

Stable water isotope climate archives in springs from the Olympic Mountains, Washington

W. C. Sidle · V. Cvetic

Received: 13 October 2009 / Accepted: 1 April 2010 / Published online: 19 June 2010
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Abstract The ^{18}O and ^2H (HDO) compositions are summarized for sampled springs ($n = 81$) within the Elwha watershed ($\approx 692 \text{ km}^2$) on the northern Olympic Peninsula. Samples, collected during 2001–2009, of springs ($n = 158$), precipitation ($n = 520$), streams ($n = 176$), and firn ($n = 3$) assisted the determinations for meteoric composition of recharge waters. The local mean water line (LMWL) is defined as $\delta^2\text{H} = 8.2\delta^{18}\text{O} - 9.3$ for the watershed. Recharge history is surmised from groundwater ages ranging from 5 ± 3 years (apparent ^{85}Kr) to $9,490 \pm 420$ ^{14}C cal years BP. About 56% of the springs were recharged over the last 1,000 years while 13% of springs were recharged over 5,000 years ago. Spring HDO values fluctuate between -11.8 to -15.6‰ $\delta^{18}\text{O}$ and -90.9 to -119.4‰ $\delta^2\text{H}$. Deuterium excess values predominate around 4–6‰. The HDO proxy records from springs suggest a pronounced paleoclimate shift in air masses near 5,000 year BP on the Peninsula.

Keywords Stable isotope · Spring · Holocene climate change · Olympic Mountains

Introduction

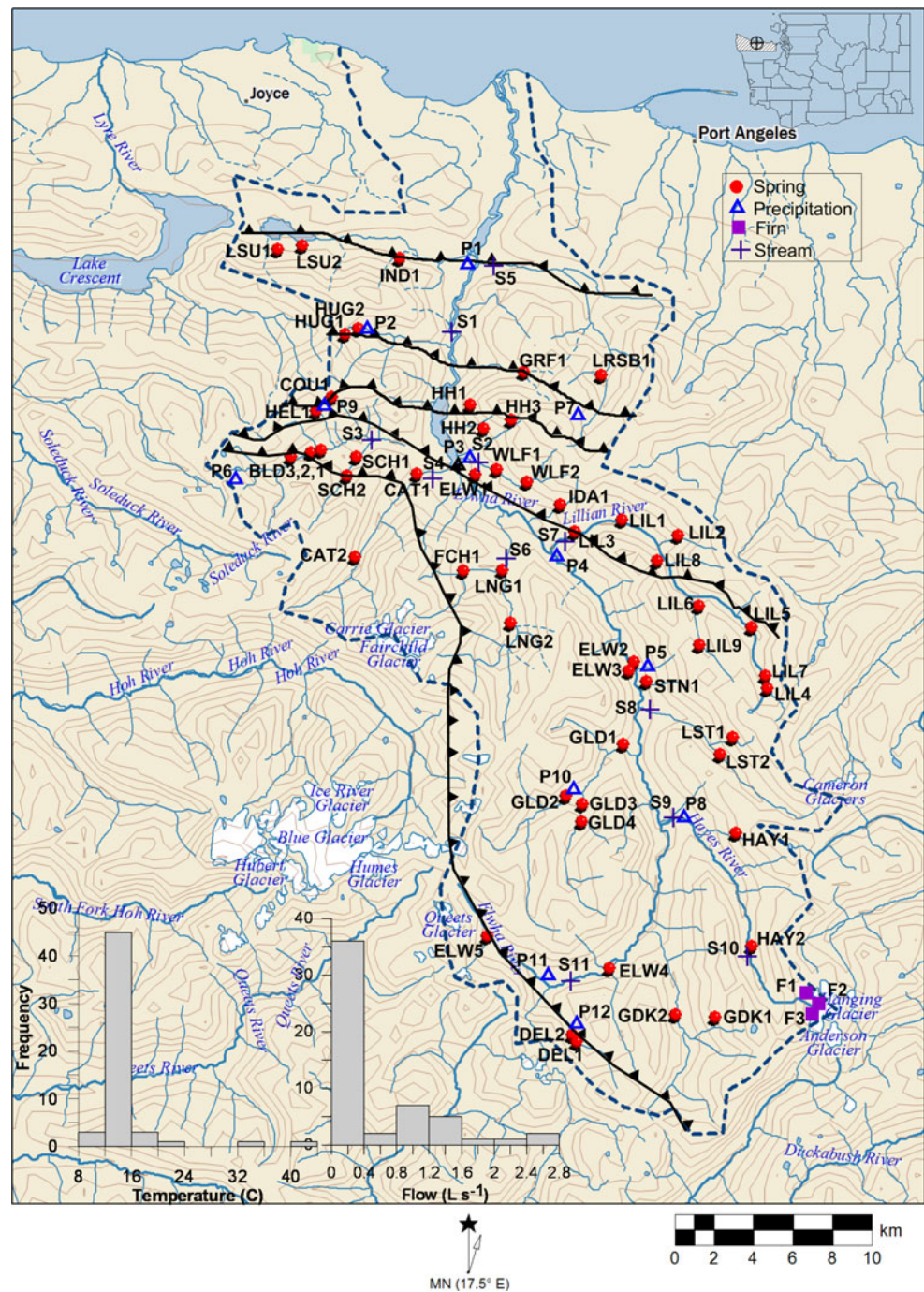
Springs offer an opportunity to sample archived climatic variables from remote watersheds on the Olympic Peninsula, Washington (Fig. 1). These include past temperature and humidity trends via the stable water isotopes, $^1\text{H}^2\text{H}^{16}\text{O}$ and $^1\text{H}_2^{18}\text{O}$ (HDO). The isotopic composition of meteoric waters behaves predictably such that the water isotopes in precipitation are depleted within cool regions and enriched within warm regions. This fundamental observation is used to document past recharge air temperature and humidity trends from groundwater (Epstein and Mayeda 1953; Araguas-Araguas et al. 2000). Examination of HDO in groundwater offers a low-resolution climate proxy though HDO is a well integrated signal of climate trends in an area since the last glacial maximum (LGM). This continental archive is used to resolve uncertainty in global climate models (GCM) (e.g., Henderson-Sellers et al. 2004; Fekete et al. 2006; Hoffman et al. 2000). Since model simulations of the earth's gross water budget generally differ with the details of basin-scale hydrology (Allen and Ingram 2002), there needs to be validation tools for forecasting hydrological responses to climate change. HDO proxy data from watersheds across the Peninsula may document past climate trends and also assist forecasting climate change.

