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Mantle-derived helium in hot springs of the Cordillera Blanca, Peru: Implications for mantle-to-crust fluid transfer in a flat-slab subduction setting

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ABSTRACT

Fault-controlled hot springs in the Cordillera Blanca, Peru provide geochemical evidence of mantle-derived fluids in a modern flat-slab subduction setting. The Cordillera Blanca is an ~200 km-long mountain range that contains the highest peaks in the Peruvian Andes, located in an amagmatic reach of the Andean arc. The Cordillera Blanca detachment defines the southwestern edge of the range and records a progression of top-down-to-the-west ductile shear to brittle normal faulting since ~5 Ma. Hot springs, recording temperatures up to 78 °C, issue along this fault zone and are CO₂-rich, near neutral, alkaline-chloride to alkaline-carbonate waters, with elevated trace metal contents including arsenic (\leq 11 ppm). Water $\delta^{18}O_{SMOW}$ (-14.2 to -4.9%) and δD_{SMOW} (-106.2 to -74.3%), trends in elemental chemistry, and cation geothermometry collectively demonstrate mixing of hot (200–260 °C) saline fluid with cold meteoric water along the fault. Helium isotope ratios (3 He/⁴He) for dissolved gases in the waters range from 0.62 to 1.98 R_A (where R_A = air 3 He/⁴He), indicating the presence of up to 25% mantle-derived helium. Given the long duration since, and large distance to active magmatism in the region, and the possible presence of a tear in the flat slab south of the Cordillera Blanca, we suggest that mantle helium may originate from asthenosphere entering the slab tear, or from the continental mantle-lithosphere, mobilized by metasomatic fluids derived from slab dehydration.

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1. Introduction

Thermal springs in continental arc settings provide a direct window into the source and cycling of aqueous fluids and volatiles in subduction zones. Geochemical and isotopic data from hot springs and fumaroles can preserve a modern record of slab- and mantle-derived fluid sources (e.g., Sano and Marty, 1995; Fischer et al., 2002; Hilton et al., 2002; Zimmer et al., 2004) in contrast to information inferred from geochemical studies of exhumed arc rocks and xenoliths that constrain the nature of fossil fluids in subduction zones (e.g., Scambelluri and Philippot, 2001; Lee, 2005). Geophysical imaging at these margins, when available, can offer complementary information on the geometry of the subduction zone and possible locations of melts and/or other fluids. Such geophysical studies identify present-day fluids as well as structures that may control their distribution and migration through the crust to the surface, such as deep crustal faults, detachments near

* Corresponding author. *E-mail address:* dennis.newell@usu.edu (D.L. Newell). the brittle–ductile transition, and fracture meshes in the lower ductile crust (Zandt et al., 2003; Wannamaker et al., 2009; Meqbel et al., 2014).

Flat slabs represent a distinct type of low-angle subduction characterized by an absence of active continental arc magmatism and thus are unique settings to investigate subduction zone fluids. Most continental arcs involve normal (steep) subduction, slab dehydration, and release of fluids to the overlying asthenospheric wedge that leads to magmatism (e.g., Peacock, 1990). In contrast, direct contact between the down-going oceanic and overlying lithosphere during "flat-slab" subduction eliminates the asthenospheric wedge and inhibits melting and arc volcanism (Pilger, 1981). Slab-to-lithosphere fluid (water and volatiles) transfer in this setting persists and is invoked as an important mechanism for fertilizing and altering the rheology of the continental lithosphere (e.g., Humphreys et al., 2003; Lee, 2005; Hoke and Lamb, 2007; Jones et al., 2015). Approximately 10% of present-day convergent margins exhibit low-angle subduction segments (Gutscher et al., 2000); however, only three of these, located along the Andean Arc, are described as well-established flat slabs (Pérez-Gussinyé et al., 2008). Additionally, recent geophysical investigations of the Peruvian flat slab suggest that part of the slab is tearing and the downgoing plate is resuming a normal steep subduction angle (Antonijevic et al., 2015),







indicating more heterogeneity in the slab geometry than previously documented in other modern flat slabs. To date, little geochemical data is available on the nature of aqueous fluids and volatiles in modern flat-slab settings, making it challenging to evaluate the significance of fluids in this phase of the subduction cycle.

Mantle and slab-derived volatiles released to the continental lithosphere are subject to significant modification by crustal processes such as mixing, degassing, and mineralization (e.g., van Soest et al., 1998; Ray et al., 2009). Thus, most studies of volatile geochemistry at convergent margins focus on active arcs and target thermal systems proximal to volcanic centers that display relatively low crustal modification to distinguish and characterize fluids derived from the mantle wedge and subducting slab. Applying these geochemical tools to thermal systems at arcs that are amagmatic, such as present-day flat-slab settings, is particularly challenging owing to the potential for significant crustal overprinting. However, we suggest that by carefully addressing the crustal geochemical overprint, it is possible to effectively interpret volatile cycling in settings lacking active magmatism.

In this contribution, we present new He isotope (³He/⁴He) results from thermal springs issuing along a 200-km-long normal fault that bounds the highest peaks of the Peruvian Andes in the Cordillera Blanca. These data, in combination with supporting geochemical and stable isotope analyses, provide direct evidence for present-day circulation of mantle-derived fluids in an amagmatic flat-slab setting. We explore the possible origins of these fluids including mobilization of mantle He from the continental mantle lithosphere by slab-derived metasomatic fluids, and asthenosphere-derived fluids associated with the inferred tear in the Peruvian flat slab (Antonijevic et al., 2015) which may extend northward under the Cordillera Blanca.

2. Geologic setting

2.1. Subduction zone style and arc volatiles in the Andes

Shallowing of the subducting slab and eventual establishment of a flat slab are postulated to have occurred along several segments of the Andean arc, supported by observations of the eastward (down dip) migration and eventual cessation of magmatism (e.g., Hoke and Lamb, 2007), the presence of adakitic magmatism (Kay and Abbruzzi, 1996), and by geophysical imaging of present-day slabs (Gutscher et al., 2000; Antonijevic et al., 2015). Presently, there are three segments of flat-slab subduction that are characteristically amagmatic, separated by segments with steeper 'normal' subduction angles associated with active magmatism (Ramos and Folguera, 2009) (Fig. 1). These flat-slab segments include the Bucaramanga segment north of 5°N (not shown), the Peruvian segment between 5 and 15°S, and the Chilean segment located from 27 to 33.5°S (Gutscher et al., 2000).

