Continental-scale links between the mantle and groundwater systems of the western United States: Evidence from travertine springs and regional He isotope data

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ABSTRACT

To understand regional mantle degassing, we compiled new and existing helium isotope data measured in hot springs, gas fields, and travertine-depositing cool springs and compared these geochemical data with mantle velocity structure determined from tomographic studies. These data suggest heterogeneous mantle degassing, with regions of highest $^3He/^4He$ in groundwaters (hence, highest mantle helium contribution) corresponding to regions of lowest mantle velocity, a reflection of tectonically active and partially molten mantle. New He isotope and water chemistry data from travertine-depositing cool springs of the western United States show marked variability consistent with mixing between surface water recharge and inputs from deep crustal and mantle sources. The deeply sourced end-member fluids of these mixing trends have high $^3He/^4He$, high dissolved CO_2, and high salinity compared to shallow recharge waters, and commonly have elevated trace element concentrations. Consequently, these fluids cause degradation of water quality in western U.S. aquifers. Our conclusions highlight a connection between neotectonics (e.g., mantle degassing) and water quality in the western United States.

INTRODUCTION

Distributed deformation associated with the western North American plate margin extends >1000 km inboard from the San Andreas fault zone to the Rocky Mountain and western Great Plains regions. This region forms an orogenic plateau with high average heat flow and is characterized by relatively low upper mantle P-wave velocities with marked heterogeneity (Godey et al., 2003; Humphreys et al., 2003). Progressive geochemical depletion of the upper mantle during generation of basaltic melt likely occurred in several episodes since the Proterozoic (Karlstrom et al., 2005). The mantle was hydrated by flat-slab subduction during the Laramide orogeny (Humphreys et al., 2003) and now is partially molten, leading to small-scale convective exchange between an upwelling asthenosphere (Gao et al., 2004) and compositionally variable lithosphere (Dueker et al., 2001; Karlstrom et al., 2005). The mantle underlying western North America is marked by one of the largest known shear wave velocity contrasts on Earth (van der Lee and Nolet, 1997). At the continental scale, this transition reflects the heterogeneous thinning and warming of North America's lithospheric keel as the plate moved southwest in absolute plate motion in the Cenozoic into a wide zone of warm asthenosphere (CD-ROM Working Group, 2002).

We hypothesize that CO_2-rich mineral springs and related travertine deposits in the western United States are a manifestation of this mantle tectonism, and hence the geochemistry of spring waters and gases can be used in conjunction with geophysical data sets to understand mantle heterogeneity and the processes of lithosphere-asthenosphere interaction. We report new water and gas chemistry with associated carbon and helium isotope data in the context of a synthesis of the existing noble gas isotope chemistry database for western North America. Our literature synthesis (Table DR1[1]) builds on previous work in the area, with the regional helium isotope data presented in the context of a tomographic image of today's mantle. We also show that travertine-depositing cool springs contain mantle-derived volatiles in a variety of locations and tectonic settings throughout the western United States, such that many aquifer systems are influenced by mixing of deeply sourced and circulated waters.

HE ISOTOPES—BACKGROUND

The isotope geochemistry of noble gases is a sensitive tracer of mantle-derived volatiles even with a large input of volatiles derived from Earth's crust. This is because the mantle has retained a significant fraction of the terrestrial inventory of the primordial isotope ^3He acquired during Earth formation (Clarke et al., 1969), and it is still leaking to Earth's surface. In contrast, the crust has been extensively reworked over geological time and has retained very little ^3He: its helium inventory is dominated by radiogenic ^4He produced from the decay of U- and Th-series nuclides. Consequently, helium presently emanating from regions of mantle melting, such as mid-oceanic ridges or helium trapped in glass and phenocrysts in mid-oceanic-ridge basalts (MORB), is characterized by a relatively high $^3He/^4He$ ratio (R) of 8 ± 1 times that of air (R_A), which has a $^3He/^4He$ ratio of 1.4×10^{-6} (Graham, 2002). Indeed, values as high as 37 × R_A have been observed in some ocean island basalts (Hilton et al., 1999) and are thought to be related to deep plumes tapping less degassed mantle reservoirs. When mantle-derived fluids are injected into the crust, mantle helium becomes progressively diluted by crustal helium characterized by low $^3He/^4He$ ratios of ~0.02 R_A. Therefore, any value higher than 0.1

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[1] GSA Data Repository Item 2005199, a description of sampling and analytical methods and geochemical data tables DR1–DR3, is available online at www.geosociety.org/pubs/ft2005.htm or on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA, or editing@geosociety.org.