Previous HDO proxy climate change studies on the Peninsula are rare and have been limited to tree-ring cellulose (Feng and Epstein 1996; Shu et al. 2005). These studies have potentially high resolution but over a short time period. Other HDO analyses reported from the Peninsula include isolated vegetation and surface waters as part of national topic reviews (Welker 2000; Kendall and Coplen 2001). Published HDO analyses in groundwater from the Peninsula are not known either from springs or wells. This research represents part of the first systematic

W. C. Sidle (✉)
National Risk Management Research Laboratory,
Water Supply and Water Resources Division,
U.S. Environmental Protection Agency,
Cincinnati, OH 45268, USA
e-mail: sidle.william@epa.gov

V. Cvetic
Groundwater Research Co, P.O. Box 136B,
Port Angeles, WA 98363, USA

Fig. 1 Location of sampled spring clusters, precipitation, firn, and streams within the Elwha watershed, Washington. Shown are traces of major thrust faults and relative percent frequency histograms of spring outlet temperatures (C) and spring flow rates ($L s^{-1}$)



mapping of springs, with their chemical and isotopic analyses, on the Peninsula.

The report objective is to provide first an appropriate geologic background in which the sampled springs are located and where groundwater is being transported. Next, present-day HDO analyses are examined from precipitation, streams, and firn in order to understand the range of values that could enter recharge waters from current air masses on the Peninsula. Given a record of Holocene groundwater ages (Sidle 2009), springs are explored as

proxies for paleoclimate trends (e.g., Moberg et al. 2005) in this representative watershed (Fig. 1).

Research setting

Watershed hydrogeology and spring characteristics

The Elwha watershed ($\approx 692 \text{ km}^2$) is the largest watershed located on the northern Olympic Peninsula in northwestern

Washington State, USA (Fig. 1). It is situated within the Westerlies-Oceanic precipitation regime (Barry and Chorley 1987), with precipitation ranging from 200 to 355 cm year⁻¹. Much of the orographic precipitation occurs as snow in the alpine and subalpine elevations, and as rain within the montane elevations. Recharge areas where significant snow accumulates range in elevation from $\approx 1,400$ to 2,100 m across the watershed. Combinations of a large recharge area, high recharge rate, and high fracture permeability concentrate volumes of water at a spring (e.g., Manga 2001).

Groundwater investigations are unknown in this wilderness area of the Olympic Mountains, so springs are essential in understanding mode of flow transport, source areas, and age. Most springs were newly discovered during this ongoing geologic mapping of the Elwha watershed. At least 52 springs (Fig. 1), some occurring as spring clusters raising the total to 81 individual springs, have thus far been identified. The Elwha springs predominantly issue from fractured metamorphosed sediments and volcanic rock assemblages. These springs are structurally controlled (Bryan 1919; Pitts and Alfaro 2001) and permit continuous flow from recharge areas, particularly along faulted contacts. In fractured rocks, the interconnected discontinuities are the pathway for fluid flow with solid rock blocks being impermeable. The continuum approach assumes that the fractured mass is hydraulically equivalent to a porous medium (e.g., Domenico and Schwartz 1990).

Spring flow rates varied little over the three hydrologic years of sampling 2006–2009. No discernable flow patterns or flow periodicities were observed. Mean flow rates (Table 1) range from seeps (Meinzer 1927) of less than 0.1 L s⁻¹ to pooled springs of nearly 2.5 L s⁻¹ in the Elwha watershed. Frequency histograms of the spring flows and outlet temperatures appear in Fig. 1. Most spring discharges are about 0.2 L s⁻¹ and are cold springs. Measured temperatures (Table 1) of groundwater flow range from 11.2 to 41.0°C. Spring outlet temperatures most commonly reflect predominant ambient groundwater temperatures which are near 13.5°C. New thermal discharges (i.e., 5°C above the mean annual air temperature) (White 1957; Reed 1983) were discovered and are not limited to the well-known Olympic Hot Springs (Campbell et al. 1970; Schoeffel 1971) within this watershed.

Geologic summary

The importance of structures on groundwater flow is deduced from regional tectonics of the Olympic Mountains. The Olympic Mountains expose the Cascadia subduction complex of largely marine trench sediments uplifted about 12 Ma (Brandon and Calderwood 1990). The Cenozoic core of accretionary wedges, Olympic

Subduction Complex (OSC) (Brandon and Vance 1992), was highly folded and intensely sheared. Imbricated thrust faulting juxtaposed complex OSC Eocene–Miocene sedimentary assemblages with early and middle Eocene oceanic basalts (Brown et al. 1960) and late Eocene through early Pliocene marine sediments, also known as peripheral rocks, (Tabor and Cady 1978a; Snavely et al. 1980; Suczek et al. 1994). This Coast Range terrane structurally overlies the OSC. Underplating onto the OSC has resulted in progressively younger and somewhat continuous sediment sequences westward of the fractured core assemblages. Similarly, metamorphic grades weaken westward to zeolite facies.

A generalized bedrock geology map (Fig. 2a), employing the nomenclature of Tabor and Cady (1978a), of the Elwha watershed illustrates contrasting rock units bounded by high-angle reverse faults. These rock units are grouped into assemblages or terranes based on their provenance yet the timing of their accretion is uncertain (Brandon et al. 1998). The mid-Tertiary volcanic arc deposits include *Trtl/Tlc/Tal* non-deformed coastal sediments, *Tcb* lava flows, and *Tbm* trench sediments belonging to the Coast Range terrane. These older rocks are thrust over younger marine sediments forming the core of the Olympic Mountains. This core of accreted wedges includes sheared, highly folded, and highly disrupted marine sediments of the *Tnm/Tnmu/Tnt* units and the *Tes/Tess/Tgs* units. These units form part of the *Needles-Gray Wolf Lithic Assemblage* and *Elwha Lithic Assemblage* that make up much of the megascale arcuate fold-like structure (Tabor and Cady 1978b) surrounding tectonically broken assemblages of the OSC wedges. Marine sediments of the *Two/Twoa/Twog* units are less disrupted and areas of continuous bedding can be recognized. These rocks were grouped into the *Western Olympic Lithic Assemblage*.

Note that some springs appear to be associated with some major mid-Cenozoic, imbricated thrust faults. These are noted in Fig. 2a and locally named herein as (1) Indian Cr.–Little R. fault (alias Lake Cr.–Boundary Cr. fault); (2) Hughes Cr.–Griff Cr. fault (alias Crescent fault); (3) Stukey Cr.–Hurricane Ridge fault; (4) Boulder Cr.–Lillian R. fault (alias Gray Wolf fault) (Radford and Sidle 1979); and (5) Boulder Hot Springs–Delabarre Cr. fault. Many sympathetic high-angle faults are associated with these thrust sheets (Tabor and Cady 1978b) but are not published.

