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8-2011

# Evaporative Enrichment of Oxygen-18 and Deuterium in Lake Waters on the Tibetan Plateau

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The final publication is available at Springer via <http://dx.doi.org/10.1007/s10933-011-9540-y>

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## Recommended Citation

Yuan F, Sheng Y, Yao T, Fan C, Li J, Zhao H, Lei Y. 2011. Evaporative enrichment of oxygen-18 and deuterium in lake waters on the Tibetan Plateau. *J Paleolimnol.* 46(2):291-307.

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**Authors**

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# Evaporative enrichment of oxygen-18 and deuterium in lake waters on the Tibetan Plateau

Fasong Yuan · Yongwei Sheng · Tandong Yao ·  
Chaojun Fan · Junli Li · Hui Zhao · Yanbin Lei

**Abstract** Stable isotopes ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) are useful tracers for investigating hydrologic and climatic variability on a variety of temporal and spatial scales. Since the early isotopic studies on mountainous glaciers in the late 1960s, a great deal of information has been generated on the isotopic composition of rainfall, snow, ice, surface waters, and lake carbonate sediments across the Tibetan Plateau. However, measurements of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake water are scarce. Here we present a new dataset of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake waters collected from 27 lakes across the plateau during a reconnaissance survey in summer 2009.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake water range from  $-19.9$  to  $6.6\text{‰}$  and from  $-153$  to  $-16\text{‰}$ , respectively.

The average values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are  $-6.4$  and  $-72\text{‰}$ , considerably greater than those of precipitation observed in this region. The derived Tibetan lake water line,  $\delta\text{D} = 5.2\delta^{18}\text{O} - 38.9$ , is significantly different from the global meteoric water line. Most of the lakes, including some freshwater lakes, contain water with negative values of  $d$ -excess ( $d$ ). There is a negative correlation between  $d$  and total dissolved solids (TDS). Each of these findings indicates that evaporation-induced isotopic enrichment prevails in Tibetan lakes. Moreover, we develop an isotope modeling scheme to calculate E/P ratios for Tibetan lakes, using a combination of existing isotopic fractionation equations and the Rayleigh distillation model. We use the intersection of the local evaporation line and GMWL as a first approximation of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake water inputs to infer an E/P ratio for each lake. Our modeling

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calculations reveal that although variable from lake to lake, the water budget across the plateau is positive, with an average E/P of 0.52. This is in good agreement with other observational and model data that show varying degrees of increases in lake size from satellite imagery and significant decreases in lake salinity in many lakes on the plateau over the last several decades. Together with the new isotopic dataset, the proposed modeling framework can be used to examine and quantify past changes in a lake's hydrologic balance from the isotopic record of downcore carbonate sediments in the region.

**Keywords** Stable isotope · Deuterium excess · Total dissolved solids · Evaporative enrichment · Lake water · Isotopic model · Tibetan Plateau

## Introduction

Studies of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of natural waters can provide information on the climate today and in the past, because mechanisms associated with hydrological cycles, including the water source, trajectory, and other hydroclimatic processes, all affect the isotopic composition of meteoric waters (Friedman 1983). Precipitation derived from different atmospheric circulation patterns usually has a distinctive isotopic signature. In the American Southwest, for example, the average  $\delta^{18}\text{O}$  values of precipitation from the Pacific North are  $\sim 4\text{‰}$  more negative than those ( $-3\text{‰}$ ) from the Gulf of Mexico (Welker 2000; Yuan and Miyamoto 2008). On the Tibetan Plateau, such investigations were first carried out in the Mount Everest region in the late 1960s (Zhang et al. 1973). Since the first station at Lhasa was established by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) global network of isotopes in precipitation (GNIP) in 1986, there have been over a dozen monitoring stations across the plateau that provide a continuous isotopic record of precipitation with a time span over 10 years (Yao et al. 2009). As a result of these monitoring efforts, observations similar to those made about moisture sources for the American Southwest can be made about moisture sources for the Tibetan Plateau. For example, the average  $\delta^{18}\text{O}$  values of precipitation from the Asia monsoon are  $8\text{‰}$  more negative than those ( $-7.7\text{‰}$ ) from the westerlies (Yao et al. 2009).

Lakes, especially those in hydrologically closed basins, are natural integrators of surficial processes and thus important information sources for paleoclimate reconstruction (Forester 1987). Variations in  $\delta^{18}\text{O}$  of lake carbonate sediments are associated with changes in  $\delta^{18}\text{O}$  of lake water ( $\delta^{18}\text{O}_{\text{L}}$ ) and water temperature in the past and therefore are used to infer past changes in climatic, hydrologic and even tectonic variables, including temperature (von Grafenstein et al. 1999; Huang et al. 2002), altitude (Rowley et al. 2001; Rowley and Currie 2006), precipitation regimes (Kirby et al. 2001; Stevens and Dean 2008), and hydrologic balance (Benson et al. 2002; Yuan et al. 2004; Gibson et al. 2005). Tibetan lakes have recently become a hotspot of paleoclimate research because (1) there are nearly 1,100 lakes with a surface area of over  $1\text{ km}^2$  (Yao 2008) (2) most of the lakes are in hydrologically closed basins with minimal anthropogenic disturbances, and (3) the closed-basin lakes are more sensitive to climate change. A number of stable isotope records from lake sediments have been generated across the plateau (Lister et al. 1991; Fontes et al. 1996; Holmes et al. 2007). These studies have provided important information for paleoclimate reconstruction in this region. But there exists an information gap between instrumental isotopic data of precipitation and isotope records of lake sediments over the Tibetan Plateau.

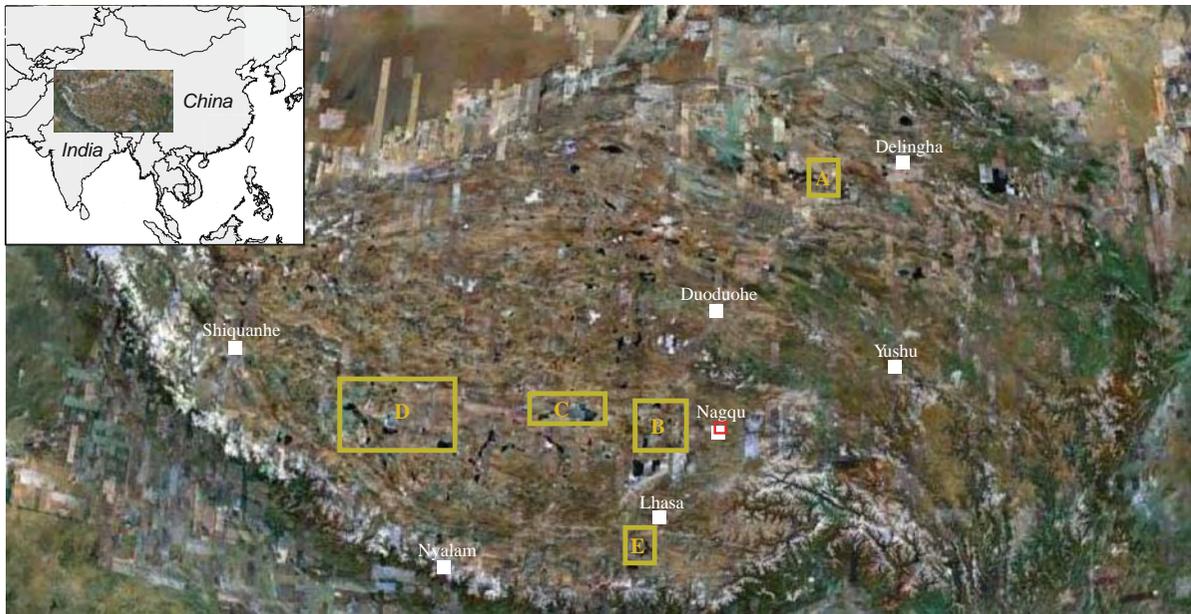
In this study, we focus on evaporation-induced isotopic enrichment in Tibetan lakes and report our attempts to improve our understanding of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in modern lake waters, which helps to bridge the information gap between instrumental isotopic data of precipitation and isotope records of carbonate sediments from lakes on the Tibetan Plateau. Objectives of this work are (1) to characterize the lake-water isotopic geochemistry of the plateau, which complements existing data on the isotopic composition of precipitation and stream waters, (2) to develop an isotope modeling framework to calculate the E/P ratio of lakes using measurable environmental variables (i.e.  $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) and through an optimization procedure for unknown parameters, and (3) to demonstrate the usefulness of the lake-water isotopic data and the isotope modeling framework for interpreting and reconstructing the E/P balance history from the isotopic composition of downcore carbonate sediments from Tibetan lakes.

