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Stable hydrogen and oxygen isotope ratios of bottled waters of the world

Gabriel J. Bowen[1]*, David A. Winter[2], Howard J. Spero[2], Robert A. Zierenberg[2], Mathew D. Reeder[3], Thure E. Cerling[1,3] and James R. Ehleringer[1,4]

[1]Biology Department, University of Utah, Salt Lake City, UT 84112, USA
[2]Department of Geology, University of Calfornia, Davis, CA 95616, USA
[3]Geology and Geophysics, University of Utah, Salt Lake City, UT 84112, USA
[4]IsoForensics Inc., 423 Wakara Way, Salt Lake City, UT 84108, USA

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Bottled and packaged waters are an increasingly significant component of the human diet. These products are regulated at the regional, national, and international levels, and determining the authenticity of marketing and labeling claims represents a challenge to regulatory agencies. Here, we present a dataset of stable isotope ratios for bottled waters sampled worldwide, and consider potential applications of such data for regulatory, forensic and geochemical standardization applications. The hydrogen and oxygen isotope ratios of 234 samples of bottled water range from −147‰ to +15‰ and from −19.1‰ to +3.0‰, respectively. These values fall within and span most of the normal range for meteoric waters, indicating that these commercially available products represent a source of waters for use as laboratory working standards in applications requiring standardization over a large range of isotope ratios. The measured values of bottled water samples cluster along the global meteoric water line, suggesting that bottled water isotope ratios preserve information about the water sources from which they were derived. Using the dataset, we demonstrate how bottled water isotope ratios provide evidence for substantial evaporative enrichment of water sources prior to bottling and for the marketing of waters derived from mountain and lowland sources under the same name. Comparison of bottled water isotope ratios with natural environmental water isotope ratios demonstrates that on average the isotopic composition of bottled water tends to be similar to the composition of naturally available local water sources, suggesting that in many cases bottled water need not be considered as an isotopically distinct component of the human diet. Our findings suggest that stable isotope ratios of bottled water have the power to distinguish ultimate (e.g., recharge) and proximal (e.g., reservoir) sources of bottled water and constitute a potential tool for use in the regulatory monitoring of water products.

Bottled or packaged waters represent an increasingly important component of human dietary intake worldwide. According to the International Bottled Water Association,[1] annual consumption of bottled water in the United States reached an average of 90 liters per person during the year 2004. In theory, bottled waters can represent a reliable, quality-assured source of water, but in practice they also present the potential for fraud and product misrepresentation that may be physically or economically harmful to consumers. The collection and processing of bottled water can in some cases be detrimental to the environment, and monitoring and authentication is critical to ensuring that bottled water production does not damage unique or sensitive water sources. Authentication of bottled water, along with many other food products, represents an important and growing challenge to agencies that monitor and assure the quality, authenticity and region of origin of consumer goods in the United States, the European Union, and countries around the world.[2,3]

The naturally occurring light stable isotopes of hydrogen and oxygen represent one possible tool for the authentication of bottled water sources.[4] The isotopic ratio ($R = {}^2H/{}^1H$ or ${}^{18}O/{}^{16}O$; reported as δ^2H or $\delta^{18}O$, where $\delta = (R_{sample} - R_{standard})/R_{standard} \times 1000$) of fresh water varies widely and systematically across the earth as a result of the spatially and temporally variable climatic patterns which govern the delivery of precipitated water to geographic regions.[5] Strong trends in δ^2H and $\delta^{18}O$ values occur with increases in latitude, altitude, and continentality,[5–7] and these patterns are relatively well known and documented as maps of precipitation stable isotope ratios.[6–9] An additional parameter, deuterium excess (d, where $d = \delta^2H - 8 \times \delta^{18}O$), reflects the effects of re-evaporation off the continents on water sources. Values of d for meteoric waters average +10‰ globally,[10] with significantly lower values characterizing

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**Correspondence to*: G. J. Bowen, Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112, USA.
E-mail: gbowen@biology.utah.edu

partially evaporated waters and higher values being indicative of recycled moisture. Where extraction and purification processes do not modify the isotopic composition of bottled waters, the known geospatial variation in natural water isotope ratios constitutes a tracer of the water source, even if the water is bottled far from that source.

Many treatment methods used to purify bottled water, such as filtration, ultraviolet sterilization, and ozone treatment, should involve minimal loss or addition of elemental H and O or molecular water, and therefore have little to no effect on the isotope ratios of bottled water. Two other purification processes, reverse osmosis and distillation, may involve the loss of some molecular water and therefore carry the potential for modification of source water isotope ratios. Although reverse osmosis involves the separation and extraction of two hydrous phases (pure water and waste water), this separation occurs under extreme pressure gradients. Most mass transfer of water during the reverse osmotic procedure is therefore likely to occur by viscous flow and without significant isotopic fractionation (see, however, Coplen and Hanshaw[11]). Distillation, less commonly used in commercial applications due to its low energy efficiency, provides the potential for fractionation of the hydrogen and oxygen isotopes if the distillation process is not carried to completion. Because some commercial water purification plants, particularly those dealing with waters having high solute loads (e.g., seawater desalination plants), discard a large fraction (up to ~85%) of water as waste,[12] distillation represents the purification method with the greatest potential to modify source-water isotope ratios.

