rocks, mantle fluids, and lithospheric (crustal) helium production, and can vary over several orders of magnitude. The $^3He_{trit}$ component for samples with large concentrations of total helium (more than an order of magnitude above atmospheric solubility) or mantle-derived fluids with high $^3He/^4He$ ratios are sensitive to the assumed terrigenic $^3He/^4He$ ratio, making dating problematic.

Results

Mosteiros Basin

During this study, seven groundwater stable isotope samples were collected and analyzed from wells and springs in Mosteiros Basin (Table 1). Except for well FF 06, the stable isotope ratios fall within a fairly tight cluster on or near the global meteoric water line (Fig. 7), with $\delta^{18}O$ values of −3.4 to −3.8‰ and δ^2H values of −15 to −21‰ (Table 2). Precipitation samples for stable isotope analysis within Mosteiros Basin were not collected during this study. Stable isotope values in Fogo precipitation were previously reported at Cha das Caldeiras ($\delta^{18}O$ of −7.0‰, δ^2H of −45‰) and at Achada Fora on the west side of Fogo ($\delta^{18}O$ of −4.0‰, δ^2H of −30‰; Barmen et al. 1990). Because of the small seasonal fluctuation in average daily air temperature, it is assumed that stable isotopes in precipitation do not vary much during the year. This is supported by stable isotope values of groundwater samples from the Monte Vermelho spring, which did not vary substantially between a wet and dry season; $\delta^{18}O$ and δ^2H values ranged between −3.76 to −3.78‰ and −18 to −21‰, respectively, during sampling in August and December 2005. A previous groundwater isotopic study by Kallrén and Schreiber (1988) reported similar values in October 1987 ($\delta^{18}O$ of −3.9‰, δ^2H of −22‰). The groundwater sample from FF 06 is much more depleted ($\delta^{18}O$ of −5.1‰, δ^2H of −28‰), indicating a higher altitude precipitation source of recharge to this well compared to other wells. This site is located southeast of the other wells and Monte Vermelho spring, and closer to the high-altitude Cha das Caldeiras caldera (Fig. 3).

Although no precipitation ^3H samples were collected in Mosteiros Basin, two dryland (rain-fed only) agricultural products were analyzed from Cha das Caldeiras that provide average seasonal values: 2005 vintage wine (2004 growing season) and fruit juice from the 2005 growing season. These samples had ^3H concentrations of 3.0 and 1.0 TU, respectively (Table 2), indicating that precipitation ^3H concentrations on Fogo have declined only slightly since previous sampling in the 1980s (Akiti 1985, Barmen et al. 1990). Groundwater ^3H concentrations in samples collected from Mosteiros Basin during this study ranged from about 0.2 to 1.2 TU. As discussed earlier (see section Sampling and methods), it is assumed that values less than 0.3 TU indicate groundwater recharge that occurred prior to the early 1950s. Groundwater from wells FF 06, FF 21, and FF 29 all had ^3H concentrations less than 0.3 TU. Groundwater from well FF 07 had a ^3H concentration of 1.2 TU, indicating either uniform post-1950s recharge or a mixture of pre- and post-1950s recharge; well FF 22 and Monte Vermelho spring had ^3H concentrations between 0.4 and 0.8 TU, likely indicating a

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Table 1 Selected field measurements of water in the Mosteiros, Ribeira Paul, and Ribeira Fajã Basins, Cape Verde

Name	Sample type	Basin	Latitude (degrees/ minutes/ seconds)	Longitude (degrees/ minutes/ seconds)	Date	Altitude (m)	Barometric pressure (mm Hg)	Total dissolved gas pressure (mm Hg)	Dissolved oxygen (mg/L)	Specific conductance (μS/cm)	pH (standard units)	Temp. (°C)
Monte Vermelho	Spring	Mosteiros	150254	242147	12/8/2005	5	–	–	–	200	7.2	–
					2/12/2005		758	763	7.6	210	7.3	22.2
FF 06	Well	Mosteiros	150133	0241908	2/12/2005	60	755	758	5.6	2280	6.8	20.3
FF 07	Well	Mosteiros	150221	0242014	2/12/2005	20	758	747	7.5	2240	7.8	22.8
FF 21	Well	Mosteiros	150246	0242104	11/8/2005	40	757	766	7.1	870	7.0	23.0
FF 22	Well	Mosteiros	150246	0242104	3/12/2005	40	758	756	7.1	700	7.4	22.4
FF 29	Well	Mosteiros	150229	0242043	3/12/2005	60	754	758	6.4	1,440	7.4	22.7
Cha das Caldeiras wine	Precip.	Mosteiros	145830	0242150	2004	1,650	–	–	–	–	–	–
Cha das Caldeiras juice	Precip.	Mosteiros	145830	0242150	2005	1,650	–	–	–	–	–	–
Dragueiro No. 1	Spring	Paul	170816	0250231	8/12/2005	270	738	721	3.0	375	7.1	23.4
NA 21	Spring	Paul	170834	0250234	6/8/2005	440	743	729	4.6	265	7.0	23.7
Passagem	Spring	Paul	170756	0250232	4/8/2005	300	741	730	5.7	510	7.2	22.6
Seladinha	Spring	Paul	170711	0250249	8/12/2005	460	720	712	6.5	450	7.8	21.3
Tabulera	Spring	Paul	170654	0250328	4/8/2005	840	694	689	7.5	220	7.6	18.9
FA 57	Well	Paul	170820	0250140	8/8/2005	80	–	–	–	580	7.1	–
					7/12/2005	80	753	777	5.0	580	7.4	24.0
FA 93	Well	Paul	170849	0250104	5/8/2005	20	762	745	5.3	710	7.2	23.0
Cabouco stream	Stream (below spring)	Paul	170755	0250245	14/6/2006	560	–	–	–	–	–	–
Oio de Agua stream	Stream (below spring)	Paul	170624	0250320	14/6/2006	955	–	–	–	–	–	–
Morcas stream	Stream (below spring)	Paul	170628	0250302	14/6/2006	710	–	–	–	–	–	–
Zeagrios No. 5 stream	Stream (below spring)	Paul	170636	0250230	14/6/2006	750	–	–	–	–	–	–
João Deaninha stream	Stream (below spring)	Paul	170648	0250227	14/6/2006	740	–	–	–	–	–	–
Calistrinho stream	Stream (below spring)	Paul	170650	0250243	14/6/2006	500	–	–	–	–	–	–
Cringa stream	Stream (below spring)	Paul	170656	0250259	14/6/2006	560	–	–	–	–	–	–
Côvada Claro stream	Stream (below spring)	Paul	170646	0250239	14/6/2006	550	–	–	–	–	–	–
Ribeira Grande	Precip.	Paul	171049	0250356	22/11/2005	18	–	–	–	–	–	–
					24/11/2005		–	–	–	–	–	–
Vila das Pombas	Precip.	Paul	170851	0250048	24/11/2005	10	–	–	–	–	–	–
G. Fajã-Monte Gordo	Spring	Fajã	163845	0241927	18/8/2005	270	738	737	7.2	380	7.8	21.3
					14/12/2005		737	744	7.9	380	8.3	21.3
G. Fajã-Cruz Roque	Spring	Fajã	163845	0241927	15/12/2005	267	–	–	–	440	–	–
G. Faja-Lombo Pelado	Spring	Fajã	163845	0241927	15/12/2005	265	–	–	–	550	–	–
FN 39	Well	Fajã	163950	0241914	13/12/2005	90	755	760	5.7	500	7.6	23.9
Posto Fajã	Precip.	Fajã	163829	0242012	16/9/2005	410	–	–	–	–	–	–