## Study area

The Tibetan Plateau, situated in central Asia, is the largest and highest plateau on Earth, with an area of over 2.5 million km<sup>2</sup> and an average elevation of over 4,000 m (Yao 2008). Geologically, it consists of four blocks or terranes accreted successively to Eurasia, namely the Songpan–Ganzi flysch complex, the Qiangtang Terrane, the Lhasa Terrane, and the Himalaya (Dewey et al. 1988). Except for one lake (Qarhan Salt Lake) in the northeastern corner of the plateau, all the lakes sampled are located in the Lhasa Terrane and southern Tibet (Fig. 1). The main rock units exposed in the Lhasa Terrane include Jurassic–Cretaceous sedimentary and igneous rocks (north), Carboniferous–Permian metasedimentary and lower Cretaceous volcano–sedimentary rocks (central), and Cretaceous–early Tertiary Gandese batholiths and volcanic rocks (south) (Leier et al. 2007; Zhu et al. 2009).

The climate on the plateau, though varying considerably from west to east and from north to south, is characteristically cold and dry with seasonal winds, strong solar radiation, and a large diurnal

temperature cycle. Annual precipitation ranges from less than 20 cm at Delingha in the northern plateau to over 50 cm at Nyalam in the southern plateau (Zhang et al. 2001), from less than 10 cm at Shiquanhe in the western plateau (Yu et al. 2007, 2009) to 47 cm at Yushu in the eastern plateau (Yu et al. 2006a; Tian et al. 2008c). Most (over 80%) of the precipitation occurs during the summer, from June to September (Yeh and Gao 1979). The precipitation regime in this region is regulated primarily by the westerlies and the Asian monsoon system, which are usually characterized by a distinctive  $\delta^{18}\text{O}$  signature (Araguas–Araguas et al. 1998; Johnson and Ingram 2004). There are three atmospheric circulation zones over the plateau: (1) the monsoon-dominated precipitation zone south of 30°N with an average  $\delta^{18}\text{O}$  value of  $-16.2\text{‰}$ , (2) the westerly-dominated precipitation zone north of 35°N with an average  $\delta^{18}\text{O}$  value of  $-7.7\text{‰}$ , and (3) the transitional precipitation zone between 30°N and 35°N with an average  $\delta^{18}\text{O}$  value of  $-11.8\text{‰}$  (Yao et al. 2009). Although variable from lake to lake, the mean annual air temperature is 1.5°C in central Tibet and the mean summer surface water temperature is 13.5°C (Liu et al. 2009). Most lakes on



**Fig. 1** Google Earth map showing locations of lake groups and precipitation monitoring stations. *Group A*: Qarhan Salt Lake; *Group B*: Zige Tangco, Daru Co, Bong Co, Pung Co, and Bam Co; *Group C*: Serbug Co, Bangkog Co, and Dagze Co; *Group D*: Dong Co, Zhaixi Co, Dawa Co, Qingmuke Co,

Angku Co, Qigai Co, Zhari Namco, Merqung Co, Taro Co, Zabuye Caka, Rinqin Xubco, Ngangla Ringco, Garing Co, and Youbu Co; *Group E*: Chen Co, Bajiu Co, Yamdrok Co, and Kongmu Co. Red open square denotes approximate location of Ahung Co

the plateau freeze during the winter (December–April). Evaporation is fairly strong over the entire plateau with an average rate of 170 cm/year, as indicated by pan evaporation data (Zhang et al. 2007). The evaporation rate of Yamdrok Co (southern Tibet) is around 130 cm/year (Tian et al. 2008a), comparable to that found in the western margin of the Great Basin in the United States (Yuan et al. 2006a).

## Materials and methods

### Field work and sampling

A reconnaissance survey of 27 lakes along a south-north transect from 28.8° to 36.85°N and a west-east transect from 83.4° to 91.1°E (Fig. 1) on the Tibetan Plateau was jointly carried out by the University of California, Los Angeles (UCLA) and the Institute of Tibetan Plateau Research in summer 2009. The 27 lakes are quite diverse in size, with lake surface areas ranging from 6 to 1,000 km<sup>2</sup>. Most lakes sampled can be categorized as high-altitude lakes with elevations of over 4,400 m.

Water pH, temperature, and electrical conductivity were measured in situ using a handheld meter with probe. Water samples were hand-dipped along the lake shore at a water depth of 10–15 cm where relatively clean water was found. Clean water bottles were slowly filled completely to minimize post-sampling alteration in water isotopic composition. The water samples were collected in 500-mL wide-mouth plastic bottles.

### Analytical methods

Each water sample was later partitioned into two halves for chemical and isotopic analyses. Chemical analyses of major ion concentrations in the water samples were conducted at Xinjiang Institute of Ecology and Geography in China. Methods used include double indicator titration for total alkalinity (carbonate and bicarbonate), silver nitrate titration for chloride, barium chromate photometry for sulfate, and atomic absorption spectroscopy for Na, K, Ca, and Mg. The analytical errors were 5% for anions and 10% for cations.

Approximately 1 mL of water was subsampled and passed through a 0.45- $\mu$ m filter immediately

upon arrival at Cleveland State University. Isotopic analysis was carried out at Duke University, using a Thermo Finnigan TC/EA with GC-PAL autosampler attached to a Thermo Finnigan Delta Plus XL continuous flow mass spectrometer via a ConFlo III interface. Stable isotope values are reported using the standard  $\delta$  notion relative to the NIST/IAEA reference material V-SMOW. The analytical precisions were  $\pm 0.1$  and  $\pm 1.5\%$  for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively.

### Modeling methods

Lake isotopic enrichment may be described by the Rayleigh equation (Rayleigh 1896),

$$\ln\left(\frac{R_L}{R_L^0}\right) = (\alpha^* - 1) \ln f \quad (1)$$

where  $R_L^0$  is the isotopic ratio of the initial bulk lake water,  $R_L$  is the instantaneous isotopic ratio of lake water,  $f$  is the fraction of water remaining in the lake and is equivalent to  $1 - E/P$ , and  $\alpha^*$  is the vapor-liquid isotopic fractionation factor (i.e.  $\alpha^* < 1$ ).

The isotopic fractionation factor during evaporation is controlled exclusively by equilibrium and kinetic processes. Craig and Gordon (1965) developed a linear resistance evaporation model to formulate equations for this isotopic fractionation factor, which relates the isotopic ratio of instantaneous water vapor leaving a water surface to measurable environmental parameters. Based on the same evaporation theory, Benson and White (1994) derived an alternative equation as follows.

$$\alpha^* = \alpha_{\text{kin}}^* \left[ \frac{\alpha_{\text{eq}}^* - \frac{hf_a R_a}{R_L}}{1 - h + \alpha_{\text{kin}}^* h(1 - f_a)} \right] \quad (2)$$

where  $h$  is the relative humidity,  $R_a$  is the isotope ratio of the atmospheric water vapor,  $R_L$  is the instantaneous isotopic ratio of lake water,  $f_a$  is the fraction of advected atmospheric water vapor in the boundary layer over the lake,  $\alpha_{\text{eq}}^*$  is the equilibrium fractionation factor, and  $\alpha_{\text{kin}}^*$  is the kinetic fractionation factor.

The equilibrium fractionation factor is dependent on the water temperature at the evaporating surface. Empirical equations are given to determine the equilibrium fractionation factor for  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , respectively (Majoube 1971).

$$\frac{1}{\alpha_{\text{eq}}^*} = \exp\left(\frac{1137}{T^2} - \frac{0.4156}{T} - \frac{2.0667}{1000}\right) \quad (3)$$

$$\frac{1}{\alpha_{\text{eq}}^*} = \exp\left(\frac{24844}{T^2} - \frac{76.248}{T} + \frac{52.61}{1000}\right) \quad (4)$$

where  $T$  is the air-water interface temperature in °K.

The kinetic fractionation factor is determined largely by the molecular transport properties (e.g. diffusivity) of the water isotopomers (Hendricks 1999). This isotopic fractionation factor may be approximated by (Stewart 1975):

$$\alpha_{\text{kin}}^* = \left[\frac{D_{\text{H}}}{D_{\text{L}}}\right]^n \quad (5)$$

where  $D_{\text{H}}$  is the diffusivity of the heavy isotopomer,  $D_{\text{L}}$  is the diffusivity of the light isotopomer, and  $n$  is a parameter with a range of 0–1, which reflects the relative importance of molecular over turbulent diffusion.  $D_{\text{H}}/D_{\text{L}}$  values are 0.969 and 0.984 for  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  and  $\text{HD}^{16}\text{O}/\text{H}_2^{16}\text{O}$ , respectively (Cappa et al. 2003).