To our knowledge, no comprehensive or current database of bottled water stable isotope ratios exists. A primary goal here is to present a first isotopic characterization of bottled waters sourced and distributed from locations around the world. We present measured isotope ratios for a large number of bottled waters, and we compare these with estimated natural water isotope ratios for reported source and known purchase locations of the waters, where these are available. The patterns revealed by this analysis, as well as notable exceptions to those patterns, provide a foundation for the application of light stable isotopes in the authentication of bottled waters. In addition, they isotopically characterize a dietary element that represents a significant fraction of water intake for many humans, with implications for criminal forensic applications that rely on isotopic relations between human body tissues and diet. Lastly, the data presented here may be useful in guiding laboratories in the selection of bottled waters for use as working standards.

EXPERIMENTAL

Samples of bottled waters were collected between 1998 and 2005 through personal purchases and solicitation of colleagues, family and coworkers. Water samples were stored in their original, unopened bottles from the time of purchase until the time of analysis. Information on purchase location was recorded when known, and information on water source location was taken from bottle labels where indicated.

Aliquots of the bottled water samples were prepared for hydrogen and oxygen isotope ratio determination via either manual or automated preparation methods at the University of Utah (UU) or the University of California, Davis (UCD). For samples analyzed using manual preparation methods, hydrogen and oxygen isotope ratios were determined from individual aliquots of the bottled water sample. Hydrogen isotope ratios were determined by mass spectrometric analysis of H_2 gas produced by a modification of the method of Coleman *et al.*,[13] in which a volume of 2 μL of water is reduced on 100 mg of Indiana University Zn reagent at 500°C (UU). Oxygen isotope ratio determination was made by analysis of CO_2 equilibrated with sample water using either dual viscous inlet[14] (UCD and UU) or continuous flow[15] (UU) methods. Measurement precision, based on the repeated analysis of internal standard waters, for the off-line preparations was ~1.5 and 0.2‰ for δ^2H and $\delta^{18}O$, respectively (1σ).

For analysis via the automated method two techniques were used. At UU, a single 0.5 μL aliquot of water was injected onto a column of glassy carbon held at 1400°C to produce H_2 and CO gases.[16] These were separated chromatographically in a helium carrier gas stream and introduced sequentially into the ion source of an isotope ratio mass spectrometer (Delta +XL; ThermoFinnigan, Bremen, Germany) for isotope ratio determination. Samples analyzed using this method were measured in duplicate, with an average precision (1σ) of 1.3‰ and 0.17‰ for δ^2H and $\delta^{18}O$, respectively, based on 750 duplicate analyses of an internal standard water. At UCD, 3 or 5 mL of sample were pipetted into reaction vessels for δ^2H or $\delta^{18}O$ analyses, respectively. Sample vials were then attached to an on-line automated equilibration system, evacuated through capillaries, backfilled with 0.6 atm of either CO_2 or H_2 and agitated at 18°C for 10 or 5 h, respectively. For the δ^2H analyses, a Finnigan proprietary platinum embedded graphite rod was placed into each reaction bottle to catalyze the equilibration of H_2 with H_2O. Equilibrated gas was analyzed on a Finnigan MAT 251 and converted into SMOW using a regression derived from three calibrated laboratory standards run in duplicate with each analysis run. Average precision ($\pm 1\sigma$) of the UCD analyses is 1.0‰ and 0.05‰ for δ^2H and $\delta^{18}O$, respectively.

Because the data presented here were generated using several analytical methods in two laboratories over the course of >5 years, we conducted a cross-calibration test to determine the degree to which these measurements were comparable. Three water standards from the UU laboratory were analyzed by UCD in May/June of 2005. These standards span a range of 123‰ for δ^2H and 16.3‰ for $\delta^{18}O$. At the UU laboratory, the two standards with end-member compositions are used to calibrate each batch of analyses, and the third, intermediate, water is analyzed daily as an internal check. Throughout the time period during which the bottled water samples were analyzed, the measured value for this standard, as determined using either UU analytical method, has been constant to within analytical uncertainty. The analyses conducted at UCD gave $\delta^{18}O$ values that were indistinguishable from the UU values for all three standards. Hydrogen isotope ratios determined at UCD were within analytical uncertainty of the UU values for the heavy and intermediate standards, and were 1.7‰ lighter than the UU value for the light standard. Given the range of standard δ^2H

values, this difference amounts to a deviation of <1.4% between the two laboratories, a difference we consider to be minor for the application presented here.

The ultimate source of all meteoric water (and of geospatial variation in the isotope ratios thereof) is atmospheric precipitation, and so to investigate the fidelity of the isotopic signature of bottled water with respect to this source we compared bottled water δ^2H and δ^{18}O values with estimated mean annual precipitation isotope ratios for source and purchase locations. Precipitation isotope ratio estimates were generated from a global dataset by detrended interpolation.[8] The database of precipitation isotope observations represented the most recent compilation maintained as of 5/1/2005,[17] and included data from the Global Network for Isotopes in Precipitation[18] and the work of individual authors.

RESULTS AND DISCUSSION

Our collection of bottled waters includes 234 unique samples marketed under at least 136 distinct names. Available records of source and purchase locations suggest that our sample set includes bottled waters sourced from at least 99 unique locations in 35 countries and purchased in at least 61 different locations in 26 countries (Table 1).

Measured stable isotope ratios of our bottled water samples (Fig. 1) range from −147‰ to +15‰ for δ^2H (mean = −58‰) and from −19.1‰ to +3.0‰ for δ^{18}O (mean = −8.0‰). The deuterium excess for individual samples ranges from −17‰ to +31‰, with an average value of +8‰ (Fig. 2). The distribution of deuterium excess values is Gaussian (excess kurtosis = 0) but moderately left-skewed (Fig. 2). Hydrogen and oxygen isotope ratios for the bottled water samples exhibit significant covariance with the estimated isotope ratios of precipitation water both at source and at purchase locations (Fig. 3; F-test, all values of $p < 10^{-8}$).