Altitude: *m* meters; specific conductance: *μS/cm* microsiemens per centimeter at 25°C; temperature: °*C* degrees Celsius

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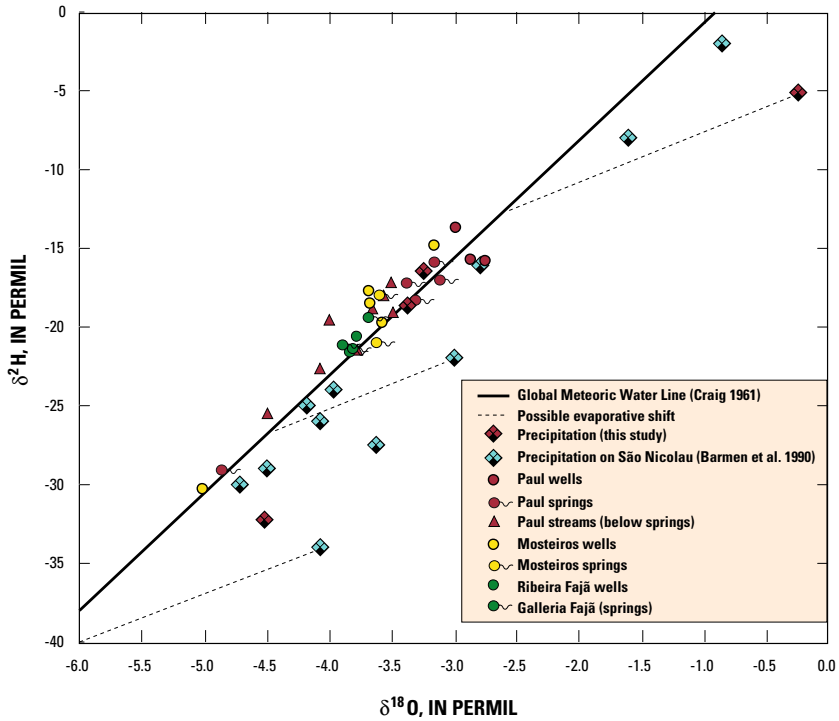

Fig. 7 Relation between $\delta^{18}O$ and $\delta^{2}H$ values in precipitation, wells, springs, and streams of the Mosteiros, Ribeira Paul, and Ribeira Fajã Basins, Cape Verde

mixture of pre- and post-1950s recharge. Similarly, a sample collected from Monte Vermelho spring in 1980 had a reported ^{3}H concentration of less than 2 TU (Barmen et al. 1990), which would be equivalent to a decay-corrected 2005 concentration of <0.5 TU.

Elevated dissolved ^{4}He concentrations and R/R_a ratios were measured in water from all of the wells sampled in Mosteiros (Fig. 8; Table 2), likely associated with recent volcanic activity of the island. The ^{4}He concentrations from these wells are as much as an order of magnitude higher than typical concentrations measured in atmospherically equilibrated groundwater. Similarly, the dissolved $^{3}He/^{4}He$ ratios of samples from these wells are as much as 8.3 R_a. This is consistent with values for mantle-derived helium. Because of its sensitivity to non-atmospheric sources of helium, $^{3}H/^{3}He_{trit}$ dating of these samples was not possible. The ^{3}He and ^{4}He concentrations of these and other mantle-influenced samples, however, are very useful for constraining the $^{3}H/^{3}He_{trit}$ age of Monte Vermelho spring and groundwater from other basins not significantly affected by helium derived from the mantle. The relation between R/R_a and the fraction of ^{4}He derived from atmospheric gases in groundwater samples from Mosteiros and the other two basins is shown in Fig. 9. The samples not affected by mantle helium sources are those having a fraction of ^{4}He derived from the atmosphere equal to about 1.0 and an R/R_a of 1. The samples that are affected by mantle helium plot along a linear trend of increasing R/R_a with a decreasing fraction of ^{4}He derived from the atmosphere. The extrapolation of this straight line to a zero fraction of atmospherically derived ^{4}He yields a y-intercept ($^{3}He/^{4}He$ ratio) of about 1.3×10^{-5} or 9 R_a, very similar to the mean $^{3}He/^{4}He$ ratio of 8.8 R_a from 11 rock samples of Santo Antão and Fogo (Christensen et al. 2001) and values of 9.5 to 9.7 R_a reported from hydrothermal springs within the Taburiente Caldera of La Palma, Canary Islands (Perez et al. 1994, 1996; Hilton et al. 2000). The value of 9 R_a was used, therefore, as the end-member terrigenic $^{3}He/^{4}He$ ratio in dating corrections for those groundwater samples not significantly affected by terrigenically derived helium. Using the terrigenic $^{3}He/^{4}He$ ratio of 9 R_a for calculating $^{3}He_{trit}$, the Monte Vermelho spring sample collected in December 2005 has an apparent age of 5–50 years, indicating at least some post-1950s recharge (Table 2).

Ribeira Paul Basin

Both precipitation and groundwater stable isotope samples were collected from Ribeira Paul Basin during this study. Two precipitation samples collected in or near Ribeira Paul during a 3-day rain event in late November 2005 plot along the meteoric water line but are generally more enriched than the groundwater samples from Ribeira Paul, likely because of the lower altitude of the rain-collection site compared to the groundwater sites. A third precipitation sample collected during the storm is isotopically depleted ($\delta^{18}O$ of −4.62‰, $\delta^{2}H$ of −32.1‰) but also shows a shift off the meteoric water line, possibly caused by evaporation occurring between the rain event and sample processing. Groundwater stable isotope samples collected from two wells, five springs, and eight spring-

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Table 2 Stable isotopes, tritium, helium, and apparent recharge age and year of water in the Mosteiros, Ribeira Paul, and Ribeira Fajã Basins, Cape Verde