## Results

There are great variations in water chemistry of lakes on the plateau (Table 1). Lake water samples tested include fresh water and saline water, with TDS values ranging from 0.2 g/L (Bong Co) to 295 g/L (Zabuye Caka). The coefficient of variation in TDS is 2.46. Most of the lake waters are mildly alkaline, with pH over 8 and below 10.  $\text{Na}^+$  and  $\text{K}^+$  are dominant cations, and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are dominant anions in many lake waters.

The analytical results of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  also show great variations (Table 2), with values ranging from  $-19.9$  to  $6.6\text{‰}$  in  $\delta^{18}\text{O}$  and from  $-153$  to  $-16\text{‰}$  in  $\delta\text{D}$ . The average  $\delta^{18}\text{O}$  value of lake waters is  $-6.4\text{‰}$ , considerably greater than that of precipitation (i.e.  $-15\text{‰}$ ) in this region. The coefficient of variation of  $\delta^{18}\text{O}$  is 0.68.

The deuterium enrichment ( $d$ -excess or  $d$ ), defined as  $d = \delta\text{D} - 8\delta^{18}\text{O}$  (Dansgaard 1964), is the intercept of the GMWL.  $d$  values of lake waters on the plateau change from  $-69\text{‰}$  in Qarhan Salt Lake to  $6\text{‰}$  in Gyrging Co, with an average of  $-21\text{‰}$ , substantially lower than the average  $d$  values ( $10\text{‰}$ ) of precipitation over the world.

There is a strong correlation ( $\delta\text{D} = 5.2\delta^{18}\text{O} - 38.9$ ,  $r = 0.98$ ,  $N = 30$ ) between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of

lake waters from the plateau (Fig. 2). Not surprisingly, open lakes (i.e. lakes with outlets) usually contain relatively low values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  compared to hydrologically closed lakes. The Tibetan lake water line (TLWL) as illustrated in Fig. 2 deviates significantly from the GMWL. Additionally, there is a statistically-significant negative log-linear correlation between  $d$  and TDS of lake waters from the plateau (Fig. 3).

## Discussion

### Relation between of $\delta^{18}\text{O}$ and $\delta\text{D}$

$\delta^{18}\text{O}$  and  $\delta\text{D}$  values of global meteoric waters change in a systematic manner, which follows the GMWL of  $\delta\text{D} = 8\delta^{18}\text{O} + 10$ , as defined by Craig (1961), Rozanski et al. (1993). Although the exact relation between of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in precipitation may change from region to region, the local meteoric water line (LMWL) of isotopic data from the Tibetan Plateau is fairly consistent and close to the GMWL. Isotopic data from the GNIP station at Lhasa show a LMWL of  $\delta\text{D} = 7.9\delta^{18}\text{O} + 10.2$ . The LMWL in other parts of the plateau has been reported as follows: (1)  $\delta\text{D} = 8.5\delta^{18}\text{O} + 15.2$  at Delingha in the northern plateau (Tian et al. 2001), (2)  $\delta\text{D} = 8.2\delta^{18}\text{O} + 17.5$  at Tuotuohe in the central plateau (Tian et al. 2001), and (3)  $\delta\text{D} = 8.1\delta^{18}\text{O} + 8.0$  at Shiquanhe in the western plateau (Yu et al. 2007).

Recently, Hren et al. (2009) developed a Tibetan river water line (TRWL) of  $\delta\text{D} = 8.5\delta^{18}\text{O} + 17.5$  based on  $\delta^{18}\text{O}$  and  $\delta\text{D}$  data from 191 streams across the plateau. The isotopic data from the current study show a distinct Tibetan lake water line (TLWL) with a slope of 5.2 (Fig. 2), deviating significantly from the TRWL, the LMWLs, and the GMWL. The deviation is interpreted to indicate the presence of evaporation because evaporation-induced isotopic fractionation usually causes deuterium enrichment in water vapor and subsequently an isotopic enrichment of  $^{18}\text{O}/^{16}\text{O}$  relative to D/H in lake water.

### Correlation of $d$ and TDS

Diffusion of  $\text{H}_2^{18}\text{O}$  relative to  $\text{H}_2^{16}\text{O}$  is slower than that of  $\text{HD}^{16}\text{O}$  relative to  $\text{H}_2^{16}\text{O}$  during evaporation occurring at the air–water interface (Cappa et al. 2003). This

**Table 1** Temperature, pH and major ion water chemistry of lakes on the Tibetan Plateau

Sample No.	Lake name or site description	T (°C)	pH (S.U.)	CO <sub>3</sub> (mg/L)	HCO <sub>3</sub> (mg/L)	Cl (mg/L)	SO <sub>4</sub> (mg/L)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	TDS (g/L)
TP-01	Qarhan Salt Lake	9.0	5.7	—	352	150,591	8,958	76	508	6,445	97,156	264.1
TP-02	Zige Tangco	9.1	9.9	121	1,529	2,295	8,793	95	277	742	5,302	19.2
TP-03	Daru Co	16.7	9.1	45	178	853	4,248	76	392	301	1,686	7.8
TP-04	Bong Co (outlet)	16.9	8.8	4	40	93	44	15	21	27	27	0.3
TP-05	Bong Co (NW)	16.4	8.4	3	46	14	112	19	12	21	26	0.3
TP-06	Bong Co (mid-W)	16.4	8.1	—	44	14	129	17	17	10	29	0.3
TP-07	Bong Co (SW)	17.5	8.2	—	35	29	80	15	13	14	21	0.2
TP-08	Pung Co	16.8	9.7	445	2,176	861	3,997	76	242	357	2,881	11.0
TP-09	Bam Co	16.0	9.6	112	483	1,362	4,195	76	196	292	2,533	9.2
TP-10	Bangkog Co	16.5	9.5	125	400	6,310	11,284	57	346	1,252	8,288	28.1
TP-11	Serbug Co	9.8	9.5	173	457	545	2,281	76	265	220	1,034	5.1
TP-12	Dagze Co	9.7	9.9	64	770	1,434	11,354	76	92	471	6,171	20.4
TP-13	Dong Co	10.2	8.9	13	277	11,115	29,610	95	993	5,011	16,576	63.7
TP-14	Zhaixi Co	10.1	9.4	208	580	2,151	9,870	57	358	1,006	5,170	19.4
TP-15	Dawa Co	10.5	9.3	112	272	3,155	14,193	57	542	945	7,390	26.7
TP-16	Qingmuke Co	10.8	9.6	52	158	574	3,145	57	346	214	1,134	5.7
TP-17	Angku Co	10.5	9.1	17	53	337	893	23	35	84	539	2.0
TP-18	Qigai Co	11.7	9.6	9	26	22	170	15	12	5	70	0.3
TP-19	Zhari Namco	10.7	9.5	147	396	1,219	7,567	57	231	353	3,970	13.9
TP-20	Merqung Co	10.0	9.2	61	457	2,510	3,179	23	14	219	3,187	9.7
TP-21	Taro Co	11.5	8.8	17	62	115	249	11	25	36	148	0.7
TP-22	Zabuye Caka	20.4	9.4	372	2,061	157,762	15,174	227	58	21,170	97,723	294.5
TP-23	Rinqin Xubco	19.8	9.4	86	237	495	1,560	76	69	88	954	3.6
TP-24	Ngangla Ringco	19.3	9.4	61	501	3,155	9,002	57	254	418	5,803	19.3
TP-25	Garing Co	20.8	8.4	3	43	14	132	23	20	8	23	0.3
TP-26	Youtu Co	20.4	9.6	177	870	3,514	8,616	57	208	458	6,143	20.0
TP-27	Chen Co	20.5	8.5	3	35	72	503	57	47	18	138	0.9
TP-28	Bajiu Co	21.3	9.2	17	44	29	157	38	36	8	8	0.3
TP-29	Yamdruk Co	22.2	9.0	26	110	115	722	19	98	33	256	1.4
TP-30	Kongmu Co	21.5	9.6	4	22	36	129	17	8	9	57	0.3

**Table 2** Sample sites, lake areas, and  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ , and TDS of lake waters from the Tibetan Plateau

