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The Influence of Sublacustrine Hydrothermal Vent Fluids on the Geochemistry of Yellowstone Lake

By Laurie S. Balistrieri, Wayne C. Shanks, III, Russell L. Cuhel, Carmen Aguilar, and J. Val Klump

Chapter F *of*
**Integrated Geoscience Studies in the Greater Yellowstone Area—
Volcanic, Tectonic, and Hydrothermal Processes in the Yellowstone
Geoecosystem**

Edited by Lisa A. Morgan

U.S. Geological Survey Professional Paper 1717

U.S. Department of the Interior
U.S. Geological Survey

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Abstract

The geochemical composition of Yellowstone Lake water is strongly influenced by sublacustrine hydrothermal vent activity. The evidence for this conclusion is twofold. First, mass-balance calculations indicate that the outflow from Yellowstone Lake is enriched in dissolved As, B, Cl, Cs, Ge, Li, Mo, Sb, and W relative to inflowing waters. Calculations involving stable isotopes of hydrogen and oxygen (δD and $\delta^{18}O$, respectively) and mass-balances indicate about 13 percent evapoconcentration in the lake, which is inadequate to account for the enrichment of these elements in the water column. Second, linear relationships between the concentration of Cl and many other elements in the lake and in hydrothermal vent fluids suggest that Yellowstone Lake water is a mixture of inflowing surface water and hydrothermal source fluid. The conservative behavior of many elements is further demonstrated in mixing experiments that utilize subaerial geyser fluids and Yellowstone River water sampled at the lake outlet.

The hydrothermal source fluid feeding the lake is identified by comparing theoretical predictions of the Cl and δD content of boiled, deep, thermal-reservoir fluid with observed compositions of water-column, pore-water, and vent samples from Yellowstone Lake. This comparison indicates that the hydrothermal source fluid has a temperature of 220°C and a Cl content of 570 mg/kg (~16 mM or millimoles per liter) and it evolved by boiling of a deep reservoir fluid with δD equal to –149 per mil and Cl content of 310 mg/kg. The concentrations of other elements in the hydrothermal source fluid are estimated using the observed linear relationships between Cl and other elements in lake and hydrothermal vent fluids. These concentrations indicate strong enrichment of Cl, Si, B, Li, Na, K, Rb, As, Ge, Mo, Sb, and W in sublacustrine hydrothermal vent fluids. In general, the composition of the hydrothermal source fluid is similar to the composition of subaerial geyser water in Yellowstone National Park (the Park).

[1] U.S. Geological Survey, University of Washington, School of Oceanography, Box 355351, Seattle, WA 98195.

[2] U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225.

[3] Great Lakes Water Institute, University of Wisconsin-Milwaukee, Milwaukee, WI 53201.

The Cl concentration in the hydrothermal source fluid indicates that Yellowstone Lake water is about 1 percent hydrothermal source fluid and 99 percent inflowing stream water. The flux of hydrothermal source fluid into the lake is about 8×10^9 kg of water per year, based on mass-balance calculations for Cl. If the concentration of Cl in deep reservoir fluid, rather than in hydrothermal source fluid, is used, then the flow is calculated to be 1.5×10^{10} kg of water per year. Using the latter estimate, sublacustrine vents in Yellowstone Lake account for ~10 percent of the total flux of deep, thermal reservoir water in the Park, as estimated from Cl in streams (Friedman and Norton, 2000, this volume). Although the volumetric input of water into the lake from hydrothermal vents is small, the impact of the vent fluids on the geochemistry of Yellowstone Lake is large because of the great enrichment of many elements in these fluids. Because about 41 million kg per day of element-enriched deep thermal water flows into the lake, and recent swath sonar studies show the presence of numerous newly recognized hydrothermal features, Yellowstone Lake should be considered one of the most significant hydrothermal basins in the Park.

Introduction

Isotopic and geochemical studies suggest that the spectacular subaerial thermal basins in Yellowstone National Park (the Park) are a result of interaction between deeply recharged meteoric water and a magma chamber in the upper crust beneath the Yellowstone caldera (Fournier and others, 1979; Fournier, 1989, 2000). A deep, hot (360°C), and Cl-enriched (~9 mM Cl) reservoir (Rye and Truesdell, 1993, this volume) is thought to feed a series of intermediate reservoirs that vary in temperature and composition because of conductive cooling to surrounding rocks, boiling and steam separation, and mixing and dilution of ascending hydrothermal fluids with colder meteoric water (Truesdell and others, 1977; Fournier and others, 1979). These processes, in addition to water-rock interactions and mineral precipitation, result in the diverse geochemical compositions of subaerial geysers in Yellowstone National Park.

The work of White and others (1988) and Fournier (1989) indicates the presence of three main types of hydrothermal waters and their hybrids within the Park. The first main type typically is boiling springs that are characterized by nearly neutral pH and high concentrations of Cl, B, alkali metals (for example, Li, Na, K), As, and Si. The boiling springs deposit siliceous sinter and consist primarily of the concentrated liquid that remains after boiling and steam separation of ascending thermal fluids. The second type of hydrothermal water is acidic, and it has high concentrations of SO_4 and NH_4. This water contains volatile gases (CO_2, H_2S, and NH_3) that separate from boiling, chloride-rich ascending fluids and then condense into colder meteoric waters. Such solutions are acidic due to addition of hydrogen ions during the dissolution of CO_2 and the dissolution and oxidation of H_2S (Xu and others, 1998). Fe, Al, Ca, and Mg are generally in greater concentrations than Na and K. These steam-heated, acid-sulfate waters tend to be above shallow, boiling, and chloride-rich fluids. Both types of hydrothermal waters are thought to originate from intermediate reservoirs in rhyolitic lava flows and ignimbrites and to have temperatures of 180° to 270°C. The third main type of hydrothermal fluid is mainly in the Mammoth Hot Springs area. In contrast to the other two water types, it ascends to the surface through sedimentary rocks composed of carbonates and gypsum-bearing shale. This water has nearly neutral pH; it has high concentrations of HCO_3, SO_4, Mg, and Ca and low concentrations of Si; and it originates from reservoirs with temperatures <100° to 120°C.

During the past 15 years, researchers from the University of Wisconsin-Milwaukee and Marquette University and, more recently, the U.S. Geological Survey have studied hydrothermal vents in Yellowstone Lake (Klump and others, 1988). The sublacustrine vents are thought to be submerged counterparts to the subaerial geysers that are present throughout the Park. Our integrated studies relate the geology and chemistry of the hydrothermal vents to the composition of water and solids in the lake, and also to the productivity and physiological characteristics of the biological communities in and near the hydrothermal fluids that enter the lake. This report focuses on the geochemistry of Yellowstone Lake water, the processes that control its composition, and the steady supply of potentially toxic elements to the Yellowstone Lake ecosystem by sublacustrine hydrothermal vents. Such information is critical for understanding and, ultimately, for managing the complex relationships between geology and biological communities in Yellowstone National Park.

Acknowledgments

Study Area

Yellowstone National Park is a region of young and active tectonism and volcanism that is related to its current position over the Yellowstone hotspot (Christiansen, 1984). Migration of the North American plate over the Yellowstone hotspot, beginning 16 Ma, produced a string of silicic volcanic fields containing caldera complexes along the Snake River Plain. This track of silicic magmatism is reflected in the topographically low Snake River Plain; the hotspot is now centered in the topographically high Yellowstone Plateau (Morgan and others, 1984; Morgan, 1992; Pierce and Morgan, 1992). Large-volume, high-silica, rhyolitic ignimbrites and lava flows have erupted from overlapping and nested calderas in the Yellowstone Plateau volcanic field, producing an estimated volume of rock of 6,700 km^3 (Christiansen, 1984). Major caldera-forming eruptions occurred at 2.1 Ma, 1.3 Ma, and 0.64 Ma (K-Ar ages cited in Christiansen and Blank, 1972; Obradovich, 1992; Christiansen, 2001). The 0.64-Ma Yellowstone caldera is the locus of most of the active hydrothermal activity in the Park. Seismic studies suggest that a zone of magma is present below the caldera at a depth of about 4–6 km (Christiansen, 1984; Smith and Rubin, 1994). Magmatic heat drives the abundant and spectacular hydrothermal activity of Yellowstone National Park. One area in the Park outside the Yellowstone caldera that has extensive hydrothermal activity is in the Norris-Mammoth corridor. This is a system of north-trending faults and thermal areas that extends from Norris Geyser Basin to Mammoth Hot Springs.

Located in the southeastern part of the Park (fig.1), Yellowstone Lake, at an altitude of 2,357 m and covering an area of more than 341 km^2, is the largest high-altitude lake in North America (Kaplinski, 1991). Multiple geologic forces, including volcanic, hydrothermal, and glacial activity, have

shaped the Yellowstone Lake basin. The northern portion of the lake is mostly within the 0.64-Ma Yellowstone caldera (fig. 1). The eastern and northeastern boundary of the lake is the eastern edge of the Yellowstone caldera. Mary Bay, a large scalloped embayment on the north edge of the lake, formed approximately 10.8 ka as a series of sublacustrine hydrothermal-explosion events (Wold, and others, 1977; Morgan and others, 1998). West Thumb, in the western part of Yellowstone Lake, formed when the 128-ka tuff of Bluff Point erupted, forming the West Thumb caldera (Christiansen, 1984; L.A. Morgan and W.C. McIntosh, oral communs., 1998). Areas in Yellowstone Lake that are within the Yellowstone caldera have exceptionally high heat flow (Morgan and others, 1977) and are characterized by abundant sublacustrine hydrothermal activity (Kaplinski, 1991) (fig. 1). The South and Southeast Arms of the lake are far outside the caldera boundary, are of glacial origin, and exhibit no evidence of hydrothermal activity.

Methods

Field Methods

Because there are very few water-quality data or discharge measurements for surface-water flow into Yellowstone Lake, samples were collected during August and September 1998, and July 1999, from 21 of the major streams that enter the lake. GPS measurements were obtained, and the temperature and pH of the water were determined at each site. The pH meter was calibrated each day using known buffer solutions. Either point-source or integrated water samples were collected in 500-mL polyethylene bottles and brought to a field-based laboratory for processing. The bottles had been acid-cleaned and well rinsed with distilled, deionized water before use. Estimates of discharge were made either by timing a float and determining the cross-sectional area of the stream (1998) or by measuring the flow rate at 1 to 20 locations in a cross section of the stream using a velocity meter (1999). The accuracy of the flow estimates varied between years and sampling sites because different individuals used different methods at different times, and because some streams could not be waded.

A large-volume (20 L) sample from the Yellowstone River at its outlet from Yellowstone Lake (near Fishing Bridge) was placed into a plastic cubitainer in July of 1999. The sample was collected using teflon tubing, an in-line 0.45-μm filter capsule, and a peristaltic pump. The sample was returned to the field-based laboratory for processing and for use in the mixing experiments described below. Because the U.S. Geological Survey (USGS) gages the Yellowstone River at its outlet from the lake (station 06186500), continuous discharge measurements from this site are available (http://mt.water.usgs.gov; accessed 8/2000). Outflows from the lake during our sampling periods were 52 ± 3 and 156 ± 9 m³/s in 1998 and 1999, respectively.

Hydrothermal vent samples for this study were collected in West Thumb, in Mary Bay, and near Stevenson Island in the summers of 1996 through 1999 (fig. 1). The West Thumb vent samples were from several vent fields at depths of 29–53 m. Vent fluids were collected nearshore off Steamboat Point and near Pelican Creek. These were shallow vents with depths of 7–10 m. Hydrothermal fluids were also collected from a deep hole in Mary Bay at depths of 48–54 m. Samples collected near Stevenson Island were from the deepest vents (95–110 m). All vent samples were collected with a tethered and submersible remotely operated vehicle (ROV) designed and piloted by Dave Lovalvo of Eastern Oceanics, Inc. Klump and others (1992) described an early version of that vehicle. Although the exact set-up of the vehicle varied from year to year, it always collected vent-fluid samples using piston-operated plastic syringes that were connected by polypropylene tubing to an articulated and extensible probe. The temperature of the vent was continuously monitored during sample collection, and the probe was maintained in position using electrical and video connections to the surface. After retrieval of the ROV, samples were transferred through three-way valves from the syringes on the vehicle into other syringes for biological and chemical measurements. The vent samples were returned to the field-based laboratory for processing.

Samples from different depths in the water column of Yellowstone Lake were collected in Southeast Arm, West Thumb, and Mary Bay in July 1997 and 1998, and near Stevenson Island in July 1998, using a trace-metal-clean hydrobottle (no internal cords) attached either to a Kevlar line, a HYDROLAB™ cable, or the hydrowire on the research boat. All wire types produced consistent results, with no evidence of contamination for the elements of interest. The water-column samples in Mary Bay were collected directly above the vents in the deep hole in Mary Bay. The water-column samples near Stevenson Island were collected close to, but not directly above, the vents that were sampled. In contrast, water-column samples from West Thumb were collected 3–4 km from the sampled hydrothermal vent fields. Water-column samples from Southeast Arm were collected at least 10 km from any known hydrothermal vents. Water-column samples were placed in 500-mL acid-cleaned and well-rinsed polyethylene bottles on board the boat and returned to the field-based laboratory. In-place measurements of temperature, pH, conductivity, redox potential, and dissolved oxygen concentrations in the water column were taken as a function of depth, using a HYDROLAB™, prior to collection of water samples. Those profiles were used to determine the depths for collection of the water samples and to confirm that the entire water column was oxic at every site.

Lake-bottom sediment was collected in Mary Bay and West Thumb using a gravity corer. Pore water was obtained from cores at the field-based laboratory, using the whole-core squeezing method of Jahnke (1988). The pore water was filtered through acid-washed, 0.2-μm disposable filters.