Recent 3D geophysical investigations of the Peruvian flat slab suggest that part of the slab north of the Nazca ridge may be sinking and tearing today (Fig. 1 contours), possibly capturing a transition back to normal steep subduction (Antonijevic et al., 2015). The northern end of these investigations is located approximately 1–2° south of the Cordillera Blanca, so it is unknown if this tear extends beneath our study region. Prior 2D seismic tomography of the Peruvian flat slab noted a 'sag' region between the Nazca ridge and Inca Plateau (Gutscher et al., 2000), broadly beneath the Cordillera Blanca, but their survey lacks the resolution to resolve a tear in the slab.

The transition between steep and flat-slab subduction zones in the Andes is exemplified in the Altiplano–Puna plateau (Fig. 1). Here, past normal arc magmatism shifted to an amagmatic flat-slab phase at ~35 Ma that persisted for approximately 10 million years before returning to steeper subduction and the magmatic activity observed today (Hoke and Lamb, 2007). During flat-slab subduction, dehydration of the slab is postulated to have fertilized and weakened the overlying lithosphere leading to continental mantle lithosphere delamination and uplift of the plateau (Hoke and Lamb, 2007). Antonijevic et al.

(2015) document a potential present-day transition from flat to steep subduction in the Peruvian segment, and postulate that this tear initiated due to the loss of buoyancy in the slab following the passing of the Nazca ridge as it subducted obliquely beneath South America. However, it is unknown if similar geodynamic processes impacted the Altiplano– Puna plateau region in the past, and it is unknown what role fluids may have in the observed foundering of the Peruvian slab.

Detailed volatile studies constrain the source of Andean arc fluids along the magmatically active segments of Ecuador, Bolivia, and Chile (Fig. 1, Table S1). Helium isotope ratios track the mixing of upper mantle-derived helium (8 R_A, the measured ³He/⁴He ratio reported relative to the air ratio of 1.4×10^{-6}) and radiogenic He characteristic of the crust (0.02–0.1 R_A) (Ozima and Podosek, 1983). The largest mantle contributions are found at thermal features associated with active volcanoes. However, significant He isotope ratio variability between thermal features is observed due to admixtures between meteoric groundwater and crustal contamination of mantle-derived melts. In contrast, studies reporting helium isotope ratios and/or other volatile data from thermal springs within the flat-slab segments of the Andean arc are very limited. Hilton et al. (1993) report 1.45 RA from Baños Toros located in the Chilean flat-slab segment (Fig. 1). Assuming mixing between crustal (0.02 R_A) and asthenospheric mantle (8 R_A) helium sources, this equates to approximately 18% mantle-derived helium. Helium isotope ratios are not reported for thermal springs along the Bucaramanga or Peruvian flat-slab segments. Peruvian Geological Survey reports (e.g., Huaccan, 2000) provide elemental chemistry from hot springs throughout Peru, but no isotopic or volatile data are reported.

2.2. The Cordillera Blanca

The Cordillera Blanca (CB) massif is a northwest-trending range with numerous peaks between 5 and 6.7 km in elevation (Fig. 2). It is composed primarily of the CB batholith, which was emplaced into shallow crustal levels (~3 kbar) at 8.2 \pm 0.2 Ma (McNulty et al., 1998; McNulty and Farber, 2002). A 200-km-long extensional detachment fault that bounds the southwestern margin of the range (Fig. 2) preserves deformation during top-to-the-west sense of shear (McNulty and Farber, 2002). Together with steeper, brittle normal faults, these features have accommodated syn-convergent extension in the highest elevations of Peru since ~5.4 Ma (Giovanni et al., 2010). Hot springs issue along the Cordillera Blanca detachment fault system. Two springs emanate from the main detachment fault near the northern end of the CB, and others issue from mapped or inferred faults in the hanging wall of the detachment (Fig. 2).

3. Methods and materials

3.1. Water and dissolved gas sampling

Samples were collected as close to the spring sources as possible. Water samples were collected in 60 and 125 ml high-density polyethylene bottles. Samples for carbonate alkalinity and anion analysis were collected unfiltered with no headspace. Samples for cation analysis were field filtered using 0.45 µm syringe filters and were preserved with concentrated trace metal grade HNO₃. Samples for stable oxygen and hydrogen isotope ratio determination were collected in 12 ml glass septa vials with no headspace. Water or gas samples for He isotope analysis were collected in 12 in. × 3/8 in. OD (~30 cm × 0.95 cm) copper tubes that were sealed with refrigeration clamps after purging with spring waters/gases. Gas splits for carbon stable isotope analysis of total dissolved CO₂ were prepared during the gas purification and extraction procedure used for helium isotopes. He and CO₂ collection protocols follow closely those described in Hilton et al. (2002).



Fig. 1. Andean arc showing current flat slab segments, the locations of subducted oceanic ridges and plateaux (Gutscher et al., 2000), and slab depth contours (km) based on earthquake depths (Antonijevic et al., 2015) along the present-day location of the Nazca ridge. ³He/⁴He results (air-corrected) from this study are shown in the box compared to a compilation of published data from the Andes (see Table S-1 for data and citations). The extent of the Altiplano–Puna plateau is based on Allmendinger et al. (1997).