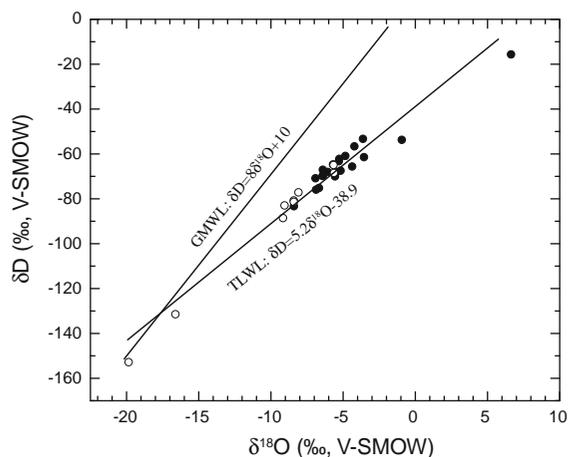
Sample No.	Lake name or site description	Sampling date	Latitude ( $^{\circ}\text{N}$ )	Longitude ( $^{\circ}\text{E}$ )	Altitude (a.m.s.l.)	Lake area ( $\text{km}^2$ )	$\delta\text{D}$ (‰)	$\delta^{18}\text{O}$ (‰)	$d$ (‰)
TP-01	Qarhan Salt Lake	08/08/09	36.850	95.200	2,685	–	–15.6	6.63	–68.7
TP-02	Zige Tangco	08/15/09	32.039	90.809	4,575	233	–68.0	–6.07	–19.5
TP-03	Daru Co	08/16/09	31.749	90.734	4,697	70	–69.8	–6.43	–18.4
TP-04	Bong Co (outlet)	08/17/09	31.304	90.976	4,639	–	–77.1	–8.09	–12.4
TP-05	Bong Co (NW)	08/17/09	31.232	91.104	4,679	143	–80.7	–8.42	–13.4
TP-06	Bong Co (mid-W)	08/17/09	31.209	91.094	4,679	–	–81.4	–8.42	–14.0
TP-07	Bong Co (SW)	08/17/09	31.182	91.096	4,679	–	–88.6	–9.16	–15.2
TP-08	Pung Co	08/17/09	31.396	90.933	4,541	176	–60.9	–4.85	–22.1
TP-09	Bam Co	08/17/09	31.362	90.635	4,576	251	–70.9	–6.92	–15.5
TP-10	Bangkog Co	08/19/09	31.745	89.431	4,531	357	–62.2	–5.26	–20.1
TP-11	Serbug Co	08/21/09	32.021	88.282	4,529	86	–67.0	–6.41	–15.8
TP-12	Dagze Co	08/22/09	31.878	87.644	4,478	290	–69.5	–6.38	–18.4
TP-13	Dong Co	08/25/09	32.124	84.737	4,405	101	–53.3	–3.63	–24.3
TP-14	Zhaixi Co	08/26/09	32.164	85.137	4,432	48	–63.2	–5.30	–20.8
TP-15	Dawa Co	08/26/09	31.234	85.030	4,636	116	–75.9	–6.87	–20.9
TP-16	Qingmuke Co	08/26/09	31.232	85.083	4,638	6	–61.4	–3.56	–33.0
TP-17	Angku Co	08/28/09	31.212	85.475	4,670	32	–83.3	–8.41	–16.1
TP-18	Qigai Co	08/28/09	31.203	85.497	4,667	18	–82.9	–9.06	–10.5
TP-19	Zhari Namco	08/28/09	31.078	85.406	4,624	1,000	–75.2	–6.67	–21.8
TP-20	Merqung Co	08/29/09	31.103	84.571	4,680	64	–67.5	–5.18	–26.0
TP-21	Taro Co	08/29/09	31.129	84.314	4,579	485	–68.5	–5.63	–23.4
TP-22	Zabuye Caka	08/31/09	31.404	84.019	4,436	295	–53.7	–0.94	–46.2
TP-23	Rinqin Xubco	08/30/09	31.331	83.423	4,766	187	–64.7	–5.70	–19.1
TP-24	Ngangla Ringco	08/30/09	31.444	83.368	4,724	498	–56.6	–4.22	–22.9
TP-25	Garing Co	09/02/09	30.805	84.975	4,665	62	–152.8	–19.85	6.0
TP-26	Youbu Co	09/02/09	30.823	84.822	4,664	64	–65.6	–4.37	–30.6
TP-27	Chen Co	09/04/09	28.962	90.489	4,434	40	–70.0	–5.56	–25.5
TP-28	Bajiu Co	09/04/09	28.757	90.872	4,520	32	–64.9	–5.66	–19.6
TP-29	Yamdruk Co	09/04/09	28.780	90.613	4,458	555	–68.0	–5.48	–24.2
TP-30	Kongmu Co	09/04/09	29.004	90.394	4,450	38	–131.4	–16.61	1.4

kinetic process results in a phenomenon called deuterium enrichment in precipitation. The average  $d$  value of precipitation around the globe is relatively constant (close to 10‰). The average  $d$  values of precipitation over the Tibetan Plateau are  $10 \pm 2\%$  (Tian et al. 2001), consistent with the global mean value of 10‰. However, most of the lake waters sampled contain a negative  $d$  value, further suggesting the prevalence of evaporation in Tibetan lakes.

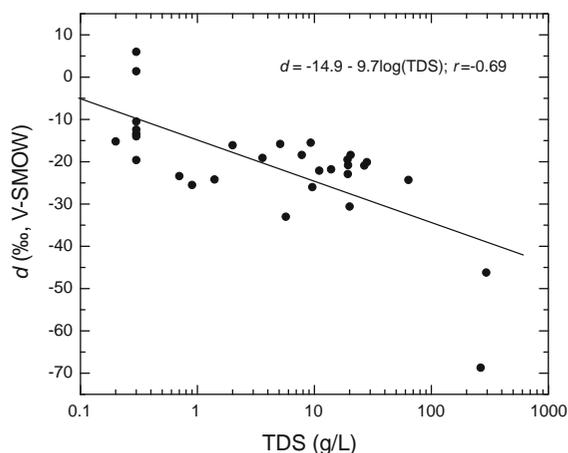
As discussed above, kinetic isotope fractionation during evaporation causes a differential isotope enrichment of  $^{18}\text{O}/^{16}\text{O}$  relative to D/H in water vapor leaving the lake surface, leading to deuterium

depletion in lake water (i.e. a negative value of  $d$ ). When evaporative enrichment takes place, the  $d$  values of lake water become more negative. On the other hand, evaporative water loss would lead to chemical enrichment of dissolved ions (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ ). With greater evaporative water loss, the TDS concentrations of lake water increase. This not only explains why there is a negative correlation between  $d$  and TDS, but also suggests that evaporation is an important player that regulates chemical and isotopic composition of lake waters on the plateau.

We also note that there are many irregularities in the relationship of  $d$  and TDS in lake waters from the



**Fig. 2** Relationship of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in surface waters from open lakes (i.e. lakes with outlets) (*open circles*) and closed-basin lakes (*filled circles*) in the Tibetan Plateau



**Fig. 3** Correlation of deuterium excess ( $d$ ) and TDS in surface waters from Tibetan lakes

plateau. This may be due in part to the fact that the lake population in this study is rather diverse in terms of lake size, salinity, and hydrologic settings. Although many lakes on the plateau are remnants of the late Pleistocene great lakes (Shi et al. 2001), each lake has its own evolutionary history due to different geohydrologic settings. For example, some lakes have similar  $d$  values of  $-20 \pm 2\text{‰}$ , but contain significantly different values of TDS, ranging from 0.3 g/L at Bajiu Co to 28.1 g/L at Bangkog Co. Some of these irregularities may be attributed to geothermal activities along tectonically active zones (Zheng 1997). Freshwater lakes presumably contain a more positive value of  $d$  due to a shorter residence time. However, the data

from this study indicate that some freshwater lakes have similarly low salinity (0.3 g/L), but significantly different  $d$  values, e.g. Kongmu Co (1.4‰), Bajiu Co ( $-19.6\text{‰}$ ), Garing Co (6‰), Qigai Co ( $-10.5\text{‰}$ ), and Bong Co ( $-12.4$  to  $-15.2\text{‰}$ ). This suggests that some freshwater lakes receive meteoric waters that have experienced certain degrees of evaporative isotopic enrichment before entering the lake.