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R_A, which lies above the range typical of various crustal lithologies, is considered to have a significant mantle He component (Ballentine et al., 2002). Conversely, areas like the Canadian Shield that have a thick, cool lithosphere and are tectonically quiescent have $^3He/^4He$ ratios ~0.02 R_A, implying that groundwater and gas reservoirs have been insulated for long periods from mantle volatile additions.

Across western North America, mantle-derived helium and elevated CO_2 levels have long been identified in fluids and gases at major volcanic centers, faults, and hydrothermal systems associated with mantle partial melting and high heat flow (Ballentine et al., 2002; Craig et al., 1978; Hilton et al., 2002; Kennedy et al., 1987, 2002; Welhan et al., 1988, and references therein). Helium-3 flux has also been used to understand magmatism in extensional tectonic settings (e.g., Oxburgh and O'Nions, 1987; Torgersen, 1993). Natural gas fields have been the focus of noble gas research and clearly show the presence of mantle-derived volatiles (Ballentine et al., 2000, 2001; Caffee et al., 1999; Hiyagon and Kennedy, 1992; Jenden et al., 1988; Kennedy et al., 2002; Poreda et al., 1986; Torgersen and Kennedy, 1999). Mantle-derived helium has been identified in the San Andreas and Walker Lane fault zones of California and Nevada (Kennedy et al., 1997; Kulongoski et al., 2005; Sorey et al., 1993; Welhan et al., 1988), suggesting that faults can serve as conduits for mantle volatiles without active magmatism.

UNDERSTANDING THE FLUX OF MANTLE VOLATILES THROUGH THE CRUST

Interpretation of the variation in helium isotopic ratios measured in groundwaters and gases is complicated by the factors that can affect the ratio during volatile movement from the mantle through the crust. Assuming the MORB value for the mantle end-member under the western United States (e.g., Ballentine et al., 2005), the factors that can lower the isotopic value below 8 R_A include alpha recoil addition of ^4He from uranium-series radioactive decay during movement through the crust, dilution by stored crustal helium (0.02 R_A), and addition from old magmatic systems that have been diluted by the same processes (Ballentine and Burnard, 2002; Torgersen, 1993). Thus, one must understand not only the initial mantle helium isotope input but the residence time, fluid flow rate, and mixing history through the crust, as well as the distribution and age of magmatic intrusions and variation in U and Th in the crust (Kennedy et al., 1997; Torgersen, 1993; Torgersen et al., 1995).

Helium does not move alone from the mantle, but travels with CO_2 and other components. Helium is a trace gas in spring gases, whereas CO_2 can comprise over 99% of the gas phase in some springs. Quantifying the CO_2 flux from the mantle is not simple, due to mixing of CO_2 from other sources such as metamorphic decarbonation of carbonate bedrock, CO_2 gas reservoirs, organically derived CO_2, and atmospheric CO_2 (Polyak et al., 2000; Sano and Marty, 1995; Sherwood Lollar et al., 1997). MORB has a narrow range of $CO_2/^3He$ ratios ($2–7 \times 10^9$), whereas crustal fluids are characterized by higher $CO_2/^3He$ ratios ($10^{11}–10^{13}$) (O'Nions and Oxburgh, 1988; Sherwood Lollar et al., 1997). The combination of $\delta^{13}CO_2$ measurements and the $CO_2/^3He$ ratio has been used successfully to resolve the relative contribution of mantle CO_2 to fluids and gases (e.g., Sano and Marty, 1995).

TRAVERTINE SPRINGS OF THE WESTERN UNITED STATES

Travertine deposition is driven by the degassing of CO_2-charged groundwater as it emerges at springs. Although it is commonly suggested in the literature that CO_2 is derived from meteoric or near-surface biological sources (e.g., Szabo, 1990), the models of Liu et al. (2003), Siegel et al. (2004) and Crossey et al. (2006) suggest that travertine-depositing springs often contain deep geological or endogenic sources of CO_2.