Name	δ^2H (‰)	$\delta^{18}O$ (‰)	$N_2/^{40}Ar$	^3H and precision (TU)	^4He (cm^3STP/g)	R/R_a	^{20}Ne (cm^3STP/g)	$^4He_{terr}$ (cm^3STP/g)	$^3He_{trit}$ (TU)	Apparent $^3H/^3He$ age (year)	Apparent recharge year
Monte Vermelho spring	−21.0	−3.78	–	0.8±0.1	–	–	–	–	–	–	Post-1950s[a]
	−18.0	−3.76	37.2	0.4±0.1	4.49E-08	1.028	1.17E-07	<1.0E-10	0–6	5–50	Post-1950s
FF 06 well	−30.4	−5.08	–	0.2±0.1	–	–	–	–	–	–	Pre-1950s[a]
FF 07 well	−14.8	−3.35	38.6	1.2±0.1	5.43E-08	1.893	1.82E-07	5.0E-09	NMF	NMF	Post-1950s[a]
FF 21 well	−19.7	−3.74	38.1	0.3±0.1	2.20E-07	7.540	1.69E-07	1.7E-07	NMF	NMF	Pre-1950s[a]
FF 22 well	−18.5	−3.83	39.0	0.9±0.2	1.71E-07	7.002	1.66E-07	1.3E-07	NMF	NMF	Post-1950s[a]
FF 29 well	−17.7	−3.84	37.9	0.2±0.1	4.31E-07	8.296	1.93E-07	3.8E-07	NMF	NMF	Pre-1950s[a]
Cha das Caldeiras wine	–	–	–	3.0±0.1	–	–	–	–	–	–	–
Cha das Caldeiras juice	–	–	–	1.0±0.1	–	–	–	–	–	–	–
Dragueiro No. 1 spring	−15.9	−3.34	38.7	0.5±0.1	5.08E-08	1.039	1.91E-07	<1.0E-10	1–5	15–45	Post-1950s
NA 21 spring	−17.0	−3.30	38.2	0.7±0.1	4.47E-08	1.004	1.64E-07	3.5E-10	0–0.3	0–10	Post-1950s
Passagem spring	−18.3	−3.48	39.1	1.2±0.1	4.51E-08	1.252	1.66E-07	<1.0E-10	6–7	30–40	Post-1950s
Seladinha spring	−17.2	−3.55	38.5	2.1±0.1	4.23E-08	0.998	1.58E-07	<1.0E-10	0–2	0–15	Post-1950s
Tabulera spring	−29.1	−4.93	39.0	0.2±0.1	4.19E-08	1.004	1.57E-07	4.9E-10	0–0.3	>50	Pre-1950s
FA 57 well	−15.7	−3.08	–	1.7±0.1	–	–	–	–	–	–	–
	−13.7	−3.19	44.8	0.9±0.1	6.09E-08	2.645	1.80E-07	1.1E-08	NMF	NMF	Post-1950s[a]
FA 93 well	−15.8	−2.97	40.4	1.3±0.1	4.98E-08	1.071	1.82E-07	4.4E-10	0–2	0–20	Post-1950s
Cabouco stream	−17.4	−3.49	–	–	–	–	–	–	–	–	–
Oio de Agua stream	−25.5	−4.51	–	–	–	–	–	–	–	–	–
Morcas stream	−22.6	−4.08	–	–	–	–	–	–	–	–	–
Zeagrios No. 5 stream	−19.6	−4.01	–	–	–	–	–	–	–	–	–
João Deaninha stream	−18.8	−3.74	–	–	–	–	–	–	–	–	–
Calistrinho stream	−17.8	−3.58	–	–	–	–	–	–	–	–	–
Cringa stream	−18.9	−3.47	–	–	–	–	–	–	–	–	–
Côvada Claro stream	−21.6	−3.79	–	–	–	–	–	–	–	–	–
Ribeira Grande precipitation	−16.3	−3.43	–	–	–	–	–	–	–	–	–
	−18.5	−3.55	–	1.1±0.1	–	–	–	–	–	–	–
Vila das Pombas precipitation	−32.1	−4.62	–	1.4±0.1	–	–	–	–	–	–	–
G. Fajã - Monte Gordo spring	−21.6	−3.98	37.9	0.2±0.1	6.04E-08	3.330	1.74E-07	1.4E-08	NMF	NMF	Pre-1950s[a]
	−21.3	−4.04	40.2	0.0±0.1	5.77E-08	3.421	1.54E-07	1.4E-08	NMF	NMF	Pre-1950s[a]
G. Fajã-Cruz Roque spring	−21.3	−3.95	–	0.0±0.1	–	–	–	–	–	–	Pre-1950s[a]
G. Faja-Lombo Pelado spring	−19.4	−3.84	–	0.0±0.1	–	–	–	–	–	–	Pre-1950s[a]
FN 39 well	−20.6	−3.93	37.1	0.3±0.1	4.44E-08	1.003	1.69E-07	<1.0E-10	0–8	> 50	Pre-1950s
Posto Fajã precipitation	−5.0	−0.63	–	–	–	–	–	–	–	–	–

[a] Apparent recharge year is only based on ^3H concentration

δ^2H and $\delta^{18}O$: ‰ permil; $N_2/^{40}Ar$: based on data from Heilweil et al. 2006, their Table 5; ^3H and precision: *TU* tritium units; ^4He**:** *cm^3 STP/g* cubic centimeters at standard temperature and pressure, per gram; R/R_a: measured $^3He/^4He$ values relative to the helium isotopic ratio of air; *$^3He_{trit}$*: tritiogenic helium; *TU* tritium units; $^3He_{trit}$ and apparent ^3He Age: ranges based on terrigenic $^3He/^4He$ values between 1.3×10^{-5} and 1×10^{-8}; *NMF* not meaningful

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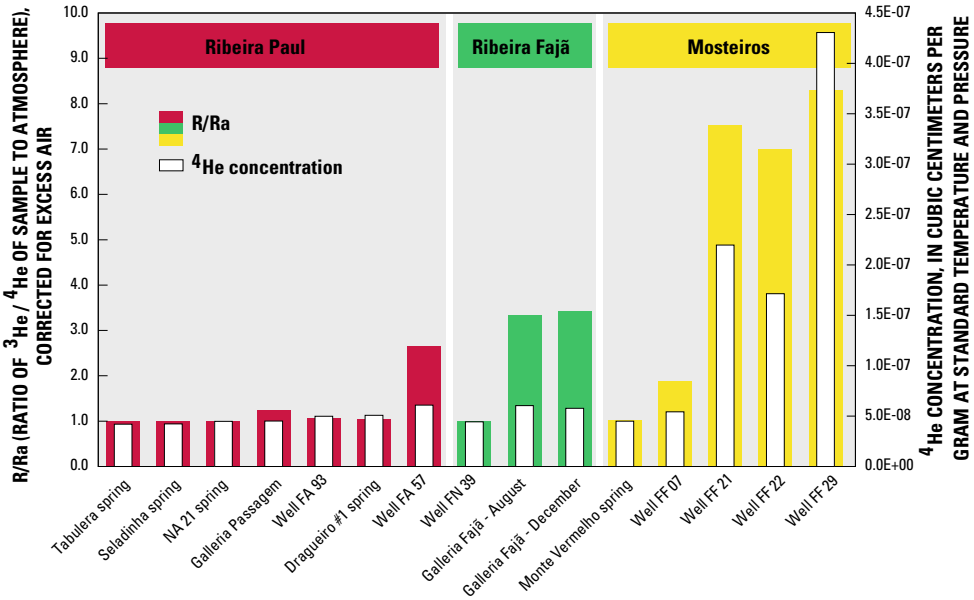