### Modeling E/P ratio

#### $\delta^{18}\text{O}$ and $\delta\text{D}$ of lake inputs

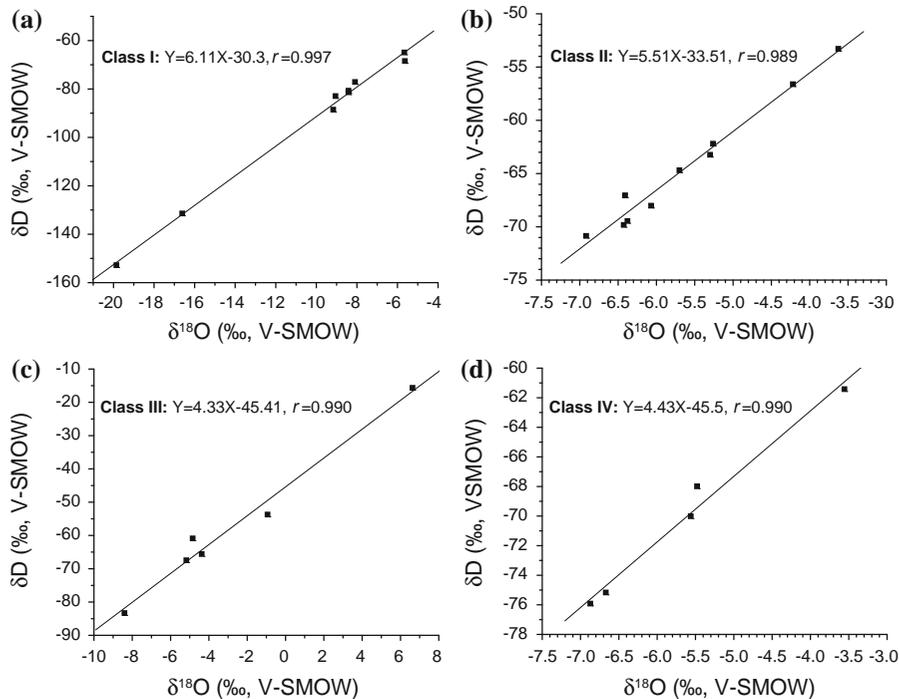
Lake inputs include precipitation on the lake surface, stream discharge, and groundwater flow. Stream discharge may account for the majority of lake water inputs for many lakes on the plateau (Yao 2008). Based on data collected from streams and rivers across the plateau (Hren et al. 2009),  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of Tibetan streams range from  $-20.8$  to  $-5.8\text{‰}$  and from  $-165$  to  $-33\text{‰}$ . The average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values are  $-14.0$  and  $-102\text{‰}$ , which are consistent with  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of precipitation observed in the region. The average  $d$  value is  $10.5\text{‰}$ , also consistent with the average  $d$  values of precipitation observed in this region and around the world. Nevertheless, there are great variations in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of stream waters. It would be inappropriate to use the average values of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in stream waters as lake inputs for a particular lake because each lake may have a drainage basin with different hydrologic, ecologic, and geomorphologic settings. Alternatively, researchers rely on the intersection of the local evaporation line (LEL) with the LMWL to provide a simple approximation of the weight-averaged  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of lake water inputs (Edwards et al. 2004). The weighted average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake inputs for Tibetan lakes are estimated to be  $-17.5$  and  $-130\text{‰}$ , using the intersection of the TLWL and the GMWL. These values are significantly lower than the average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of local precipitation and stream waters. This may be ascribed to the fact that (1) a majority of the lakes sampled are located in the southern part of the plateau, (2) a portion of the lakes sampled are fed by snowmelt from high mountainous glaciers on the plateau, and (3) the isotopic composition of precipitation in the southern Tibetan Plateau and snowmelt from mountainous glaciers is considerably lower than that in other parts of the region.

The inferred  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of  $-17.5$  and  $-130\text{‰}$  reflect the flow-weighted-average isotopic composition of lake inputs from all the lakes sampled in the plateau and thus may be representative for a majority of the lakes studied, but not all, because of inter-lake variations. To improve our approximation of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake inputs, we categorized the lakes sampled into four classes based on salinity (or TDS), lake dynamics (i.e. changes in lake surface area over the last 30–40 years inferred from satellite imagery), and geomorphologic settings. Class I lakes are open or throughflow lakes that contain freshwater (TDS  $< 1.0$  g/L) and that maintain a relatively constant lake surface area. Class II lakes are closed-basin saline lakes that experienced significant lake expansions. Class III lakes are terminal saline lakes that receive isotopically-enriched waters from one or multiple lakes in the upper watersheds and have experienced significant lake expansions over the last three decades. Class IV lakes are closed-basin saline lakes with little change in lake size. We reconstructed four lake water lines (LWL) for the four classes of lakes in Fig. 4. Each class has a different LWL from the TLWL. The slope of the LWL from Class II lakes is close to that of the TLWL. The slope of the LWL from

Class I lakes is significantly greater than that of the TLWL while the slopes of the LWLs from Classes III and IV are significantly lower than that of the TLWL. It turns out that the inferred  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake inputs of Class II lakes are identical to those inferred from the TLWL ( $\delta^{18}\text{O} = -17.5\text{‰}$ ;  $\delta\text{D} = -130\text{‰}$ ). Class I lakes have the lowest inferred  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake inputs ( $\delta^{18}\text{O} = -21.3\text{‰}$ ;  $\delta\text{D} = -161\text{‰}$ ) while Classes III and IV have the greatest inferred  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake inputs (Class III:  $\delta^{18}\text{O} = -15.1\text{‰}$ ,  $\delta\text{D} = -111\text{‰}$ ; Class IV:  $\delta^{18}\text{O} = -15.5\text{‰}$ ;  $\delta\text{D} = -114\text{‰}$ ).

#### $\delta^{18}\text{O}$ and $\delta\text{D}$ of ambient atmospheric vapor

The isotopic composition of ambient atmospheric vapor is an input variable that needs to be determined for quantification of the isotopic fractionation factor ( $\alpha$ ). Yin et al. (2008) reported that  $\delta^{18}\text{O}$  values of 255 atmospheric vapor samples collected from July 2005 to March 2006 at Delingha (northeast Tibetan Plateau) range from  $-39.5$  to  $1.5\text{‰}$ , with an average of  $-21.2\text{‰}$ . Yu et al. (2006b) presented a set of  $\delta^{18}\text{O}$  values of atmospheric vapor from the Nagqu River basin (central Tibet) during the late monsoonal



**Fig. 4** Relationships between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in lake waters for *Class I* (a), *Class II* (b), *Class III* (c), and *Class IV* (d)

season in 2004 (August to October), showing that  $\delta^{18}\text{O}$  values range from  $-32.4$  to  $-16.2\text{‰}$  with an average of  $-24.7\text{‰}$ . Additionally, isotopic values of atmospheric vapor in equilibrium with precipitation in saturated air can be calculated, using the longer (6 years) record of isotopic composition of precipitation from the GNIP station at Lhasa. The deduced  $\delta^{18}\text{O}$  value is  $-25.4\text{‰}$ , slightly more negative than the average value of  $-24.7\text{‰}$  found in central Tibet. Considering the contrasting climatic settings across the plateau, we assign  $-25.0\text{‰}$  to  $\delta^{18}\text{O}$  and infer the average  $\delta\text{D}$  value of atmospheric vapor in the region by assuming the average  $d$  value of the atmospheric vapor is 10, because the majority of lakes sampled are located in southern and central Tibet.

### *Model parameters*

The mean annual air temperature is around  $3^\circ\text{C}$  in this region, but the mean surface water temperature during evaporation seasons is substantially higher. The annual mean surface water temperature during summer is around  $13.5^\circ\text{C}$  at Cona Lake (central Tibet) (Wang and Dou 1998; Liu et al. 2009). Tian et al. (2008b) reported that the mean surface water temperature was  $15^\circ\text{C}$  in Yamdrok Co from July to September. Our field measurements show that the surface water temperature of the 27 lakes ranges from  $9.0^\circ\text{C}$  in Qarhan Salt Lake to  $22.2^\circ\text{C}$  in Yamdrok Co, with an average of  $15.1^\circ\text{C}$  (Table 1). Because the measurements were taken in the warmest part of the year (August and September), the annual mean surface water temperature of the 27 lakes would be lower than this value.

The annual mean relative humidity ( $h$ ) is about 0.5 in the Nagqu River basin (Yu et al. 2006b). Based on data from a meteorological monitoring station at Amdo (central Tibet), Liu et al. (2009) reported that the average  $h$  value was around 0.62 during non-freezing seasons in 2000. The  $h$  values range from 0.2 to 0.7 at a meteorological monitoring station in the Yamdrok Co basin (southern Tibet) and the average  $h$  value is estimated to be about 0.56 during non-freezing seasons (Tian et al. 2008b).

The fraction of advected atmospheric vapor ( $f_a$ ) theoretically ranges from 0 to 1. But studies from Pyramid Lake (western United States) indicate that most of water vapor overlying the water surface is derived from the lake, i.e.  $f_a$  is less than 0.25 (Benson and White 1994). The values of parameter  $n$  could

theoretically range from 0 (a state of completely turbulent diffusion) to 1 (completely molecular diffusion). Experimental and modeling studies suggest that it may have a relatively small range from 0.3 to 0.4 (Cappa et al. 2003).  $f_a$  and  $n$  are important parameters to account for the kinetic isotope fractionation. Both are related to the local wind speed.