Worldwide, there is recognition that travertine deposits are associated with faulting and extensional settings (Hancock et al., 1999). In the western United States, active travertine-depositing hot and cool springs (Fig. 1) are associated with basement-penetrating normal faults and lavas associated with extensional tectonics. The association of travertine deposits with hot springs and lavas suggests a link to high crustal heat flow. However, cool travertine springs are

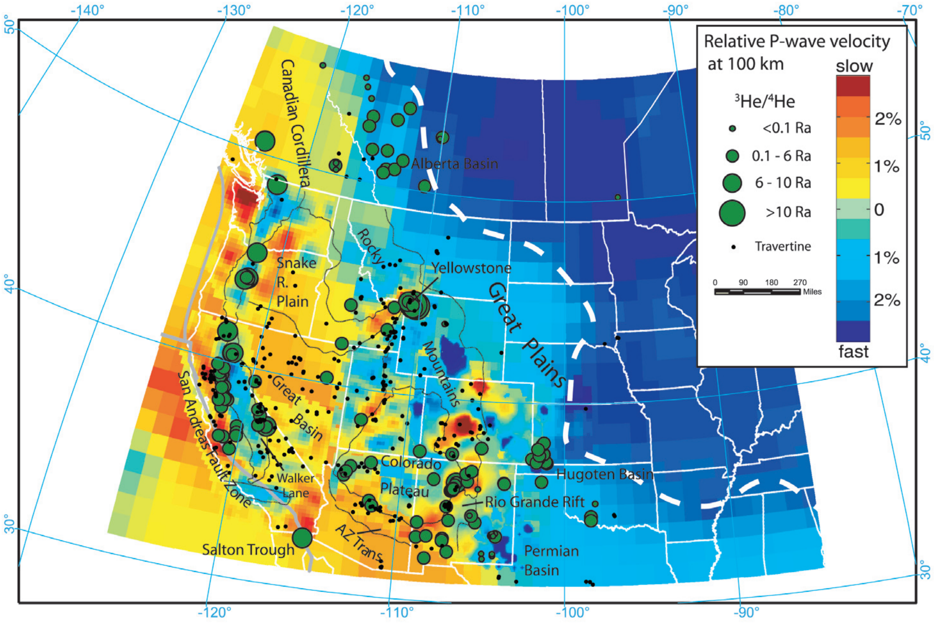

Figure 1. $^3He/^4He$ values (R/R_A notation) for hot springs, cool mineral springs, gas fields, and groundwater for the western United States and Canada. Helium isotopic values are overlain on P-wave velocity mantle tomography at 100 km depth (modified from: Humphreys et al., 2003). Blue: interpreted as high velocity, old, and cold lithosphere at 100 km depths. Yellow to red: lower velocity and warmer lithosphere and/or asthenosphere at 100 km depths, interpreted to be locally partially molten (Humphreys and Dueker, 1994). Tectonic provinces outlined in black (e.g., Rio Grande rift); white dashed line depicts our interpretation of the eastward transition from the tectonically active western U.S. mantle to the tectonically quiescent mantle. Dots show locations of western U.S. travertine deposits (Buchanan and Swain, 1998; Feth and Barnes, 1979; Heitmuller and Reece, 2003; Johnson and McCormick, 2005; Love and Chafetz, 1988).

also found in these settings, and they have similar water chemistries to hot springs. Hot springs have been sampled extensively for He isotopes as part of geothermal exploration in the western United States, especially in the Great Basin (e.g., Kennedy et al., 1996). Our work focuses on characterizing cool springs and expanding the geochemical database on travertine-depositing systems of the southwestern United States, and it highlights a direct link between neotectonics and gas and water chemistry in western U.S. aquifers.

RESULTS

New ^{3}He/^{4}He data from springs in the Arizona Transition zone, the Colorado Plateau, and the Rio Grande rift have R_A values that range from 0.08 to 1.16 R_A (Table 1). These data are merged with published values from hot springs, cool springs, geothermal wells, and gas field wells of western North America (Table DR1; see footnote 1) and are overlain on an image of the mantle velocity field at 100 km depth (Fig. 1) (Humphreys et al., 2003). Our new data are important in reinforcing the regional extent of mantle degassing and in reemphasizing that mantle helium is present in a wide variety of both thermal and nonthermal springs.

Water-free gases measured in spring waters range up to 99% by volume CO_2 and average 45%. In contrast, typical shallow groundwaters containing dissolved gases from a meteoric or soil-gas origin have <1% by volume CO_2. A plot of nitrogen, argon, and helium shows our data in terms of potential gas source based on tectonic setting (Giggenbach, 1992). These data show a trend in source ranging from air-saturated groundwater to an end member composition dominated by crustal or mantle-derived volatiles (Fig. 2; Table DR2 [see footnote 1]). The $CO_2/^3He$ ratios for these springs range from 2.02×10^9 to 5.1×10^{12} (Table 1; Table DR1 [see footnote 1]), falling within both the mantle and crustal ranges. Their $\delta^{13}CO_2$ values range from −12.7 to −1.0‰ Peedee belemnite (Table 1), spanning the range between marine carbonates (0 ± 2‰) and the mantle (−6 ± 3‰) (Hoefs, 1987; Sano and Marty, 1995; Trull et al., 1993), with the more negative values indicating some influence by organic carbon sources (−20 to −30‰). While these analyses cannot quantitatively determine the source of the CO_2 present, they support the hypothesis that some of the CO_2 is mantle-derived.