3.2. Chemical and isotopic analysis

Water temperature, pH and conductivity were measured using an Oakton pH/cond/T portable meter. Major and trace element concentrations in spring waters were analyzed at the Utah State University (USU) Water Research Laboratory using a Dionex Ion Chromatograph (anions) and Agilent ICP-MS (cations). Total alkalinity was measured by manual colorimetric titration. The δ^{13} C values of the total dissolved CO₂ were measured at the Scripps Institution of Oceanography using a ThermoFinnigan DeltaPlus isotope ratio mass spectrometer (IRMS). Results are reported in per mil (‰) relative to the PDB scale with an uncertainty of ±0.1‰ based on repeat analysis of NBS carbonate standards. The δ^{18} O and δ D of water samples were determined at the USU Department of Geology Stable Isotope Laboratory using a ThermoScientific Delta V Advantage IRMS with a GasBench II interface. Oxygen and hydrogen isotope ratios were



Fig. 2. Hot springs of the Cordillera Blanca investigated during this study. Results shown include measured temperature, the Na–K temperature estimates in parenthesis, the air-corrected ³He/⁴He (R_C/R_A) values, and As concentration (ppb). Surface geology modified from Giovanni et al. (2010).

determined by continuous flow IRMS using CO₂ equilibration and H₂ equilibration with Pt reduction, respectively. Results are reported in per mil (‰) relative to SMOW based on in-house standards. $\delta^{18}O$ and δD uncertainties were \pm 0.06‰ and \pm 2.0‰, respectively, determined by repeat measurements of internal water standards calibrated to VSMOW and VSLAP, and replicate sample analyses.

Helium isotope ratios were measured at the Fluids and Volatiles Laboratory at Scripps Institution of Oceanography using gas extraction, purification, and analytical procedures described in Shaw et al. (2003). Measured ³He/⁴He ratios (R) are reported relative to air (R_A) which has a value of 1.4×10^{-6} (Ozima and Podosek, 1983). These ratios are corrected for atmospheric contamination of dissolved helium using ((R / R_A * X) - 1) / (X - 1) where X is the air-normalized He/Ne ratio multiplied by β_{Ne}/β_{He} , where β_{Ne} and β_{He} are the Bunsen solubility

coefficients for neon and helium in pure water (Weiss, 1971; Hilton, 1996) at a temperature of 15 °C. Resulting air corrected values are reported as R_C/R_A in Table 1.

4. Results and discussion

4.1. Geochemistry of Cordillera Blanca hot springs

4.1.1. Aqueous geochemistry and geothermometry

The 8 hot spring locations investigated here range in temperature, pH, and specific conductance with values from 38 to 78 °C, 5.0–6.6, and 700–23,000 μ S, respectively (Fig. 2, Table S2a). For comparison to the hot springs and to represent meteoric recharge infiltrating along the fault, cold springs, streams, and lakes were also sampled and

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Cordillera Blanca hot spring $^{3}\text{He}/^{4}\text{He}$ ratios, and carbon isotope ratios of CO_2. a, b, c, d

Spring (Baños)	Sample ID	R/R_A	X ^a	$\begin{array}{c} R_{C}/R_{A}{}^{b} \\ (\pm 1\sigma) \end{array}$	$\frac{CO_2/^3He}{(\times 10^{12})}$	[⁴ He] _m (cm ³ STP/gH ₂ O)	[⁴ He] _c ^c (cm ³ STP/gH ₂ O)	δ ¹³ C _{CO2} ^d (‰) PDB
Olleros	CB05	1.05	5.43	1.06 ± 0.24	10.3	7.08E-08	5.77E-08	-7.82
Olleros	CB06	1.8	36.9	1.82 ± 0.55	39.1	9.89E-09	9.63E-09	-10.30
Merced	CB07	0.7	5.07	0.62 ± 0.17	27.3	2.40E-08	1.93E-08	-6.28
Chancos	CB08a	1.24	3.65	1.33 ± 0.31	4.22	4.18E-08	3.03E-08	-9.06
Chancos	CB08b	0.9	3.51	0.85 ± 0.24	19.2	3.32E-08	2.38E-08	-9.72
Monterrey	CB09	1.27	13.2	1.30 ± 0.30	2.44	1.10E-07	1.02E - 07	-9.96
Huancarhuaz — g	CB11g	1.95	36.7	1.98 ± 0.40	0.269	-	-	-14.49
Huancarhuaz	CB11	1.66	5.28	1.81 ± 0.46	6.85	7.08E-08	5.77E-08	-10.75
Aquilina	CB14	1.78	53.7	1.79 ± 0.40	0.609	1.94E-07	1.90E-07	-10.74

g – gas sample; all others water samples.

 $^{a} \overline{X} = (^{4}\text{He}/^{20}\text{Ne})_{\text{measured}} / (^{4}\text{He}/^{20}\text{Ne})_{\text{air}} \times \beta \text{Ne}/\beta \text{He}; \beta = \text{Bunsen coefficient from Weiss} (1971): groundwater recharge temperature of 15 °C.$

^b R_c/R_A is the air-corrected He isotope ratio = [$(R_m \land R_A \times X) - 1$] \land (X - 1). R_m is measured ³He/⁴He ratio divided by the ³He/⁴He in air ($R_A = 1.4 \times 10^{-6}$).

^c Dissolved He concentrations are air-corrected where $[He]_{c} = ([He]_{m} \times (X - 1)) / X$.

 $^d~\delta^{13}C$ errors are estimated at $\pm 0.10\%$ based on repeat NBS standard runs.

analyzed during this study. Most thermal springs were degassing (bubbling) at their source (although this study focused on dissolved gas samples), and exhibited travertine accumulations. The springs emanate along an ~200 km NW–SE transect with flow paths through different geological units (phyllites, carbonates, and igneous rocks), and the aqueous chemistry can be explained by a binary mixture of an alkaline-chloride type saline groundwater with low salinity Ca–Na bicarbonate waters (Table S2b, Fig. S1). Local meteoric waters



Fig. 3. A) Cross plot of dissolved HCO₃⁻ versus dissolved Cl⁻. These data are interpreted as representing mixing between saline and dilute end-members. B) δ^{18} O and δ D of CB hot springs and local, cold meteoric water from this study and Mark and McKenzie (2007). Local meteoric water lines and *x* are defined by meteoric waters from the glaciated Cordillera Blanca (w, r² = 0.75) and the Rio Santa and non-glaciated Cordillera Negra (x, r² = 0.98); GMWL – global meteoric water line (Craig, 1961). CB hot springs fall on trend *y* (slope 3.2, r² = 0.85). Included on the plot are the isotope compositions of "metamorphic fluids" (Sharp, 2006) and 'andesite water' (Giggenbach, 1992).