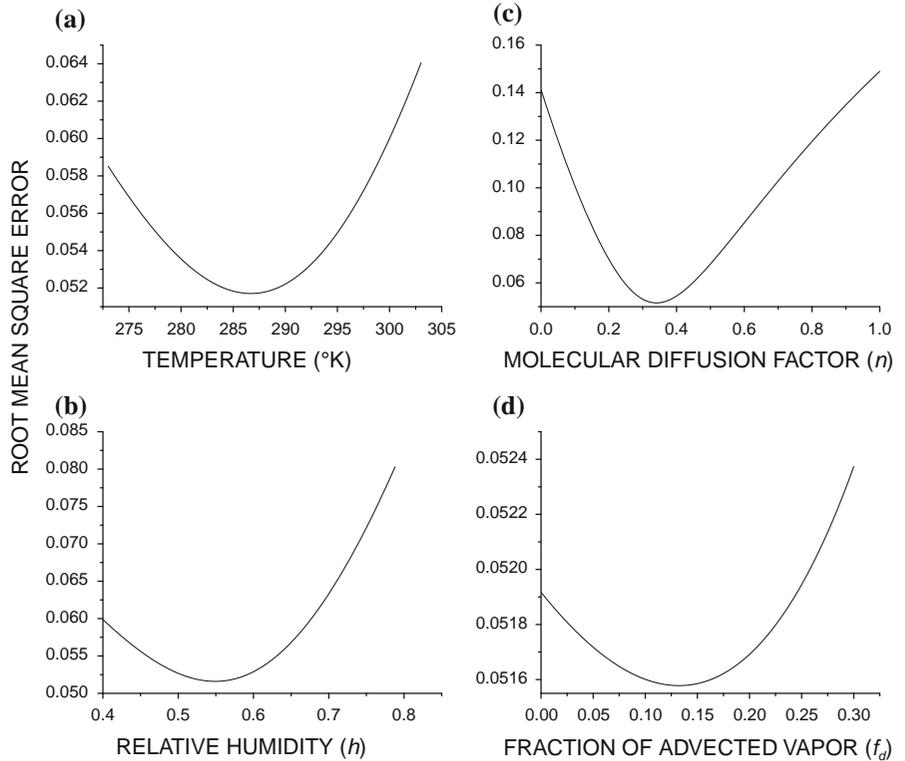
### *Model implementation and assessment*

The model was coded and implemented using combined features of spreadsheet and macros of Microsoft Office Excel 2007. The initial values of model parameters ( $T$ ,  $h$ ,  $n$ , and  $f_a$ ) were assigned to any number within their individual ranges described above. We calculated the root mean square error (RMSE), i.e. the relative error between  $\delta^{18}\text{O}$ -inferred E/P and  $\delta\text{D}$ -inferred E/P, to optimize the values for the four model parameters (Fig. 5). Finally, we used the optimal values:  $T = 13.5^\circ\text{C}$ ,  $n = 0.34$ ;  $h = 0.55$ , and  $f_a = 0.13$  to calculate E/P ratios for the 27 lakes (Table S1).

The average value of E/P inferred is 0.52, ranging from 0.09 in Garing Co to 0.74 in Qarhan Salt Lake. The model appears to perform well in the following aspects. First, there exist the optimal values for the four model parameters in their individual ranges, which appear to be realistic for Tibetan lakes in this study. For example, the optimal value of  $T$  is  $13.5^\circ\text{C}$ , which is close to what we estimated previously.  $h$  falls on the midpoint of the humidity range from 0.5 to 0.6.  $n$  is close to the middle of the interval of 0.3–0.4 used by Cappa et al. (2003).  $f_a$  is slightly higher than the value of 0.1 used in a hydrologic-isotopic-balance model for Pyramid Lake (Benson and Paillet 2002). It is reasonable to have a slightly higher value of  $f_a$  because of much more windy climate conditions prevailing on the plateau. Second, the average relative error of  $\delta^{18}\text{O}$ -inferred E/P and  $\delta\text{D}$ -inferred E/P is 4.6%, with a maximum of 9.5% (Table S1). The model works particularly well for Class II lakes because their relative errors do not exceed 3.0%. Lastly, we calculated E/P ratio for Cona Lake, a lake that has been investigated using a steady-state isotopic model (Liu et al. 2009), and found that our inferred E/P ratio is 0.26, slightly higher than their estimated E/P value of 0.24.

To evaluate the relative significance of the four model parameters ( $T$ ,  $h$ ,  $n$ , and  $f_a$ ), we performed a suite of model sensitivity tests, in which we let one

**Fig. 5** Optimization of model parameter values of surface water temperature (a), relative humidity (b), molecular diffusion factor (c), and fraction of advected vapor (d). The optimization was based on the minimization of the root-mean-square relative error between  $\delta^{18}\text{O}$ -inferred E/P and  $\delta\text{D}$ -inferred E/P



parameter change and set the other three parameters constant (using the optimal values), and then calculated the mean E/P ratio for all the lakes. Results from the sensitivity tests (Fig. 6) indicate that 1)  $f_a$  is the least sensitive parameter, with an average slope of 0.003% E/P per 1%  $f_a$ , 2)  $T$  is the most sensitive parameter, with an average slope of 0.3% E/P per 1°K, and 3)  $h$  and  $n$  are two parameters with identical moderate sensitivity (slope = 0.15% E/P per 1%  $h$  or  $n$ ). Since the RMSE is used to find the optimal values of the four parameters, the E/P quantification error associated with uncertainties in the values of the model parameters is overall minimal.

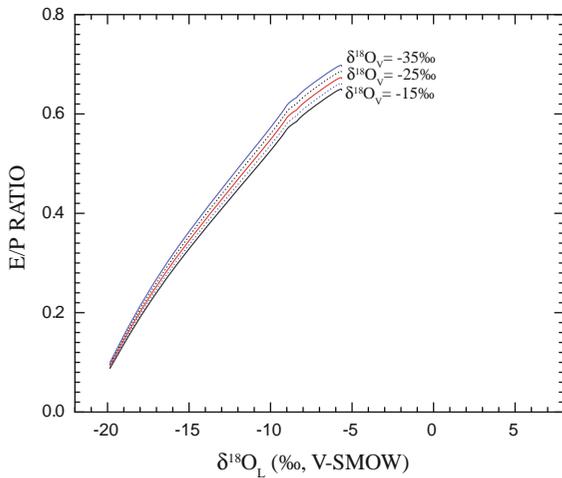
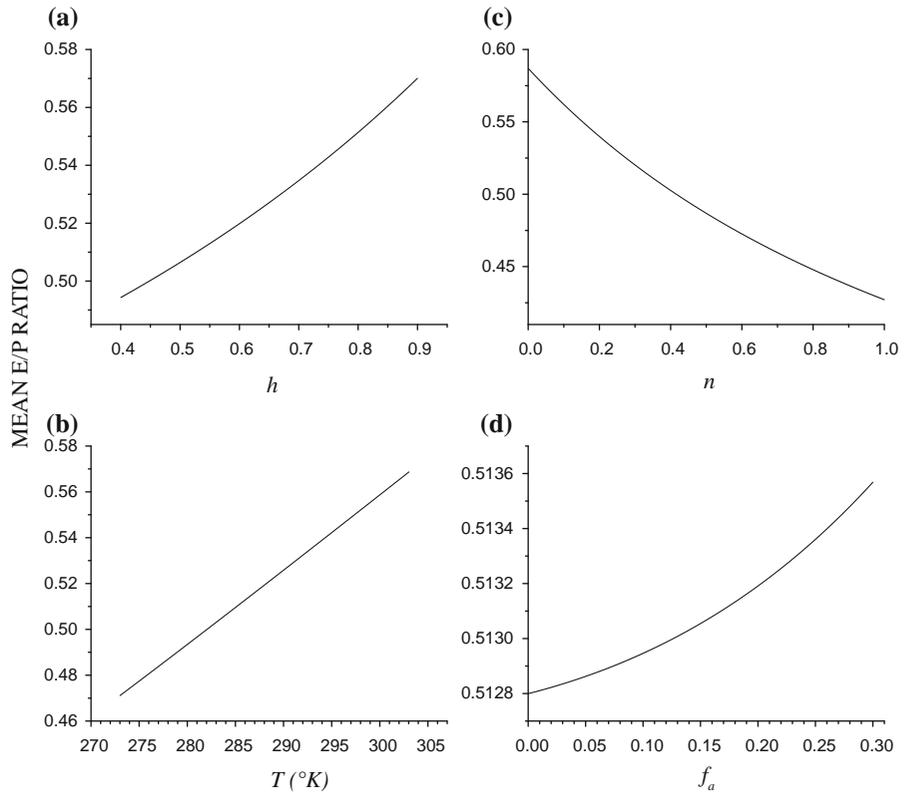
It is worth noting that the model lacks sensitivity to changes in  $f_a$  and that the  $f_a$  value chosen is fairly low. This may be explained by the Benson and White (1994) hypothesis that the base of the mixed air layer contains water vapor mostly (if not entirely) derived from the underlying lake surface during evaporation. The actual value of  $f_a$  depends on the existence and thickness of a thin layer of lake-derived water vapor and is a function of wind speed,  $h$ , and evaporation rate (Benson and White 1994). For example, with lower wind speed, higher  $h$ , and higher evaporation

rate ( $E$ ), the thickness of the thin layer (or film) increases and  $f_a$  decreases.