Fig. 8 Ratio of $^3He/^4He$ in groundwater to atmospheric $^3He/^4He$ and total ^4He concentration in groundwater from the Mosteiros, Ribeira Paul, and Ribeira Fajã Basins, Cape Verde

fed streams (collected during the dry season and assumed to represent groundwater discharge) in Ribeira Paul Basin generally plot along the global meteoric water line (Fig. 7). The most-depleted groundwater values ($\delta^{18}O$ of −4.93‰, δ^2H of −29.1‰) were measured at Tabulera spring, the highest-altitude site within the basin (Fig. 4). The least depleted groundwater values ($\delta^{18}O$ of −3.19‰, δ^2H of −13.7‰) were measured at well FA 57, lower in the basin. The eight spring-fed stream samples had isotopic compositions similar to the wells and springs in the basin, with $\delta^{18}O$ and δ^2H values of −3.5 to −4.5‰ and −17.4 to −25.5‰, respectively.

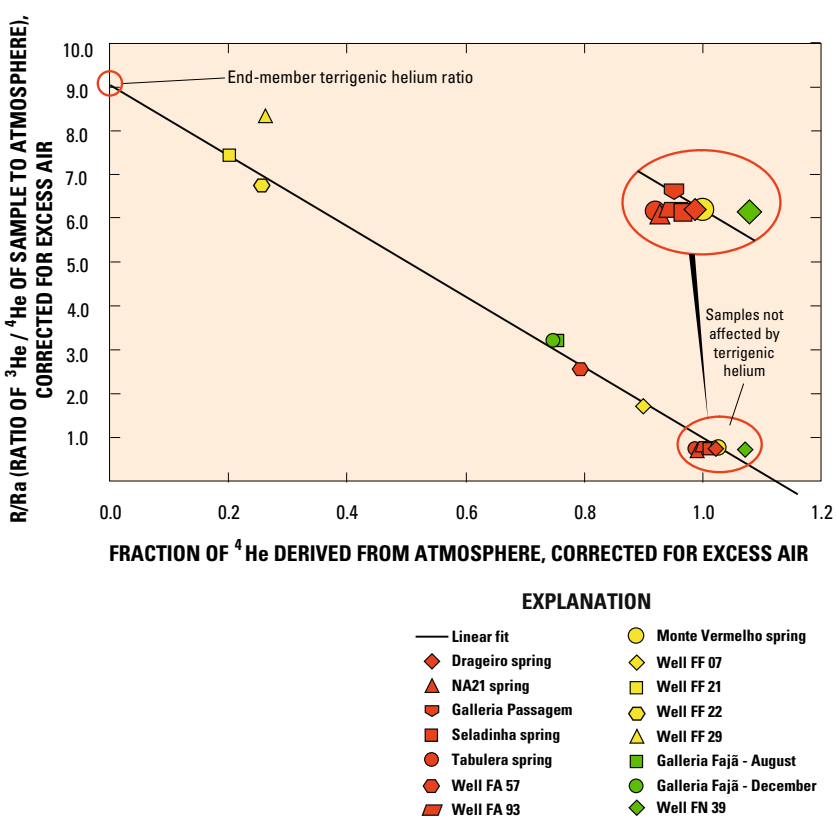

Fig. 9 Relation between $^3He/^4He$ and fraction of ^4He derived from atmospheric gases in groundwater from the Mosteiros, Ribeira Paul, and Ribeira Fajã Basins, Cape Verde

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Two precipitation ^3H samples were collected in and near Ribeira Paul Basin during the rain event of late November 2005. These samples had ^3H concentrations of 1.1–1.4 TU (Table 2). Groundwater ^3H concentrations of samples collected in the basin ranged from 0.2 to 2.1 TU. Tabulera spring was the only groundwater site in Ribeira Paul having ^3H concentrations less than 0.3 TU, indicating that groundwater recharge supplying this spring occurred prior to the early 1950s. The other springs and wells in Ribeira Paul Basin had ^3H concentrations ranging from 0.5 to 2.1 TU, indicating at least some fraction of modern recharge.

The $^3H/^3He_{trit}$ ages at five springs and one well in Ribeira Paul Basin are consistent with the ^3H concentrations and indicate that groundwater is a mixture of pre- and post-1950s recharge. Water collected from Tabulera spring had an apparent age of more than 50 years, indicating recharge prior to the 1950s. Water collected from springs Dragueiro No. 1, NA 21, Passagem, Seladinha, and well FA 93 all have apparent ages of less than 50 years (Table 2). Compared with Mosteiros Basin, there is less influence of mantle-derived helium on groundwater in Ribeira Paul Basin, with only one well (FA 57) having ^4He slightly above atmospheric equilibration and a $^3He/^4He$ ratio of about 2.6 R_a (Figs. 8 and 9; Table 2). Because of this terrigenic ^4He, $^3H/^3He_{trit}$ dating at this site was not possible. The recharge source to the only other well in Ribeira Paul Basin (FA 93) is assumed to be surface water from the adjacent stream, derived from recent precipitation. The sample had no $^3He_{trit}$ and a ^3H concentration of 1.3 TU, within the range of current ^3H concentrations in precipitation. Because this young water comes from a shallow well (21-m depth) adjacent to the stream, it indicates the potential for anthropogenic contamination from upstream sources such as nitrates or pathogenic bacteria. The measured specific conductance of water from this well also was higher than in any other location in Ribeira Paul Basin.

Ribeira Fajã Basin

While only one precipitation sample was collected for stable isotope analysis within Ribeira Fajã Basin ($\delta^{18}O$ of −0.6‰, δ^2H of −5.0‰), stable isotope ratios for São Nicolau precipitation were previously reported for the ten largest precipitation events of 1981 ($\delta^{18}O$ of −1.2 to −4.8‰, δ^2H of −2 to −30‰; Barmen et al. 1990). Groundwater stable isotope samples collected from the Galleria Fajã tunnel and well FN 39 all plot along the meteoric water line within a narrow range ($\delta^{18}O$ of −3.84 to −4.04‰, δ^2H of −19.4 to −21.6‰), indicating a similar source of precipitation recharging the aquifer for these two locations (Fig. 7). The stable isotope ratios of groundwater from Ribeira Fajã Basin are generally more depleted than the other two basins, even though the average altitude of the basin is much lower than that of both the Mosteiros and Ribeira Paul Basins (Table 2). This indicates either that the majority of recharge in the Ribeira Fajã Basin is from higher-altitude precipitation or the atmospheric patterns result in more isotopically depleted air masses entering the basin.