(e.g., Lochocota, Fig. S1) are Ca–Na bicarbonate type. Dissolved bicarbonate also follows this binary mixing trend (Fig. 3A). Notable trace elements include iron, arsenic (up to 10,800 ppb), thallium, antimony, and zinc (Table S2c).

Near-neutral, alkaline-chloride to alkaline-bicarbonate waters can provide reliable geothermal reservoir temperatures using Na–K and K–Mg geoindicators depending on the degree of equilibration between the water and the host rock mineralogy (Giggenbach, 1988). CB hot springs plot in the "partial equilibration" field of a ternary diagram comparing Na–K and K–Mg temperature calculations with estimates ranging from 200 to 275 and 72–174 °C, respectively (Fig. 4). For these samples, the Na–K results provide the best estimate of the higher temperature history of fluids; whereas, the K–Mg results are unreliable because they are susceptible to re-equilibration due to cooling and mixing with lower temperature ground waters. The results form a trend between partially equilibrated hot fluids and immature ground waters (Fig. 4), further supporting the interpretation that the hot springs represent mixing between deeply circulated saline fluids and shallow groundwater.

4.1.2. Stable isotope geochemistry (δ^{18} O, δ D, δ^{13} C and 3 He/ 4 He)

Oxygen (δ^{18} O) and hydrogen (δ D) stable isotope ratios from the 8 hot spring locations range from -14.2 to -4.9 and -106.2 to -74.3% (SMOW), respectively (Fig. 3B, Table S3). We also report new δ^{18} O and δ D values from 10 locations (streams, lakes, cold springs)



Fig. 4. Ternary diagram combining the Na–K and K–Mg geothermometers (modified from Giggenbach, 1988). The two thermometers intersect at the same temperature along the 'Full Equilibration Line'. The Baños Olleros, Huancarhuaz, and Monterrey samples plot on the 260 °C Na–K isotherm within the 'Partial Equilibration' field. Baños Aquilina falls on the 200 °C Na–K isotherm.

in the Cordillera Blanca representative of local meteoric water located between 2600 and 4740 m above sea level (Fig. 3B, Table S3). These meteoric water values are combined with those reported by Mark and McKenzie (2007) to define two local meteoric water lines (LMWLs) (Fig. 3B LMWLs w and x). Meteoric waters draining predominantly glaciated portions of the CB define a LMWL (w) with a slope of 6.7. Meteoric waters (cold springs, streams) from the Cordillera Negra (non-glaciated) and the Rio Santa (Fig. 2) constrain a LMWL (x) with a shallower slope of 5.9.

The hot spring samples have stable isotope ratios that vary from similar to local meteoric water (either LMWL w or x) to significantly enriched in ¹⁸O and ²H with respect to LMW. Considered as a data set, the hot spring δD and $\delta^{18}O$ values form a linear trend (slope = 3.2) (Table S3, Fig. 3B y). This trend could be due to enrichment from a kinetic isotope effect driven by surface evaporation (Craig et al., 1963). In geothermal systems the δ^{18} O can be increased by high temperature exchange between meteoric water and silicate bedrock (Craig, 1963), and increases in both δ^{18} O and δ D can be due to high temperature steam separation at depth (Giggenbach and Stewart, 1982), or mixing with brines equilibrated with metamorphic or igneous rocks at high temperatures (Sheppard, 1986). Near surface evaporation is unlikely to be important because these groundwater samples were collected at their discharge point at the surface; however, this process cannot be completely ruled out. Groundwater exchange with silicate bedrock causing increases in δ^{18} O would result in horizontal pathways from meteoric isotope compositions that are not represented in the current data set (Fig. 3B, e.g., path z). Steam separation at depth has been observed in other geothermal systems to produce similar trends (slope < 3.6) in δ^{18} O and δ D (Giggenbach and Stewart, 1982; Giggenbach, 1992). Groundwater mixing with isotopically distinct brines is also consistent with observed trends' in major ion chemistry (e.g., Fig. 3A). Thus, the plausible origins of the trend in hot spring isotope O and H ratios are mixing between meteoric recharge and brine, steam separation at depth, and possibly evaporation in the near surface.

Carbon stable isotope ratios of the total dissolved CO_2 ($\delta^{13}C_{CO2}$) range from -10.75 to -6.28‰ (Table 1, Fig. 5B). At Baños Huancarhuaz, the δ^{13} C values of both the total dissolved CO₂ and exsolving CO₂ gas were measured at -10.75 and -14.49% (Table 1), respectively. This difference is larger than expected for equilibrium fractionation between these species at the temperature and chemistry of this hot spring (3.74 vs. ~2.1‰), likely indicating some disequilibrium during degassing. Air-corrected ³He/⁴He ratios of dissolved gases in the springs vary from 0.62 to 1.98 R_A (Table 1). Using the highest aircorrected ${}^{3}\text{He}/{}^{4}\text{He}$ (1.98 R_A) value, this equates to ~25% mantlederived helium assuming a two-component mixture of a MORB mantle source (8 R_A) and crustal He (0.02 R_A) (Fig. 5A). This estimate would increase to 30-50% if helium originates from the continental mantle lithosphere (4–6 R_A) (Dodson et al., 1998; Gautheron and Moreira, 2002). Along volcanic arcs, the $CO_2/{}^3$ He ratio is used along with $\delta^{13}C_{CO2}$ to constrain the CO₂ source (Sano and Marty, 1995), and with ³He/⁴He to document mixing between mantle and crustal volatiles (O'Nions and Oxburgh, 1988). CB hot spring $CO_2/{}^3$ He ratios of dissolved gases vary