To evaluate the influence of the isotopic composition of ambient atmospheric water vapor ( $\delta^{18}\text{O}_V$ ), we assigned five different values ( $-15$ ,  $-20$ ,  $-25$ ,  $-30$  and  $-35$ ‰) of  $\delta^{18}\text{O}_V$  and calculated the E/P ratios for Class I lakes under different  $\delta^{18}\text{O}_V$  conditions (Fig. 7). The influence of  $\delta^{18}\text{O}_V$  on the modeled E/P ratio increases as a lake becomes more isotopically-enriched. In the case of Class I lakes, the error is up to  $\pm 2.5\%$  E/P when  $\delta^{18}\text{O}_V$  has an uncertainty up to  $\pm 10$ ‰. This translates to 0.25% E/P per 1‰  $\delta^{18}\text{O}_V$ , suggesting the E/P quantification error induced by uncertainties of  $\delta^{18}\text{O}_V$  is also minimal.

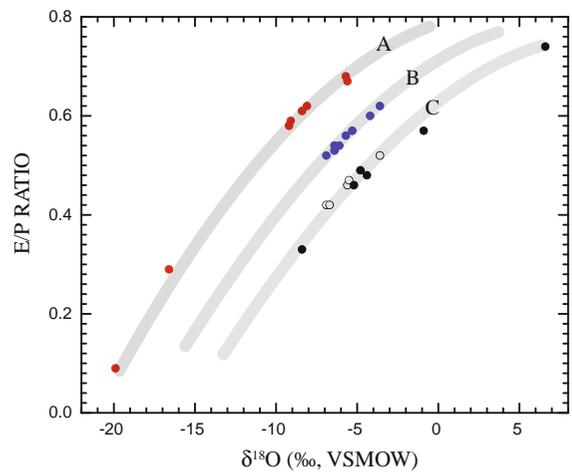
We also evaluated the effects of the isotopic composition of lake inputs ( $\delta^{18}\text{O}_I$ ) and lake waters ( $\delta^{18}\text{O}_L$ ) on quantification of the E/P ratios for the Tibetan lakes. Based on the modeled E/P results (Table S1), there are three nearly parallel lines in Fig. 8, reflecting different isotopic composition of lake inputs. Line A is derived from Class I lakes that have an inferred  $\delta^{18}\text{O}_I$  of  $-21.3$ ‰. Line B is derived from Class II lakes that have an inferred  $\delta^{18}\text{O}_I$  of  $-17.5$ ‰. Line C is derived from lakes in Classes III

**Fig. 6** Plots of sensitivity of model parameter values to the mean E/P ratio of Tibetan lakes. **a** Modeled E/P sensitivity to relative humidity. **b** Modeled E/P sensitivity to surface water temperature. **c** Modeled E/P sensitivity to molecular diffusion factor. **d** Modeled E/P sensitivity to the fraction of advected water vapor



**Fig. 7** Modeled E/P sensitivity to the isotope composition of free atmospheric vapor

and IV whose average inferred  $\delta^{18}O_I$  is  $-15.3\text{‰}$ . The effect of  $\delta^{18}O_I$  on the inferred E/P ratios is substantial, but not linear. The difference in  $\delta^{18}O_I$  between Lines A and B is  $3.8\text{‰}$ , which leads to 11%



**Fig. 8** Plot of modeled E/P ratio versus  $\delta^{18}O$  of lake water ( $\delta^{18}O_L$ ). Lines A, B, and C represent generalized relationships of modeled E/P and  $\delta^{18}O_L$ , corresponding different  $\delta^{18}O$  of lake inputs ( $\delta^{18}O_I$ ).  $\delta^{18}O_I$  values for Lines A, B, and C are  $-21.3$ ,  $-17.5$ , and  $-15.3\text{‰}$ . Red filled circles denote Class I lakes, blue filled circles denote Class II lakes, black filled circles denote Class III lakes, and open circles denote Class IV lakes

difference in E/P ratio (equivalent to 2.9% E/P per 1‰  $\delta^{18}\text{O}_\text{I}$ ), whilst the difference in  $\delta^{18}\text{O}_\text{I}$  between Lines B and C is 2.2‰, which leads to 12% difference in E/P ratio (equivalent to 5.4% E/P per 1‰  $\delta^{18}\text{O}_\text{I}$ ). On the other hand, the effect of the  $\delta^{18}\text{O}_\text{L}$  on inferred E/P ratios is also substantial, but not linear. The slope in Fig. 8 decreases as  $\delta^{18}\text{O}_\text{L}$  increases and a 1‰ error in  $\delta^{18}\text{O}_\text{L}$  translates to a 2.6–4.1% error in the modeled E/P ratio. This analysis indicates that uncertainties in  $\delta^{18}\text{O}_\text{I}$  and  $\delta^{18}\text{O}_\text{L}$  are the major sources of error in the modeled E/P ratio.

The modeling calculations allow us to conclude that although variable from lake to lake, the water budget across the southern Tibetan Plateau is positive, with an average E/P of 0.52. This is consistent with other observational data. For example, many Tibetan lakes have experienced varying degrees of expansion in the last three decades (Wu et al. 2005; Bianduo et al. 2009). Comparison of our TDS values with the published data collected in the 1960s–1970s (Zheng 1997) indicates that over half of the studied lakes have become less salty over the last several decades. Moreover, our estimates of E/P are in line with a pronounced positive water budget signature over the Tibetan Plateau in the global E/P balance map (Trenberth et al. 2006). The analysis of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake waters may serve as a useful tool to provide independent E/P estimates for studies in the global water cycle, particularly for remote regions like the Tibetan Plateau where instrumental observations are very limited.

#### Implications for paleoenvironmental studies

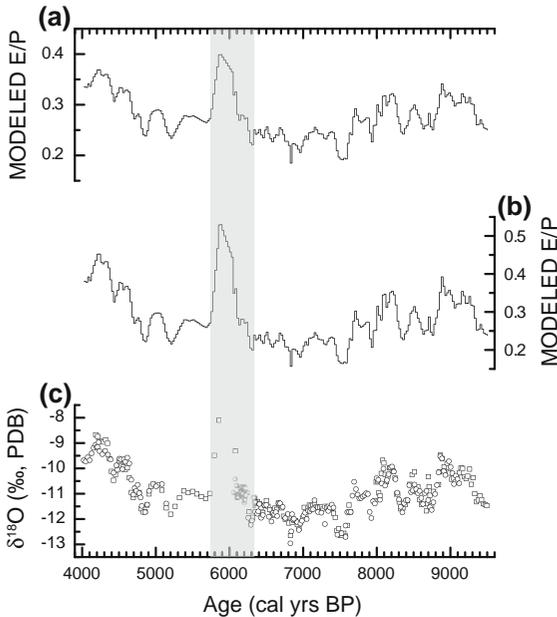
It is evident that there are varying degrees of uncertainties in the modeled results of E/P ratios. Most of the uncertainties are induced by the simple approximation of  $\delta^{18}\text{O}_\text{I}$ . The  $\delta^{18}\text{O}_\text{I}$  values inferred for each class represent the  $\delta^{18}\text{O}$  value of composite meteoric waters entering a drainage basin instead of a single lake. For example,  $\delta^{18}\text{O}_\text{I}$  values inferred for Class I lakes reflect the  $\delta^{18}\text{O}$  values of composite meteoric waters including snowmelt from mountainous glaciers. The meteoric waters may have experienced significant evaporative isotopic enrichment before entering a throughflow lake. As a result, the relatively high E/P ratios inferred for Class I lakes are interpreted to reflect the hydrologic balance

conditions at watershed scales, but do not necessarily indicate the degree of isotopic enrichment occurring within these lakes.

In fact, variations in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake waters are attributed to surficial processes in a lake (lake process) and its catchment (catchment process). Lake processes, e.g. precipitation and evaporation at the lake surface, surface and subsurface inflow and outflow (stream and groundwater flows), and seasonal stratification and turnover, regulate variations in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake water. Catchment processes modify the isotopic signatures of precipitation through evaporative enrichment and selective utilization of soil water by plants (Gat 1995). There are some similarities between the two processes because both are regulated by regional climate variability. However, there are some discrepancies between the two processes because the catchment process is also affected by ecologic and morphologic factors such as vegetation cover and drainage pattern. Thus, some of the variations in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake waters can be caused by non-climatic factors (e.g. landslides, dams, and river diversion).