Groundwater ^3H concentrations from samples collected in Ribeira Fajã Basin were all ≤ 0.3 TU, indicative of groundwater recharge occurring prior to the early 1950s. The two helium samples collected in Galleria Fajã indicate mantle influence, with $^3He/^4He$ ratios greater than 3.0 R_a (Fig. 8; Table 2). Because of this terrigenic helium source, $^3H/^3He_{trit}$ dating of the Galleria Fajã samples was not possible. Water from well FN 39, however, does not appear to be influenced by mantle helium; the estimated $^3He_{trit}$ concentration of 0 to 8 TU results in an apparent age of greater than 50 years.

Discussion

Recharge sources, flow paths, and residence times

Oxygen, hydrogen, and helium isotopes, along with field parameters from the Cape Verde basins investigated during this study provide valuable insight with respect to sources of recharge, infiltration mechanisms, flow paths, and residence times. Stable isotope concentrations of precipitation and groundwater generally plot on or near the global meteoric water line defined by Craig (1961). The deuterium excess value, *d*, defined by Dansgaard (1964) as being equal to $\delta^2H - 8(\delta^{18}O)$, ranges from 8 to 13 with a mean value of 10.6 (n=28). Only four stable isotope precipitation samples were collected during this study; ten samples were previously collected on Sao Nicolau (Barmen et al. 1990; Fig. 7). While these 14 samples are not sufficient to define an altitude gradient, other studies of tropical rain found altitude $\delta^{18}O$ gradients of −1 to −3‰/km (Gonfiantini et al. 2001). Akiti (1985) collected five precipitation stable isotope samples on the nearby island of Santiago, which showed an amount effect (increased isotopic depletion with larger rain events). Precipitation samples from the Sahel region of Nigeria (at a latitude of 13°N, similar to Cape Verde) also showed a $\delta^{18}O$ amount effect associated with monsoon rains, which was more clearly discernable than other seasonal and temperature effects (Goni et al. 2001). Compared to the large variation found in precipitation samples ($\delta^{18}O$ of −1 to −5‰), groundwater samples are more isotopically depleted ($\delta^{18}O$ of −3 to −5‰). Groundwater δ^2H values range from −3.7 to −5.1‰ for Mosteiros Basin, −3.0 to −4.9‰ for Ribeira Paul Basin, and −3.8 to −4.0‰ for Ribeira Fajã Basin (Table 2). While some of the precipitation samples show evidence of evaporation, none of the groundwater samples indicate an evaporative shift. This suggests that most infiltration and recharge occurs rapidly and in place (i.e., at higher altitudes) rather than as downstream focused infiltration of runoff.

^3H values of less than 0.3 TU at seven wells and springs in the three Cape Verde study basins indicate pre-bomb era recharge and groundwater residence times of more than 50 years; ^3H values up to 2 TU at the other nine sites suggest at least some recent recharge. $^3H/^3He_{trit}$ dating was used to refine groundwater residence times or

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verify the existence of older water at seven of these sites. As previously discussed, $^3H/^3He$ dating was not possible at six sites because of large concentrations of terrigenic ^4He.

The combination of low ^3H concentrations (less than 1 TU except for well FF 07) and isotopically depleted stable isotopic signatures of groundwater in Mosteiros Basin generally indicate high-elevation recharge and long flow paths/residence times. In contrast, a larger range of $\delta^{18}O$ and δ^2H values, higher ^3H concentrations (0.5 to 2.1 TU), and younger $^3H/^3He_{trit}$ ages of groundwater from Ribeira Paul Basin indicate a predominance of post-1950s recharge (except for Tabulera spring) and shorter flow paths/residence times. Similar to Mosteiros, the groundwater sites sampled in Ribeira Fajã Basin have low ^3H concentrations (≤0.3 TU), pre-1950s $^3H/^3He_{trit}$ ages and relatively depleted $\delta^{18}O$ and δ^2H values, indicative of higher elevation recharge and long flow paths/residence times.

The islands of Cape Verde are located along a volcanically active hot spot. Measured field parameters and environmental tracers, however, show that deep geothermal circulation is not an important process, in contrast to other active oceanic hot spots like New Zealand (Kühn and Stöfen 2005), Iceland (Sigvaldason 1966) or the nearby Canary Islands (Albert-Beltran et al. 1990; Valentín et al. 1990). Groundwater stable isotopes from Cape Verde generally plot on or near the global meteoric water line with a $\delta^{18}O/\delta^2H$ slope of about 8 (Fig. 7), in contrast to a slope of about 3 (characteristic of evaporation at near-boiling temperatures) commonly associated with geothermal systems (Criss 1995). Measured groundwater pH values are near-neutral to slightly alkaline, ranging from 6.8 to 8.3 (Table 1), whereas geothermal waters associated with other hot spots typically have low pH (Wood 2006). Groundwater temperatures range from about 19 to 24°C, similar to mean annual air temperatures rather than the characteristic warmer temperatures associated with deep geothermal circulation. During sampling there was no observed bubbling (often an indicator of CO_2 outgassing). Measured in situ total dissolved-gas pressures for groundwater in all three watersheds varied from 700 to 770 mm Hg and generally were similar to atmospheric pressures at each site (Table 1). Total dissolved-gas pressures much higher than atmospheric pressure may be indicative of high P_{CO2} (partial pressure of CO_2) associated with geothermal fluids (Chiodini et al. 1995). For a geothermal field in Italy, Dallai et al. (2005) report high $N_2/^{40}Ar$ ratios of 47–4,197, indicating the presence of radiogenic ^{40}Ar and excess N_2. In contrast, all $N_2/^{40}Ar$ ratios from the three Cape Verde watersheds range from about 37 to 45 (Table 2).

Susceptibility to contamination and artificial recharge potential

Because of the future potential for groundwater development in Cape Verde, there are concerns regarding aquifer susceptibility to anthropogenic contamination and saltwater intrusion with increased well withdrawals. Additional surface impoundments along ephemeral washes to artificially enhance groundwater recharge are also being planned. While additional site-specific studies are needed to adequately address these issues, the environmental tracers utilized in this study provide information that can be used to make some generalized interpretations.