Water analyses from these springs indicate that they are generally <30 °C, range in pH between 6 and 7, have alkalinities between 300 and 3000 mg/l, and have total dissolved solids up to 23,000 ppm. Chemistry for selected springs found in the Rio Grande rift is provided in Table DR3 (these springs are representative for travertine-springs of the southwestern United States). Major ion chemistry shows trends between Ca-Mg-HCO_3 and Na-Cl-SO_4 type waters (Fig. 3) that range from dilute to saline. Springs have arsenic contents ranging from <5 ppb to >5000 ppb. Similar mixing trends are present in the Grand Canyon and lead to the inference that there are different endogenic water end members that mix with the more dilute waters from surface recharge to explain the observed wide range of water compositions (Crossey et al., 2006).

CORRELATION OF HELIUM ISOTOPIC VARIATIONS WITH TECTONIC PROVINCE

Although the distribution of ^{3}He/^{4}He data is highly variable among tectonic provinces, in general the highest mantle helium contributions correlate to the youngest and most active tectonic regions and the domains of lowest mantle velocity (Fig. 1). Exceptions to this exist because of mixing that can affect helium isotopic value during movement through the crust. In Yellowstone National Park, ^{3}He/^{4}He ratios as high as 16 R_A are observed (Craig et al., 1978; Kennedy et al., 1987); these values suggest that Yellowstone represents a high-^{3}He plume end member such as is found in Hawaii and Iceland (see review by Graham, 2002). All other localities in the western United States show ^{3}He/^{4}He values ≤8 R_A. Therefore, we assume that helium in the western United States is a mixture between a mantle end member with a

TABLE 1. NEW ^{3}He/^{4}He AND $\delta^{13}CO_2$ VALUES FOR SPRINGS AND GROUNDWATER OF SOUTHWEST U.S.

Location	Rc/Ra[*]	1σ	X[†]	$CO_2/^3He$ ($\times 10^9$)	$\delta^{13}CO_2$ (‰ PDB)
New Mexico					
Montezuma Hot Spring (BM 290 1957)[§]	0.083	0.007	1818.91	nr	nr
Upper Owl Spring[§]	0.384	0.031	37.34	nr	nr
Manby Hot Spr Pool—near bathhouse[§]	0.316	0.015	1332.05	nr	nr
Manby Hot Spr Pool—S of bathhouse[§]	0.301	0.011	799.87	nr	nr
Ponce de Leon Hot Spr—hottest in concrete[§]	0.199	0.008	1956.96	nr	nr
No Name Spring—S of John Dunn Bridge[§]	0.09	0.006	7139.41	nr	nr
Tierra Amarilla Anticline—Grassy Spring	0.198	0.004	1330.24	42	–4.6
La Madera Spring	0.33	0.005	148.24	456	–2.2
Salt Spr—Jemez Pueblo	0.114	0.002	641.04	133	nr
Salado Arroyo Spring	0.606	0.024	11.37	5100	–1.0
Lucero Uplift unnamed mineral spring[§]	0.47	0.03	2666.02	nr	nr
Truth or Consequences Artesian Well[§]	0.37	0.02	724.30	nr	nr
Geronimo Hot Spring—Truth or Consequences[§]	0.41	0.02	372.35	nr	nr
Radium Spring—Resort bath house[§]	0.35	0.02	540.23	nr	nr
Roy Smith Well—Radium Spring Area[§]	0.292	0.012	2299.29	nr	nr
Well #10 Burgette Greenhouse Lightening Dock[§]	0.679	0.044	736.77	nr	nr
Well #1 Burgette Greenhouse Lightening Dock[§]	0.724	0.052	531.47	nr	nr
Well #4 Doc Cambell's Gila Hot Springs[§]	0.112	0.007	399.29	nr	nr
Lightfeather Hot Spring[§]	0.107	0.009	705.99	nr	nr
Turkey Creek Hot Spr—Upper Spring[§]	0.159	0.014	69.22	nr	nr
Bubbles Spring Lower Frisco Area[§]	0.425	0.022	97.79	nr	nr
Lower Frisco Hot Spring[§]	0.35	0.021	42.95	nr	nr
Upper Frisco Hot Spring[§]	0.363	0.038	6.75	nr	nr
Sedillo Spring Socorro[§]	0.4	0.023	0.36	nr	nr
Colorado					
Pagosa Hot Spring travertine summit[§]	0.093	0.006	7139.12	nr	nr
Pagosa Hot Spring—S of main terrace[§]	0.113	0.01	1421.58	nr	nr
Arizona (Verde Valley)					
Fossil Creek, upper orifice	0.31	0.005	1805.57	2.02	–11.7
Fossil Creek, downstream	0.975	0.052	3.32	nr	–12.7
Montezuma Well	1.162	0.02	21.07	500	–7.6

Note: nr—not reported; Spr—Spring.