Fig. 5. A) ³He/⁴He (R/R_A, uncorrected for air contribution) vs. He/Ne mixing diagram showing the CB hot springs (diamonds) compared to Baños Toros in the Chilean flat slab, and other Andean arc data (Table S-1). End members include ASW (air saturated water; 1 R_A, He/Ne = 0.32), crust (0.02 R_A, He/Ne > 1000), and mantle (8 R_A, He/Ne > 1000). B) $CO_2/^3$ He vs. $\delta^{13}C_{CO2}$ mixing diagram between mantle, crustal sedimentary (organic), and crustal carbonate-derived CO₂ end-members (after Sano and Marty, 1995). CB hot springs (diamonds) plot as a mixture of crustal sedimentary and carbonate sources with minor mantle contributions. Baños Aquilina (Aq), Baños Huancarhuaz (Hc), and Baños Olleros (Ol) are highlighted to guide discussions in text. Open system degassing trajectories (dashed arrows, with percent degassed shown) originate from Aq showing how degassing at 78 and 180 °C modifies the CO₂/³He ratios and $\delta^{13}C_{CO2}$ values of residual dissolved gases (see text for details of degassing model). Also shown are trajectories originating from Aq for the residual fluid composition due to progressive calcite precipitation at 78 and ~180 °C. Hc_w and Hc_g are dissolved gas in water and free gas samples, respectively. C) ³He/⁴He (R_c/R_A) vs. CO₂/³He for CB hot springs (diamonds). Also shown are binary mixing curves between a mantle end-member (8 R_A and 2 × 10⁹) and a range of crustal end-members (0.02 R_A, and CO₂/³He 10¹⁰-10¹⁵). The horizontal dashed line from Aq to Ol indicates how degassing impacts CO₂/³He ratios. D) CO₂/³He vs. dissolved He showing inverse relationship in CB hot springs data (diamonds). Open system degassing from Aq for 78 and 180 °C are shown as dashed lines (see text for details of model). Also included on panels B, C, and D are representative data from active arcs including the Andes (Ecuador, Northern Chile, Central Chile, and the Chile Southern Volcanic Zone – SVZ), Indonesia, and Lesser Antilles (see Table S1 for data and citatir

from 6.09×10^{11} to 3.91×10^{13} (Table 1), and when combined with the $\delta^{13}C_{CO2}$ suggest a carbon source dominated by mixing of sedimentary (organic and carbonate) crustal sources (Fig. 5B). For example, applying a three-component mixing model using upper mantle ($\delta^{13}C = -6.5\%$, $CO_2/^3He = 2 \times 10^9$), crustal organic sedimentary (-20% and 1×10^{13}), and crustal carbonate (0%, 1×10^{13}) end-members (after Sano and Marty, 1995), the carbon at Baños Aquilina (Aq) is a mix of 54% organic sediments, 46% carbonates, and ~0.3% mantle-derived carbon. The ³He/⁴He and $CO_2/^3$ He ratios of CB hot springs plot on binary mixing curves between a mantle end member ($8 R_A$, 2×10^9) and a range of crustal end members ($0.02 R_A$, $\sim 10^{13}$ –> 10^{15}) (Fig. 5C). For a comparison to active volcanic arcs, published data from locations along the Andean Arc (Ecuador, and northern, central, and southern volcanic zones of Chile), Indonesia, and the Lesser Antilles are also plotted in Fig. 5 (Table S1).

4.2. Modification of volatile geochemistry in the crust

The above analysis of ${}^{3}\text{He}/{}^{4}\text{He}$, CO₂/ ${}^{3}\text{He}$, and $\delta^{13}\text{C}_{\text{CO2}}$ (Fig.5A–C) assumes that mixing between mantle and different crustal reservoirs is the only process controlling the dissolved gas ratios. However, mixing does not fully explain the inverse relationship displayed in Fig. 5D or the very low helium concentrations observed in some samples. In addition to mixing, modification of dissolved gas and stable isotope ratios due to degassing, gas dissolution, temperature variability, and mineralization is observed at active volcanic arcs (van Soest et al., 1998; Shaw et al., 2003; Ray et al., 2009) and a variety of continental settings (Gilfillan et al., 2009; de Leeuw et al., 2010). Similar inverse correlations between $CO_2/^3$ He and dissolved He at some active arc segments (Fig. 5D: SVZ Chile, Indonesia, and Lesser Antilles) has been interpreted as a degassing signal. Solubility differences between He and CO₂ lead to preferential He loss during degassing, resulting in the higher $CO_2/^3$ He ratios correlating with lower total dissolved He (van Soest et al., 1998). Degassing and loss of CO₂ in the geothermal system should also change the residual total dissolved CO_2 to higher $\delta^{13}C$ values, depending on the temperature, and the coupled variability in $CO_2/^3$ He and δ^{13} C observed in some active arc settings is attributed to both mixing and degassing (Fig. 5B). It is important to note that extensive carbonate mineralization during fluid ascent would lower the $CO_2/^3$ He ratio, have no impact on dissolved He, and depending on temperature, result in trends to lower residual $\delta^{13}C_{CO2}$ values.

To evaluate the impact of open system degassing on the observed Cordillera Blanca hot spring $CO_2/^3$ He versus $\delta^{13}C_{CO2}$ and the $CO_2/^3$ He versus He relationships (Fig. 5B, D), we have applied the Rayleigh fractionation approach used in previous studies addressing degassing in geothermal systems related to volcanic arcs, active faults in continental settings, and at natural CO_2 gas domes (Gilfillan et al., 2009; Ray et al., 2009; de Leeuw et al., 2010). Our approach is summarized below:

Fractionation of the $CO_2/^3$ He ratio during progressive degassing is calculated using the following Rayleigh equation (e.g., Hilton et al., 1998; de Leeuw et al., 2010):

$$(\mathrm{CO}_2/\mathrm{He})_f = (\mathrm{CO}_2/\mathrm{He})_i \times \mathrm{F}^{(\alpha-1)} \tag{1}$$

where *i* and *f* indicate the starting (initial) and residual CO₂/He of the dissolved gases in the hot spring water for some fraction (F, from 1 to 0) of the total helium remaining in solution. Alpha (α) is the temperature dependent fractionation factor between He and CO₂, and is the ratio of their solubility constants in water (He/CO₂). The solubility constant (Bunsen coefficient) for He in water at the desired temperature is calculated using Weiss (1971). We use the tabulations by Duan and Sun (2003) for the solubility of CO₂ in water as a function of temperature and pressure. Degassing fractionation between ³He and ⁴He is not considered due to the negligible solubility difference between these isotopes (Weiss, 1970), and the lack of inverse correlation between ³He/⁴He and He in this data set (Fig. S2).