Water samples from two subaerial geysers were collected from West Thumb Geyser Basin (Black Pool and Vandalized Pool) in September of 1998, using a plastic bottle. They were immediately filtered on-site using a 0.45-μm filter. During July of 1999, water samples were collected from three subaerial

YELLOWSTONE NATIONAL PARK

YELLOWSTONE LAKE BATHYMETRY

WEST THUMB

NORTHERN YELLOWSTONE LAKE
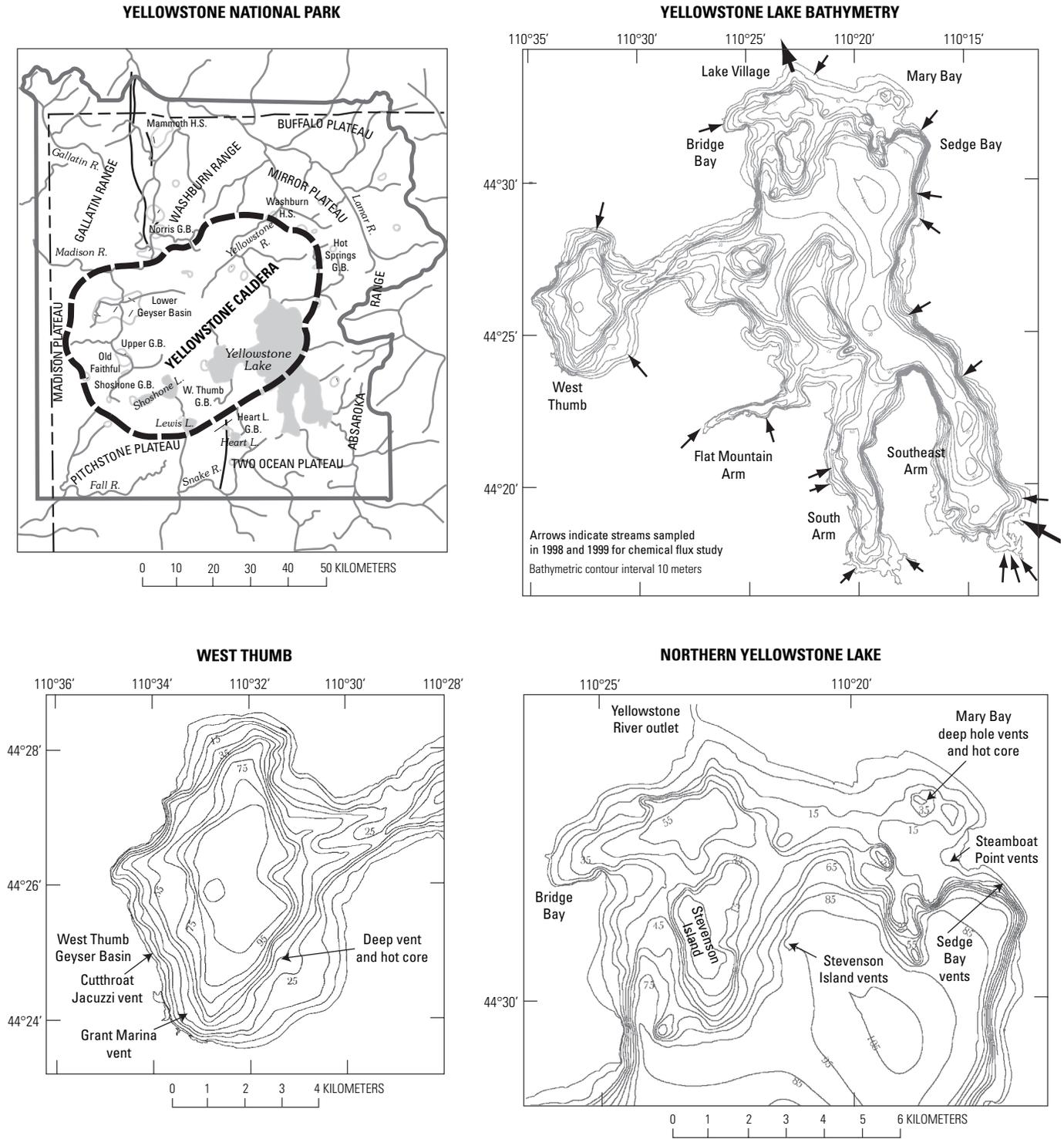
Figure 1. Maps of Yellowstone National Park and Yellowstone Lake with detailed maps of West Thumb and northern Yellowstone Lake showing locations of the sampling sites. G.B., geyser basin; H.S., hot spring; R., River; L., Lake. Base bathymetry from Kalinski (1991).

geysers in Norris Geyser Basin (Green Dragon, Echinus, and Porkchop Geysers) and from Black Pool at West Thumb Geyser Basin using a peristaltic pump loaded with teflon tubing and an in-line 0.45-µm filter capsule. These particular geysers were chosen because they are indicative of the spectrum of hydrothermal fluids observed in the Park. Water samples from Porkchop, Black Pool, and Vandalized Pool are neutral to alkaline and Cl-rich. The hydrothermal fluids from Green Dragon and Echinus are acidic and enriched in SO_4 and Cl. Geyser waters collected in 1999 were immediately mixed with filtered water collected from the Yellowstone River in 500-mL polyethylene bottles in proportions ranging from 0 to 100 percent geyser water. The temperatures of the mixtures were maintained by insulating the bottles. The samples were processed at the field-based laboratory less than 2 hours after mixing.

Laboratory Methods

Values of pH of vent fluids, water-column samples, and mixed solutions were determined at the field-based laboratory after standardizing a pH meter and electrode using six buffer solutions ranging from pH 1.68 to 10. Subsamples of all water samples except pore water were taken for analysis of dissolved elements, Hg, anions, isotopes ($\delta^{18}O$ and δD), and either alkalinity or dissolved inorganic carbon. Because of the limited volumes of pore water, only selected samples were analyzed for anions and isotopes. Samples for anion and dissolved-element determinations were obtained by filtering the water through 0.45-µm disposable nylon filters into new polyethylene bottles for anions; into acid-cleaned, well-rinsed polyethylene bottles for dissolved elements; and into acid-cleaned glass bottles with teflon caps for Hg. Anion samples were kept cool, whereas samples to be analyzed for dissolved elements were preserved by adding one drop of re-distilled concentrated nitric acid per 10 mL of solution. Samples for dissolved Hg analyses were preserved with 1.5 mL-Ultrex concentrated HNO_3, saturated with sodium dichromate, per 60 mL of sample. Anion analyses of vent, water-column, and pore-water samples were done by ion chromatography at the field-based laboratory; anion analyses of the river water and mixing experiments were done by ion chromatography in the USGS laboratories in Denver, Colo. Dissolved elements were determined at the USGS laboratories in Denver, using inductively coupled plasma–atomic emission spectrometry (ICP–AES) (major ions and B), inductively coupled plasma–mass spectrometry (ICP–MS) (minor elements), and cold vapor generation with atomic-fluorescence detection (Hg). Samples for water isotopes ($\delta^{18}O$ and δD) were placed in 20-mL glass scintillation vials, tightly capped, and analyzed at the USGS laboratories in Denver by isotope-ratio mass spectrometry. Water samples were prepared for hydrogen-isotopic analyses using the Zn reduction technique, and for oxygen-isotope analyses using an automated CO_2 equilibration technique. Values of $\delta^{18}O$ and δD are relative to Vienna Standard Mean Ocean Water (VSMOW); they have reproducibility of approximately 0.1 and 1.0 per mil, respectively. Alkalinity was

determined using either a Chemetrics test kit (stream samples) or by Gran titration (mixing experiment samples) (Stumm and Morgan, 1996) at the field-based laboratory. The dissolved inorganic carbon or sum CO_2 content of the vent fluids and water-column samples was determined by flow-injection analyses at the field-based laboratory.

Blank samples using distilled, deionized water were included with each batch of 20 samples. The blank samples had element concentrations below detection limits. Standard reference solutions, either from the USGS or from the National Institute of Standards and Technology, were included in each batch of samples to determine accuracy and precision of the ICP-AES and ICP-MS analyses.

Results and Discussion

Systematics of Stable Isotopes ($\delta^{18}O$ and δD)

Hydrogen and oxygen isotopes are powerful tools for understanding the origin and evolution of waters in and around Yellowstone Lake. A plot of δD versus $\delta^{18}O$ clearly indicates that Yellowstone Lake deep waters plot off the global meteoric water line of Craig (1961), along an evaporation trend with a slope of about 5 (fig. 2). In contrast, samples from the majority of streams that drain into Yellowstone Lake have isotope values of typical atmospheric waters that plot on or near the global meteoric water line. Examination of the data for lake water reveals three important observations: (1) lake water is progressively more evaporated with increased distance from the Yellowstone River inlet, which is at the south end of Southeast Arm (fig. 1), (2) sublacustrine hydrothermal vent water is mainly lake water, probably due to mixing in the shallow subsurface or entrainment of lake water during sampling of the hydrothermal vent fluids, and (3) vent-water samples and water-column samples above vent sites tend to form nearly vertical arrays that indicate mixing with water whose composition is similar to the thermal pore water collected from Mary Bay and West Thumb sediments. Pore-water samples were collected from near-surface sediments as close as possible to known sublacustrine vent sites.

Studies by Craig and others (1963), Craig and Gordon (1965), and Gilath and Gonfiantini (1983) showed that the effects of evaporation, which are dependent on both kinetic and equilibrium liquid-vapor isotope-fractionation effects, can be calculated if temperature, relative humidity, and the isotopic values (oxygen or hydrogen isotopes) of surface inflow waters and atmospheric vapor are known. In practice, the isotope values of atmospheric vapor are calculated assuming equilibrium with precipitation. Krabbenhoft and others (1990) showed that the equilibrium assumption is valid, at least for $\delta^{18}O$ calculations. Parameters used in stable-isotopic-evaporation calculations are listed in table 1. Using the equations in Gilath and Gonfiantini (1983) and the appropriate $\delta^{18}O$ data, we calculate that Yellowstone Lake water has evaporated approximately 13 percent
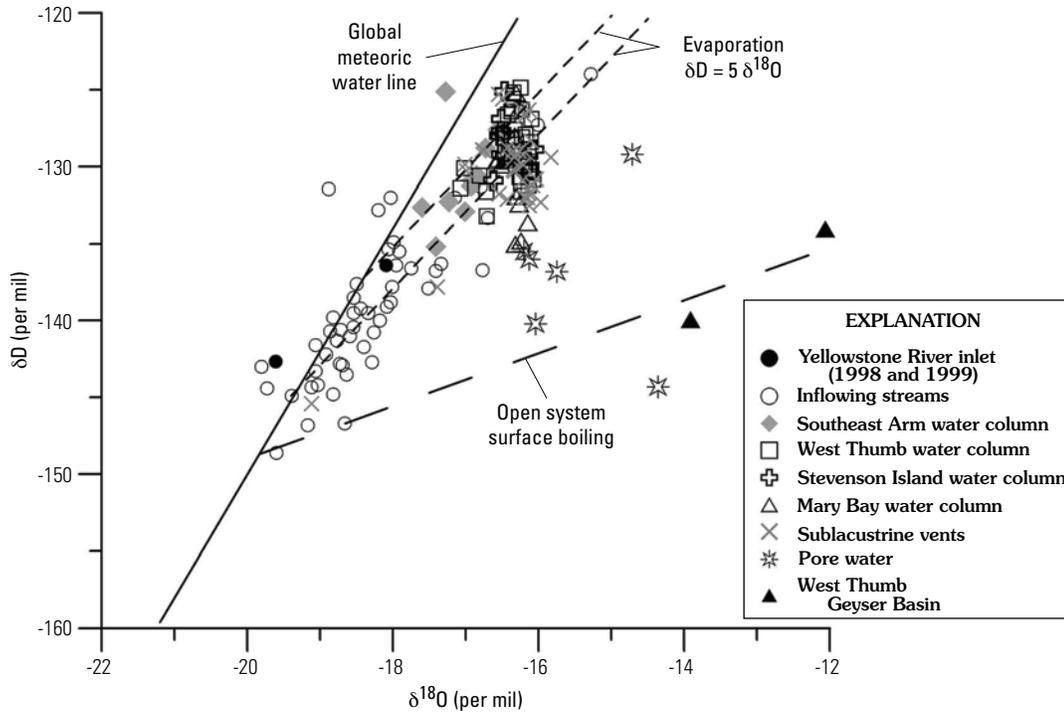
Figure 2. Hydrogen- and oxygen-isotope compositions of Yellowstone Lake (water columns in Southeast Arm, West Thumb, near Stevenson Island, and Mary Bay), inflowing streams, and sublacustrine hydrothermal vent fluids. Cl-rich pore waters collected near sublacustrine hydrothermal vents and two subaerial geyser waters from West Thumb Geyser Basin are shown for comparison.

during the 14±3-year residence time of the water in the lake. Hostetler and Giorgi (1995) compiled and calculated meteorological data for Yellowstone Lake, and their estimates of evaporation from meteorological data allow a direct comparison with estimates from stable-isotope fractionation. Using Kaplinski's (1991) estimate of total lake volume and the mean annual evaporation rate for Yellowstone Lake based on the global-climate model of Hostetler and Giorgi (1995), we calculate net evaporation during the 14-year residence time of about 16 percent, very similar to that estimated from the isotopic calculations (table 1). Furthermore, the simulations and meteorological data of Hostetler and Giorgi (1995) indicate that the volume of water lost due to evaporation and gained from precipitation is 3–4 times less than the volume of water flowing into and out of the lake. Thus, evaporation is very important in controlling the stable-isotopic composition of Yellowstone Lake water, but it is not the major flux of water from the lake.

Mass-Balance Calculations

Mass-balance calculations are used to identify elements for which hydrothermal vents may be an important source to Yellowstone Lake. These calculations consider the change in concentration of an element or species in a system as a function of time (Schnoor, 1996). The change in concentration as a function of time is the difference between the inputs (or sources) and outputs (or sinks) of elements or species to the system. For Yellowstone Lake, we consider only changes in dissolved concentrations of elements or species. Figure 3 illustrates potential sources and sinks of dissolved elements or species to Yellowstone Lake. Potential sources include precipitation

(rain and snow), inflowing streams, and hydrothermal vents. Potential sinks for this system are evaporation, outflow via the Yellowstone River at the north end of the lake, and removal processes occurring within the lake that transform dissolved elements into particulate elements (for example, mineral precipitation, adsorption, or biological uptake). Ground water may be an important potential source or sink of elements. However, its impact is not known because a thorough hydrologic balance and detailed analyses of ground-water compositions have not yet been done for this system.