Rules and exceptions for bottled water isotopes

The hydrogen and oxygen isotope ratios of our bottled water samples lie within a range of values typical of ‘normal’ meteoric waters.[7,10,19,20] Most samples cluster near the global meteoric water line[10] ($\delta^2\mathrm{H} = 8 \times \delta^{18}\mathrm{O} + 10$) when plotted in $\delta^2\mathrm{H}/\delta^{18}\mathrm{O}$ space (Fig. 1). These observations imply that the δ^2H and δ^{18}O values of the bottled waters might reflect a relatively unaltered source water signature. The significant relationship between the bottled water isotope ratios and the estimated isotope ratios of precipitation at the reported source locations also supports this implication. Plots of bottled water vs. source precipitation isotopes, however, reveal a significant amount of variation around the 1:1 relationship expected for perfect incorporation of the local precipitation signal in bottled water (Figs. 3(A) and 3(B)). These deviations may reflect natural, hydrological modification of the precipitation-derived isotopic label prior to extraction of the water for bottling or discrepancies between the reported and true sources of bottled water.

Source water relationships

Hydrological mixing and post-precipitation processes, including evaporation of subaerially exposed water, cause the isotope ratios of surface and groundwater reservoirs to deviate from those of local precipitation to varying degrees.[20] The left-skewed distribution of *d* values and the high (positive) δ^{18}O values of some samples suggest that evaporative processes were important in modifying the stable isotope ratios of some of the bottled waters in our sample set. Within our sample set, a group of nine bottled waters from India (group 1; Figs. 1, 3A and 3B)) can be used to illustrate the isotopic evidence of evaporative effects. These samples include some of the most ^{2}H- and ^{18}O-enriched samples in our dataset, including three of four samples with measured δ^{18}O values above 0‰, and several samples which lie well off of the 1:1 bottled water to source precipitation isotope ratio relationship (Figs. 3(A) and 3(B)). The average *d* value for the samples (−5‰; min = −16‰, max = +3‰) is significantly less than that for estimated mean annual precipitation at the source locations (+10‰; Student’s t-test, $p \ll 0.001$), indicating substantial evaporation of the source waters prior to bottling. Labels from the sampled bottles detail the treatment methods applied to these samples, and indicate that none of the waters were distilled. Partial evaporation of natural water sources in the seasonally dry regions of India from which the samples originated constitutes a likely explanation for the positive offset of isotope ratios for many of the bottled waters in this group relative to those of local precipitation.

The isotope ratios for a second set of bottled water samples in our collection display clear evidence for bottling of at least two distinct water sources, despite their labels indicating a single, common, bottling location. Seven waters in group 2 (Figs. 3(A) and 3(B)) were marketed under a common label by a bottler in western Argentina. The isotope ratios for these waters cluster in two subgroups. Average values for the subgroups are −57‰ (δ^2H; $n = 2$, range = 0.3‰) and −7.8‰ (δ^{18}O; $n = 1$) for the isotopically heavy subgroup and −132‰ ($n = 4$, range = 1.8‰) and −16.2‰ ($n = 1$) for the light subgroup. Four samples of a second brand of bottled water, the label of which indicates that it is bottled at the same location, give average values of −112‰ ($n = 4$, range = 8.8‰) and −14.2‰ ($n = 3$, range = 1.1‰). Single-factor analysis of variance confirms that the δ^2H values of these three subgroups represent statistically distinct populations ($p \ll 0.001$).

The Argentinean samples originated from a region in which two major sources of water are exploited: basinal groundwater and impounded Andean runoff.[21] Neither source is likely to exhibit seasonal isotopic variation of the order observed in the bottled water sample set; groundwater should mix and integrate water derived from throughout the seasonal cycle, whereas the major rivers of this region are fed year-round primarily by melting mountain snow and glacial ice. Basinal groundwater is likely to be derived primarily from infiltration of basinal precipitation, and thus represents a truly ‘local’ water resource. The estimated water isotope ratios for lowland precipitation at the bottling location (−47‰ and −6.6‰ for δ^2H and δ^{18}O, respectively) can be used as an estimate of the isotope ratios of water recharging the basinal aquifers. Of the bottled waters, only those from the heavy subgroup of brand 1 have isotope ratios similar to those of the local precipitation and are likely to be derived from a groundwater source. The bottling location, however,

Table 1. Measured isotope ratios for bottled waters, grouped according to the location of water source and purchase location