Fractionation of carbon stable isotope ratios will also occur during progressive loss of $CO_{2(g)}$ through either degassing or through the precipitation of calcite, and can be modeled using the following form of the Rayleigh equation (Sharp, 2006).

$$\delta^{13}C_f = \delta^{13}C_i + (1000 + \delta^{13}C_i)(F^{(\alpha-1)} - 1)$$
(2)

where *i* and *f* indicate the starting and residual δ^{13} C of the total dissolved CO₂ (total dissolved inorganic carbon, TDIC) in the spring water for some fraction (F, from 1 to 0) of the total carbon remaining in solution. Alpha (α) is the temperature dependent fractionation factor between CO_{2(g)} and TDIC ($\alpha_{CO2(g)-TDIC}$) or between calcite and TDIC ($\alpha_{CC-TDIC}$). To accurately calculate $\alpha_{CO2(g)-TDIC}$, first the temperature dependent fractionation between the dissolved carbonate species and CO₂(g), ϵ^{13} C_{TDIC-CO2(g)}, is computed (Gilfillan et al., 2009):

$$\epsilon^{13}C_{TDIC-CO2(g)} = x \big(\epsilon^{13}C_{H2CO3(aq)-CO2(g)} \big) + (1-x) \big(\epsilon^{13}C_{HCO3(aq)-CO2(g)} \big) \quad (3)$$

and,

$$\alpha_{\text{CO2-DIC}} = \exp^{(-\epsilon 13C/1000)} \tag{4}$$

where x is the mole fraction of H₂CO₃(aq) and (1 - x) is the mole fraction of HCO₃⁻(aq). The temperature specific $\epsilon^{13}C_{H2CO3(aq)-CO2(g)}$ and $\epsilon^{13}C_{H2CO3(aq)-CO2(g)}$ are calculated using the relationships in Deines et al. (1974). For the pH range (5–6.6) of the hot springs investigated, $CO_3^{2^-}(_{aq})$ is negligible and not considered. The dissolved carbonate speciation is calculated using PHREEQC (Parkhurst and Appelo, 1999) and the measured elemental chemistry, T, and pH of the spring water. The temperature specific fractionation factor between calcite and dissolved CO₂ is calculated using Bottinga (1968).

To evaluate how degassing and calcite mineralization may impact CB hot spring gas and isotope ratios, the spring with the highest dissolved He and lowest $CO_2/{}^{3}$ He ratio (Baños Aquilina, Fig. 5D "Aq") is used to represent the initial (i) condition in Eqs. (1) and (2). Degassing curves for 78 and 180 °C are plotted on Fig. 5B and D. This temperature range is chosen to represent degassing at the measured spring temperature (78 °C) and higher temperatures (and pressures) occurring at depth. The solubility constant ratio (He/CO₂) at 78 °C and 1 bar (surface) is 0.04, and 0.009 at 180 °C and 100 bar (at depth). Note that this range in temperature results only in a slight change in the degassing fractionation of the $CO_2/{}^{3}$ He ratio (Fig. 5D). In contrast, this temperature difference results in a significant difference in the fractionation of carbon isotope ratios during degassing. As shown by the two trajectories on Fig. 5B, at 78 °C the residual $\delta^{13}C_{CO2}$ becomes progressively higher, and at 180 °C there is no fractionation. The horizontal arrow on Fig. 5C is the degassing trajectory for $CO_2/{}^3$ He, assuming no fractionation of the ³He/⁴He ratio. Fig. 5B also shows calculated trajectories starting at Aq due to calcite precipitation. $CO_2/^3$ He ratios decrease due to loss of CO₂ to calcite, and below ~180 °C, carbon stable isotope ratios will decrease.

Based on this analysis, degassing provides a plausible explanation for some but not all of the trends in the data, and calcite mineralization results in trajectories that are inconsistent with the observed data. To aid in this discussion, three hot springs are circled on Fig. 5B–D: Baños Aquilina (Aq), Huancarhuaz (Hc), and Olleros (Ol), which exhibit the highest and nearly identical ³He/⁴He ratios (1.79 to 1.98 R_A), the lowest and similar $\delta^{13}C_{CO2}$ (-10.75 to -10.30%), but highly variable $CO_2/^3$ He ratios and dissolved He contents (6.09×10^{11} and 190 ncm³ STP/gH₂O to 3.91×10^{13} and 9.63 ncm³ STP/gH₂O). Fig. 5B shows that degassing from the composition measured at Aq at high temperature (180 °C) can explain the range of $CO_2/^3$ He and similar δ^{13} C; however, lower temperature degassing (e.g., 78 °C) would result in progressively higher δ^{13} C in Hc and Ol, which is not observed. Also, degassing from Aq to produce the $CO_2/^3$ He ratios at Hc and Ol (Fig. 5C) provides a more plausible explanation than interpreting this distribution as mantle mixing with 3 very different crustal reservoirs (CO₂/³He ~10¹³ to >10¹⁵). Finally, the inverse relationship between CO₂/³He and He and large range in dissolved He (Fig. 5D) is generally supported by degassing. However, the CO₂/³He ratios for Hc and Ol are higher than predicted by Rayleigh degassing alone from Aq. CO₂ addition along flow paths, or degassing from a different initial condition could explain this variability.

Compared to Aq, Hc, and Ol, the other CB hot springs characterized have a similar range of $CO_2/^3$ He, but have higher and more variable $\delta^{13}C_{CO2}$ (-9.98 to -6.28‰) and lower 3 He/ 4 He ratios (0.62 to 1.33 R_A). The isotope geochemistry of these springs does not conform to a simple degassing scenario from the composition at Aq. Degassing is necessary to produce the observed inverse relationship between $CO_2/^3$ He and He (Fig. 5D), but to explain the additional variability requires CO_2 addition, variable temperatures of degassing, and/or different initial conditions.