In Mosteiros Basin, the majority of water supply for agriculture and population centers comes from wells and springs along the northeastern coastal plain (Fig. 3). In contrast, the majority of recharge likely occurs higher in the basin and has relatively long flow paths and residence times. There likely is a low potential, therefore, for aquifer water-quality degradation from contamination by septic effluent or agricultural chemicals applied on the coastal plain. A more pressing concern is the potential for saltwater intrusion with increased groundwater extraction because of the proximity of the existing wells to the ocean. A thin lens of fresh groundwater in the Mosteiros coastal plain overlies brackish water, as indicated by an abrupt transition from freshwater (specific-conductance values of about 2,000 μS/cm) to brackish water (≥ 15,000 μS/cm) at only a few meters depth below the water table in well FF 07. This risk was illustrated during a 24-h pumping test at well FF 21, during which the specific-conductance values increased from 870 (Table 1) to about 1,500 μS/cm (Heilweil et al. 2006). Groundwater age and stable isotope values indicate that most of the groundwater currently being pumped in Mosteiros Basin is derived from recharge that entered the aquifer more than 50 years ago and in the upper parts of the watershed. This suggests that it may take decades or more for artificial recharge from sites in the upper basin to beneficially impact the coastal plain aquifer where the agricultural projects are implemented. Artificial recharge at lower altitudes nearer the production wells may produce quicker results, but may also increase susceptibility to contamination via flushing of agricultural chemicals or septic effluent. Further evaluation of vertical permeability and potential confining layers, therefore, is necessary to determine if such local artificial recharge along the coastal plain is a viable option.

$^3H/^3He_{trit}$ ages and stable isotope values of groundwater from Ribeira Paul Basin indicate a wide variation in recharge sources, groundwater flow paths, and groundwater residence times. The majority of current and planned groundwater development in the basin is from abundant springs discharging from the mid- and higher-altitude parts of the basin (Fig. 4), in the same general area where environmental tracers indicate the majority of recharge likely occurs. Both the abundance of young (post-1950s) groundwater and the location of agriculture and population centers in the upland part of the basin indicate a potential threat from agricultural chemicals or septic effluent that could degrade water quality within the aquifer. The specific conductance of groundwater measured in Ribeira Paul Basin varied from about 200 to 700 μS/cm, displaying a general increase with decreasing altitude and towards the ocean. This increase in

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solutes towards the lower end of the basin may be caused by irrigation/wastewater return flow, recharge from higher-salinity precipitation and sea spray closer to the ocean, or increased water/rock interaction via longer flow paths and slower residence times. Because of Ribeira Paul's abundant springs, there is little current or planned additional pumping from wells near the ocean; thus salt-water intrusion is currently not a concern. Groundwater ages in Ribeira Paul Basin range from pre-1950s to modern, indicating both short and long flow paths. Both the abundance of springs and the existence of some short flow paths and younger groundwater ages in Ribeira Paul Basin indicate that beneficial effects from artificial recharge may occur more quickly than in the other two basins.

Ribeira Fajã Basin has the lowest altitude, driest conditions, and most limited water resources of the three basins. The only measurable groundwater discharge is from the Galleria tunnel (Fig. 5), at higher elevation than most of the agricultural development and population centers. The combination of the upgradient location of the Galleria springs and their relatively old (pre-1950s) waters indicates that there is a relatively low potential for groundwater contamination of this primary water supply from agricultural chemicals or septic effluent. No groundwater pumping is currently occurring in Ribeira Fajã Basin, and groundwater specific conductance is generally low, increasing from about 400 μS/cm at Monte Gordo spring to 500 μS/cm at Lombo Pelado spring and well FN 39 nearer the ocean. The small amount of estimated groundwater recharge to this basin indicates that salt-water intrusion may be a concern if future production wells are located close to the coast. $^3H/^3He$ dating and stable isotope concentrations indicate that recharge to the Galleria springs occurred more than 50 years ago and possibly at higher altitudes in the watershed. The analysis of environmental tracers and hydraulic properties indicates that if artificial recharge impoundments are located in the upland part of the aquifer, they may enhance discharge from the Galleria springs. However, the effect of such recharge structures would depend on the success of locating these structures upgradient of and along groundwater flow paths intersected by these springs.

Conclusions

Oxygen, hydrogen, and helium isotopes were utilized for developing conceptual hydrogeologic models and evaluating groundwater conditions of volcanic island aquifers in Cape Verde, West Africa. Because these watersheds have sparse groundwater sampling points, the synthesis of this environmental tracer information greatly improved the understanding of these aquifer systems. Stable isotopes ($\delta^{18}O$, δ^2H) support the predominance of high-altitude precipitation and recharge, consistent with the much higher rainfall and exposed permeable basalts of the highlands. In contrast to some other volcanic islands, the combination of stable isotope ratios close to the global meteoric water line, near-neutral pH, low total dissolved gas pressures, low $N_2/^{40}Ar$ ratios, and cool temperatures of groundwater in these three watersheds do not indicate the prevalence of geothermal circulation. High ^4He and $^3He/^4He$ ratios of water from some wells and springs, however, suggest a mantle source of helium in groundwater, either through degassing or diffusion from the basaltic aquifer matrix. While these high helium concentrations preclude $^3H/^3He_{trit}$ dating at those sites, the $^3He/^4He$ ratios indicate a terrigenic end-member of about 9 R_a that was utilized for constraining groundwater residence times at other sampling points. This isotopic technique may be widely applicable for groundwater dating in other active volcanic settings. Tritium and $^3H/^3He_{trit}$ dating (where possible) suggest long groundwater residence times (>50 years) in Fajã Basin, whereas Mosteiros Basin and Ribeira Paul Basin contain both young and old groundwater flow paths and residence times. In Ribeira Fajã Basin, the upland location of the Galleria springs and their relatively old waters indicates that there is a relatively low potential for groundwater contamination of the primary water supply from septic effluent or agricultural activities.

The combination of field measurements and environmental tracer data indicate variations in both susceptibility to contamination from anthropogenic sources or saltwater intrusion and artificial recharge potential. In Mosteiros Basin, the predominance of groundwater recharge in the upper part of the watershed and discharge at lower elevations likely indicates that there is currently a low potential for aquifer water-quality degradation from surface contamination in the coastal plain. There is, however, a high potential for saltwater intrusion with increased groundwater extraction. In Ribeira Paul Basin, the upland location of agriculture and population centers indicates a potential threat from surface contamination. Because of limited groundwater pumping along the coast, saltwater intrusion in Ribeira Fajã Basin is not an immediate concern; however, the lower recharge rates in this basin suggest that saltwater intrusion may be a future concern if production wells are located close to the coast. While field and environmental tracer methods for evaluating recharge sources and groundwater residence times have certain limitations, they provide useful information for improving the conceptual understanding of groundwater systems and practical information for sustainable water management solutions, particularly where sampling points are limited.