At each spring location either a recognizable fault scarp, fault contact between smaller rock members of the mapped units, shear zone, or fractured rock unit was noted during the field investigations. For example, detailed geologic mapping (see inset Fig. 2b) during this research along a portion of the Stukey Cr.–Hurricane Ridge fault within the Boulder Cr. catchment reveals several steep reverse faults. These are crowded near the contacts between the sheared

Table 1 Sampled springs in the Elwha watershed, with identification, water temperature, flow rate, and geologic setting

ID	Spring <i>T</i> (°C)	<i>Q</i> (L s ⁻¹)	Geologic setting	ID	Spring <i>T</i> (°C)	<i>Q</i> (L s ⁻¹)	Geologic setting
HUG1	13.7	0.31	Faulted Tbm/Tcb contact	LIL5	14.2	0.06	Tnt/Tb axial hinge contact
HUG2	14.1	0.15	Faulted Tbm/Tcb contact	LIL6	11.2	0.09	Tnt/Tb axial hinge contact
GRF1	13.8	0.30	Tbm/Tcb contact	LIL7	13.6	0.12	Tnt/Tb axial hinge contact
IND1	13.9	0.70	Tcb anticlinal axis bed	LIL8	13.7	0.31	Tgs/Tnt fault contact
LRSB1	14.7	0.81	Tcs/Tcb contact	LIL9	28.3	0.16	Tnt/Tb axial hinge contact
LSU1	13.7	1.44	Faulted Tcb	LNG1	12.7	0.04	Tes/Tgs vertical contact
LSU2	14.9	0.06	Faulted Tcb	LNG2	13.3	0.06	Tes/Tb fault contact
BLD1	41.0	2.44	Olympic Spring(s); Tes/Two-Twoa contact	SCH1	14.6	0.17	Tes vertical bed
BLD2	36.7	2.49	Olympic Spring(s); Tes/Two-Twoa contact	SCH2	14.3	0.06	Tes/Twoa contact fault
BLD3	21.1	1.80	Tes/Two-Twoa contact	STN1	14.4	0.01	Tg/Tgst contact
CAT1	14.7	0.47	Tes/Two-Twoa contact	WLF1	13.9	0.37	Tnmu/Tb contact
CAT2	28.0	1.52	Two vertical bed	WLF2	14.3	0.04	Tnm/Tb contact
COU1	14.3	1.27	Tbm/Tnmu fault contact	DEL1	13.9	0.02	Twog/Tes fault contact
ELW1	13.7	0.91	Winslow Spring(?) Tnmu/Qo contact	DEL2	12.3	0.05	Twog/Tes fault contact
ELW2	13.6	0.06	Tg/Tgst contact	ELW1	13.1	1.43	Tes/Tess axial hinge contact
ELW3	13.8	0.03	Tg/Tgst contact	ELW2	13.3	0.83	Twog/Tes fault contact
FCH1	13.8	0.02	Tes/Two vertical contact	GDK1	13.2	0.20	Tes/Tb fault contact
HEL1	13.2	0.04	Tbm/Tnmu vertical contact	GDK2	12.0	0.14	Tes/Tb fault contact
HH1	13.6	0.02	Tbm/Tnmu fault contact	GLD1	12.5	0.03	Tes/Tgs vertical contact
HH2	12.8	0.28	Tbm/Tnmu vertical contact	GLD2	13.0	0.01	Tes/Tb/Tec/Tss fault contact zone
HH3	13.2	0.25	Tb/Tnmu contact	GLD3	12.9	0.04	Tes/Tb/Tec/Tss fault contact zone
IDA1	13.2	0.01	Tnt/Tnm axial hinge contact	GLD4	13.7	1.38	Tes/Tb/Tec/Tss fault contact zone
LIL1	14.7	0.04	Tgs vertical bed	HAY1	12.8	0.92	Tes/Tgs–Tb dike complex
LIL2	12.4	0.09	Tgs/Tnt fault contact	HAY2	13.9	0.28	Tes–Tb dike complex
LIL3	13.8	0.02	Tnt/Tb axial hinge contact	LST1	13.2	0.92	Tgs/Tgst/Tb axial hinge–fault contacts
LIL4	10.3	2.26	Tnt/Tb axial hinge contact	LST2	14.1	0.25	Tgs/Tgst/Tb axial hinge–fault contacts

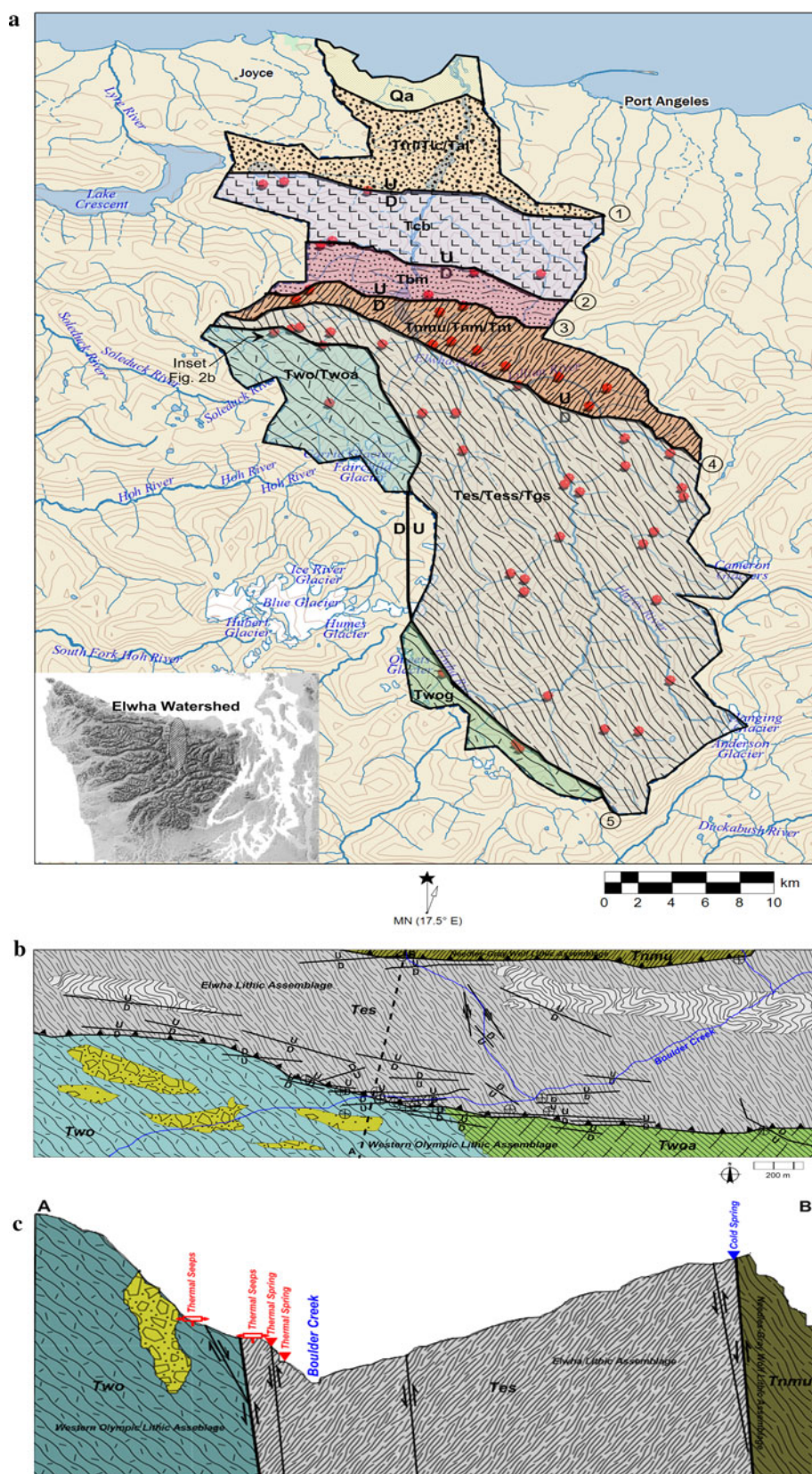
Elwha Lithic Assemblage and the less disrupted *Western Olympic Lithic Assemblage*. A cluster of spring orifices (at BLD1 and BLD2, Fig. 1) are distinct but also diffuse seepage occurs particularly within the tectonic breccia, shear zones, and highly disrupted cleavage zones. In an illustrated type cross section A–B (Fig. 2c), thermal groundwater seeps and flows from faults along the contacts of *Tes* contorted slate and phyllite with the more porous *Two* and *Twoa* non-foliated sandstones, with angular conglomerates, and argillite, respectively. Another spring with cold or ambient groundwater issues from a fault contact between the *Elwha Lithic Assemblage* and the *Needles-Gray Wolf Lithic Assemblage*.