The mathematical expression to describe changes in the concentration (C) of a dissolved element or species as a function of time (t) (that is, $\frac{\delta C}{\delta t}$ with units of moles/L/s) in terms of these potential inputs and outputs is:

$$\frac{\delta C}{\delta t} = \frac{(Qprec*Cprec)}{V} + \frac{\sum(Qin*Cin)}{V} + \frac{(Qvent*Cvent)}{V} - \frac{(Qevap*Cevap)}{V} - \frac{(Qout*Cout)}{V} - J \pm \frac{(Qgw*Cgw)}{V} \tag{1}$$

where Q is discharge in m³/s of precipitation (prec), inflow (in), hydrothermal vent water (vent), evaporation (evap), outflow (out), and ground water (gw), C is the dissolved concentration of an element or species of interest in moles/L in precipitation, inflow, hydrothermal vent water, evaporation, outflow, or ground water, J is a generic removal term in moles/L/s to account for transformations from dissolved to particulate phases, and V is the volume of the lake in m³.

Contributions from precipitation and evaporation are insignificant because their element concentrations (Drever, 1988) and discharges are very low (table 1) compared to other hydrologic components considered in equation 1. Therefore, neither evaporation nor precipitation is considered further in the

Table 1.   Volume and flux relations for water budget of Yellowstone Lake.

Average ice-free relative humidity	77%	Hostetler and Giorgi (1995)
Average ice-free annual temperature	11.6°C	Hostetler and Giorgi (1995)
$\delta^{18}O$ flow-weighted surface inflow	−19.0‰	this study
$\delta^{18}O$ atmospheric moisture*	−28.8‰	
Mean annual evaporation rate	0.19 km^3/yr	Hostetler and Giorgi (1995)
Mean annual precipitation rate	0.17 km^3/yr	Hostetler and Giorgi (1995)
Aug.–Sept. 1998 stream inflow	0.67 km^3/yr	this study
July 1999 stream inflow	3.6 km^3/yr	this study
Lake surface area	341 km^2	Kaplinski (1991)
Lake volume	16.54 km^3	Kaplinski (1991)
Discharge at USGS gaging station 06186500 Yellowstone River at Yellowstone Lake outlet	1.19±0.29 km^3/yr	USGS; from 67-year record [http://mt.water.usgs.gov]
Average residence time	14±3 yr	Calc. as volume/discharge
Net evaporation rate	1.12%/yr	
Net evaporation calculated from hydrologic data and residence time	16±3%	For one residence time of lake water
Net evaporation calculated from $\delta^{18}O$	13%	For one residence time of lake water

*Calculated by equilibrium with precipitation.

Figure 3.   A box model, the basis for the mass-balance calculations, illustrates the potential sources and sinks of elements in Yellowstone Lake.

mass-balance calculations. In addition, if we assume that the system is at steady state (that is, $\frac{\delta C}{\partial t}= 0$ or there is no change in the dissolved concentration of an element or species in lake water as a function of time), then equation 1 can be rearranged to indicate that inputs due to inflow and hydrothermal vents equal outputs by outflow and other biochemical removal processes. Ground water can act either as a source or a sink of elements.

$$\Sigma(Qin*Cin) + (Qvent*Cvent) = (Qout*Cout) \pm (Qgw*Cgw) + (J*V) \quad (2)$$

By dividing both sides of the equation by *Qout* and rearranging, the dissolved concentration of an element or species at the lake outlet can be compared with that in the flow-weighted inflow.

$$Cout - [\frac{\Sigma(Qin*Cin)}{Qout}] = \frac{(Qvent*Cvent)}{Qout} \pm \frac{(Qgw*Cgw)}{Qout} - \frac{(J*V)}{Qout} \quad (3)$$

If the dissolved concentration of a chemical species in the outflow is greater than the flow-weighted dissolved concentration of the same species in the inflow, there is a net source of that species in the lake. If the difference between the dissolved concentrations of the outflow and flow-weighted inflow is negative, then the lake is acting as a net sink for the element or species. If the dissolved concentration of a chemical species in the outflow is equal to the flow-weighted dissolved concentration of the same species in the inflow, there is no net source or sink in the lake.

The mass-balance calculations were made using two synoptic estimates of the flow and dissolved concentrations of elements or species in streams, determined during low-flow (August and September of 1998) and high-flow (July of 1999) conditions. Sampling times were chosen to represent extremes

in discharge and element or species concentrations associated with those flows, and they were intended to span the range of variations. The mass-balance calculations are instantaneous pictures. A more detailed evaluation that looks at changes in daily, monthly, or seasonal fluxes can be done only when a hydrologic balance for the lake is determined and samples for element analyses of the inflows and outflows are collected and analyzed at higher frequencies throughout a long time interval.

The Yellowstone River at its inlet to Yellowstone Lake in Southeast Arm is the major contributor (that is, 70 percent in 1998 and 86 percent in 1999) of water to the lake. Because the Yellowstone River at its inlet to Yellowstone Lake is a braided stream, it is difficult to measure its discharge without an established and calibrated gaging station. Hence, of all the terms on the left side of equation 3, the value for *Qin* likely has the largest error. We estimate this error by examining the water balance for the time intervals of our samplings. This calculation considers that the change in the volume (V) of the lake as a function of time (t) (that is, $\frac{\partial V}{\partial t}$ in units of m³/s) is equal to the discharge or flux of water into the lake minus the flux of water out of the lake, that is,

$$\frac{\partial V}{\partial t} = Qprec + Qin + Qvent - Qevap - Qout \pm Qgw \quad (4)$$

To calculate the value of *Qin* for comparison with our measured value, we used published values of *Qprec* and *Qevap* for this area (table 1) and assumed that *Qvent* and *Qgw* are negligible relative to the other discharges. In addition, the value for $\frac{\partial V}{\partial t}$ for each of the river sampling intervals (8/24–9/1/98 and 7/12–7/21/99) was estimated by first determining the relationship between gage height and discharge at Yellowstone River at its out-

let from the lake, from the long-term gaging records (http://mt.water.usgs.gov; accessed 8/2000). The change in discharge at the Yellowstone River outlet during the sampling periods was converted to a change in gage height using the relationship. Then, the change in gage height was multiplied by the surface area of the lake (table 1) to determine the change in volume during the sampling intervals. Solving equation 4 with the above assumptions yields calculated values for Q_{in}, which is the sum of all inflows, of 27 m^3/s in 1998 and 93 m^3/s in 1999. The measured values for ΣQ_{in} during our sampling periods were 21 m^3/s in 1998 and 115 m^3/s in 1999. Our measured values for ΣQ_{in} are within 22 percent of the calculated values.
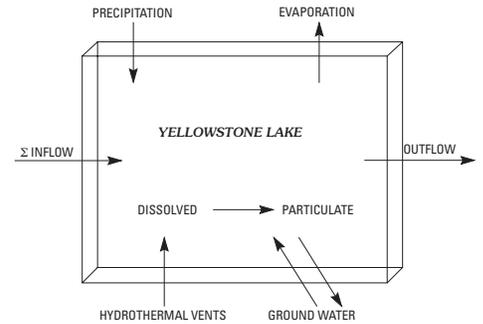
Because our discharge estimates are relatively well constrained ($\pm$22 percent), we can evaluate the role of internal sources of elements to the lake by plotting the ratio of the concentration of an element in the outflow to the concentration in the flow-weighted inflow (fig. 4). On this log plot, positive values of the ratio indicate that there is a net source of the element into the lake, whereas negative values indicate that the lake is a net sink for the element. Values of zero indicate that there is little or no net source or sink for the element, or that a small source or sink term is not resolved by this approach. Given the assumptions and error estimates above, we conservatively assume that values of the ratio within 1 log unit of zero indicate no net source or sink.

The mass-balance calculations for 1998 and 1999 indicate that many elements have larger dissolved concentrations (by at least a factor of 10) in the outflow from Yellowstone Lake

relative to the flow-weighted inflow, suggesting that there is a supply of these elements within the lake (fig. 4). The magnitude of the loading of elements or species into the lake appears to be seasonal (that is, generally loading is greater during high flow), but more detailed information about temporal changes in discharges and associated element concentrations is needed. Elements that definitely show a source within the lake (that is, log [concentration$_{outflow}$/concentration$_{flow-weighted\ inflow}$] $\geq$ 1) for one or both years include As, (possibly) B, Cl, Cs, Cu, Ge, Li, Mo, Sb, and W. Probable mechanisms for increased concentrations of many elements in the lake include evapoconcentration and supply from hydrothermal vents and ground water. The stable isotopes ($\delta^{18}O$ and δD) indicate that evapoconcentration accounts for a change of about 13 percent in the concentrations of elements during the residence time of water in the lake. This change is within our analytical error, and it is much too small to account for the results of our mass-balance calculations. Because most of these elements (As, B, Cl, Cs, Li, Mo, Sb, and W) are known signature elements for the suberial hydrothermal waters (Beeson and Bargar, 1984; Stauffer and Thompson, 1984; Sturchio and others, 1986; White and others, 1991), we conclude that enrichment of these elements in the lake outflow is due to hydrothermal input. Other elements (that is, Ce, La, Mn, Sc and U) show removal within the lake during one or both years. Processes such as oxidation and (or) mineral precipitation (Mn) or sorption by particles (Ce and U) may be responsible for dissolved-metal loss from the water column (Stumm and Morgan, 1996).
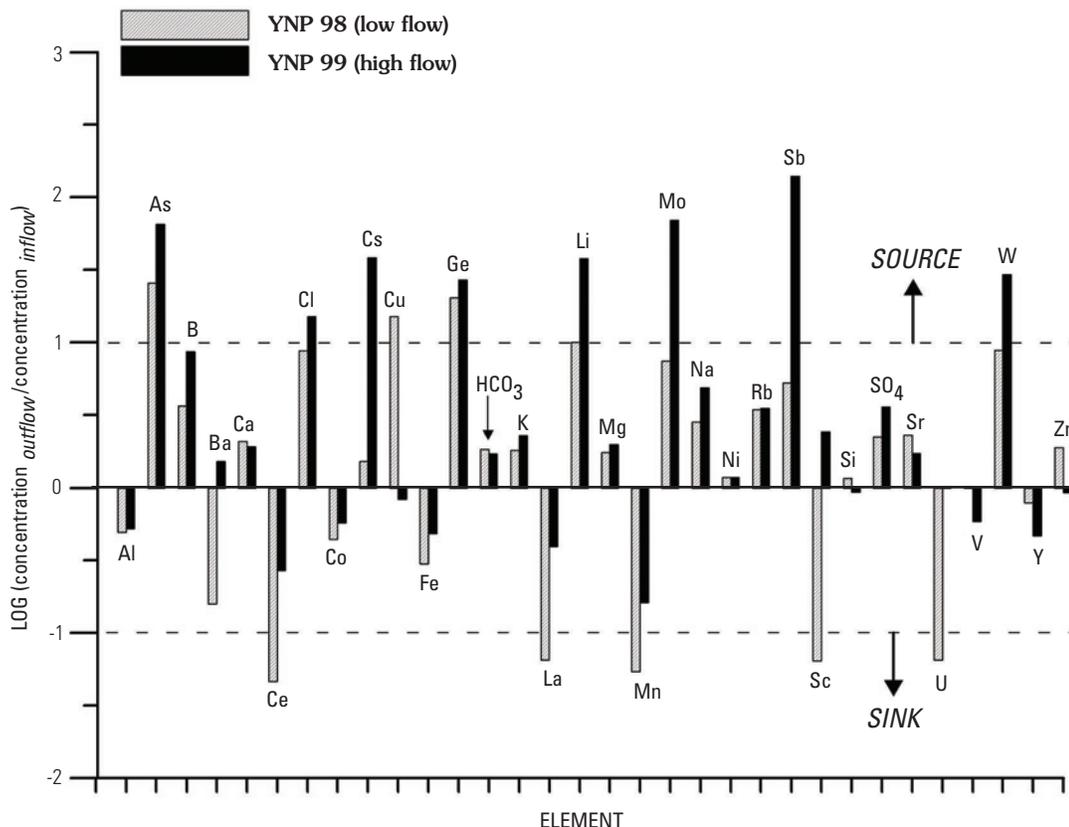
Figure 4. Results of mass-balance calculations that compare element concentrations in the flow-weighted inflow to and outflow from Yellowstone Lake. Values of the log of the ratios (concentration$_{outflow}$/concentration$_{inflow}$) $\geq$ 1 indicate a net source of elements to the lake; log ratios $\leq$ 1 indicate a net loss or sink of elements within the lake. If the log ratio = 0$\pm$1, then there is no net source or sink of elements.

Chloride Concentrations in Hydrothermal Vent Fluids and Lake Water: Mixing of End-Member Solutions

Chloride is a major indicator of hydrothermal fluids. Geochemical interpretations of geyser basin fluids indicate that the subsurface deep-reservoir fluids that feed the thermal basins in the Park contain about 10 mM (360 mg/kg) Cl (Truesdell and others, 1977; Fournier, 1989). As these fluids ascend to the surface, boiling and steam separation occur; the concentration of Cl in the boiled water can be as high as 20 to 21 mM (710 to 750 mg/kg) (Truesdell and others, 1977). Chloride concentrations in the boiled water depend on the steam-separation mechanism (that is, single stage, continuous, or a combination) and dilution by local meteoric waters.

Chloride is an excellent tracer of hydrothermal water in Yellowstone Lake because the major source of water to the lake, that is the Yellowstone River, contains almost no Cl (<6 μM or micromoles per liter). The flow-weighted inflow for August and September of 1998 and July of 1999 had Cl concentrations of 15 and 9 μM, respectively. Those values are at least three orders of magnitude smaller than Cl concentrations in the deep source water or boiled thermal water.