Source							Purchase						
			Ave		σ					Ave		σ	
City	State or Province	Country	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	City	State or province	Country	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
Esquel		Argentina	−96	−12.6			Esquel		Argentina	−97	−12.7		
Malargue		Argentina	−114	−15.0			Malargue		Argentina	−114	−15.1		
Mendoza		Argentina	−108 (10)	−13.2 (5)	28.9	3.25	Neuquen		Argentina		−11.8 (2)		0.85
Neuquen		Argentina		−12.4			Brussels		Belgium	−51	−8.1		
Preston	Victoria	Australia	−75	−10.6			Reine		Belgium	−51	−8.1		
Lindoia	Sao Paulo	Brazil	−43	−6.7			Belize City		Belize	−19	−2.3		
San Pedro		Brazil	−54	−8.1			Manaus	Amazonia	Brazil	−39	−5.9		
Bujumbura		Burundi	−29	−4.9			Bujumbura		Burundi	−29	−4.9		
Vancouver	BC	Canada	−109	−13.8			Wotton Township	Quebec	Canada	−80	−12.2		
Revelstoke	BC	Canada	−143 (2)	−18.5 (3)	4.1	1.02	Bejing		China	−66	−8.5		
Feversham	Ontario	Canada	−78	−11.1			Erenhot		China	−66 (4)	−8.9 (4)	23.8	3.16
Piedmont	Quebec	Canada	−72	−10.4 (2)		1.09	Prague		Czech Republic	−35	−6.1		
Wotton Township	Quebec	Canada	−79	−12.2			Sykarainen		Finland	−82 (2)	−10.8 (2)	22.2	3.64
Santiago		Chile	−89 (4)	−11.4 (3)	0.6	0.61	Bad Adelholzen		Germany	−20	−3.4		
Baishan		China	−60	−8.0			Bayreuth		Germany	−62	−9.4		
Hedekilden		Denmark	−54	−7.8			Reykjavik		Iceland	−57 (2)	−8.8 (2)	0.7	0.12
Siwa		Egypt	−45	−8.2			Chandigarh		India		−5.9		
Helsinki		Finland	−78	−11.3			Jaipur		India		−5.2 (2)		2.00
Chatillon-sur-Chalaronne		France	−53 (2)	−7.3	0.4		Khalapur		India	−48	−4.8		
Evian-les-Bains		France	−74	−10.7			Kulu		India	−43	−6.9		
Vergeze		France	−42	−6.3 (3)		0.02	Baghdad		Iraq	−43 (7)	−6.6 (7)	29.4	4.16
Vittel		France	−56 (2)	−7.3 (2)	0.1	0.01	Orvieto		Italy	−45	−6.6		
Gerolstein		Germany	−57 (3)	−8.5 (3)	0.8	0.01	Tokyo		Japan	−3	−1.8		
Vikos		Greece	−68	−10.9			Eldoret		Kenya	−12 (2)	−4.0 (2)	0.5	0.92
Reykjavik		Iceland	−57	−8.7			Mombasa		Kenya	−13	−3.8		
Baddi		India		−6.2 (2)		0.49	Nairobi		Kenya	−16 (6)	−3.6 (7)	4.7	0.75
Bangalore		India	−2	1.7			Nakuru		Kenya	−12	−3.6 (2)	4.2	0.05
Dhar		India	15	2.0			Thica		Kenya	−12	−3.3		
Gurgaon		India		−0.3			Auckland		New Zealand	−34	−5.6		
Hyderabad		India	−8 (3)	−0.8 (3)	9.7	0.66	Putaruru		New Zealand	−34	−5.9		
Jaipur		India		−4.7 (2)		1.38	Lahore		Pakistan	−50	−6.9		
Mumbai		India	−47	−4.8			Dealu Floreni		Romania	−53	−7.2		
Nagpur		India	−10	−1.2			Singapore		Singapore	−32	−6.0 (2)		1.10
Paonta Sahib		India	−39	−5.0			Johannesburg		South Africa	−23 (2)	−5.7 (2)	2.2	1.30
Solan		India	−4	1.0			Jeju-do		South Korea	−38	−6.4		
Dingle		Ireland	−34	−5.1			Seoul		South Korea	−60	−8.7		
Naples		Italy	−42	−6.9 (2)		0.02	Arusha		Tanzania	−76	−11.6		
Popoli		Italy	−63	−9.7			Dar Es Salaam		Tanzania	−42	−6.5		
San Pellegrino Terme		Italy	−62	−9.1 (2)		0.00	Bangkok		Thailand	−23	−4.3		