[*] Rc/Ra—Air corrected R/Ra; Ra = ^{3}He/^{4}He in air (1.4 E-6).

[†] $X = (^4He/^{20}Ne)_{measured}/(^4He/^{20}Ne)_{air} \times [\beta Ne/\beta He]$; ß—Bunsen coefficients, assuming a groundwater recharge temperature of 15 °C (Weiss, 1970).

[§] Unpublished data provided by M. Kennedy and M. van Soest.

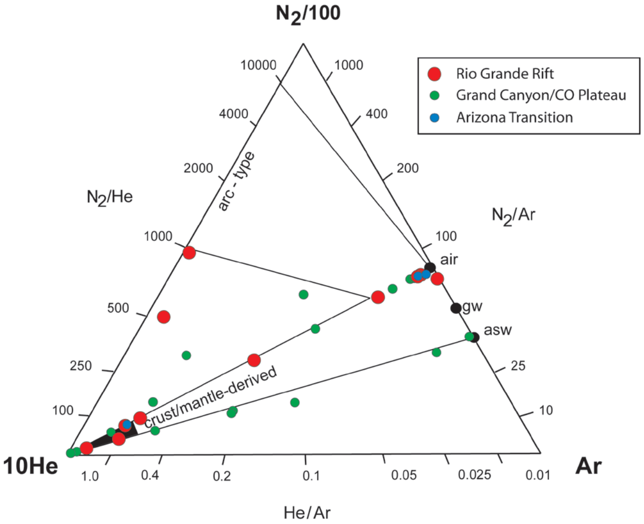

Figure 2. He-Ar-N_2 plot (after Giggenbach, 1992) for travertine-spring gases from the Rio Grande rift, Arizona Transition zone, and the Grand Canyon (Crossey et al., 2006). He values are multiplied by 10 and N_2 is divided by 100 to allow for better viewing of the data, whereas the true gas ratios are preserved on the axes. Fields for crustal and/or mantle-derived gases, air, and air-saturated groundwater (asw) are from Giggenbach (1992).

TABLE 2. SUMMARY OF HELIUM ISOTOPIC RATIOS AND PERCENT MANTLE CONTRIBUTION FOR KEY TECTONIC PROVINCES OF WESTERN NORTH AMERICA

Tectonic region	R_A range	Mantle contribution	References
Cascade volcanoes	2.2–8.1	28–100%	Craig et al., 1978; Evans et al., 2004; Welhan et al., 1988
Canadian Cordillera	0.06–6.5	0.5–80%	Clark and Phillips, 2000; Hiyagon and Kennedy, 1992
San Andreas fault zone	0.1–4.0	1–50%	Jenden et al., 1988; Kennedy et al., 1997; Kulongoski et al., 2005; Poreda et al., 1986; Torgersen and Kennedy, 1999
Salton Trough	6.3	75%	Welhan et al., 1988
Walker Lane	0.4–7.0	5–88%	Hilton, 1996; Sorey et al., 1993; Welhan et al., 1988
Great Basin	0.14–0.25	1–3%	Welhan et al., 1988
Colorado Plateau/Rocky Mountains	0.07–0.80	0.5–10%	Caffee et al., 1999; Crossey et al., 2006
Arizona Transition Zone	0.1–1.2	1–14%	Kennedy and van Soest (unpub.); this study
Valles Caldera	0.8–6.0	10–75%	Goff and Janik, 2002
Rio Grande rift	0.09–0.65	1–7%	Kennedy and van Soest unpub.; this study
Bravo Dome gas (NE New Mexico)	0.3–4.3	3–53%	Ballentine et al., 2005; Caffee et al., 1999
Great Plains gas fields	0.06–0.69	0.5–8%	Ballentine et al., 2000, 2001; Ballentine and Sherwood Lollar, 2002; Hiyagon and Kennedy, 1992

MORB-like helium isotopic composition and the crustal, radiogenic helium (0.02 R_A) reservoir (Table 2).