Normal dip faulting was recognized (Fig. 2b, c) among a few spring locations and could be flow paths for modern meteoric waters mixing with presumed older recharged spring waters. Late Quaternary faulting in the region (e.g., Wilson et al. 1979) could disrupt the archival recharge record of these springs, when past flow paths are altered. So it is vital that groundwater age determinations complement HDO sampling of these springs.

Sampling and analytical methods

Spring waters ($n = 52$) were sampled via a modified Kemmerer-type thief sampler. For seeps with low flow rates, $<0.1 \text{ L s}^{-1}$, Tygon[®] tubing was connected to 100 ml PTFE canisters, serving as reservoirs, modified after Salve (2005) to accumulate sample. The water samples for HDO were collected in triplicate in 250-mL amber glass bottles. Springs in the Elwha watershed were sampled annually ($n = 158$) from 2006 to 2009. Twelve precipitation collection stations were sampled biweekly from April to October during 2006–2009 ($n = 504$) and thus represent bulk precipitation. The precipitation samples were collected using a customized automated sequential tipping bucket, pre-treated with mineral oil to prevent evaporation. Also selected storm samples ($n = 16$) were collected. Precipitation samples were weighted to the volume collected. Surface waters ($n = 176$) were collected semi-annually at 11 streams during 2001–2009. Meltwaters were obtained from three Shelby-tube[®] cored glacial firn during 2008 near the headwaters of Mount Anderson (Fig. 1).

Fig. 2 **a** Bedrock geology of Elwha watershed. Shown are high-angle reverse faults and rock nomenclature after Tabor and Cady (1978a). **b** Example of mapped structural geology of sampled springs (see *inset* in **a**), for this project, and documentation of local assignments of the Olympic Subduction Complex (OSC) assemblages or terranes. Several sympathetic faults are mapped along the major traces of regional thrust faults. **c** Geologic cross section A–B (see Fig. 2b) illustrating springs/seeps and associated high-angle faults



Stable water isotopes were analyzed by isotope ratio mass spectrometry (IRMS) on a Thermo Scientific Delta V Plus® instrument. Preparation procedures for ^{18}O were CO_2 equilibration (Roether 1970); and for ^2H were Pt–HDO equilibration after Horita (1988). Duplicate ^2H analyses were via Cr-reduction after Gehre et al. (1996). All analyses of the light stable isotopes are provided in per mil (‰) notation and are computed against the internal IRMS standard as

$$\delta R_{\text{sample}}\text{‰} = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 10^3 \quad (1)$$

where R is a ratio (e.g., $^{18}\text{O}/^{16}\text{O}$). For ^{18}O and ^2H the Vienna Mean Standard Oceanic Water (VSMOW) is normalized to the Standard Light Antarctic Precipitation (SLAP) (Coplen 1994). IRMS analytical precision on the Elwha samples is equal to $\pm 0.02\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.6\text{‰}$ $\delta^2\text{H}$.

The sampling and experimental methods employed for measuring radioisotope ages in groundwater, that are reported herein with the HDO results, were previously completed and are summarized in Sidle et al. (2010). Briefly, the fissiogenic ^{85}Kr , ^3H , ^3H – ^3He age determinations allow modern meteoric waters ($\approx$ post nuclear age or early 1950s) to be measured. Calculated tritium ages from direct measurements of ^3H are determined from an exponential decay-recharge model (Vogel et al. 1974; Maloszewski and Zuber 1982). However, since ^3H activity was below detection limits in most spring water samples, tritogenic He (e.g., Schlosser et al. 1989) was measured and provided much of the ^3H meteoric ages. The best measure of modern meteoric recharge was via ^{85}Kr analyses (Sidle 2006), which unlike the decline of ^3H in the atmosphere, has consistently increased in the atmosphere.

Cosmogenic isotopes, ^{14}C and ^{39}Ar , permitted the determination of older groundwater amongst the springs. Apparent $^{14}\text{C}_{\text{DIC}}$ groundwater ages are corrected for the geochemical processes involving dissolution, dilution, and exchange of DIC in the system of CO_2 – HCO_3^- – CO_3^{2-} – $\text{CO}_3(\text{s})$ and its isotopic exchanges (Fontes and Garnier 1979). ^{39}Ar yields a useful time range of about 100–1,000 years BP. Variations of $^{39}\text{Ar}/\text{Ar}$ up to 7% over the last 1,000 years from cosmic ray flux are corrected in the ^{39}Ar age calculations (Oeschger et al. 1974; Loosli et al. 1992).

Results and discussion

Present HDO air mass compositions

Fractionation during condensation from the vapor masses imparts a meteoric relationship between ^{18}O and ^2H onto

recharge waters. The global meteoric water line (GMWL) provides the basis (Craig 1961; Rozanski et al. 1993) for examining the provenance of groundwater and their evolution over past time intervals. Local meteoric water lines (LMWL) will vary from the GMWL in slope and deuterium intercept. Because of Rayleigh distillation during rainout, isotopically depleted waters are associated with cool regimes and enriched waters are indicative of warm regimes.