Scorze		Italy	−56	−8.1		
Tione di Trento		Italy	−40 (3)	−5.8 (4)	2.2	0.67
Jacarta		Java	−32	−5.3		
Amman		Jordan	−30			
Petra		Jordan	−29	−5.9		
Eldoret		Kenya	−12	−3.4		
Kedong		Kenya	−25	−4.3		
Lokichogio		Kenya		−3.1		
Molo		Kenya	−16 (2)	−4.5 (2)	0.7	0.14
Mombasa		Kenya	−13	−2.9 (2)		0.77
Nairobi		Kenya	−25 (5)	−5.3 (5)	28.8	3.54
Nakuru		Kenya	−14	−3.6		
Thika		Kenya	−13	−3.3		
Ulu Tiram		Malaysia		−6.8		
Putaruru		New Zealand	−33	−5.9		
Islamabad		Pakistan	−37	−6.8		
Izvorul Alb		Romania	−53	−7.2		
Nishnij Nowgorod		Russia	−104 (3)	−11.4 (3)	0.3	0.03
Jizan		Saudia Arabia	1			
Trenta		Slovenia	−72 (4)	−10.0 (3)	2.1	0.43
Doornkloof		South Africa	−25	−4.8		
Zambra		Spain	−47			
Henniez		Switzerland	−68	−9.8		
Saxon		Switzerland	−86	−13.2		
Rayong		Thailand	−40	−5.9		
Bethania	Wales	UK	−43	−6.5		
Trofarth Spring	Wales	UK	−38	−6.7		
Blackford	Scotland	UK	−56 (2)	−8.2 (2)	0.6	0.07
Abu Dhabi		United Arab Emirates	−13	−1.9		
North Pole	AK	USA		−15.9		
Alhambra	CA	USA	−54 (2)	−7.5 (3)	3.1	0.56
Baxter	CA	USA	−72 (8)	−10.0 (6)	1.9	0.82
Brea	CA	USA	−64	−9.3		
Calistoga	CA	USA	−54 (5)	−6.9 (3)	3.4	1.28
Fresno	CA	USA	−85	−11.2 (2)		0.83
Livermore	CA	USA	−54	−7.9		
Mt. Shasta	CA	USA	−91	−12.0		
Olancha	CA	USA	−110 (2)	−13.3 (3)	0.7	2.24
Roseville	CA	USA	−71 (5)	−9.7 (4)	2.3	0.92
San Francisco	CA	USA	−55	−7.3		
Weed	CA	USA	−107	−14.5		
Denver	CO	USA	−121	−14.7		
Greenwich	CT	USA	−37 (2)	−6.6 (2)	38.7	4.22
High Springs	FL	USA	−7 (2)	−0.2 (2)	19.6	4.51
Honolulu	HI	USA	−14 (2)	−3.0 (3)	0.9	0.41
Keaau	HI	USA	−16	−3.7 (2)		0.15
Ketchum	ID	USA	−140	−18.3		
Paradise	ID	USA	−136 (2)	−17.3 (3)	2.4	0.98
Rayong		Thailand	−40	−5.9		
Broughton		UK	−45	−6.5		
Fairbanks	AK	USA		−15.9		
Flagstaff	AZ	USA	−64	−9.3		
Berkeley	CA	USA	−99 (2)	−13.3 (2)	11.2	1.80
Los Angeles	CA	USA	−110	−14.5		
San Francisco	CA	USA	−74	−11.1		
San Jose	CA	USA	−64	−9.5		
Denver	CO	USA	−121	−14.7		
Boca Garden	FL	USA	6	2.9		
Gainesville	FL	USA	−9	−3.6		
Gilchrist	FL	USA	−21	−3.4		
Lahaina	HI	USA	−12 (2)	−3.0 (2)	1.5	0.04
Boston	MA	USA	−65	−9.3		
Cambridge	MA	USA	−68	−10.3		
Shoreview	MN	USA	−72	−10.0		
Santa Fe	NM	USA	−80 (2)	−10.6 (2)	0.1	0.06
Corvallis	OR	USA	−128	−15.2		
Greenville	TN	USA		−7.3		
Salt Lake City	UT	USA	−99 (3)	−12.9 (3)	35.0	3.78
Madison	WI	USA	−57	−8.4		

Table 1. Measured isotope ratios for bottled waters, grouped according to the location of water source and purchase location

Source							Purchase						
			Ave		σ					Ave		σ	
City	State or Province	Country	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	City	State or province	Country	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
Barrington	IL	USA	−80	−11.1 (2)		1.11							
Poland Spring	ME	USA	−58 (7)	−7.9 (6)	5.8	1.57							
Rodney	MI	USA	−72	−10.0									
Culver	OR	USA	−127	−15.2									
New Tripoli	PA	USA	−46	−7.1									
South Coventry	PA	USA	−46	−5.0									
Greenville	TN	USA	−46	−7.2 (2)		0.13							
Park City	UT	USA	−118	−14.5									
Salt Lake City	UT	USA	−93 (3)	−12.8 (3)	22.5	2.37							
Amelia	VA	USA	−50	−7.8									
La Crosse	WI	USA	−57	−8.4									
Jericho	West Bank		−32	−4.3									

lies at the foot of the Andes Mountains, and within 100 km of glaciated peaks of nearly 7000 m in elevation. Two dams impound water from the major drainages in this region and provide a large fraction of the water used in the lowlands.[21] This high-altitude terrain provides a likely source for ^{2}H- and ^{18}O-depleted samples in group 2, with estimated isotope ratios for mean annual precipitation as low as −138‰ (δ^2H) and −19.1‰ ($\delta^{18}O$) for the higher parts of the range. The isotopic data, then, suggest that waters from the light subgroup of brand 1 are sourced from high-Andean water, whereas the bottled water sold as brand 2 represents either a third, distinct water source, likely recharged at intermediate elevations, or a mixture of the lowland and Andean sources used by brand 1.

As was the case for the bottled water samples from India, consideration of d values for the Argentinean waters supplements the information provided by the individual isotopes. The average d value for the heavy subgroup of brand 1 (+5‰) is indistinguishable from the estimated value of precipitation at the indicated source location (+5‰), furthering the suggestion that this subgroup represents minimally modified water from local, basinal sources. In contrast, the average d values for the light subgroup (−2‰) and the intermediate waters of brand 2 (+2‰) are much lower, suggesting some evaporation of these waters prior to bottling. The light subgroup value is at the extreme lower end of the range of values observed in arid-region rivers of the United States,[20] and, because of the high relief and short catchment lengths of rivers in this region of Argentina, we believe that it is unlikely that such low d values resulted from evaporation of waters in naturally flowing rivers. Evaporation of water during its residence in the above-mentioned mountain reservoirs, which have turnover times of the order of 2 months,[21] provides a likely mechanism for obtaining the low d values observed for these samples.