Dissolved chloride concentrations for the flow-weighted inflow waters, hydrothermal vent fluids, and lake water as a function of depth are compared in figure 5 and table 2. The vent fluids and lake water are significantly enriched in Cl relative to the inflowing water. However, the vent fluids, with a few exceptions, have about the same concentration of Cl as the lake water, and that concentration (100 to 200 μM) is substantially lower than dissolved Cl concentrations in deep thermal water (10 to 20 mM). Thus, the vent fluids that we collected appear to be highly diluted hydrothermal source water. Furthermore, Cl concentrations in the water column vary with location in the lake. This observation is not expected for a conservative element in a lake that has a water residence time of 14±3 years. These differences in Cl concentrations, as well as other elements (table 2), suggest that there is variable dilution by lake water or there are variable inputs of hydrothermal fluids into the lake.

The dilution hypothesis is supported by relationships between the concentrations of Cl and other elements in lake and vent waters. The results of the mixing experiments between Yellowstone River water and subaerial geyser fluids are also instructive. Linear relationships between Cl and other element concentrations are expected for mixing of end-member solutions when no removal reactions (for example, precipitation of minerals) occur. The slopes of such lines are indicative of the concentrations in the end-member solutions. The concentrations of selected elements that show enrichments in the outflow relative to the inflow (B, Li, As, and W) are plotted with respect to Cl in figures 6 and 7 for the flow-weighted inflow, water column, hydrothermal vent fluids, and mixing experiments. The correlation coefficients for the linear relationships between Cl and B, Li, As, and W for these solutions are significant at the 99 percent confidence interval (Rohlf and Sokal, 1995).

Other dissolved components that show linear relationships between their concentrations and Cl concentrations in lake water and vent fluids at the 99 percent confidence interval are SiO_2, Na, K, Rb, Cs, Ge, Mo, Sb, HCO_3, and SO_4. There are no correlations between dissolved Cl and the alkaline earth elements (Mg, Ca, Sr, Ba) in lake water and vent fluids. Alkaline earth elements are independent of Cl concentration, indicating that end members have very similar concentrations or that the hydrothermal source fluid has negligible concentrations of these elements. The linear relationships between Cl and many elements or species in vent fluids and lake water strongly indicate that end-member mixing is occurring and that the most likely end members that define the chemical composition of Yellowstone Lake water are inflow water and hydrothermal source fluids. This is further demonstrated by linear correlations between Cl and other elements or species, including the alkaline earth elements, for the experiments in which river water and subaerial geyser fluids were mixed.

To compare differences in the compositions of hydrothermal vent fluids and their influence on the geochemistry of the water column in the lake, we normalized element concentrations in these waters to an average concentration of Cl in the deep water of the lake. This normalization eliminates the variable dilution of these waters as end-member mixing occurs.

$$[Me^*] = \frac{[Me]}{[Cl]} * [ClDW] \tag{5}$$

where $[Me^*]$ is the normalized-element or species concentration, $[Me]$ is the measured concentration of the element or species, $[Cl]$ is the measured Cl concentration, and $[ClDW]$ is the average concentration of Cl in the deep water of Yellowstone Lake and is 140 μM.

Relationships Between Major Anions and pH in Hydrothermal Vent Fluids and Lake Water

The principal anions in the subaerial hydrothermal systems in the Park are Cl, SO_4, and HCO_3 (Henley and others, 1984). The relative proportions of those anions in hydrothermal waters and their pH reflect the processes (for example, boiling, dissolution of gases and rocks, and mixing) that occur as deep thermal fluids ascend and interact with ground water, surrounding rocks, and surface water. For example, deep thermal fluids may flow directly to the surface, producing boiling springs that have nearly neutral to alkaline pH and Cl-rich water. Acid-SO_4 waters of low pH (<3) and low Cl contents are produced when H_2S volatilizes from deep thermal fluids during boiling and then condenses into colder ground water. The H_2S can then oxidize and release hydrogen ions and SO_4 to solution. Volatilization of CO_2 from boiling thermal fluids and dissolution into ground water produces HCO_3-rich waters. Mixtures of these waters form hybrid solutions, such as acid-SO_4-Cl waters.

Table 2. Temperature and average chemical composition of Yellowstone Lake water, including streams that enter the lake (flow-weighted inflow), deep lake water (DW; >25 m deep) in Southeast Arm (SE. Arm), in West Thumb (WT), near Stevenson Island (SI), and in Mary Bay (MB), and lake-bottom hydrothermal vent fluids in West Thumb, near Stevenson Island, and in Mary Bay.

Parameter, element, or species	Units	1999 Flow-weighted inflow	SE. Arm DW	WT DW	SI DW	MB DW	WT vents	SI vents	MB nearshore vents	MB deep-hole vents
temp.	°C	14.6	4.8	7.3	9.3	12	8.7–68	15–106	28.3–93	30–103
pH		5.7	7.5	7.3	7.4	6.9	5.4–8.6	5.1–7.1	5.4–7.3	4.8–6.9
Cl	μM	8.7	120	160	140	170	50–1,150	130–140	120–140	140–170
SiO_2	μM	170	170	210	190	200	180–1,600	160–330	150–350	150–400
B	μM	1.1	7.4	8.1	7.5	9.7	3.2–68	5.7–8.3	6.5–9.2	7.4–13
Li	μM	0.8	5.7	7.9	6.5	8.1	8.8–88	6.2–7.8	4.9–7.2	4.9–8.5
Na	μM	72	350	470	400	440	440–3,900	360–420	300–390	270–430
K	μM	16	31	38	36	36	17–200	36–41	33–61	31–51
Rb	nM	13	56	69	60	68	61–550	56–69	47–96	55–85
Cs	nM	0.4	24	31	22	31	22–630	17–24	17–280	8.3–660
Mg	μM	42	98	110	110	110	8.2–120	90–130	74–140	66–120
Ca	μM	59	130	130	130	130	87–140	120–160	100–210	90–140
Sr	nM	230	500	490	490	520	75–550	470–730	410–1,140	380–730
Ba	nM	41	61	59	60	65	36–120	71–590	29–1,240	57–490
As	nM	2.9	160	270	190	240	120–2,800	130–290	88–230	49–720
Ge	nM	0.1	2.7	5.5	3.3	3.9	5.5–140	2.7–5.5	2.7–4.1	2.7–5.5
Hg	pM	<25	<25	55	<25	<25	<25–800	<25–850	<25–160	<25–140
Mo	nM	0.4	11	16	11	11	18–380	0.4–21	9.5–33	1–28
Sb	nM	<0.2	4.1	6.3	4.9	6.5	0.8–140	<0.2–7.8	<0.2–90	<0.2–107
W	nM	0.9	7.3	11	6.9	9.5	87–440	5.4–10	6.5–260	7.1–540
ΣCO_2	mM	0.25	0.62	0.69	0.69	0.79	0.76–5.5	0.64–9.8	0.92–2.4	0.83–27
HCO_3	μM	240	560	680	620	610	510–3,040	460–700	400–720	230–620
SO_4	μM	21	76	78	82	89	21–130	78–120	71–150	78–150

Figure 5. Dissolved Cl concentrations in flow-weighted inflow to Yellowstone Lake, lake water as a function of depth and location, and hydrothermal vents as a function of location. Inflow data were collected in the summers of 1998 and 1999, water-column data in the summer of 1998, and vent data in the summers of 1996–1999.
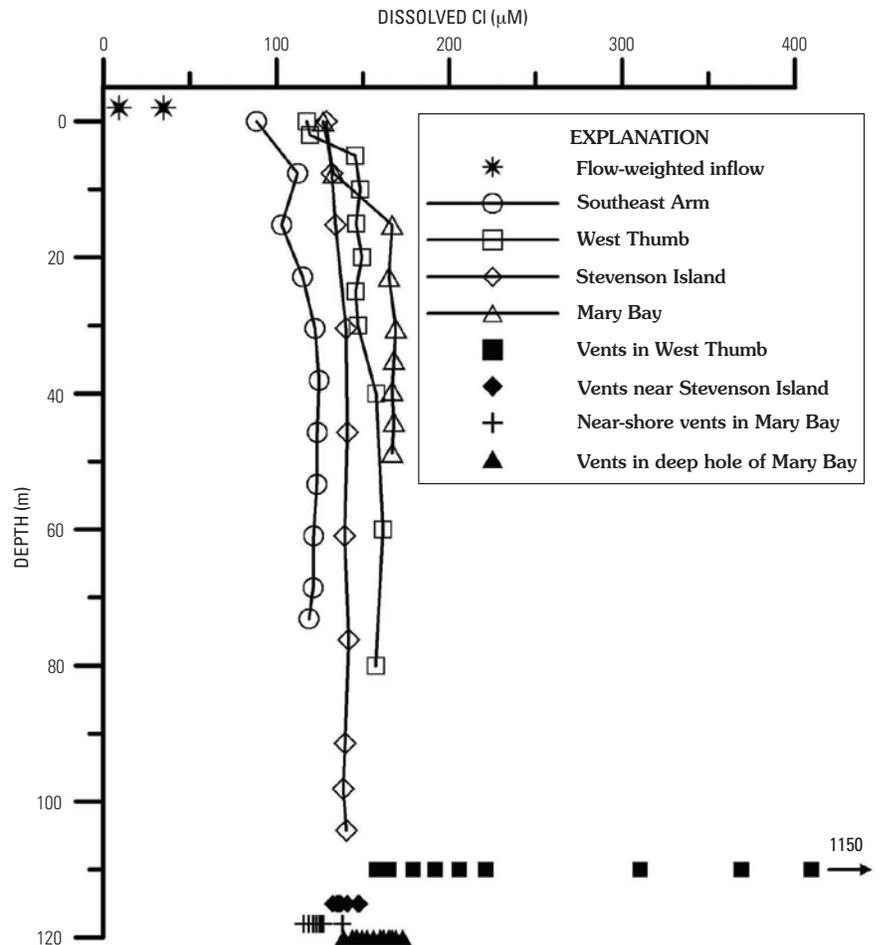
A ternary diagram illustrates the relative importance of Cl, SO_4, and HCO_3 in vent fluids and lake water (fig. 8). Data from the acid and nearly neutral geyser water collected from Norris Geyser Basin and West Thumb Geyser Basin are also plotted for comparison. The first observation is that the dominant anion in almost all vent fluids and lake water is HCO_3, whereas the water in subaerial geysers tends to be dominated by Cl (Porkchop), Cl and SO_4 (Green Dragon and Echinus), or Cl and HCO_3 (Black Pool). Second, the water from some vents near Stevenson Island and in the deep hole of Mary Bay have a larger proportion of SO_4 relative to Cl or HCO_3, whereas the water from vents in West Thumb has a larger proportion of Cl relative to SO_4 and HCO_3. This observation suggests that water in certain vents near Stevenson Island and in the deep hole of Mary Bay is influenced more by the volatile gas H_2S. The relative proportions of anions in lake water are between the proportions in the two vent types, but closer to the relative proportions observed in water from the Mary Bay and Stevenson Island vents.

The mixing lines between Yellowstone River water at the inlet to the lake and subaerial geyser water suggest that the source fluid for vents near Stevenson Island and in the deep hole of Mary Bay has a larger component of acid-SO_4-Cl water, whereas the source fluid for some vents in West Thumb has a larger component of nearly neutral, Cl-rich water. The lake water is a composite of these source fluids and inflowing surface water.

The pH of hydrothermal vent fluids is regulated by the amount of volatile gases (CO_2 and H_2S) dissolved into solution. In figure 9, normalized concentrations of total dissolved carbonate (ΣCO_2^*) are plotted with respect to pH (measured at 25°C) for the hydrothermal vents and water in Yellowstone Lake. Also shown in that figure is a prediction, using the chemical-equilibrium-modeling computer program MINEQL+ (Schecher and McAvoy, 1998), of pH based on injection of variable concentrations of CO_2 into a closed system. There is excellent agreement between the measured and predicted pH. Values of pH are lower when there are higher amounts of total-dissolved-carbonate species in solution. The contribution of H_2S, depicted by concentrations of its oxidized form (SO_4), is <13 percent of the sum of ΣCO_2^* and SO_4^*. Thus, the dominant dissolved gas controlling the pH of these waters likely is CO_2. The observed data indicate that water in all vents, except a few in West Thumb and near the shore in Mary Bay, are acidic (pH < 7). The most acidic and CO_2-enriched vents are near Stevenson Island and in the deep hole of Mary Bay. In contrast, lake water has low concentrations of total dissolved carbonate, and it is nearly neutral to alkaline.
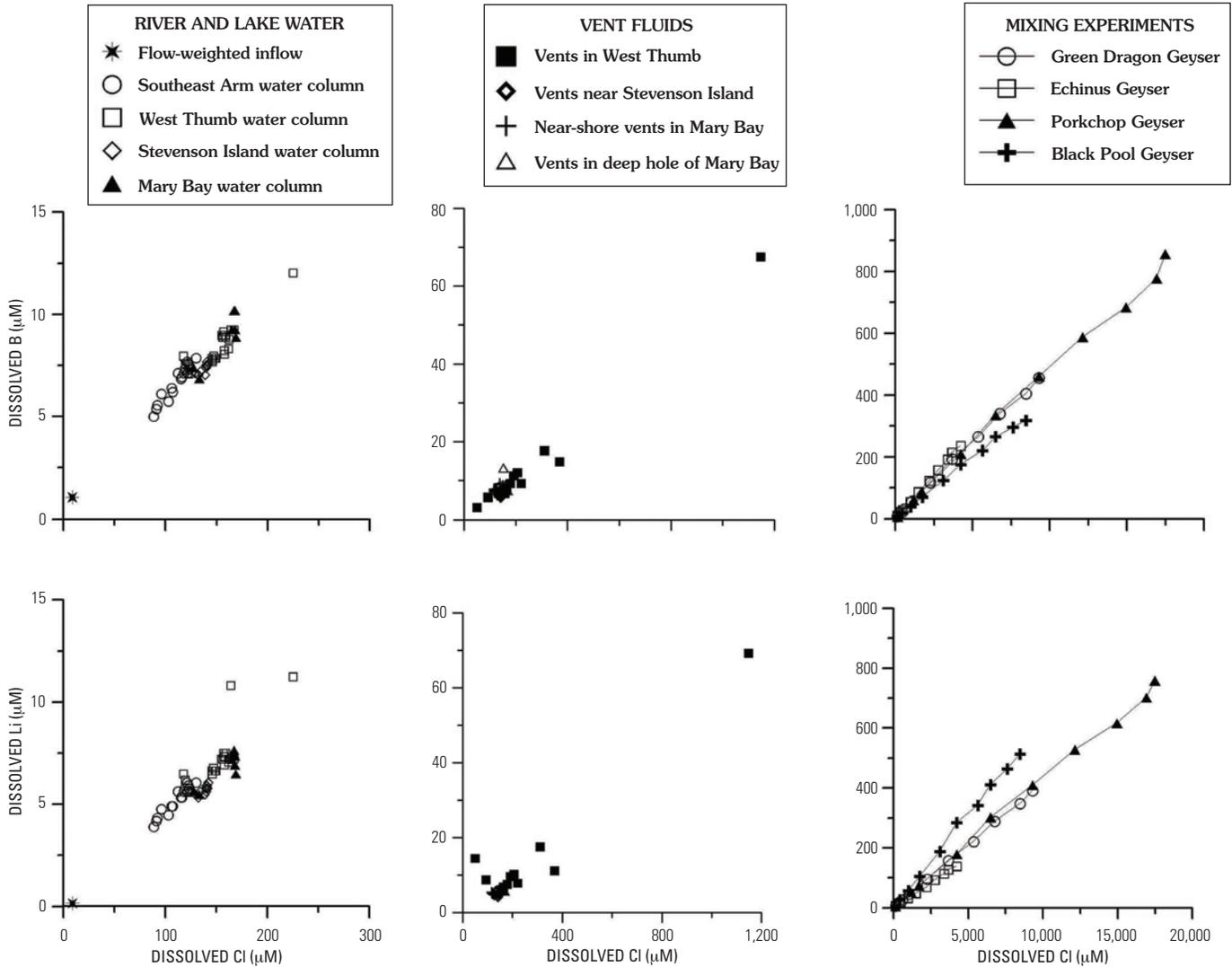
Figure 6.   Dissolved concentrations of B and Li as a function of dissolved Cl concentrations in inflow and lake water, hydrothermal vent fluids, and in the mixing experiments between Yellowstone River water and subaerial geyser fluids. Note changes in scale for both x- and y-axes.