Mean HDO values from precipitation at 12 widely distributed collection stations and from storm event temporary collectors from the lowlands into the alpine zone of the Elwha watershed (Fig. 1) are first plotted as the basis of the LMWL (Fig. 3a). These precipitation samples represent the most extensive HDO analyses ($n = 520$) on the Peninsula. The LMWL is:

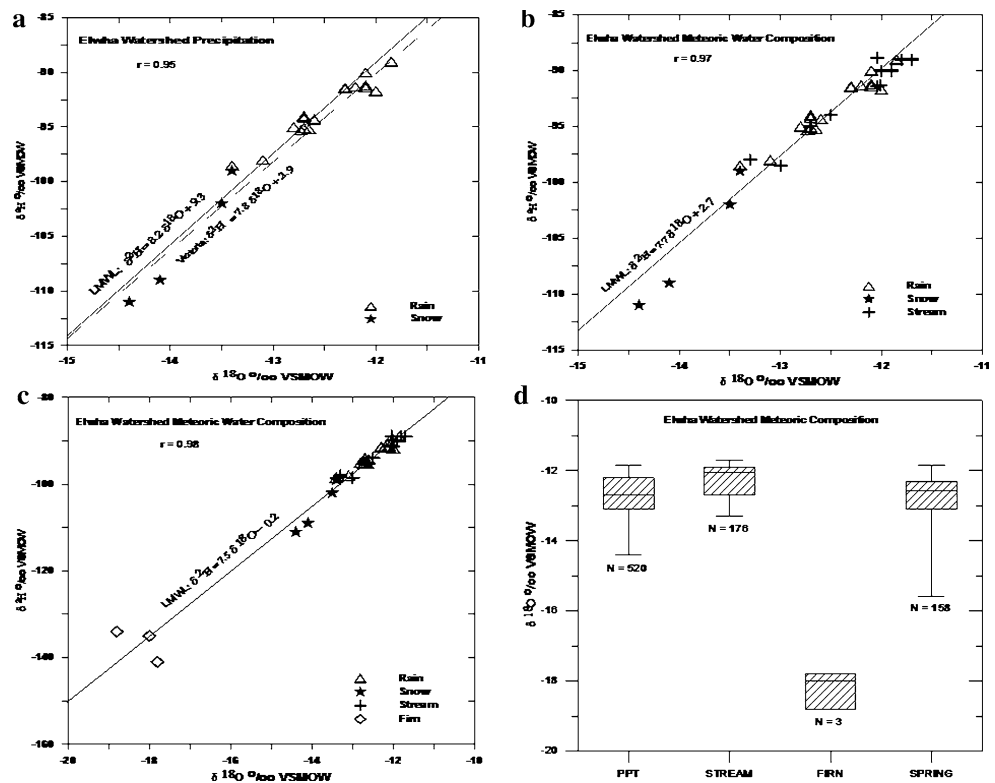
$$\delta^2\text{H} = 8.2 \delta^{18}\text{O} + 9.3 \quad r = 0.95 \quad (2)$$

For comparison, the nearest annual LMWL is that of the IAEA/GNIP (Global Network of Isotope Precipitation) station (IAEA 2009) in Victoria, British Columbia (Fig. 3a). Local precipitation collected in the Elwha watershed is similar to Victoria's coastal precipitation. This is expected as Pacific marine air mass rainout over both locales and they are close ($\approx 48^\circ 10'\text{N}$, $123^\circ 33'\text{W}$). Still the Elwha watershed LMWL is slightly steeper because many stations are located in subalpine areas which received more depleted precipitation.

Elsewhere on the Peninsula, Rozanski et al. (1993) and Welker (2000) cite a single IAEA precipitation station (discontinued in the 1960s) on Destruction Is., off the western coast of the Peninsula with a mean $\delta^{18}\text{O}$ composition of -7.6‰ . Tang et al. (2000) and Shu et al. (2005) report steeper LMWL slopes near 8.8 ± 0.4 . Their precipitation stations were collected over 2 years but from 5 locations scattered widely across the entire Peninsula in order to sample the general orographic precipitation gradient. That HDO data are not confirmed by detailed sampling in the Elwha watershed and are well removed from the established IAEA station dataset.

Expectedly, Elwha stream samples plot (Fig. 3b) similarly to precipitation and likely reflect the importance of runoff in this high rainfall regime. Presumed gaining streams also receive groundwater contributions probably from shallow fractures in this rock terrane. However without sampling groundwater directly (e.g. springs) and without recharge source information, the assumption has been that streams are dominated by direct overland runoff. The most depleted precipitation (Fig. 3a) is snow collected at stations within the subalpine zone of the Olympic Mountains. Typically, glacial firn samples, beneath massive snowpacks in the uppermost Elwha watershed, contain the most depleted HDO isotopes (Fig. 3c).

Fig. 3 **a** Scatter plot of $\delta^{18}\text{O}$ – $\delta^2\text{H}$ per mil values from the Elwha watershed precipitation. Shown is the regressed LMWL along with the IAEA LMWL of Victoria, British Columbia; **b** scatter plot of $\delta^{18}\text{O}$ – $\delta^2\text{H}$ per mil values for local streams and precipitation with the resultant LMWL; **c** scatter plot of $\delta^{18}\text{O}$ – $\delta^2\text{H}$ per mil values for glacial firn and the resultant LMWL; **d** nonparametric box and whisker plots of $\delta^{18}\text{O}$ per mil values from Elwha precipitation, streams, firn, and springs



Examination of the spread of HDO values among these Elwha meteoric waters (Fig. 3d) demonstrates that modern precipitation ranges over 2 per mil $\delta^{18}\text{O}$. The 25–75% quartiles are 12.3 to 13.1‰ $\delta^{18}\text{O}$ with the most depleted value being -14.4 ‰ $\delta^{18}\text{O}$. Knowing the present HDO composition of these modern air masses tracking across the Peninsula is useful for comparison with past meteoric waters. Such are represented by groundwater presuming that their recharge ages are significantly older than modern meteoric water. Note that the spring water 25–75% quartiles are 12.5 to 13.1‰ $\delta^{18}\text{O}$ and are almost identical to that of modern precipitation, at least over the period 2006–2009. Median spring $\delta^{18}\text{O}$ values are also slightly more enriched than the precipitation values. However it is noteworthy that some spring waters have much more depleted $\delta^{18}\text{O}$ values of -15.6 ‰.

Archived HDO spring compositions

Present meteorological processes that fractionate and partition these HDO isotopes are believed to extend in time even though air masses may change as climate fluctuates (Gourcy et al. 2005). Predominantly, isotopic compositions of young meteoric groundwater exhibit a linear correlation with the mean composition of precipitation over a recharge area, particularly in the middle and high latitudes (Jouzel et al. 2000). Inspection of the Elwha meteoric groundwater HDO values (Fig. 4) suggests a gentler slope than the

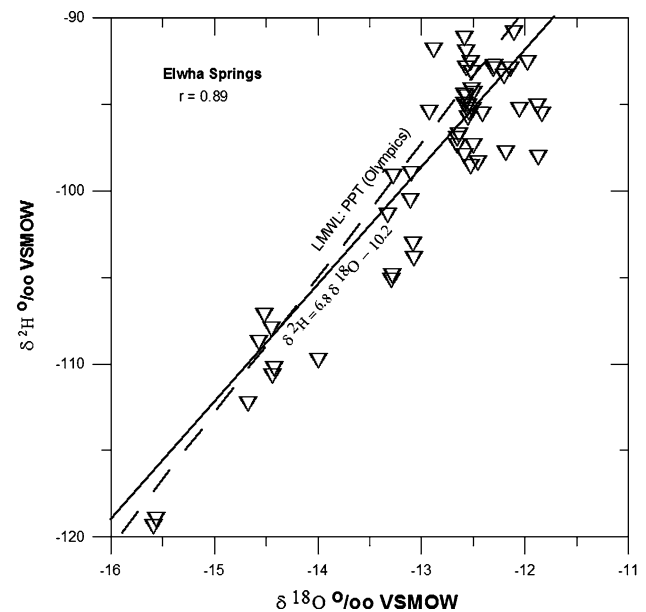


Fig. 4 Scatter plot of $\delta^{18}\text{O}$ – $\delta^2\text{H}$ per mil values from groundwater in springs within the Elwha watershed. Shown are the regressed meteoric line and the LMWL from Elwha precipitation

LMWL presently observed from precipitation and stream runoff on the Peninsula. Springs issuing today, record past recharge waters from -11.8 to -15.6 ‰ $\delta^{18}\text{O}$ and -90.9 to -119.4 ‰ $\delta^2\text{H}$. This is a large range and would be unexpected if all groundwater was similar in age and was being recharged within the Elwha watershed.