Purchase location relationships

Although not reflective of systematic natural processes, the comparison of bottled water isotope ratios with precipitation water isotope ratios at the source of purchase may provide information on general trends in the commercial distribution of water. We have shown that isotope ratios of bottled waters correlate with water isotope ratios of water sources. Because precipitation isotope ratios vary continuously across space, we might therefore hypothesize that if the isotope ratios of bottled water tend to be similar to those of precipitation at the site of purchase, this is consistent with the hypothesis that bottled water sold in a given location tends to be derived from nearby water sources. In contrast, if local precipitation and bottled water isotope ratios were not significantly correlated, this would suggest that the geographic location of bottled water sources was not related to location of purchase. A practical purpose for this exercise is the need to isotopically characterize geospatial variation in the human diet in order to facilitate forensic applications involving diet-induced geospatial variation in the isotope ratios of human body tissues.[22] If the stable isotope ratios of bottled waters are, for whatever reason, characteristically similar to those of other available dietary water sources, then the consumption of bottled water by individuals would be less likely to compromise the

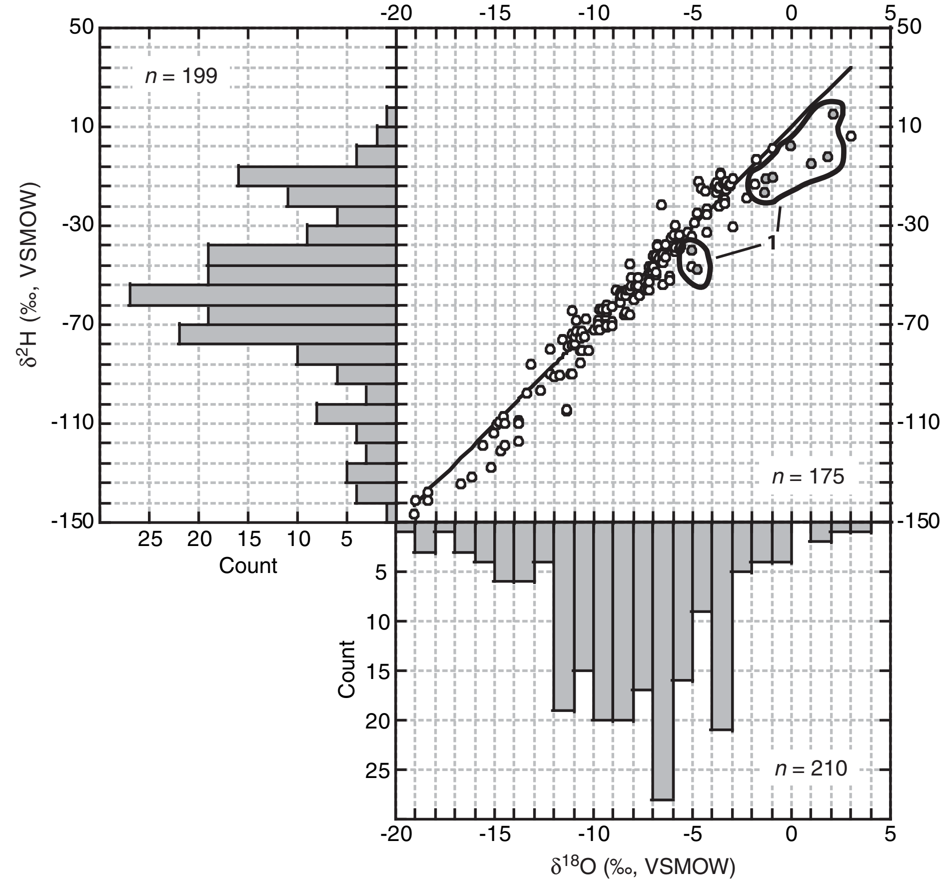

Figure 1. Hydrogen and oxygen isotope ratios of 234 bottled water samples sourced from at least 28 countries worldwide (not all samples were analyzed for both isotopes). The $\delta^2H - \delta^{18}O$ crossplot shows only samples for which both isotope ratios were determined. Samples in group 1 include a subset of bottled waters sourced in India and discussed in the text. The global meteoric water line is shown in black.

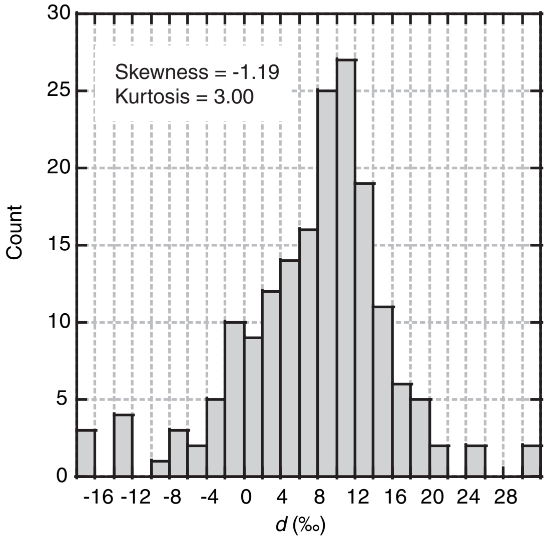

Figure 2. Frequency distribution of deuterium excess values (*d*) for 175 bottled water samples.

isotopic relations between human body tissues and their environment on which these applications are predicated.

Although our study does not constitute a complete examination of the geospatial distribution of bottled water isotope ratios, our more or less random sample of bottled waters does demonstrate a robust relationship between the isotopic composition of bottled water and that of environmental water at the location of purchase (Figs. 3(C) and 3(D)). Not only are these relationships significant, but their predictive power is as great as that of the presumably more systematic relationships between source (precipitation) water and bottled water isotope ratios.