Table 2 summarizes R_A variations in key areas of western North America, calculated in terms of percent of mantle contribution. In active tectonic areas such as the Salton Trough, San Andreas fault, Walker Lane, Cascadia, and the Canadian Cordillera, maximum R_A values are consistently high and imply at least 50% mantle contribution to the helium inventory. Lower values reported in these regions are generally interpreted to be diluted by the crustal He reservoir. Most areas of the east of Walker Lane have much lower R_A values, implying up to 14% mantle-derived helium (notable exception: the Valles Caldera). Somewhat enigmatic are areas of tectonically quiescent sedimentary basins flanking the Cordillera (Alberta basin, Kansas-Hugoton basin, and Bravo Dome) that have elevated R_A values perhaps indicative of long-term storage of mantle-derived helium.

In order to test for a direct relationship between helium isotopic composition and underlying mantle velocity, we plotted all regional helium isotopic values reported herein versus the relative P-wave mantle velocity (Fig. 4). The velocity structure used is a compilation of P-wave tomographic studies and a shear-wave velocity model for the western United States at 100 km (Dueker et al., 2001; Humphreys et al., 2003). The highest R_A values show a good correlation with mantle velocity ($r^2 = 0.83$). The correlation omits points from Cascadia, where the velocity model reflects subduction of the oceanic slab, not the state of the North American lithosphere. Points with lower R_A in each velocity domain (resolved to 0.25%) are also not included in the correlation because these data can be explained by admixture of mantle and crustal He.

MOVEMENT OF MANTLE-VOLATILES THROUGH MAGMATISM AND ACTIVE FAULTING

There is evidence that mantle volatiles can be precursors to more obvious tectonic or magmatic activity. For example, cold springs at Three Sisters, Oregon, show anomalously high CO_2 and R_A values (Evans et al., 2004), and forest kills at Mammoth Mountain were correlated with increased CO_2 emissions linked to changes in magmatic activity (Evans et al., 2002; Farrar et al., 1995). Several lines of evidence can also be used to infer that volatiles are conveyed from the middle crust to the surface via seismogenic processes: the association of travertine and travertine-depositing springs with basement-penetrating faults suggests that the faults serve as fluid conduits and that spikes in mantle helium exist in active springs along fault zones (e.g., San Andreas, Walker Lane); monitoring at tectonically active areas shows that the movement of CO_2 and mantle helium correlate with seismicity. Helium isotopes showed a rapid response to earthquake swarms at Mammoth Mountain; increases in mantle contribution correlate to magmatically driven seismic swarms (e.g., Sorey et al., 1993). Also, Kulongoski et al. (2005) concluded that mantle helium found in groundwaters of the Morongo Basin east of the San Andreas fault moved via deeply penetrating faults. They cite no evidence for active magmatism in the area and speculate that episodic seismicity and associated hydrofracturing drive volatile transfer from the mantle to the crust.

LINKING MANTLE HELIUM TO TECTONICS

It is generally agreed that helium flux from the mantle is most pronounced during partial melting (Ballentine and Burnard, 2002) and that movement through the crust is aided by fracturing (e.g., Torgersen and O'Donnell, 1991), which is supported by the existence of mantle helium up to MORB values at volcanic centers and the association of mantle helium with travertine springs and faults (e.g., Kulongoski et al., 2005). However, the presence of mantle helium in the Great Plains and Alberta Basin (Fig. 1), areas without recent tectonism and with mantle seismic velocities that preclude significant partial melt in the mantle (Humphreys and Dueker, 1994), is enigmatic. This observation has led to the interpretation that mantle volatiles trapped in some gas reservoirs are millions of years old (e.g., Ballentine et al., 2001). Ballentine et al. (2001) argue that mantle helium and CO_2 present in parts of the Permian Basin were stored for ~300 m.y. and were derived from magma degassing associated with foreland extensional basins related to the Marathon thrust belt. However, the elevated R_A values in other basins of the Great Plains do not correlate to nearby areas of magmatism nor to present-day partially molten mantle. Hiyagon and Kennedy (1992) suggest that fluids enriched in mantle volatiles entered these basins due to Laramide-to-recent compressional tectonics, a hypothesis supported by paleomagnetic studies (Enkin et al., 2000). Another explanation for the presence of mantle helium is that hydration above the Farallon slab during the Laramide orogeny may have introduced mantle volatiles that were stored in the lithosphere (Humphreys et al., 2003).