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 DOI 10.1007/s10040-009-0434-2

References

Akiti T (1985) Environmental isotope study of the groundwaters of the island of Santiago. Isotope Hydrology Section report, IAEA, Vienna, 27 pp

Albert-Beltran J, Araña V, Diez JL, Valentin A (1990) Physical-chemical conditions of the Teide volcanic system (Tenerife, Canary Islands). J Volcanol Geotherm Resour 43:321–332

Andrews JN (1985) The composition of radiogenic helium and its use to study groundwater movement in confined aquifers. Chem Geol 49:339–351

Barmen G, Joseffson G, Magnusson M, Wernersson H (1984) A hydrogeological investigation on Santiago, Cape Verde Islands. Report TVTG-5009, Lund Institute of Technology, Lund, Sweden, 43 pp

Barmen G, Carvalho V, Querido A (1990) Groundwater-related geological and isotopic investigations on the island of Fogo: an overview. Report LUTVDG/TVTG-90/3027, Lund Institute of Technology, Lund, Sweden, 72 pp

Bokuniewicz HJ (1980) Groundwater seepage into Great South Bay, New York. Estuar Coast Mar Sci 10:437–444

Breddam K, Kurz MD (2001) Helium isotope signatures of Icelandic alkaline lavas. EOS Trans Am Geophys Union 82 (47):F1315

Cable JE (1997) Magnitude and variations of groundwater seepage along a Florida marine shoreline. Biogeochemistry 38:189–205

Cabrera MC, Custodio E (2004) Groundwater flow in a volcanic-sedimentary coastal aquifer: Teide area, Gran Canaria, Canary Islands, Spain. Hydrogeol J 12(4):305–320

Cambereri TC, Eichner EM (1998) Watershed delineation and groundwater discharge to a coastal embayment. Groundwater 36 (4):626–634

Castro MC (2004) Helium sources in passive margin aquifers: new evidence for a significant mantle ^{3}He source in aquifers with unexpectedly low in situ ^{3}He/^{4}He production. Earth Planet Sci Lett 222(3–4):897–913

Chiodini GF, Frondini F, Ponziani F (1995) Deep structures and carbon dioxide degassing in central Italy. Geothermics 24 (1):81–94

Christensen BP, Holm PM, Jambon A, Wilson JR (2001) Helium, argon and lead isotopic composition of volcanics from Santo Antão and Fogo, Cape Verde Islands. Chem Geol 178:127–142

Clarke WB, Jenkins WJ, Top Z (1976) Determination of tritium by mass spectrometric measurements of ^{3}He. Int J Appl Radiat Isot 27:515–522

Craig H (1961) Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. Science 133(3467):1833–1834

Craig H, Lupton JE (1976) Primordial neon, helium, and hydrogen in oceanic basalts. Earth Planet Sci Lett 31:369–385

Criss RE (1995) Stable isotope distribution: variations from temperature, organic and water-rock interactions. In: Ahrens TJ (ed) Global earth physics: a handbook of physical constants, AGU Reference Shelf 1, American Geophysical Union, Washington, DC, pp 292–307

Cross VA, Bratton JF, Bergeron E, Meunier JK, Crusius J, Koopmans D (2006) Continuous resistivity profiling data from the Upper Neuse River Estuary, North Carolina, 2004–2005. US Geol Surv Open-File Rep 2005-1306

Dallai L, Magro G, Petrucci E, Ruggieri G (2005) Stable isotope and noble gas isotope compositions of inclusion fluids from Larderello geothermal field (Italy): constraints to fluid origin and mixing processes. J Volcanol Geotherm Res 148:152–164

Dansgaard W (1964) Stable isotopes in precipitation. Tellus 16:436–468

Descloitres M, Guerin R, Albouy Y, Tabbagh A, Ritz M (2000) Improvement in TDEM sounding interpretation in presence of induced polarization: a case study in resistive rocks of the Fogo volcano, Cape Verde Islands. J Appl Geophys 45:1–18

Farley KA, Natland JH, Craig H (1992) Binary mixing of enriched and undegassed (primitive?) mantle components (He, Sr, Nd, Pb) in Samoan lavas. Earth Planet Sci Lett 111:183–199

Farley KA, Basu AR, Craig H (1993) He, Sr, and Nd isotopic variations in lavas from the Juan Fernandez archipelago. Contrib Mineral Petrol 115:75–87

Gingerich SB, Oki DS (2000) Ground water in Hawaii. US Geol Surv Fact Sheet 126-00, 6 pp

Gonfiantini R, Roche MA, Olivry JC, Fontes JC, Zuppi GM (2001) The altitude effect on the isotopic composition of tropical rains. Chem Geol 181(1–4):147–167

Goni IB, Fellman E, Edmunds WM (2001) Rainfall geochemistry in the Sahel region of northern Nigeria. Atmos Environ 35:4331–4339

Graham DW (2002) Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts: characterization of mantle source reservoirs. In: Porcelli D, Ballentine CJ, Wieler R (eds) Noble gases in cosmochemistry and geochemistry (47). Mineralogical Society of America, Washington, DC, pp 247–317

Graham DW, Christie DM, Harpp KS, Lupton JE (1993) Mantle plume helium in submarine basalts from the Galápagos platform. Science 262:2023–2026

Haagsma B (1995) Traditional water management and state intervention: the case of Santo Antão, Cape Verde. Mt Res Dev 15(1):39–56

Heilweil VM, Earle JD, Cederberg JR, Messer MM, Jorgensen BJ, Verstraeten IM, Moura MA, Querido A, Spencer F, Osorio T (2006) Evaluation of baseline ground-water conditions in the Mosteiros, Ribeira Paul, and Ribeira Fajã Basins, Republic of Cape Verde, West Africa, 2005-06. US Geol Surv Sci Invest Rep 2006-5207, 42 pp

Hidroprojecto Engenharia E Gestão (2000) Etude d'aménagement des basins versants, phase 1: caracterisation de la situation actuelle et diagnostic, v. 2.5, Bassin de Ribeira da Fajã [Study of the installation of basin slopes, phase 1: characterization of the current location and diagnosis, v. 2.5, Basin of Ribeira da Fajã]. Republique du Cap Vert, Ministere de L'Agriculture, de L'Alimentation et de L'Environment, Lisbon

Hildenbrand A, Marlin C, Conroy A, Gillot P, Filly A, Massault M (2005) Isotopic approach of rainfall and groundwater circulation in the volcanic structure of Tahiti-Nui (French Polynesia). J Hydrol 302:187–208

Hilton DR, Barling J, Wheller GE (1995) Effect of shallow-level contamination on the helium isotope systematics of ocean-island lavas. Nature 373:330–333

Hilton DR, MacPherson CG, Elliott TR (2000) Helium isotope ratios in mafic phenocrysts and geothermal fluids from La Palma, the Canary Islands (Spain): implications for HIMU mantle sources. Geochim Cosmochim Acta 64(12):2119–2132

Institute Géographique National de France (1981) Etude des résurgences d'eau douce par thermographies [Study of fresh water recovery by thermography]. Institute Géographique National de France (IGN), Saint Mandé Cedex, France, 42 pp

Irwin A, Wilson C (1998) Cape Verde Islands. Bucks, England, Bradt, 230 pp

Izuka SK, Gingerich SB (2003) A thick lens of fresh groundwater in the southern Lijue Basin, Kauia, Hawaii, USA. Hydrogeol J 11 (2):240–248