Two groups of samples, each having a common purchase location, can be used to illustrate the potential isotopic variability of bottled waters purchased at a single location. The samples in group 3 (Figs. 3(C) and 3(D)) represent four different bottled waters purchased during a single evening at a train station in northern China. The measured isotope ratios of these samples span a relatively large range (57‰ for δ^2H, 7.5‰ for $\delta^{18}O$). Their average values (−66‰, −8.9‰), however, are indistinguishable from those of precipitation at the purchase location (−68‰, −9.8‰). Two of the four samples have isotope ratios that are very similar to the estimated precipitation at the location of purchase, and probably originated from a local water source. Of the other two samples, one has isotope ratios that are much lower than local precipitation and the other has values much higher. Source locations are not available for these waters but, given that these samples were purchased on the platform of a major

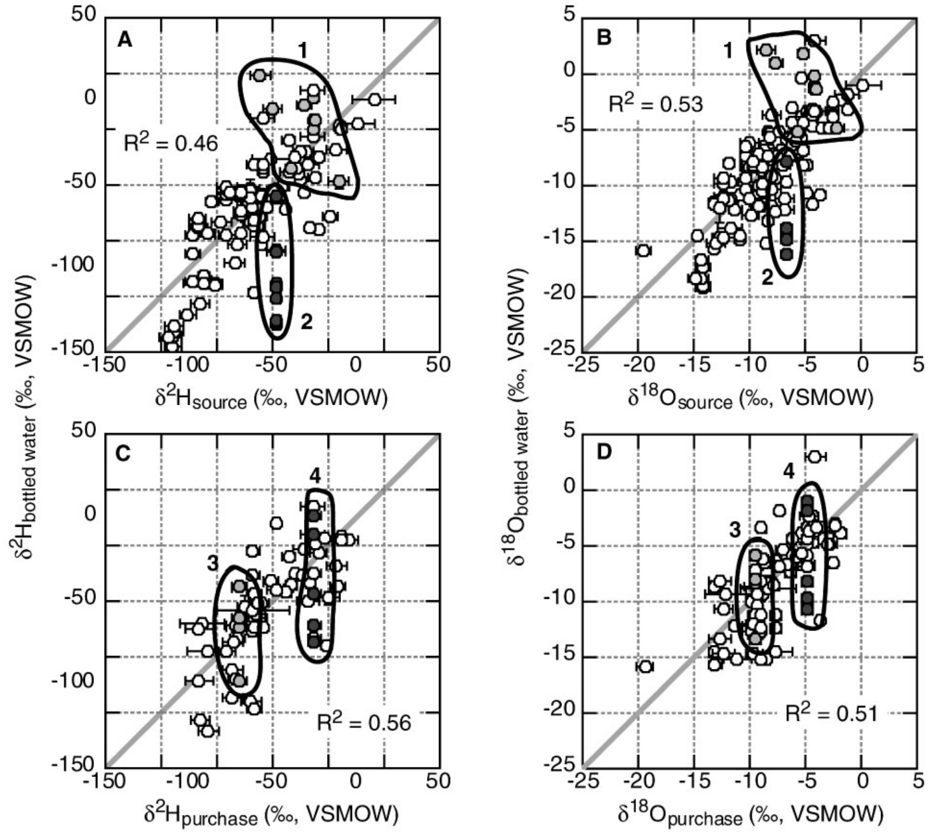

Figure 3. Measured hydrogen and oxygen isotope values of bottled waters plotted against estimated isotope ratios for mean annual precipitation at the reported source (A, B) or purchase (C, D) location. Error bars represent 95% confidence intervals on the precipitation isotope ratio estimates.[8] Sample groups 1 (light grey fill) and 2 (dark grey fill) in A and B and 3 (light grey fill) and 4 (dark grey fill) in C and D are discussed in the text. Diagonal lines correspond to a 1:1 relationship, rather than an empirical fit to the data.

north-south running rail line, our interpretation of the isotopic data is that these represent samples bottled at locations to the north and south, respectively, of the purchase location and shipped along the rail line.

The six samples comprising group 4 (Figs. 3(C) and 3(D)) were obtained from a military camp in Baghdad, Iraq. The measured isotope ratios for these samples span a large range (75‰ for δ^2H, 9.7‰ for δ^{18}O), and give average values (−45‰, −7.0‰) that are somewhat lighter than those estimated for Baghdad precipitation (−22‰, −4.8‰). Source locations are available for these samples, and suggest that none of the bottled water originated within Iraq. The lightest isotope ratios in group 4 represent waters sourced from Europe, whereas the heaviest values are from a water sample bottled in Saudi Arabia. The relatively low average isotope ratios for bottled waters in group 4 reflect the fact that three out of the six waters sampled were of European origin.

Bottled water standards

Another potential use for the dataset presented here is as a source of information for choosing bottled waters for use as laboratory consistency standards or internal working standards for the analysis of oxygen and hydrogen isotope ratios in natural water samples. Bottled waters are convenient, clean and widely available, making them an attractive source of water standards. Our data also demonstrate that the δ^2H and δ^{18}O values of commercially available bottled waters span a large range, meaning that bottled water standards, if properly chosen, could be used in the analysis of most naturally occurring waters. The data obtained here will allow isotope laboratories to choose bottled waters that closely bracket the isotope variations expected in natural waters for applications where high precision and consistency of standardization is required. Although most laboratories using bottled waters as standards choose to obtain, homogenize, and store large volumes of water suitable for long-term standardization efforts, stability of isotope ratios across batches and through time may be an important consideration in selecting waters that are likely to have isotope ratios that are reliably and consistently close to targeted standard values. Our study did not include a systematic investigation of isotope ratio variability, but we were able to estimate between-sample isotope ratio variance for some bottled water brands that were repeatedly sampled. To aid laboratories in selection of bottled waters for use as standards, we have archived our dataset of average values and variance of the isotope ratios for the water brands sampled here.[17]