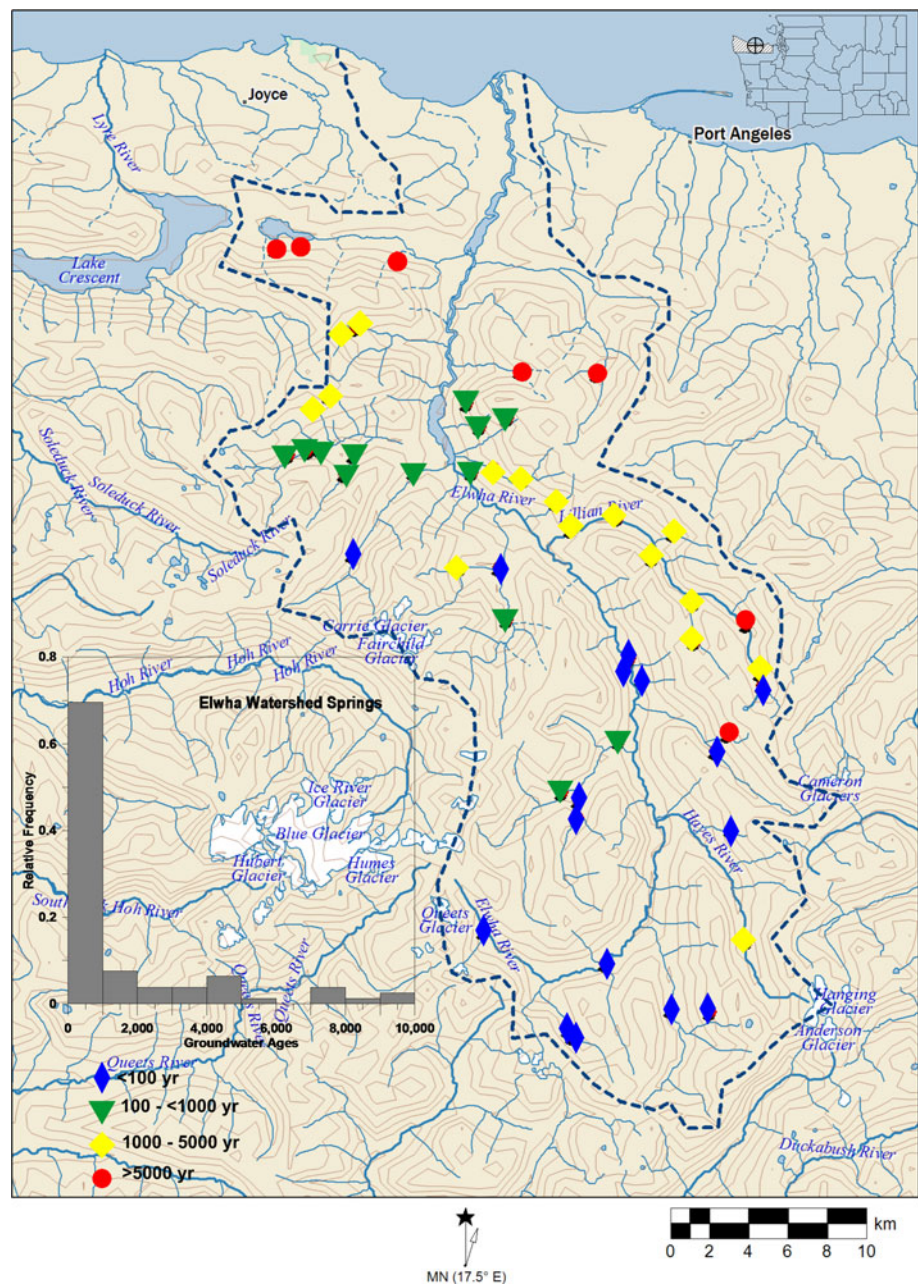
In that modern meteoric water context the observed spring water departures and separation along the LMWL in Fig. 4 for the Elwha watershed may infer 1) sample evaporation; 2) significant mixing; and/or 3) different recharge sources.

Departures below the Elwha LMWL could be due to kinetic evaporation during sampling/storage, permitting $\delta^{18}\text{O}$ enrichment. Enrichment in $\delta^2\text{H}$ among some samples could be due to heavy precipitation during storm events and/or effects of humidity (e.g. Scholl et al. 2002). Because sample evaporation was minimized in the surface water collections (Fig. 3b), it is not likely that all of the sampled

spring waters separately experienced evaporation from poor sampling or storage protocols.

Conventionally, the range of HDO among springs along the LMWL might represent mixing between present melt-water and precipitation for similar recharge-age waters. In which case it would be necessary to correct for altitude effects (e.g. Rose et al. 1996). The $\delta^{18}\text{O}/100\text{ m}$ gradient, from 16 precipitation samples collected during four storms, at Elwha locations between 247 and 1,360 m is -0.16 . This value is lower than $\delta^{18}\text{O}/100\text{ m}$ gradients calculated for a similar climate regime with similar steep topographic relief (Clark et al. 1982) within the Coast Range, British

Fig. 5 Map of grouped groundwater ages from spring clusters within the Elwha watershed. Shown is the relative frequency histogram of the Holocene groundwater ages



Columbia. Further this assumes a progressive HDO depletion in precipitation upslope. Generally only shallow and locally derived groundwater would be expected to match precipitation closely (e.g. Fritz et al. 1987). This is unrealistic for the known recharge areas because most springs are either identified with separate thrust sheets (Figs. 1, 2a) or other fractures of unknown depth, extent, and association. Moreover the springs were probably recharged at great distances through structures and not simply from nearby hillsides.

Different recharge areas for the springs could explain the observed range of groundwater HDO values in the Elwha watershed. For similar recharge-age waters the rainout from the air masses would need to be selective over different upland areas within the same watershed. Somehow the recharge waters would then be transported through various fractures in a similar time interval. This scenario is untenable because of the structural geology of this very large watershed ($\approx 692 \text{ km}^2$) which is entirely within the wet regime of the orographic rainout.