Jackson DB, Lenat JF (1989) High-level water tables on Hawaiian type volcanoes and intermediate depth geoelectric structures, Kilauea Volcano, Hawaii and Piton de la Fournaise Volcano, Isle de la Reunion. General assembly of the International Association of Volcanology and Chemistry of the Earth's Interior, Santa Fe, New Mexico, 25 June–1 July 1989. Bull New Mexico Bur Geol Min Resour 131:142

Kallrén L, Schreiber I (1988) Groundwater survey on western Fogo, Cape Verde. Report TVTG-5019, Lund Institute of Technology, Lund, Sweden, 83 pp

Kühn M, Stöfen H (2005) A reactive flow model of the geothermal reservoir Waiwera, New Zealand. Hydrogeol J 13 (4):606–626

Kurz MD, Jenkins WJ, Hart SR, Clague D (1983) Helium isotopic variations in volcanic rocks from Loihi Seamount and the island of Hawaii. Earth Planet Sci Lett 66:388–406

 DOI 10.1007/s10040-009-0434-2

Kurz MD, Kammer DP, Gulessarian A, Moore RB (1990) Helium isotopes in dated alkali basalts from Sao Miguel, Azores. EOS Trans Am Geophys Union 71:657

Langworthy M, Finan TJ (1997) Waiting for rain: agriculture and ecological imbalance in Cape Verde. Rienner, Boulder, CO, 212 pp

Lodge A, Helffrich G (2006) Depleted swell root beneath the Cape Verde Islands. Geology 34(6):449–452

Macdonald GA, Abbott AT, Peterson FL (1983) Volcanoes in the sea: the geology of Hawaii, 2nd edn. University of Hawaii Press, Honolulu, 517 pp

Mamyrin BA, Tolstikhin IN (1984) Helium isotopes in nature. Elsevier, Amsterdam, The Netherlands, 273 pp

Mazor E (1991) Applied chemical and isotopic groundwater hydrology. Halsted, New York, 274 pp

Michael HA, Lubetsky JS, Harvey CF (2003) Characterizing submarine groundwater discharge: a seepage meter study in Waquoit Bay, Massachusetts. Geophys Res Lett 30(6):1297

Mink JF (1963) Water development tunnels in a dike complex. Trans Am Geophys Union 44(1):46

Moreira M, Doucelance R, Kurz MD, Dupré B, Allégre CJ (1999) Helium and lead isotope geochemistry of the Azores Archipelago. Earth Planet Sci Lett 169:189–205

Olivry JC (1981) Estudo de precipitacões em São Nicolau, República das Ilhas de Cabo Verde [Precipitation study in São Nicolau, Republic of Cape Verde]. Office de la Recherche Scientifique et Technique outre mer centre ORSTOM, Dakar, Senegal, 55 pp

Oki DS, Gingerich SB, Whitehead RL (1999) Hawaii. In: Ground water atlas of the United States: Alaska, Hawaii, Puerto Rico and the US Virgin Islands. US Geol Surv Invest Altas 730-N, segment 13, pp N12–N22

Ozima M, Podosek FA (1983) Noble gas geochemistry. Cambridge University Press, Cambridge, 367 pp

Perez NM, Nakai S, Wakita H, Sano Y, Williams SN (1994) $^{3}He/^{4}He$ isotopic ratios in volcanic-hydrothermal discharges from the Canary Islands, Spain: implications on the origin of the volcanic activity. Mineral Mag 58:709–710

Perez NM, Nakai S, Wakiti H, Hernandez PA, Salazar JM (1996) Helium-3 emission in and around Teide volcano, Tenerife, Canary Islands, Spain. Geophys Res Lett 23:3531–3534

Peterson FL (1972) Water development on tropical volcanic islands: type example: Hawaii. Ground Water 10(5):18–23

Poreda RJ, Schilling JG, Craig H (1993) Helium isotope ratios in Easter microplate basalts. Earth Planet Sci Lett 119(3):319–329

Prada SN, da Silva MO, Cruz JV (2005) Groundwater behavior in Madeira, volcanic island (Portugal). Hydrogeol J 13(5–6):800–812

Révész K, Coplen TB (2008) Determination of the $\delta(^{18}O/^{16}O)$ of water: RSIL lab code 489. In: Révész K, Coplen TB (eds) Methods of the Reston Stable Isotope Laboratory: U.S. Geological Survey Techniques and Methods, 10–C2, pp 28

Saar MO, Castro MC, Hall CM, Manga M, Rose TP (2005) Quantifying magmatic, crustal, and atmospheric helium contributions to volcanic aquifers using all stable noble gases: implications for magmatism and groundwater flow. Geochem Geophys Geosys 6(3). doi:10.1029/2004GC000828

Santos FM, Almeida EP, Gomes M, Pina A (2006) Hydrogeological investigation in Santiago Island (Cabo Verde) using magnetotellurics and VLF methods. J Afr Earth Sci 45(4–5): 421–430

Scholl MA, Gingerich SB, Tribble GW (2002) The influence of microclimates and fog on stable isotope signatures used in interpretation of regional hydrology: East Maui, Hawaii. J Hydrol 264:170–184

Sheldon A (2002) Diffusion of radiogenic helium in shallow ground water: implications for crustal degassing. PhD Thesis, University of Utah, Utah, 185 pp

Sigvaldason GE (1966) Chemistry of thermal waters and gases in Iceland. Bull Volcanol 29(1):589–604

Solomon DK, Cook PG (2000) ^{3}H and ^{3}He. In: Cook PG, Herczeg AL (eds) Environmental tracers in subsurface hydrology. Kluwer, Boston, pp 397–424

Stute M, Schlosser P (2000) Atmospheric noble gases. In: Cook PG, Herczeg AL (eds) Environmental tracers in subsurface hydrology. Kluwer, Boston, MA, pp 349–377

Tolstikhin IN, Kamenskiy IL, Forjaz V, Polyak BG, Kononov VI, Kudrayavtsev DI (1991) Helium isotopes in gases of Sao Miguel Island, The Azores Plateau. Int Geol Rev 33(9):930–940

Vailleux Y, Bourguet L (1974) La mise en valeur des eaux souterraines dans l'archipel du Cap Vert [The development of groundwater in the archipelago of Cape Verde]. Final Mission Report 140, BURGEAP, Ministerio da Coordenacão Interterritorial, Brigada de Aguas Subterraneas do Cabo Verde, Paris, 291 pp

Valentín A, Albert-Beltran J, Diez JL (1990) Geochemical and geothermal constrains on magma bodies associated with historic activity, Tenerife (Canary Islands). J Volcanol Geotherm Resour 44:251–264

Weiss RF (1968) Piggyback samplers for dissolved gas studies on sealed water samples. Deep Sea Res 15:695–699

Wood SA (2006) Rare earth element systematics of acidic geothermal waters from Taupo Volcanic Zone, New Zealand. J Geochem Expl 89(1–3):424–427

 DOI 10.1007/s10040-009-0434-2