Normalized Concentrations of Elements in Hydrothermal Vent Fluids and Lake Water

The anion and pH data for hydrothermal vents in Yellowstone Lake suggest that there are some differences in the compositions of source fluids to the lake and that the compositions of the source fluids may vary as a function of location within the lake. To further explore these differences, we examined the concentrations of SiO_2, B, alkali metals (Li, Na, K, Rb, Cs), alkaline earth elements (Mg, Ca, Sr, Ba), trace anions and mercury (As, Ge, Hg, Mo, Sb, W), species related to gas dissolution (HCO_3, SO_4), and redox-sensitive species (Fe, Mn) in inflow water, lake water, and hydrothermal vent fluids. Because lake water is a variable mixture of inflow water and hydrothermal source fluids and vent fluids are variable mixtures of lake water and hydrothermal source fluids, we evaluated their Cl-normalized concentrations

as a function of depth and location for lake water and as a function of location for vent water. The concentrations of elements in flow-weighted inflow water were not normalized because this water is an end-member fluid. The comparisons of different water are intended to emphasize the influence of hydrothermal vent fluids on the composition of Yellowstone Lake water and to characterize the geochemical signature of hydrothermal source fluids to the lake water.

SiO_2

The flow-weighted inflow concentration of SiO_2 (fig. 10) is slightly lower than the average, but within the range, of the Cl-normalized concentration in the water column of the lake (170 compared to 200±20 µM). The concentration of SiO_2* as a function of depth in Yellowstone Lake water is fairly uniform, with a variation of only 12 percent about the mean.

Figure 7. Dissolved concentrations of As and W as a function of dissolved Cl concentrations in inflow and lake water, hydrothermal vent fluids, and in the mixing experiments between Yellowstone River water and subaerial geyser fluids. Note changes in scale for both x- and y-axes.
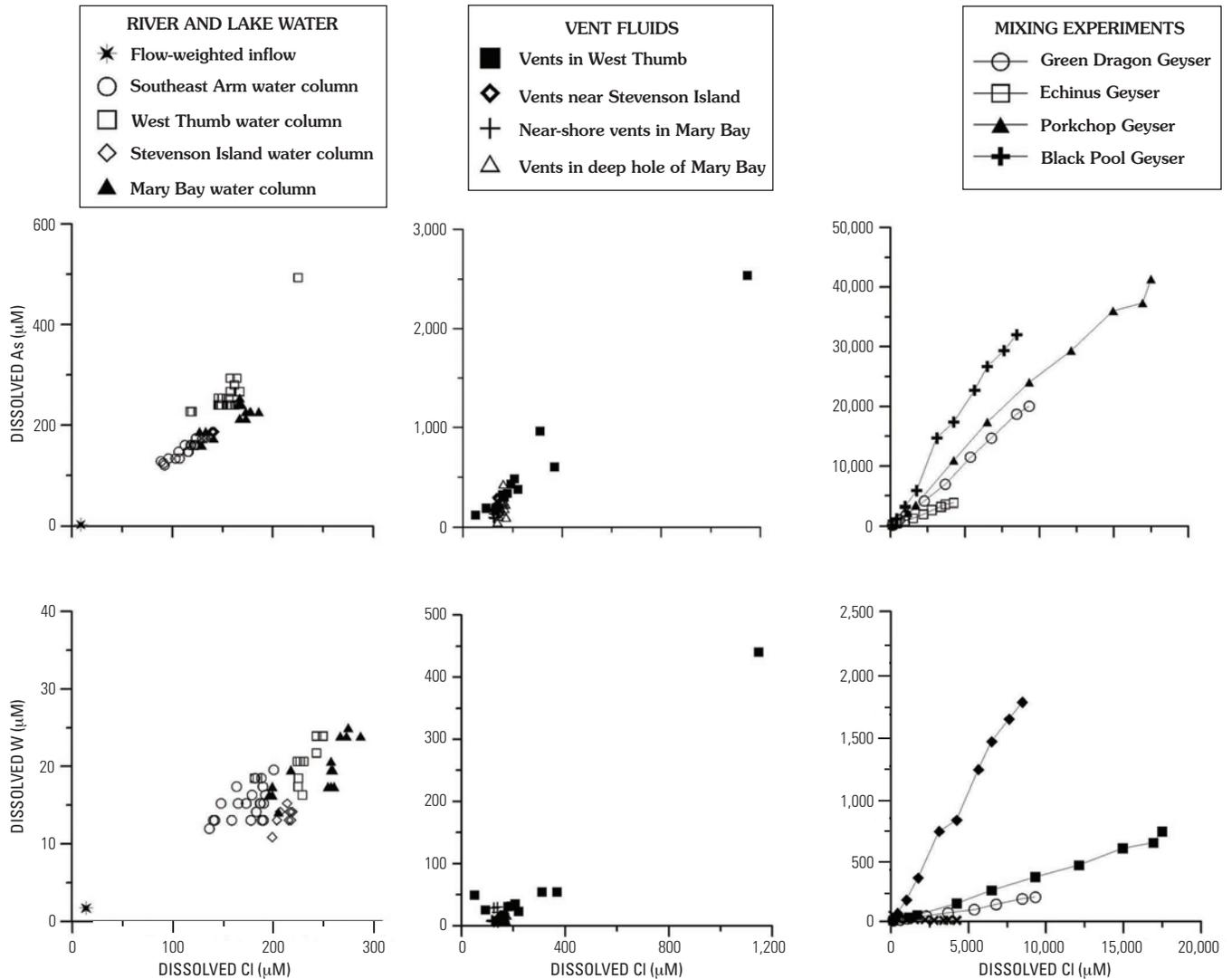
Several of the hydrothermal vent fluids, particularly those in Mary Bay and near Stevenson Island, show some enrichment in SiO_2* relative to lake water.

B and Alkali Metals

Lake water is enriched in all of these elements, relative to the flow-weighted inflow water (fig. 11). The average Cl-normalized concentrations of B, Li, and Rb in the water column of Yellowstone Lake are 7.9 µM B*, 6.3 µM Li*, and 63 µM Rb*. There is little variation (<8 percent) in Cl-normalized concentrations with depth or location for these elements throughout the lake. This observation is consistent with the small variations in the average concentrations of these elements (6.6–8.6 µM B*, 4.8–6.2 µM Li*, 61–68 µM Rb*) in hydrothermal vent fluids collected from different sites in the lake.

The average concentration of Na* in lake water is 390±40 µM, with water below the thermocline (>15 m) in Mary Bay at the low end of the range and water in Southeast Arm at the high end of the range. Concentrations of Na* in vent fluids from different sites are generally similar.

Concentrations of K* in the water column are 41±6 µM (15 percent variation), with the deep water of Mary Bay and West Thumb at the lower end of the range, compared to lake water near Stevenson Island. Water in Southeast Arm appears to be more enriched in K, compared to water in the other areas. Water from some vents in West Thumb and the deep hole in Mary Bay has lower concentrations of K* than water from other vents.

Vent fluids from sites that are generally more acidic and enriched in CO_2 (Mary Bay and Stevenson Island; see fig. 9) tend to have lower concentrations of Cs* than do fluids from more neutral West Thumb vents (average concentrations of 21–25 µM compared to 39 µM). However, the influence of

Figure 8. Ternary diagram showing relationships between dissolved Cl, SO_4, and HCO_3 in inflow, hydrothermal, and lake water. Data for subaerial geysers in Norris Geyser Basin (Green Dragon, Echinus, Porkchop) and West Thumb Geyser Basin (Black Pool) are plotted for comparison.

EXPLANATION
- □ Vents in West Thumb
- ◇ Vents near Stevenson Island
- + Near-shore vents in Mary Bay
- △ Vents in deep hole of Mary Bay
- ▲ Green Dragon Geyser
- ● Echinus Geyser
- ✕ Porchop Geyser
- ▼ Black Pool Geyser
- ✳ Flow-weighted inflow
- ⊠ Yellowstone River Inlet 1997–99
- ○ Yellowstone Lake
- — Mixing of geyser water with inlet water
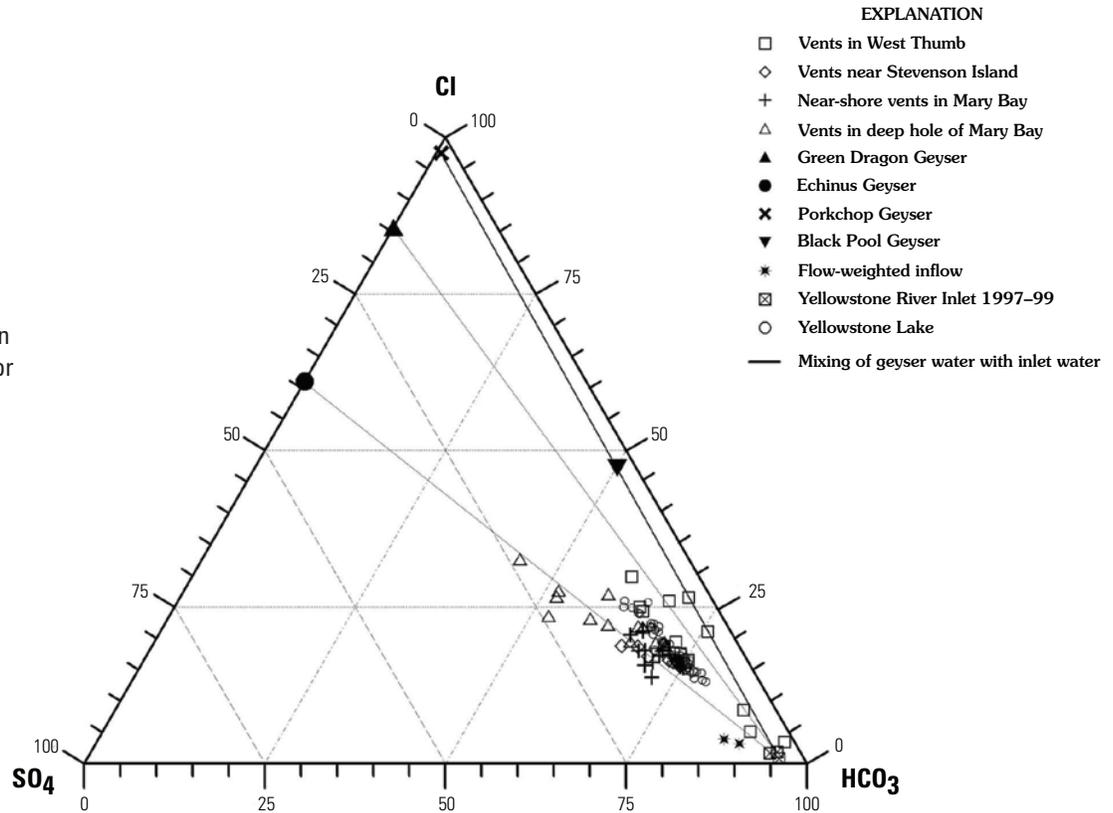
vent fluids on the concentration of Cs* in the water column is small (26±3 µM). Concentrations in the water column near Stevenson Island are slightly lower than those at other sites in the lake.

The above data suggest that the composition of the hydrothermal source fluid is similar in its B, Li, Na, K, and Rb contents throughout the lake. Only the vent-water data for Cs* suggest that slightly more enriched vent fluids are present in West Thumb, compared to the other vent sites.

Alkaline Earth Elements

Concentrations of alkaline earth elements (fig. 12), especially Mg, Ca, and Sr, in flow-weighted inflow water tend to be lower than those in the water column. Water-column profiles of Mg*, Ca*, Sr*, and Ba* indicate that the average concentrations are 110 µM, 130 µM, 510 nM (nanomoles per liter), and 64 nM, respectively, and the profiles show variations of only 11–13 percent in concentration with depth and location. Although these variations are small, the deep water in Mary Bay and West Thumb has lower concentrations of these elements, relative to those of deep water near Stevenson Island and in Southeast Arm.