Instead, the Elwha spring water HDO regression line slope (Fig. 4) may be an artifact of different recharge events over a long time interval that is the Holocene. As such the HDO shifts might record variable episodes of temperate and cool regimes during rainout over the Olympic Mountains in the past. Still it would appear that many past recharge waters archived in these Elwha spring waters had similar HDO compositions to current air masses (Fig. 3d). The exceptions (Figs. 3d, 4) though indicate cooler rainy regimes than present. Recharge-age determinations for these springs are crucial to resolve the climate implications, if any, for these observed HDO shifts.

In fact the recharge ages of these 52 spring clusters ($n = 81$) vary (Fig. 5) from modern meteoric water to about 9,500 years BP, roughly after the LGM on the Peninsula. About 56% of the springs received their recharge in less than 1,000 years BP with 25% being modern meteoric water. About 13% of the sampled springs have groundwater ages over 5,000 years BP. The youngest sampled spring has a recharge age of 5 ± 3 years (^{85}Kr apparent age) while the oldest spring water was recharged $9,490 \pm 420 \text{ }^{14}\text{C}$ cal years BP (Sidle 2009). The age-distribution map in Fig. 5 illustrates that most but not all of the oldest groundwater are flowing from springs in the lowlands or foothills within the Elwha watershed. Young spring waters sampled were expectedly most common within the upper reaches of the watershed. Note the wide distribution of recharge ages recorded in springs apparently aligned along the Boulder Cr.–Lillian R. thrust fault (alias Gray Wolf fault) and its presumed sympathetic reverse faults.

The distributions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions over the Holocene recharge events recorded in the sampled springs

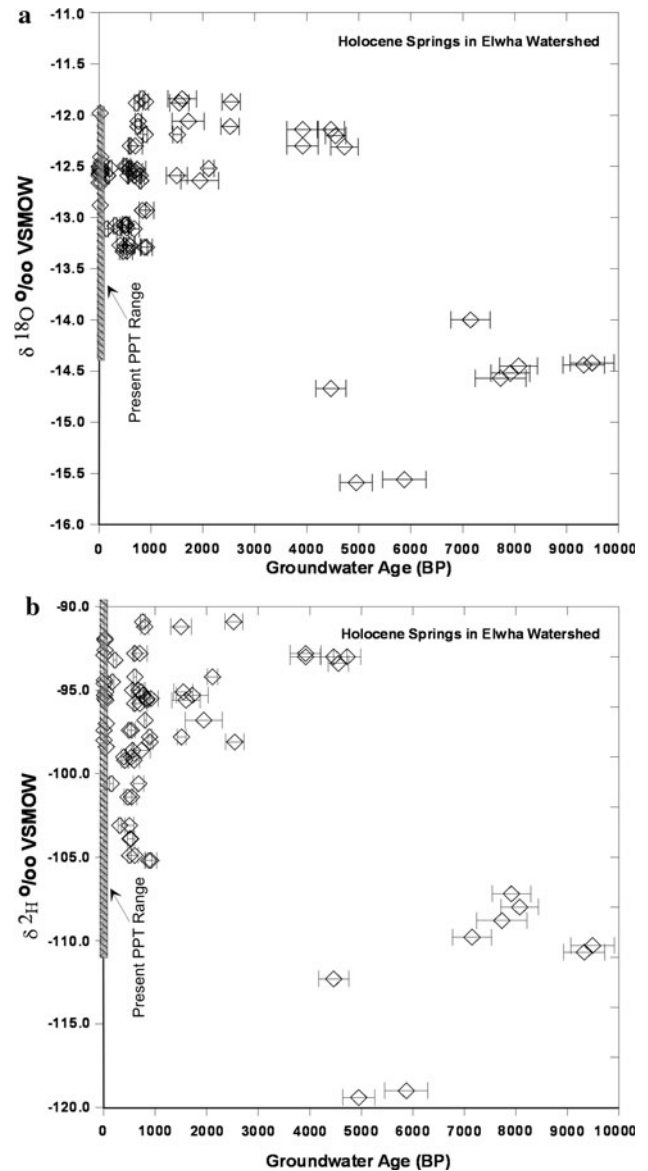


Fig. 6 **a** Scatter plot of Holocene groundwater ages– $\delta^{18}\text{O}$ per mil values for the Elwha springs. Shown is the range of modern precipitation HDO values; **b** scatter plot of Holocene groundwater ages– $\delta^2\text{H}$ per mil values for the Elwha springs

are plotted in Fig. 6a, b. Note that spring waters sampled do not represent a continuum throughout the Holocene. The gaps between the ages plotted result from not locating groundwater discharging from that time period within the Elwha watershed. It would be fortuitous to encounter a complete history of recharge from springs.

The wide ranges of present precipitation $^{18}\text{O}\text{‰}$ ($\bar{x} = -12.8 \pm 0.8$; median 12.57) and $^2\text{H}\text{‰}$ ($\bar{x} = -98.3 \pm 6.2$; median 95.8), which include snow, are similar to most of spring recharge HDO values since about 5,000 years BP. However, during infiltration of precipitation to the saturated zone seasonal mixing occurs while the

net contribution is volume-weighted (Gat 1971). That average recharge composition then may be an integrated HDO signature in that parcel of groundwater being transported toward a spring. Still the mean or median of present precipitation (Fig. 6a, b) does closely match much of the mid-Holocene to modern meteoric waters now discharging at springs within the Elwha watershed. Finer-age resolutions over the last millennium (Fig. 7) confirm wide

fluctuations of these air masses but that are similar to present climate conditions on the Peninsula.

The most pronounced paleoclimate shift, as inferred from the HDO data from the Elwha springs, appears to have occurred after a protracted cool regime after the LGM to possibly 5,000 years BP. Illustrated in Fig. 8 the HDO depletions are over 2‰ ^{18}O and over 10‰ ^2H . This might suggest that the source of the air masses had changed possibly in response to oceanic surface water warming. Some (e.g., Pisias et al. 2001; Bartlein et al. 1998) have

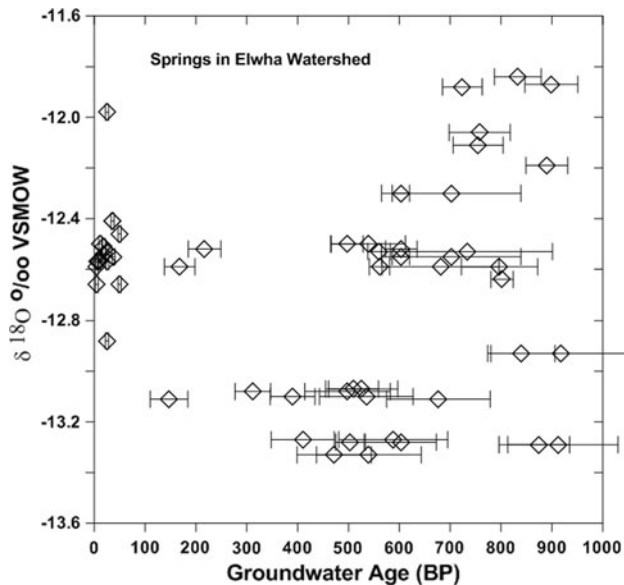


Fig. 7 Scatter plot of last millennium groundwater ages– $\delta^{18}\text{O}$ per mil values for the Elwha springs