Abrupt (km- to 10-km-scale) mantle velocity transitions between velocity domains have been imaged by recent detailed tomographic studies (Dueker et al., 2001; Gao et al., 2004). The extent to which these transitions represent old compositional provinces, such as across paleosuture zones (Dueker et al., 2001; Karlstrom et al., 2005) versus active small scale asthenospheric convection (e.g., Gao et al., 2004), remains a first-order problem in understanding the western U.S. mantle and lithosphere-asthenosphere interactions. Perhaps the velocity transition beneath the western Great Plains (Fig. 1, light blues to greens, marked by white dashed line) is linked to the presence of mantle volatiles in basins, reflecting convective heat loss as the mantle starts to heat but before it melts. Mantle-derived helium may be a harbinger of mantle tectonism, hinting at slow eastward warming and subsequent dismemberment of the old, cold keel of the North American plate.

LINKS BETWEEN MANTLE DEGASSING AND WATER QUALITY

During the ascent of fluids carrying mantle-derived volatiles, rock-fluid interaction occurs, as does mixing between shallow groundwater, basement fluids, and sedimentary basin brines. Evidence for mixing along flow-paths exists in the geochemical data from travertine-depositing springs in the Rio Grande rift and Colorado Plateau. Data show mixing of saline and dilute end members that potentially relates to local tectonic province (Fig. 2). In the Grand Canyon, radiogenic $^{87}Sr/^{86}Sr$ ratios derived from Precambrian basement show simi-

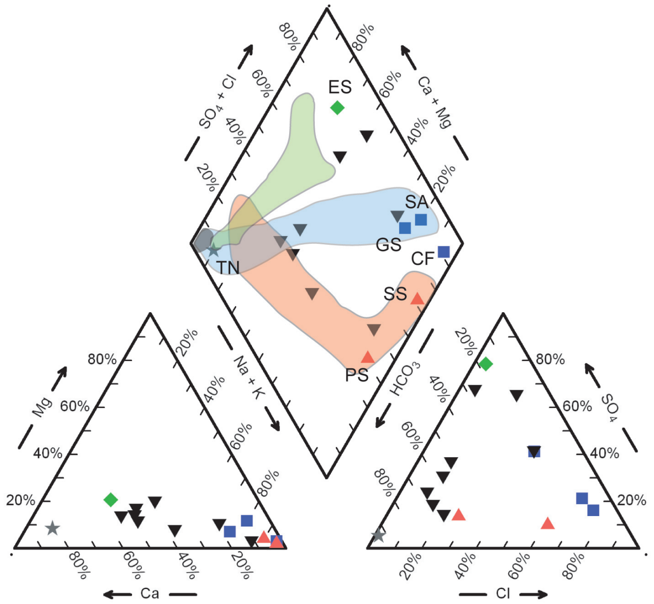

Figure 3. Piper diagram displaying the normalized concentrations in milliequivalents per liter of major cations and anions, which are projected graphically into the quadrilateral (after Piper, 1944). Observed mixing trends from tectonic subprovinces from the Grand Canyon are shown as shaded fields (from Crossey et al., 2006); representative end members from the Rio Grande rift (labels refer to data in Table DR3 [see text footnote 1]) are shown as points. Also included are average water chemistries from hydrologic zones in the Albuquerque basin (black triangles) (from Plummer et al., 2004). Recharge waters (gray + star) appear to be mixing with end members (sulfate—green + diamond; chloride—blue + square; mixed chloride-bicarbonate—red + triangle); groundwaters in the Albuquerque basin fall within these trends.