4.3. Cordillera Blanca detachment geothermal system

The trend in oxygen and hydrogen isotope ratios, mixing relationships in the major ion chemistry, elevated fluid temperature estimates from geothermometry, and the presence of elevated trace metal contents collectively support a mixture of shallow meteoric recharge with deeply circulated saline ground waters. The distribution of hot springs along the Cordillera Blanca detachment fault zone is likely controlled by the location of individual subsurface hydrothermal groundwater cells and the permeability discontinuities between fault rocks and the host rocks (e.g., Forster and Smith, 1989). Here, we make a first-order estimate of the hydrothermal fluid circulation depth by using the maximum temperatures calculated using hot spring geothermometry (200-275 °C), and applying a geothermal gradient of 25 °C/km to suggest that ground waters may be circulating to depths of 8-11 km. Heat flow in the region is estimated to be low (McNulty and Farber, 2002); however, direct measurements near the Cordillera Blanca detachment are not available. Thus, a locally higher thermal gradient associated with the Cordillera Blanca detachment and batholith is possible and would decrease the fluid circulation depth estimate.

Based on the analysis in Section 4.2, the isotope geochemistry of Baños Aquilina has experienced the least amount of crustal overprinting of the hot springs investigated. Thus, we hypothesize that the ${}^{3}\text{He}/{}^{4}\text{He}$, $CO_2/{}^{3}He$, and $\delta^{13}C_{CO2}$ values measured at this spring are the most representative of fluids moving from depth along the Cordillera Blanca detachment fault zone. In summary, hydrothermal fluids may be advecting from depths of 8-11 km, and carry a mix of mantle and crustal derived helium, with CO₂ derived primarily from carbonate and organic sedimentary crustal sources. The estimated proportions of mantlederived helium and carbon are ~25% and ~0.3%, respectively. These estimates assume asthenospheric end-member compositions for He and C, and that degassing has not impacted the isotope geochemistry of Aq. The proportion of mantle-derived carbon would increase if Aq has been impacted significantly by degassing. Similarly, the fraction of mantle-derived helium would increase if values more consistent with the continental mantle-lithosphere were used as a mixing end-member.

4.4. Mantle helium in Cordillera Blanca detachment hydrothermal fluids

Possible origins for the mantle-derived helium in these hydrothermal fluids include residual fluids in the crust from earlier arc magmatism (>5 Ma), young fluids in the crust derived from a residual, thin mantle wedge or from upwelling asthenosphere accessing a tear in the flat slab (e.g., Antonijevic et al., 2015), or continental lithospheric mantle helium mobilized by metasomatic fluids released from the slab due to dehydration. Each of these possibilities will be considered with respect to available geophysical and geochemical constraints.

The most recent magmatic activity in the CB region was the eruption of a tuff at ca. 5.4 Ma that predates extension in the area, the formation of the Cordillera Blanca detachment fault, and unroofing of the CB massif (Giovanni et al., 2010). Regionally, this period of activity is interpreted to represent the waning stages of arc magmatism during the transition to flat-slab subduction. To evaluate if present-day ${}^{3}\text{He}/{}^{4}\text{He}$ ratios (~1.8 R_A) could be a residual stain from this magmatism, we have calculated the reduction of an original mantle ratio (8 R_A) due to radiogenic ${}^{4}\text{He}$ production in the crust, modifying the approach presented in Kulongoski et al. (2005).

$${}^{4}\text{He}_{rad} = {}^{4}\text{He}_{prod} \times (1-\Phi)/\Phi \tag{5}$$

$${}^{3}\text{He}/{}^{4}\text{He}_{r} = {}^{3}\text{He}_{m}/({}^{4}\text{He}_{rad} \times t + {}^{4}\text{He}_{m})$$
 (6)

where ⁴He_{rad} is the rate of ⁴He production and accumulation in crustal pore fluids (mol gH_2O^{-1} year⁻¹), ⁴He_{prod} is the production rate for the crust (mol g^{-1} year⁻¹), Φ is the porosity of the crustal rocks, ³He/⁴He_r is the present-day residual isotope ratio after ⁴He ingrowth, ${}^{3}\text{He}_{M}$ and ${}^{4}\text{He}_{M}$ are the concentrations (mol g⁻¹) introduced by the magmatism, and t is years since the magmatic event. Assuming introduction of mantle fluids at 5.4 Ma, with a ${}^{3}\text{He}/{}^{4}\text{He}$ of 1.1×10^{-5} (8 R_{A}) , ⁴He of ~1300 ncm³ STP gH₂O⁻¹ (4.1 × 10¹¹ mol g⁻¹) based on average mantle values observed along the Chile SVZ (Fig. 5D, Table S1), average radiogenic production rates for ⁴He in the crust $(\sim 1.6 \times 10^{-17} \text{ mol g}^{-1} \text{ year}^{-1})$ (after Ballentine and Burnard, 2002), and a crustal porosity of 5%, the residual 3 He/ 4 He ratio from this event is estimated as 3.4×10^{-7} (0.25 R_A). This calculation does not consider the impact of mixing with the crustal helium reservoir that would further reduce the ratio. Therefore, radiogenic ingrowth of ⁴He combined with mixing with meteoric groundwater would have long since diluted a mantle He signature from this magmatic pulse. For the observed ratios to be the product of mantle-derived magmatism, the event would need to have occurred < 500 ka.

Mantle helium in crustal fluids in the absence of recent magmatism has been documented at major strike-slip faults such as the San Andreas Fault (Kennedy et al., 1997; Kulongoski et al., 2013), the Anatolian Fault (Güleç et al., 2002; Doğan et al., 2009; de Leeuw et al., 2010), and Karakoram Fault (Klemperer et al., 2013). In each case, the observed values require a continuous vertical fluid flux (<10 to 147 mm year⁻¹) or much more rapid episodic flux of mantle helium from depth (Kennedy et al., 1997). The implication is that fluid pressures and permeability along these fault systems are high enough to move mantlederived fluids from the asthenosphere through the ductile crust to the surface. Applying a similar model to the Cordillera Blanca detachment is complicated for several reasons. In strike-slip settings, a nearvertical fault is presumably providing a pathway from the asthenosphere to the shallow crust. However, the CB detachment is a low to moderate angle normal fault that penetrates to an unknown depth, but likely penetrates deep into the upper crust (McNulty and Farber, 2002). Additionally, the degassing documented in the Cordillera Blanca springs complicates the flux calculation because it requires an estimate of the mantle-derived helium concentration, and estimating a pre-degassing He concentration is highly uncertain. However, we suggest that a similar magnitude of mantle helium flux must exist to transport these fluids into the Cordillera Blanca detachment and produce the values observed in the hot springs. Based on this assessment, the question remains: is the mantle helium originating from underlying asthenosphere or from the mantle lithosphere?