The isotope composition of lake sedimentary carbonates is determined primarily by lake-water isotopic composition. The effect of water temperature on  $\delta^{18}\text{O}$  values of sedimentary carbonates is considered minimal since for every 1°C increase in water temperature there is a corresponding 0.21‰ decrease in the  $\delta^{18}\text{O}$  value of sedimentary carbonates (O'Neil et al. 1969). For this reason, isotope records of lake sediments are commonly interpreted to indicate past changes in the basin's E/P ratio or hydrologic balance (Ricketts and Anderson 1998; Benson et al. 2002; Benson and Paillet 2002; Yuan et al. 2006a, b). As discussed above, the isotopic enrichment observed in lake water and downcore sediments reflects the hydrologic balance of the lake's drainage basin. This implies that sediment records from some throughflow lakes on the plateau can be a valuable source of information on past changes in the basin's hydrologic balance even though some of the changes may be caused by non-climate factors. For example, Ahung Co is such a small (area = 3.6 km<sup>2</sup>), shallow (maximal water depth = 1.5 m) lake, with a small surface outlet, located in central Tibet (Morrill 2004). Geochemical measurements of downcore sediments show that lake level has fluctuated as a result of several century-scale wet-dry climatic oscillations

since the early Holocene (Morrill et al. 2006). To constrain past hydrologic variability, we calculated the E/P from isotopic records using the isotope modeling framework and parameter values derived from isotopic composition of lake waters on the plateau. As highlighted in Fig. 9, there is an abrupt 4‰ increase in  $\delta^{18}\text{O}$  in the middle Holocene ( $\sim 6,000$  years BP). Modeled results show a corresponding 0.15 increase in E/P, equivalent to 4% increase in E/P per 1‰ increase in  $\delta^{18}\text{O}$ . This is in good agreement with the spatial variability in E/P derived from  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake waters on the plateau (Table S1). Also, we calculated the E/P from the  $\delta^{18}\text{O}$  record of the lake using a water mass and isotopic mass balance model (Fig. 9b) (Gibson and Edwards 2002; Edwards et al. 2004). Although



**Fig. 9** Comparison of  $\delta^{18}\text{O}$  records with modeled E/P results for Ahung Co. **a** Modeled E/P time series from  $\delta^{18}\text{O}$  records of sedimentary carbonates in Ahung Co. **b** Modeled E/P results using an isotopic mass balance approach (Gonfiantini 1986; Gibson and Edwards 2002),  $E/P = (\delta_I - \delta_L)/(\delta_E - \delta_L)$ , where subscripts denote inflow ( $I$ ), lake ( $L$ ), and evaporation ( $E$ ). **c** Carbonate  $\delta^{18}\text{O}$  records from lake sediments (*Core 2A: open squares; Core 3A: open circles*) of Ahung Co, central Tibet (Morrill et al. 2006).  $\delta^{18}\text{O}$  of paleolake water ( $\delta_w$ ) is deduced from  $\delta^{18}\text{O}$  of sedimentary carbonates ( $\delta_c$ ), using  $T = 16.0 - 4.14(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$  (Anderson and Arthur 1983), where  $T$  is water temperature ( $22.5^\circ\text{C}$ ) when carbonate forms (Galat and Jacobson 1985). Note that  $\delta^{18}\text{O}$  values of lake inputs are assumed to be similar to those of Cona Lake

the results from the mass balance model contain a larger magnitude of variability, the average E/P values throughout the record from the two models are almost identical. The results from the two models agree well when E/P is relatively low (i.e.  $<0.4$ ), but differ greatly with increasing  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake waters. This implies that the E/P signal from our modeling approach may reflect the average E/P values for a longer time scale (i.e. residence time of a corresponding lake).

Lastly, we want to emphasize that this isotopic enrichment model, like many others, requires several implicit assumptions. First, we assume that lake water is well-mixed or at least mixed once a year. Stratification may develop in many lakes in the summer and winter. For example, data from Lake Puma Yumco (southern Tibet) show thermal stratification develops while chemical stratification is not evident during the summer (Zhu et al. 2010). This isotopic model may not be appropriate for deep saline lakes in which prolonged stratification may develop. Second, the isotopic model requires the lake system of interest to be hydrologically closed or at least partially closed. In other words, the model may not work for throughflow reservoirs which act like a river channel. Third, we assume that the average  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of lake inputs are relatively constant at yearly to decadal timescales. This may be invalid for lakes which receive meteoric waters with significant low  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values because of intensified monsoonal activities or extraordinary snowmelt from mountainous glaciers due to the recent global warming. Abrupt changes in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of source meteoric waters could also confound the interpretation of isotope records from downcore sedimentary carbonates. Researchers usually depend on other proxy records from lake sediments in the region to evaluate the effects of the source-water isotopic changes on the basin's E/P or hydrologic balance.

## Conclusions

This study presents a new isotopic dataset and a modeling framework to quantify the E/P ratio from evaporation-induced isotopic enrichment in lake waters on the Tibetan Plateau. The isotopic data of this study show that lake waters from Tibetan lakes contain a wide range of composition, with  $\delta^{18}\text{O}$

ranging from  $-19.9$  to  $6.6\text{‰}$  and  $\delta D$  from  $-153$  to  $-16\text{‰}$ . The average value of  $\delta^{18}\text{O}$  in the waters is  $-6.4\text{‰}$ , which is larger than that of meteoric waters in this region. Analysis of the relationships of  $\delta^{18}\text{O}$  and  $\delta D$  in meteoric waters on the plateau indicates that the TLWL deviates significantly from the GMWL, the TRWL, and the LMWLs. The average value of  $d$  in Tibetan lakes is  $-21\text{‰}$ , significantly lower than that of precipitation. Each of these facts reflects the process of evaporation in Tibetan lakes. Moreover, there is a negative correlation between  $d$  and TDS in Tibetan lake waters, further attesting to the fact that evaporative enrichment prevails in lake waters across the plateau.

On the basis of existing isotopic fractionation equations and the Rayleigh model, we put together a new isotopic modeling framework to quantify E/P from isotopic enrichment in lake waters on the plateau. As a first approximation, we used the intersection of the local evaporation line (LEL) and GMWL to deduce  $\delta^{18}\text{O}$  and  $\delta D$  values of lake water inputs. The average  $\delta^{18}\text{O}$  and  $\delta D$  values of ambient atmospheric vapor are estimated using published data from the Nagqu River basin (central Tibet). The values of four model parameters were optimized through the minimization of the RMSE, i.e. the relative error between  $\delta^{18}\text{O}$ -inferred E/P and  $\delta D$ -inferred E/P. The results from the modeling calculations indicate that the average E/P ratio is 0.52, ranging from 0.09 to 0.74. The major source of modeling uncertainty is from the approximation of  $\delta^{18}\text{O}$  and  $\delta D$  values of lake water inputs, in which every 1‰ error in  $\delta^{18}\text{O}_I$  could lead to up to 5% error in the modeled E/P. Because of inter-lake variations in  $\delta^{18}\text{O}_I$ , the modeled E/P ratio for individual lakes is tentative and subject to adjustment once the LEL for each lake is constructed.

This study could have multiple implications for paleoenvironmental studies in the region. First, most of the Tibetan lakes contain lake water with varying degrees of evaporation-induced isotopic enrichment. This implies that  $\delta^{18}\text{O}$  of lake water and sediments is an indicator of a lake's hydrologic balance. Second, some of the isotopic enrichment found in  $\delta^{18}\text{O}$  of lake water and sediments may occur in meteoric waters before entering a lake. This implies that some signals found in downcore sediments may be caused by catchment processes such as changes in vegetation cover and drainage pattern due to seismic activities.

Third, past changes in hydrologic balance can be evaluated quantitatively from downcore  $\delta^{18}\text{O}$  records using the proposed isotope model. Lastly, changes in the isotopic composition of source meteoric waters would have a significant impact on the modeled E/P. This highlights the importance of multi-proxy records from lake sediments in the region.

**Acknowledgments** This paper has benefited from the valuable inputs by Editors J. Holmes and M. Brenner who reviewed an earlier version of this manuscript. We gratefully acknowledge the logistic support provided by staff from the Institute of Tibetan Plateau Research, Chinese Academy of Sciences. The field work was in part sponsored by a NASA New Investigator award NNX06AE58G (Y. Sheng). The isotopic analysis at Duke University was supported by an NSF grant EAR-0902895 (F. Yuan).

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