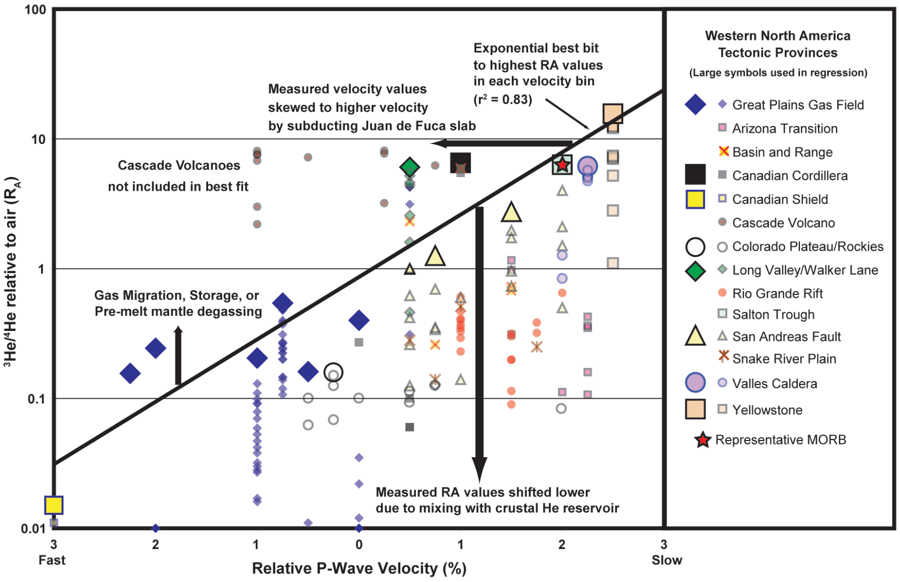

Figure 4. Correlation between relative P-wave mantle velocity at 100 km (Fig. 1) and $^3He/^4He$ ratios (R_A) for the different tectonic provinces of western North America. Note log scale for R_A values. An exponential fit (r^2 = 0.83) was applied using the maximum reported R_A for each mantle velocity domain (resolved to 0.25%). Cascadia is not included in the correlation; see discussion in text. R_A values that plot below the trend line are interpreted to represent the dilution of mantle derived fluids carrying ^3He by the crustal He reservoir. Points lying above the trend line have higher R_A values than would be predicted based on seismic velocity. Reasons may include migration of gases from regions overlying seismically slower mantle, long-term storage of gases, or perhaps degassing of mantle prior to formation of partial melt.

lar mixing trends between deep and shallow waters (Crossey et al., 2006). Thus, these springs are the surface expression of groundwaters altered by complicated mixing pathways as well as the introduction of mantle-derived fluids, and we argue that these processes are occurring within groundwaters throughout the western United States.

Our data show that CO_2-charged groundwaters carrying mantle volatiles are saline, of poor quality, and are elevated in trace metals, such as arsenic (Tables DR2 and DR3 [see footnote 1]). Arsenic contents were found to exceed the U.S. drinking water standard of 10 ppb in some springs (EPA, 2004). These results are similar to travertine-spring data reported from the Grand Canyon, where springs are often saline and have arsenic and uranium contents of several parts per million (Crossey et al., 2006; Monroe et al., 2005). Rio Grande surface water quality degrades from north to south, as traced by increasing salinity, a trend often attributed to effects of agriculture and evapotranspiration. But based on water chemistry and conservative tracers, it has been suggested that the upwelling of deep sedimentary basin brines at the terminus of Rio Grande rift basins is degrading downstream water quality (Phillips et al., 2003). However, our findings show that the mixing of basin brines alone cannot explain the spring geochemistry. Groundwater in the Albuquerque basin varies widely in composition and quality (Plummer et al., 2004), and travertine-depositing springs along the Rio Grande rift encompass the distribution of these water types (Fig. 3), although the travertine springs have much higher total dissolved solids. Rio Grande rift springs also have similar water chemistry to endogenic end members identified in the Grand Canyon (Fig. 3) (Crossey et al., 2006). Endogenic water volumes are small, but their impact on water quality appears to be significant and potentially quantifiable utilizing a suite of geochemical tracers such as trace metals, chloride, and sulfate. The variability observed between endogenic fluid end members and apparent correlation with tectonic province (e.g., sulfate versus chloride rich end members; Fig. 3) is compelling, leading us to hypothesize a mantle source for some of these constituents. However, it is also equally plausible that the mixing trends seen in each tectonic province are a function of different fluid mixing pathways and rock-water interaction, which is the cornerstone of most existing interpretations (e.g., Plummer et al., 2004). Yet, most existing models fail to include deeply derived inputs, such as the CO_2 and He data presented herein, and struggle to explain observations such as highly divergent chemical characteristics within individual aquifers.

CONCLUSIONS

We emphasize three main conclusions: (1) Based on new data, we show that travertine depositing springs (in addition to the hot springs and gas fields that have been the focus of work by others) provide an important record of regional mantle degassing for the western United States. Based on the distribution of travertine and travertine-springs, the entire mantle under the western United States may be heterogeneously degassing. (2) In the context of regional degassing, we combine our new data with previous work to provide a synthesis of helium isotopic data in the western United States and use mantle tomography to provide spatial context to broad scale tectonic processes (Fig. 1). To a first order, regional low mantle velocity in the western United States agrees with the observed regional degassing, evidenced by mantle helium in springs and groundwater (Figs. 1 and 4). (3) By combining water and gas chemistry for the travertine-depositing springs, we show that mantle degassing may be associated with a diffuse degradation of water quality in western U.S. aquifers. Understanding the controls on water quality in this region will continue to be a priority because of increasing population, periodic drought, and rapidly depleting high-quality groundwater resources.

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