Geophysical investigations (seismic and 2D tomography) constrain the general geometry and depth of flat slabs along the Andean margin (Gutscher et al., 2000). These authors show that the top of the Peruvian flat slab beneath the Cordillera Blanca region (~8.5–10°S) has a depth of ~100 km, and is located in a broad 'sag' in the subducting plate observed between the Inca plateau and Nazca ridge. These geophysical data do not resolve the presence of asthenospheric mantle below the region. However, they have been interpreted to show slab steepening and 're-subduction' starting ~600 km east of the trench, and ~300 km east of the Cordillera Blanca massif. The transition to steep subduction and appearance of an asthenospheric wedge in the north (\sim 5°S) and south (\sim 15°S) are 500–750 km from the Cordillera Blanca massif (Gutscher et al., 2000). Using these geophysical constraints, mantle helium derived from an underlying residual or distal asthenospheric wedge is unlikely.

However, as presented in Section 2.1, the recent higher resolution 3D seismic tomography of the Peruvian segment has identified a possible arc-parallel tear (Fig. 1) in the subducting slab north of the Nazca ridge between ~14 and 11°S (Antonijevic et al., 2015). These results also indicate the presence of asthenosphere in the tear that is in contact with the continental lithosphere. Antonijevic et al. (2015) hypothesize that the tear may continue to the north, but their data array does not extend far enough northward to constrain the presence of a tear or asthenosphere below the Cordillera Blanca. Interestingly, these authors also note the presence of a localized high heat flow anomaly above the northern end of the asthenosphere filled tear. As mentioned previously, heat flow near the Cordillera Blanca is considered low, but is based on sparse data (McNulty and Farber, 2002). Speculatively, the hydrothermal systems identified in our study may be indicative of localized higher heat flow anomalies. Although direct supporting geophysical evidence is not available, it is possible that the mantlehelium observed in the Cordillera Blanca region is related to a northward extension of the imaged slab tear and associated asthenosphere in contact with the lithosphere.

Another possible origin of the mantle helium observed in the CB hot springs is the continental mantle lithosphere, with He mobilized by fluids released from the subducting flat slab. Temperatures at the base of the continental lithosphere ~300 km from the trench in an established flat slab setting (>5 Myr since closing of mantle wedge) are likely too low (~600 °C) (Gutscher et al., 2000) to create melts, although aqueous/supercritical fluids will be released from the slab to the overlying lithosphere at these temperatures (e.g., Mungall, 2002). Due to the low angle of subduction, dehydration of the slab is likely to occur along the subduction interface for long distances inland from the trench (Pérez-Gussinyé et al., 2008; Jones et al., 2011). For example, dehydration of the Laramide-aged (late Cretaceous- early Tertiary) flat slab is postulated to have hydrated parts of the North American lithosphere for over 1000 km from the plate boundary (Humphreys et al., 2003; Jones et al., 2011). Additionally, mineral-fluid reactions (metasomatism) preserved in lower crustal (~40 km) xenoliths from the eastern parts of the North American Cordillera are attributed to fluid release from the Laramide flat slab, suggesting that aqueous fluids derived from the mantle lithosphere were responsible for altering the lower crust (Jones et al., 2015). We suggest that continental mantlelithosphere metasomatism during upward migration of slab-derived aqueous fluids is also a possible mechanism to release mantle-helium to deep fluids that then can migrate into shallow hydrothermal systems.

4.5. Transport of mantle-derived fluids through the lithosphere

Migration of slab-derived fluids across the brittle-ductile transition into the upper crust has been imaged above a newly forming subduction zone in New Zealand using magnetotelluric methods, and such fluids are hypothesized to be moving via developing fault-fracture meshes (Wannamaker et al., 2009). This mechanism is analogous to the faultvalve model that drives flow by fluid overpressurization and stress switching in a megathrust setting (Sibson, 2013). Similarly, Kennedy and van Soest (2007) argue that elevated levels of mantle-derived helium in the western U.S. are associated with high extensional and shear strain gradients that modify the permeability of the brittle-ductile transition, allowing movement of mantle-derived fluids into the shallow crust and associated brittle fault zones. Importantly, the formation of ore deposits has been attributed to metal-bearing fluids crossing the brittle-ductile transition via fracture systems during stress switching cycles in compressional settings, such as forearcs (e.g., Sibson, 2013). Mungall (2002) hypothesized that supercritical fluids (or melts) derived from subducting slabs can be sources of chalcophile elements in hydrothermal systems in flat slab settings. Our results further support these mechanisms for fluid transfer from mantle and slab depths into the brittle crust and to the surface, and show that this is a "plausible process", even in settings with thick crust that lack active magmatism and associated conduits.

5. Conclusions

Here we document the presence of up to 25% mantle-derived helium in hot springs issuing from the Cordillera Blanca detachment fault system in a flat-slab subduction setting. These results begin to fill an important geochemical data gap for this unique tectonic setting. Recognition of mantle-derived fluids in this region of the Peruvian flat slab may represent the geochemical manifestation of migration of slab-derived fluids through the lithosphere, or the postulated tear in the slab and transition to steep subduction and the reestablishment of an asthenospheric wedge (Antonijevic et al., 2015). Our results provide support of existing ideas for the role of fluid dehydration from a flat slab in the subduction zone cycle. In this scenario, the addition of mantle- and slab-derived fluids may weaken the continental lithosphere and impact deformation, uplift, and future magmatic activity, as hypothesized for ancient systems including the North American Cordillera (Humphreys et al., 2003; Jones et al., 2015) and the Altiplano–Puna plateau of the Andes (Hoke and Lamb, 2007; Garzione et al., 2008).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.chemgeo.2015.10.003.

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