The hydrothermal vent fluids may have some influence on water-column geochemistry at some sites. Although the Cl-normalized concentrations of the alkaline earth elements vary widely, vent fluids in West Thumb and the deep hole in Mary Bay generally have lower average concentrations of Mg*, Ca*, and Sr*, compared to concentrations in vent fluids near Stevenson Island and near the shore in Mary Bay (65–83 µM versus 110 µM Mg*,

82–100 µM versus 140 µM Ca*, and 330–470 nM versus 580–590 nM Sr*). Large concentrations of Ba* are present in some hydrothermal vent fluids near Stevenson Island and in the deep hole of Mary Bay.

Trace Anions and Mercury

Concentrations of As*, Ge*, Mo*, Sb*, and W* in the water column of Yellowstone Lake (fig. 13) are higher than those in flow-weighted inflow water. Concentrations of Hg in flow-weighted inflow water and water-column samples are below or very close to the detection limit (< 25 pM or picomoles per liter). However, Hg* concentrations in vent water are as high as 320 pM.

The average Cl-normalized concentrations of As, Ge, Mo, Sb, and W in lake water are 210 nM, 3.7 nM, 12 nM, 5.2 nM, and 8.4 nM, respectively. Variations with depth and location range from a low of 10 percent for Sb* to a high of 20 percent for Ge*. The water column in West Thumb generally has the highest concentrations of these elements.

All of the trace elements and mercury show large variations in their Cl-normalized concentrations in the hydrothermal vent fluids. In general, concentrations of all these elements tend to be higher in vent fluids from West Thumb, compared to the other sites (average concentrations: 290 nM versus 170–220 nM As*, 7.6 nM versus 3.3–3.9 nM Ge*, 53 pM versus 16–34 pM Hg*, 22 nM versus 6–17 nM Mo*, 9.9 nM versus 4.1–6.5 nM Sb*, and 22 nM versus 8.5–13 nM W*). The vent fluids, enriched in As, Ge, Mo, and W in West Thumb, appear to enrich the water column at that site, relative to other sites in the lake.

Species Related to Gas Dissolution

The water column of Yellowstone Lake is enriched in SO_4, ΣCO_2, and HCO_3 (fig. 14) relative to flow-weighted inflow water (table 2), and the profiles show a variation of 8 percent in SO_4^*, 7 percent in ΣCO_2^*, and 12 percent in HCO_3^* concentrations as a function of depth and location. Average Cl-normalized concentrations of lake water are 81 μM SO_4^*, 0.69 mM ΣCO_2^*, and 640 μM HCO_3^*. However, HCO_3^* concentrations indicate that there is less HCO_3 at depth at the station over the deep hole of Mary Bay compared to concentrations at other locations in the lake.

The hydrothermal vent fluids show clear differences in SO_4^* concentrations as a function of location in the lake. Hydrothermal vent fluids in West Thumb have lower concentrations (51 ± 20 μM) than do fluids from vents near Stevenson Island and in Mary Bay (93–100 ± 20 μM). Some vent fluids in Mary Bay and near Stevenson Island are greatly enriched in ΣCO_2^* and, as indicated previously, dissolution of CO_2 probably is responsible for the low pH values of these fluids. Vent water in West Thumb and in the deep hole in Mary Bay tends to have lower average concentrations of HCO_3^* (390–460 μM) than does water from vents near Stevenson Island and near the shore in Mary Bay (590–620 μM).

Redox-Sensitive Species

In contrast to most of the other examined elements, the concentrations of Fe and Mn (fig. 15) in the flow-weighted inflow are generally greater than or equal to Cl-normalized concentrations in the water column. The water-column data indicate that there are differences between sites. There are enrichments in the very bottom water for Fe or below the thermocline for Mn at the site over the deep hole in Mary Bay, whereas enrichments in Mn are present in the bottom water near Stevenson Island.

Hydrothermal vent fluids near Stevenson Island and in the deep hole of Mary Bay are significantly enriched in Fe (13–20 times the average concentration in lake water) and Mn (15–28 times the average concentration in lake water). This suggests that both Fe and Mn are in their reduced forms in the vent fluids, and they oxidize and precipitate when they mix with oxic lake water. The different behaviors of Fe and Mn with depth in the water column in both Mary Bay and near Stevenson Island likely reflect the fact that the oxidation rate of Fe is faster than that of Mn (Stumm and Morgan, 1996). The difference in oxidation rates allows dissolved Mn to diffuse higher in the water column before it is removed by oxidation and precipitation.
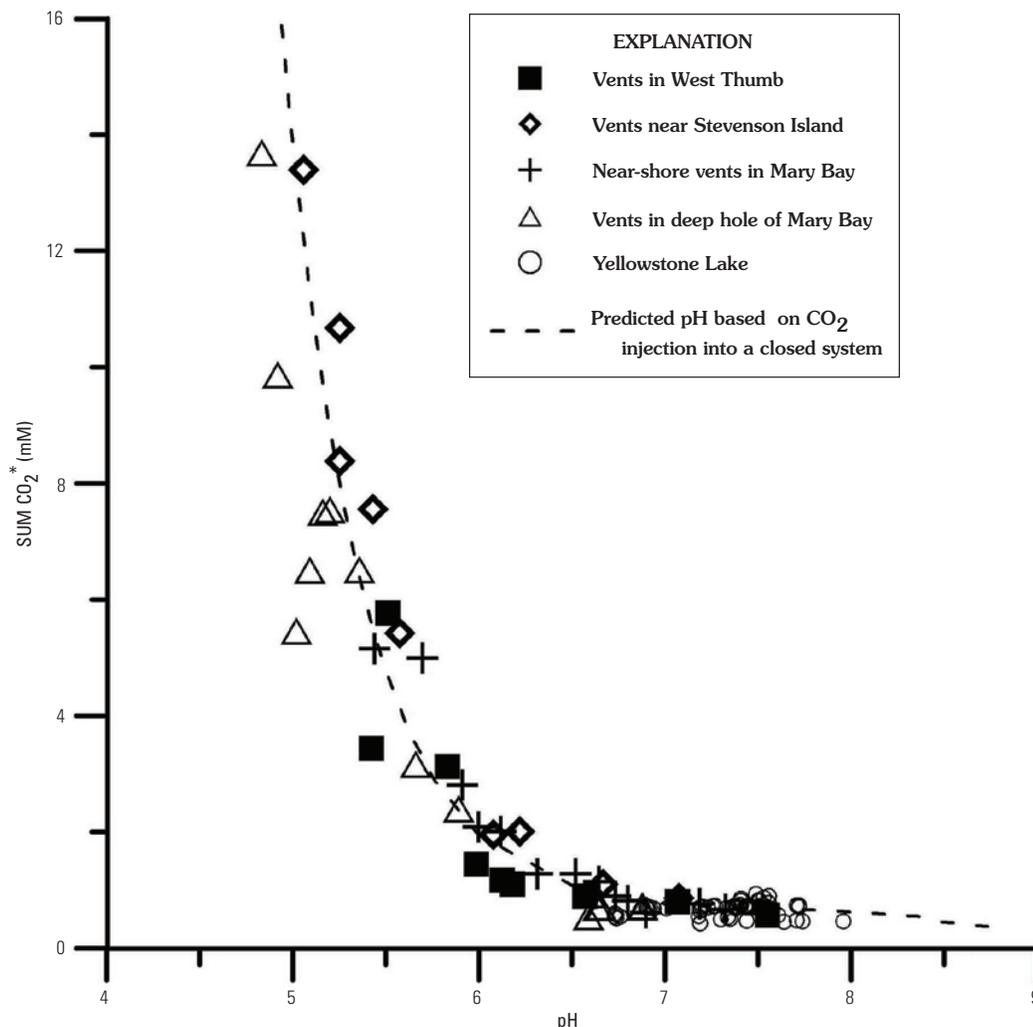
Figure 9. Cl-normalized concentrations of total dissolved inorganic carbon (ΣCO_2^*) versus pH for hydrothermal vent fluids and lake water in Yellowstone Lake. The dashed line is a prediction of pH for variable injections of CO_2 into a closed system.

EXPLANATION

■   Vents in West Thumb

◇   Vents near Stevenson Island

+   Near-shore vents in Mary Bay

△   Vents in deep hole of Mary Bay

○   Yellowstone Lake

- - -   Predicted pH based on CO_2 injection into a closed system

Element Enrichment Due to Hydrothermal Activity

The above observations indicate that Yellowstone Lake water is enriched in some elements and species (Cl, B, alkali metals, alkaline earth elements, As, Ge, Mo, Sb, W, SO_4, and HCO_3) relative to concentrations in inflowing waters. This enrichment includes water in Southeast Arm that is outside of the caldera and away from known hydrothermal activity. Although there may be some local influences of hydrothermal inputs on some water-column profiles, in general, these elements and species tend to vary little in concentration (less than 13 percent for major ions and up to 20 percent for minor ions) with location or depth in the lake, if dilution effects are taken into account. Enrichment of these elements and species in the lake is consistent with the mass-balance calculations that use only inflow and outflow concentrations and water fluxes. Only two elements (Fe and Mn) show variations with depth and location in the lake when dilution effects are considered. These variations are due to processes that affect the speciation of the elements after they enter the lake.
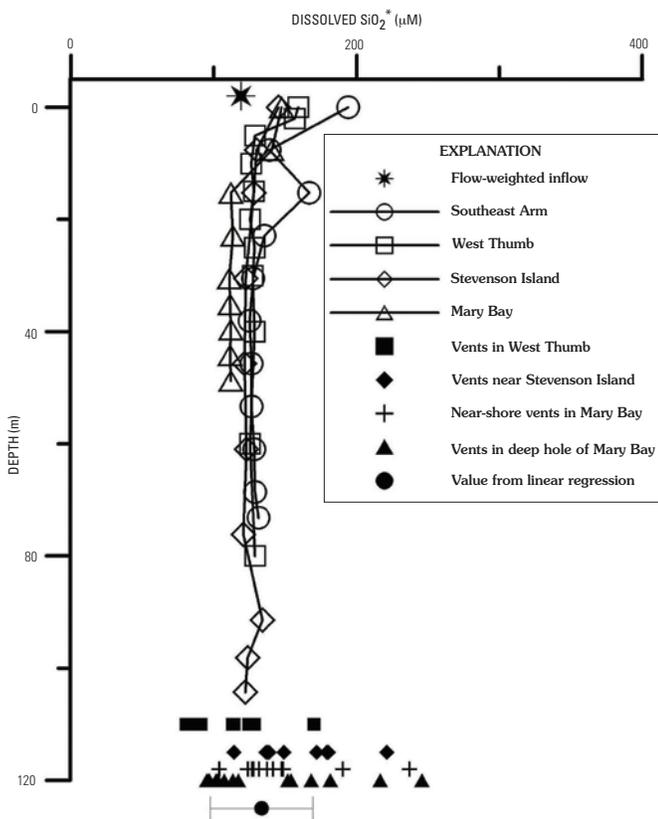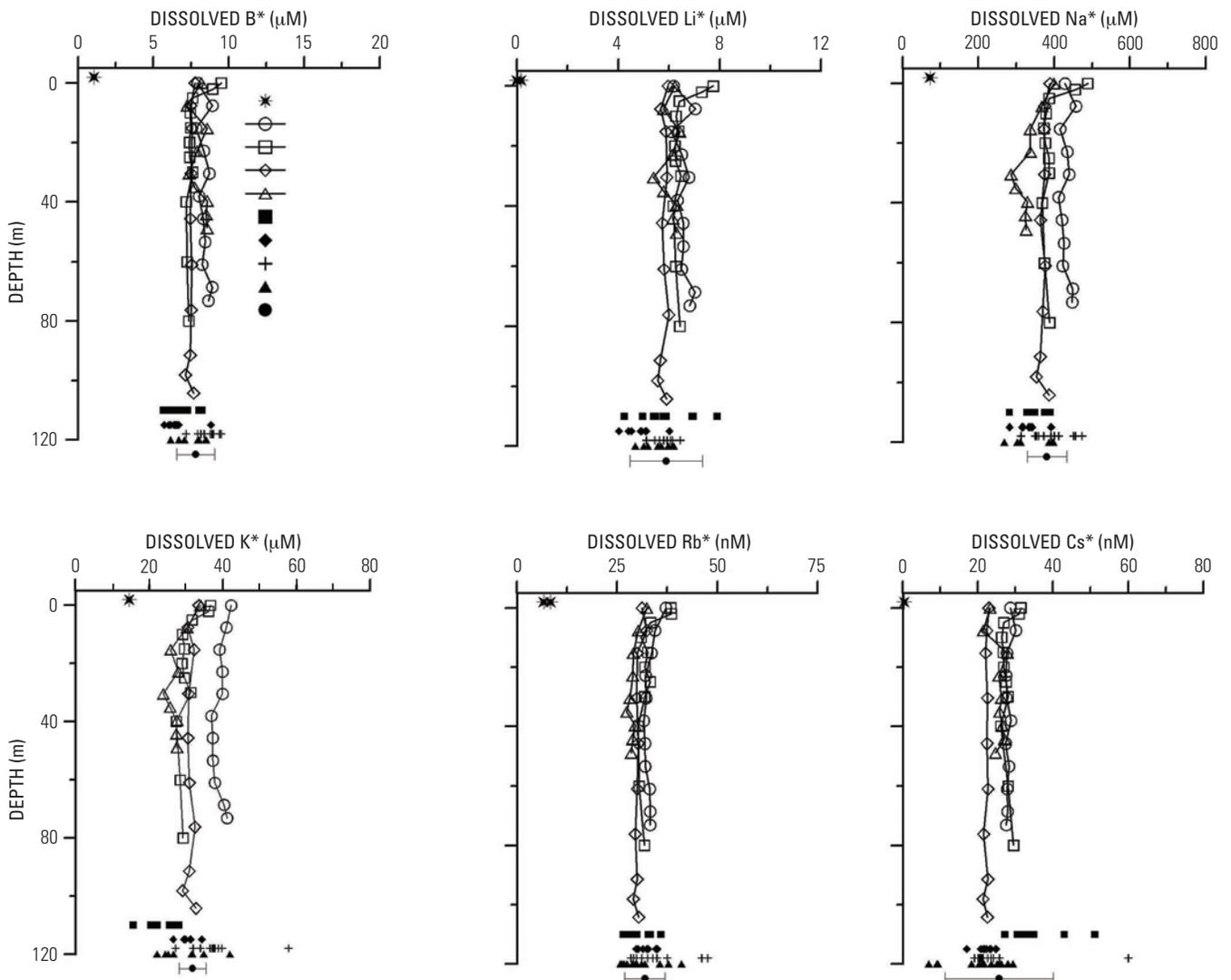

Figure 10.   Cl-normalized concentrations of dissolved SiO_2 in inflowing waters to Yellowstone Lake, lake water as a function of depth and location, and hydrothermal vents as a function of location. The average value and standard deviation determined from the Cl-element regression at 140 µM (micromoles per liter) Cl are also shown.