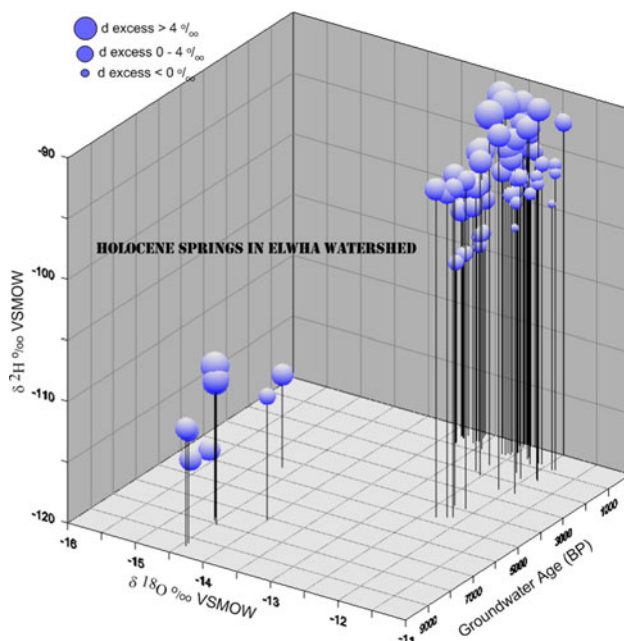


Fig. 8 Bubble plot of HDO and deuterium excess values from the Elwha springs during the Holocene

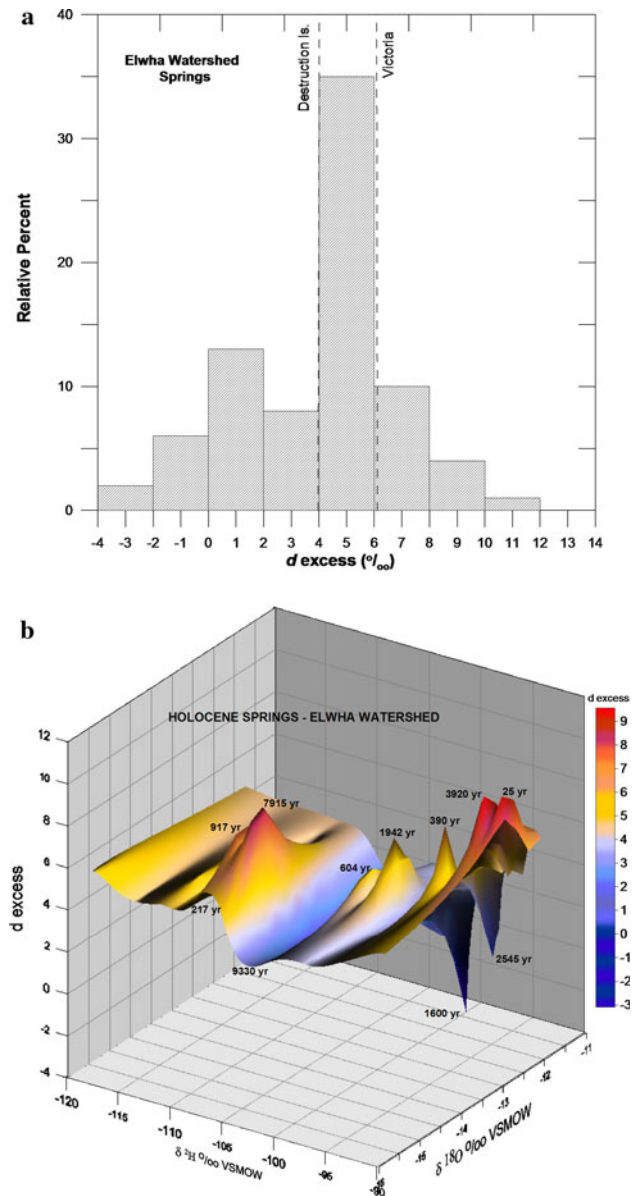


Fig. 9 **a** Relative percent frequency histogram of deuterium excess values from the Elwha springs. Noted are recent d-excess values of precipitation at Victoria, British Columbia and Destruction Island, Washington; **b** Surface plot of deuterium excess values from the Elwha springs during the Holocene

reasoned from radiolarian and pollen proxies in marine sediment cores that climate simulations suggest continental climate changes related to Pacific Northwest coastal upwelling at wavelengths >3,000 years over the last 150 kyr. A review of mid-Holocene warm periods from Greenland ice cores (e.g., Huntley et al. 2002), vegetation proxies in the Americas (e.g., Grimm et al. 2001), and limnology proxies in the Americas (e.g., Fritz et al. 2001) suggest one or two warming periods between 6,500 and 4,500 years BP. These temperature optima are observed more prominently in various climate proxies in Europe (e.g., Negendank 2004).

Finally, shifts in the air masses and resultant rainout over recharge areas should also be reflected in humidity changes. Deuterium excess has been used as a predictor of shifts in air mass systems (e.g., Jouzel et al. 2000). Today's d-excess on the Peninsula ranges closely between 4 and 6‰ (Fig. 9a) and is the apparent dominant mode also from the archived HDO values in the Elwha springs. However, the d-excess surface plot (Fig. 9b) illustrates the chronic fluctuations over the Holocene ages with no obvious spike near 5,000 years BP. It remains unclear whether a possible shift in marine air mass patterns equates with increased precipitation.

Conclusions

The HDO proxy data from springs in the Elwha watershed suggest that present-day marine air masses, tracking across the Peninsula, may have persisted at least for 5,000 years. An apparent pronounced climate shift occurred in the mid-Holocene on the Peninsula but the duration of the transition from a much cooler regime is unknown from available groundwater ages. Other local proxy information is not available for confirmation of this paleoclimate episode although other cited global proxies broadly support the timeline for a temperature optimum. Future investigations of the stable water isotope climate archives in springs from other watersheds on the Peninsula may improve the age-resolution of the recharge waters and an understanding of the natural variations underpinning these past climate shifts.

Acknowledgments This article is published posthumously. Sadly, Dr. William C. Sidle passed away on March 14, 2010. Bill's enormous contribution to EPA's mission cannot be overstated. Please direct all inquiries on this work to Christopher A. Impellitteri (impellitteri.christopher@epa.gov). Cooperation of the US National Park Service, US Forest Service, and many private land owners are appreciated. Special thanks are given to the field crews for sampling and on-site analyses in challenging terrain throughout the seasons. Special thanks to R. Kolmar (Ohio State University), and W. Huang-Lee (Princeton University). Any opinions expressed in this paper are those of the authors and do not, necessarily, reflect the official positions and policies of the USEPA. Any mention of commercial

products or trade names does not constitute endorsement or recommendation by the USEPA.

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