CONCLUSIONS

Our sample of bottled waters from around the world documents the range and patterns of stable hydrogen and oxygen isotopic variability in commercially marketed water. In addition to their use in identifying standards for water isotope ratio analysis, isotope ratio data for these waters promise to be applicable in two ways: as a tool for authenticating and understanding the source of bottled water products, and as a means of characterizing an increasingly important component of the human diet. Examples such as our case studies of Indian and Argentinean bottled waters demonstrate both the complexity and the power of stable isotopes as tools for authentication or monitoring of bottled water products. These properties derive from the fact that water isotopes serve as tracers of ultimate source of waters, reflecting the location of water recharge rather than extraction. Furthermore, the isotopic signal of source can be subtly or substantially modified by post-precipitation processes such as evaporation. Two arguments can be advanced as to why these properties of the water isotope tracer method do not compromise the value of the method. First, one major concern of the agencies that regulate bottled water production is that extraction and packaging of water be done in an environmentally conscious manner. This concern involves the whole of the hydrological systems which might potentially be affected by bottled water production, and stable water isotopes provide a link between a bottled water product and the hydrological system from which it is derived. The ability to investigate and verify claims about the water resources being tapped by bottled water production, as for instance in our case study of Argentinian waters, is thus a potentially important tool for regulatory agencies. Second, the power of the isotope tracer method for bottled water authentication will grow as further information is collected. Our analysis was based on comparing measured bottled water isotope ratios with a generalized grid of precipitation isotope ratios. Future development of the method could focus on establishing a catalogue of source water isotope ratios that could, for instance, enable authorities to distinguish between natural spring and municipal water sources present in the same general location.

Two case studies in which we examined the isotopic ratios of numerous bottled waters purchased at a single location clearly demonstrated that transport of water products can lead to substantial differences between the stable isotope ratios of bottled water and of environmental water at the location of purchase. Our case studies focused on extreme cases, however, in which transport of water products over long distances was expected (waters purchased at a station on a major north-south rail line and a military camp in the Middle East). Despite this, however, in both cases the range of bottled water isotope ratios observed spanned the estimated values for environmental water at the location of purchase, and the average values for the set of bottled waters were not very different than the local water values. This suggests a general tendency, even in these extreme cases, for marketeers to make available the conveniently obtained bottled water products from all surrounding sources, with the consequence that the array of available products tends to represent the range of water isotope ratios characteristic of the region of purchase. Although concerted consumption of exotic, designer brands of water may represent an isotopically distinct dietary component in some individuals, in most cases the isotopic intake of individuals resulting from consumption of locally purchased bottled water should be approximated reasonably well by the isotope ratios of other local water resources.

This first compilation of data on the stable isotope ratios of bottled waters of the world demonstrates that isotope ratio analysis represents a potentially powerful tool for regulatory monitoring of bottled water products. Isotopic signatures of source water are preserved in bottled water, and can provide information on the ultimate (recharge) and proximal (reservoir) sources of bottled water. Further characterization of water sources is needed to fully exploit the potential of this tool, but our dataset allows us to say with confidence that significant relationships exist between bottled and environmental waters and that these relationships are worthy of further investigation.

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REFERENCES

1. Available: http://www.bottledwater.org.
2. Rossmann A. *Food Rev. Int*. 2001; **17**: 347.
3. Dennis MJ. *The Analyst* 1998; **123**: 121R.
4. Ingraham NL, Matthews RA, McFadyen R, Franks AL. *Environ. Eng. Geosci*. 2004; **10**: 361.
5. Dansgaard W. *Tellus* 1964; **16**: 436.
6. Bowen GJ, Wilkinson B. *Geology* 2002; **30**: 315.
7. Rozanski K, Araguas-Araguas L, Gonfiantini R. In *Climate Change in Continental Isotopic Records*, Swart PK, Lohmann KC, McKenzie J, Savin S (eds). American Geophysical Union: Washington, DC, 1993; 1–36.
8. Bowen GJ, Revenaugh J. *Water Resour. Res*. 2003; **39**, 1299. DOI: 10.129/2003WR002086.
9. Bowen GJ, Wassenaar LI, Hobson KA. *Oecologia* 2005; **143**: 337.
10. Craig H. *Science* 1961; **133**: 1702.
11. Coplen TB, Hanshaw BB. *Geochim. Cosmochim. Acta* 1973; **37**: 2295.
12. Wanger AL, Dettmer A, Luster T. *Draft Report on Seawater Desalination and the California Costal Act*. California Coastal Commission: San Francisco. 2003; 56.
13. Coleman MI, Shepard TJ, Durham JJ, Rouse JE, Moore GR. *Anal. Chem*. 1982; **54**: 993.
14. Epstein S, Mayeda T. *Geochim. Cosmochim. Acta* 1953; **4**: 213.
15. Fessenden JE, Cook CS, Lott MJ, Ehleringer JR. *Rapid Commun. Mass Spectrom*. 2002; **16**: 1257.
16. Sharp ZD, Atudorei V, Durakiewicz T. *Chem. Geol*. 2001; **178**: 197.
17. Available: http://www.WaterIsotopes.org.
18. IAEA/WMO. Global Network for Isotopes in Precipitation, the GNIP Database, 2004. Available: http://isohis.iaea.org/.
19. Dansgaard W. *Geochim. Cosmochim. Acta* 1954; **6**: 241.
20. Kendall C, Coplen TB. *Hydrolog. Process*. 2001; **15**: 1363.
21. Araujo ED, Bertranou A. *Systemic Study of Water Management Regimes: Mendoza, Argentina*. South American Technical Advisory Committee, Global Water Partnership. 2004; 102.
22. Longinelli A. *Geochim. Cosmochim. Acta* 1984; **48**: 385.