Our studies of lake water, stream water, and hydrothermal vent fluids indicate that there is enrichment of As, B, Cl, Cs, Ge, Hg, Li, Mo, Sb, and W in lake water and in sublacustrine hot springs. What is the significance of this list of elements? All of these elements are relatively mobile in the aqueous environment: Cs, Hg, and Li exist as cations; Cl is a simple anion; and As, B, Ge, Mo, Sb, and W exist as oxyanions. Consequently, all of these elements are likely to remain in solution in the Yellowstone River for considerable distances downstream from Yellowstone Lake. Table 3 summarizes established regulatory limits on these elements in drinking water and seafood, and it summarizes known human health effects of these elements. Some elements (As, Hg, Li, Mo, and Sb) are toxic or potentially toxic above specified concentrations, but only dissolved concentrations of Sb in Yellowstone Lake and in hydrothermal vent fluids exceed presently established limits for Sb in drinking water. Dissolved As and Sb in subaerial geyser fluids sampled in Norris and West Thumb Geyser Basins and Cl concentrations in fluids sampled in West Thumb Geyser Basin exceed current drinking-water standards, and those element concentrations may have important local consequences for biota in the Greater Yellowstone ecosystem.

δD and Cl: An Estimate of the Concentration of Cl in the Hydrothermal Source Fluid to the Lake

Truesdell and others (1977) presented an elegant quantitative description of the effect of subsurface boiling on the isotopic and Cl composition of subaerial hydrothermal water in Yellowstone National Park. Their calculations showed that the δD values of hydrothermal fluids are a function of the boiling mechanism. They considered two end-member boiling mechanisms—single-stage steam separation, wherein steam remains mixed with the water until it separates at a given temperature, and continuous steam separation, wherein steam separates from solution as it is formed. Although concentrations of dissolved Cl are about the same for the two mechanisms, values of δD are considerably lower for continuous separation compared to values for the single-stage steam-separation mechanism. One assumption of these calculations is that there is a single, deep, thermal reservoir containing fluid with the following characteristics: 360°C, 310 mg/kg Cl (8.7 mM Cl), and –149 per mil δD. Analyses of δD and $\delta^{18}O$ of recharge waters in the Park indicate that this deep reservoir fluid is isotopically lighter than recharge waters in the caldera, and either it has a remote recharge area in the northwest corner of the Park or it has a residual component of water from the last glacial event (Rye and Truesdell, 1993; this volume). In the Truesdell and others (1977) model calculations, deep reservoir fluid ascends to the surface while boiling. Mixing between deep thermal water and cold, dilute local meteoric water (5°C, 2 mg/kg Cl [56 µM Cl] and a range of δD values [–142 to –133 per mil]) is also considered. Such mixtures then can ascend to the surface with additional boiling.
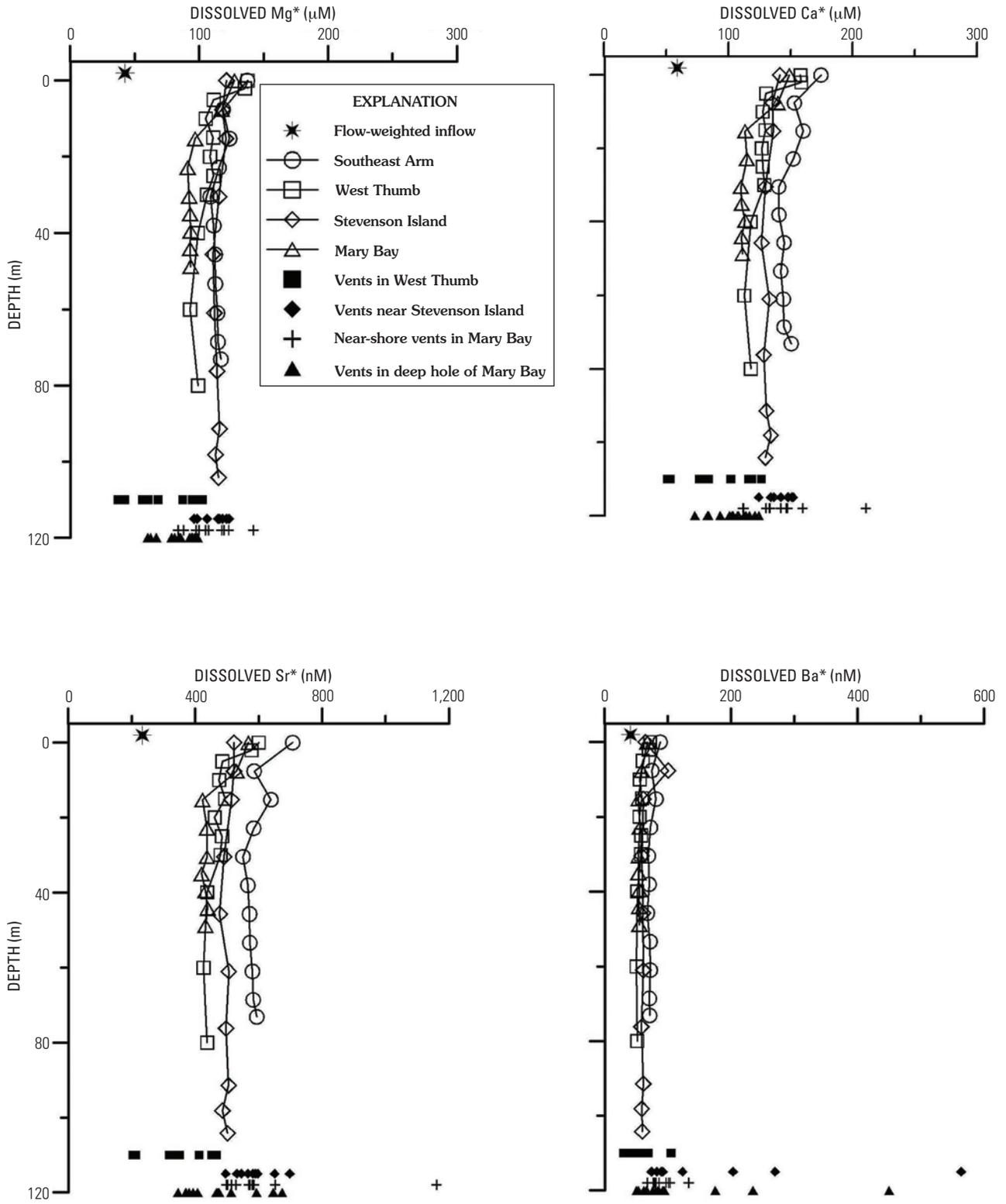
Figure 11. Cl-normalized concentrations of dissolved B, Li, Na, K, Rb, and Cs in inflowing waters to Yellowstone Lake, lake water as a function of depth and location, and hydrothermal vent fluids as a function of location. The average values and standard deviations determined from the Cl-element regression at 140 μM (micromoles per liter) Cl are also shown.

We use the approach of Truesdell and others (1977), with modifications, and our isotopic and Cl data for inflow water, water-column samples, pore water from shallow sediments, and hydrothermal vent fluids in Yellowstone Lake to estimate a value for the concentration of Cl in the end-member hydrothermal-source fluid to the lake. First, we calculate the composition of water produced by mixing between deep thermal water and meteoric water that has the composition of our flow-weighed inflow water (5°C, 1.4 mg/kg Cl [39 μM Cl], -141 per mil δD). The solid line with open diamonds in figure 16, along with associated temperatures of the mixtures, shows this process.

Next, we reproduce the Truesdell and others (1977) boiling curves for continuous and single-stage steam separation for deep thermal fluid. Calculations are done at 5°C intervals for continuous steam separation. The solid lines with open circles and open squares, along with associated

temperatures, represent boiling of the deep thermal fluid by continuous steam separation and single-stage steam separation, respectively (fig. 16).

The next step is to calculate the Cl-δD compositions for situations in which first there is mixing between meteoric water and deep thermal fluid, and then there is boiling to a temperature of 220°C by the two different steam-separation mechanisms. These cases are depicted in figure 16 by solid lines with closed triangles (continuous separation) and open triangles (single-stage separation). Temperatures of the mixtures before boiling are given in parentheses above the open triangles. We chose a boiling temperature of 220°C, for reasons that will be apparent later. The calculations were done for a range of boiling temperatures, but those results would further complicate the figure and are not included in the figure.

Figure 12. Cl-normalized concentrations of dissolved Mg, Ca, Sr, and Ba in inflowing waters to Yellowstone Lake, lake water as a function of depth and location, and hydrothermal vent fluids as a function of location.
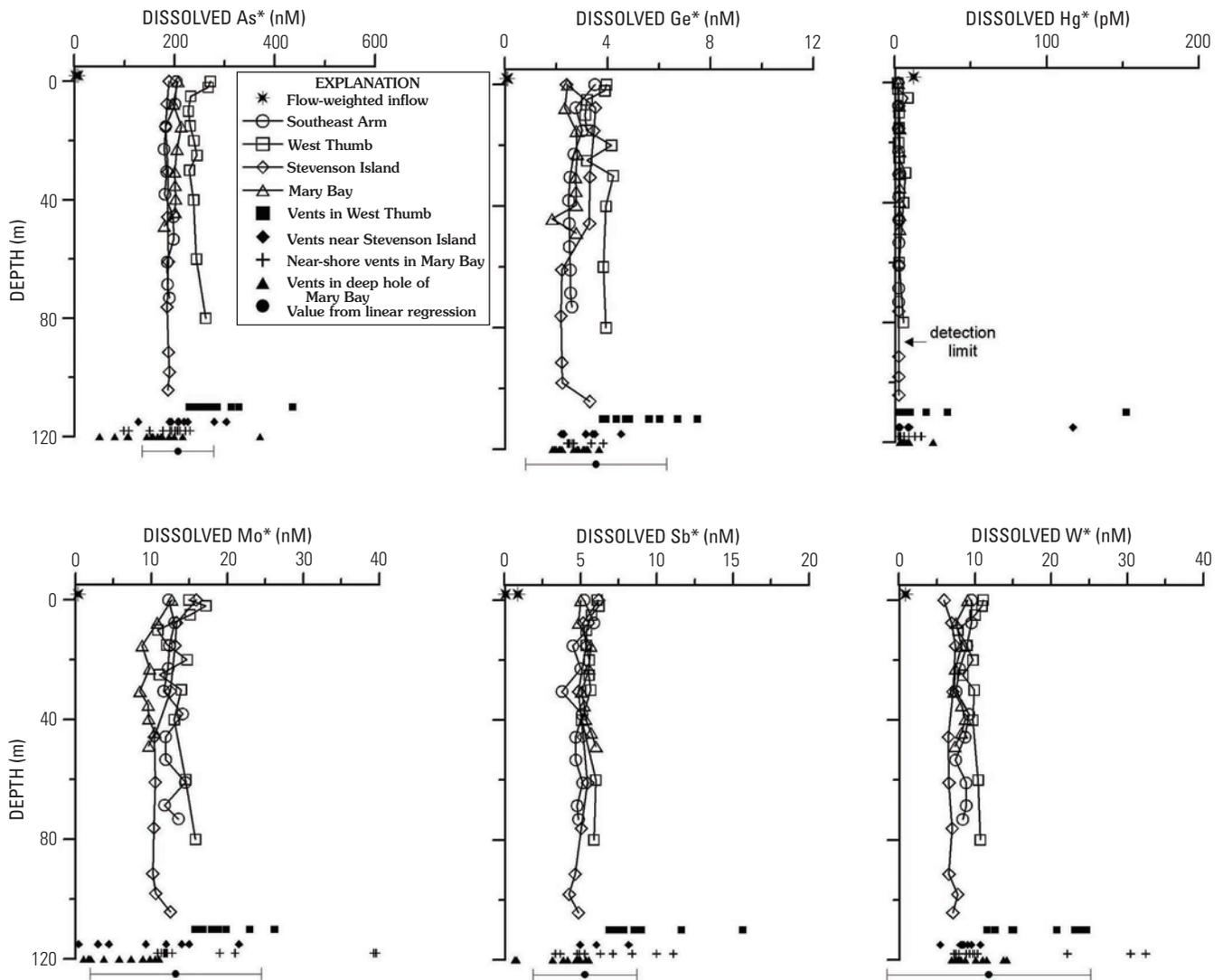
Figure 13. Cl-normalized concentrations of dissolved As, Ge, Hg, Mo, Sb, and W in inflowing waters to Yellowstone Lake, lake water as a function of depth and location, and hydrothermal vent fluids as a function of location. The average values and standard deviations determined from the Cl-element regression at 140 µM (micromoles per liter) Cl are also shown.

Our final theoretical consideration is mixing between boiled thermal water and bottom water of Yellowstone Lake. The bottom water of Yellowstone Lake contains 4.4–5.9 mg/kg Cl (~120–170 µM Cl), and it has δD values that range from –128 to –131 per mil. The temperature of the bottom water ranges from 4.8°C to 12°C, depending on location. We use the temperature of bottom water in Mary Bay (12°C) in our calculations of mixing because some of our pore-water data are from that site. Mixing between Yellowstone Lake bottom water and hydrothermal waters that boil at a variety of temperatures and by different mechanisms can be portrayed by a series of straight lines between end members. For simplicity, only mixing between the bottom water of Yellowstone Lake and boiled deep thermal water with continuous steam separation to 220°C is shown in figure 16 (dashed lines). The temperatures of the mixtures are indicated by stars along the dashed line and are given as numbers in brackets.

Boiling and mixing calculations provide the theoretical framework needed to calculate a value for the Cl concentration in the hydrothermal source water to the lake. As indicated earlier, almost all of the collected hydrothermal vent fluids are very dilute, with Cl-δD values not much different from those of lake water (fig. 16). On the other hand, one vent sample and several pore-water samples have higher Cl concentrations and lower values of δD than other samples. These values, along with values for the most concentrated vent fluids in West Thumb and the lower range of values from Yellowstone Lake bottom water, form a straight line. This line best represents mixing between the bottom water of Yellowstone Lake and boiled deep thermal water. This boiled deep thermal water is the hydrothermal source fluid to the lake. The line intersects the boiling curves at 220°C, for both steam-separation mechanisms. The Cl concentrations for boiled thermal water at 220°C are 553 mg/kg (~15.6 mM) for single-stage steam
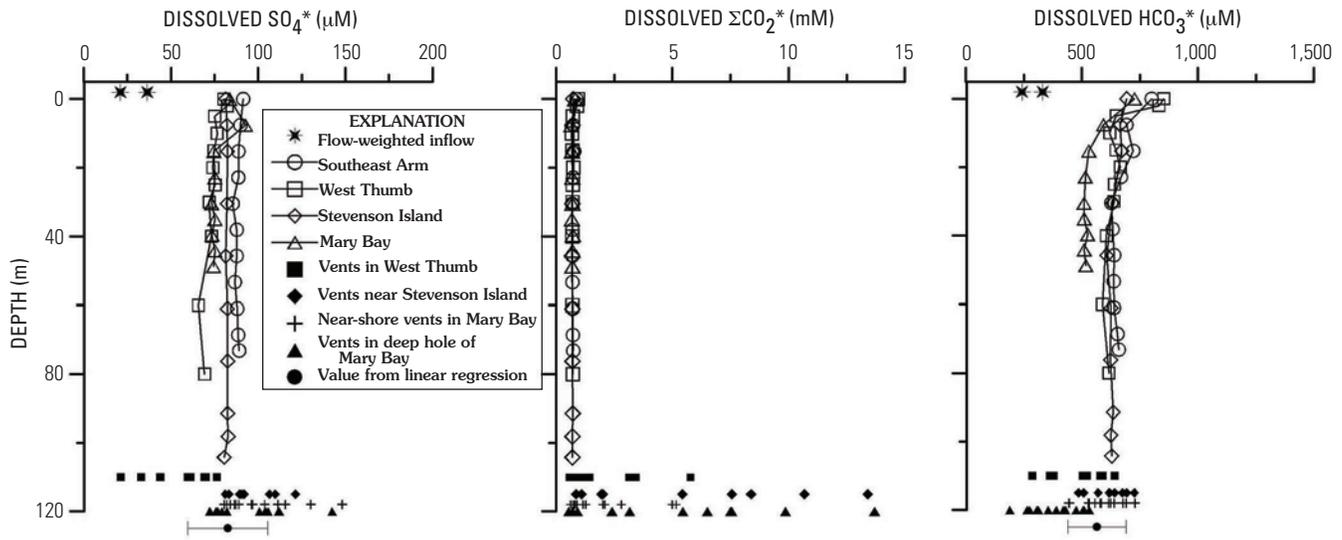
Figure 14. Cl-normalized concentrations of dissolved SO_4, ΣCO_2, and HCO_3 in inflowing waters to Yellowstone Lake, lake water as a function of depth and location, and hydrothermal vent fluids as a function of location. The average values and standard deviations determined from the Cl-element regression at 140 µM (micromoles per liter) Cl are also shown.
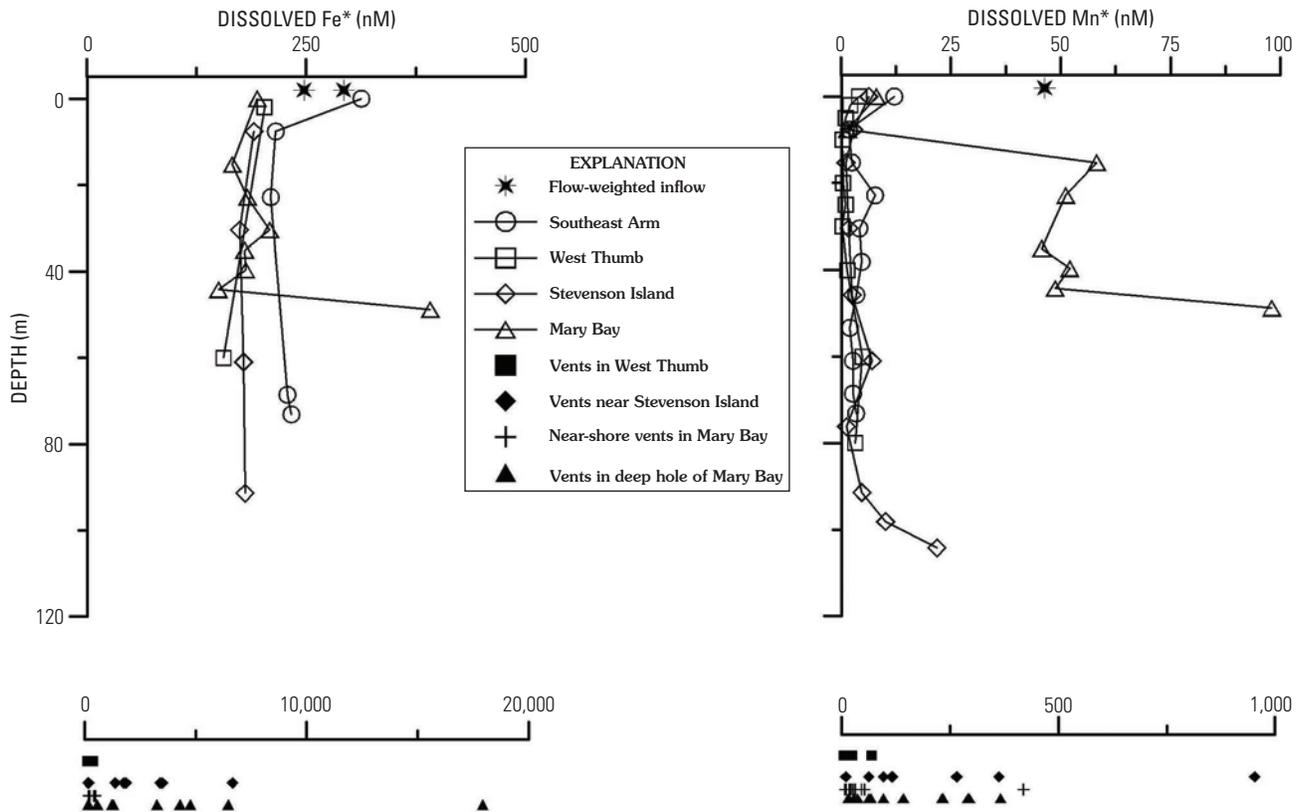
Figure 15. Cl-normalized concentrations of dissolved Fe and Mn in inflowing waters to Yellowstone Lake, lake water as a function of depth and location, and hydrothermal vent fluids as a function of location. Note the change in concentration scales.

separation and 586 mg/kg (~16.5 mM) for continuous steam separation. We interpret this to mean that deep thermal reservoir fluid boils with steam loss from about 360°C to 220°C during ascent, and then it mixes with cold ambient lake water.

Is 220°C a reasonable boiling temperature for the hydrothermal fluids entering the bottom of Yellowstone Lake? Using the relationship between boiling-point and depth (or pressure) in Henley and others (1984), we calculate that the boiling-point temperatures at the depths of the lake-bottom vents are 105°C for the shallow (7–10 m) vents in Mary Bay, 158°–160°C for vents in the deep hole of Mary Bay, 140–160°C for vents at depths of 29–53 m in West Thumb, and 180°–185°C for the deep (95–110 m) vents near Stevenson Island. These boiling temperatures compare with 93°C temperatures for the subaerial geysers in Yellowstone National Park. The estimated boiling temperature of the hydrothermal source fluid to the lake (220°C) therefore is higher than expected from the calculated boiling-point temperatures at lake-bottom pressures for all sampled vents. This difference suggests that either mixing with lake water occurs in the shallow subsurface beneath the lake bottom or that submersible sampling of vent fluids has not allowed measurement of the maximum temperatures of venting.

A check on the estimated 220°C temperature can be made by calculating the temperature along the mixing line between bottom water in Mary Bay (12°C) and the hydrothermal end member (220°C) and then comparing those temperatures to the temperature of the pore water and sediment at the bottom of the core from Mary Bay (270 mg/kg Cl [~7.7 mM Cl], −140.2 per mil δD). The Cl and δD values place the pore water exactly on the mixing line (fig. 16). Unfortunately, it was not possible to measure the temperature of the pore water and sediment at the bottom of the core. However, some constraints on the temperature can be made by observations at the time of core collection. The core was too hot to touch and the core liner was severely deformed by the heat. The melting point for cellulose acetate butyrate, the material of core liners, is >135°C (http://hazard.com/msds). Calculations for temperatures of mixtures of bottom water from Mary Bay and the boiled thermal water place the temperature of the deepest pore-water sample between 95°C and 137°C (fig. 15), close to the temperature at which core liner melts. This temperature exceeds the maximum measured vent-fluid temperatures in the deep hole in Mary Bay (103°C), suggesting there is mixing of lake water and hydrothermal fluids below the sediment-water interface.

Concentrations of Selected Elements and Species in Boiled Hydrothermal Source Fluid to the Lake

If our assessment of the Cl-δD relationships and pore-water data is correct, then we can estimate the concentrations of some elements in the hydrothermal source fluid to the lake from linear relationships between Cl and elements in lake water and vent fluids. The extrapolations take us far beyond the measured Cl concentrations in lake water and vent fluids. However, the laboratory experiments indicate that mixing of dilute Yellowstone River water and element-enriched geyser water with Cl concentrations between 4.2 mM and 19 mM (150 mg/kg and 660 mg/kg) results in no observed losses for the elements of interest. In other words, only dilution is occurring, and all of the examined elements or species behave conservatively. Hence, there is experimental justification for extrapolating beyond the range of Cl and element concentrations in the lake and vent waters.

Table 3. Regulatory limits and potential health-related effects of certain elements.

[Data from Smith and Huyck (1999) and references cited therein, with additional information from EPA and FDA Web sites. MCL, maximum contaminant level; [+], primary EPA standard; [#], secondary EPA standard; *, shellfish; **, methyl mercury in fish (usually approximates total mercury); P, possible or suspected; Y, proven or established; T, toxic metals with multiple effects; S, special conditions required; t, metals with potential for toxicity; E, embryocidal. Leaders (--) indicate no known health effect. Little or no data are available for health effects of Cs, Ge, or W]

| Element	EPA drinking water MCL (mg/L)	FDA action levels in seafood (mg/kg wet weight)	Essential for human health	Toxicity	Carcinogenic	Teratogenic (interferes with growth of embryo or fetus)
As	0.050[+]	76–86*	P	T	Y	Y/E
B	--	--	P	--	--	--
Cl	250[#]	--	Y	--	--	--
Cs	--	--	--	--	--	--
Ge	--	--	--	--	--	--
Hg	0.002[+]	1.0**	--	T	--	Y/E
Li	--	--	P	S	--	--
Mo	--	--	Y	t	--	Y
Sb	0.006[+]	--	--	t	--	--
W	--	--	--	--	--	--

The predicted concentrations of selected elements and species in the boiled hydrothermal source fluid to the lake are compared to the observed compositions of selected subaerial geyser fluids in Yellowstone National Park (table 4). The concentrations of elements in the hydrothermal source fluid were calculated by assuming that the Cl concentration in the fluid is 16 mM (570 mg/kg), which is the average of the values predicted for deep thermal water boiled from 360°C to 220°C by single-stage and continuous steam separation. If the elements and species of interest, except those affected by gas loss (HCO_3 and SO_4), are conservative during the boiling process, then we can also estimate the compositions of selected elements in the deep thermal fluid by assuming that the Cl concentration is 8.7 mM (310 mg/kg) (table 4). This solution is the parent fluid for the boiled hydrothermal water entering the lake, and it is more dilute because it has not yet lost water through steam separation.

The ratios of the predicted compositions of hydrothermal source fluids or measured compositions of subaerial geyser fluids to the predicted composition of deep thermal fluid are presented in figure 17. On this log plot, a value of zero indicates that the concentration of an element in a given fluid (that is, hydrothermal source fluid or subaerial geyser water) is the same as that in the deep thermal fluid. Values greater than zero indicate that an element is enriched relative to the parent fluid.

Enrichment occurs if the element remains in solution and is concentrated during steam loss. Values less than zero indicate that the element is depleted in a given fluid relative to the parent fluid. Elements may be lost from solution during steam separation by adsorption, precipitation, or volatilization. The comparisons indicate that the compositions of all the hydrothermal fluids are within a factor of 2 to 5 for many elements (Cl, Si, B, Li, Na, K, Rb, and As) (fig. 17). Concentrations of Ge, Mo, Sb, and W in the hydrothermal source fluid to the lake and in the neutral to alkaline subaerial geyser fluids are generally within a factor of 2 to 5 of the concentrations in the deep thermal fluid. The predicted hydrothermal source fluid and the deep thermal reservoir fluid are greatly enriched (>10 to >100 times) in Mo, Sb, and W relative to the acid-Cl-SO_4 subaerial geyser waters.

Another test of the predicted composition of the hydrothermal source fluid to Yellowstone Lake is to calculate the in-place temperature for a hydrothermal fluid of such composition using chemical geothermometers. Using the equations in Fournier (1981) and Kharaka and Mariner (1988), equilibrium temperatures are predicted to be 158°C (Na-K), 202°C (amorphous SiO_2), 277°C (quartz with maximum steam loss), and 331°C (chalcedony) for the geothermometers. Calculations using the Na-K-Ca or Mg geothermometers could not be done because we do not have estimates for the concentrations of alkaline earth elements in
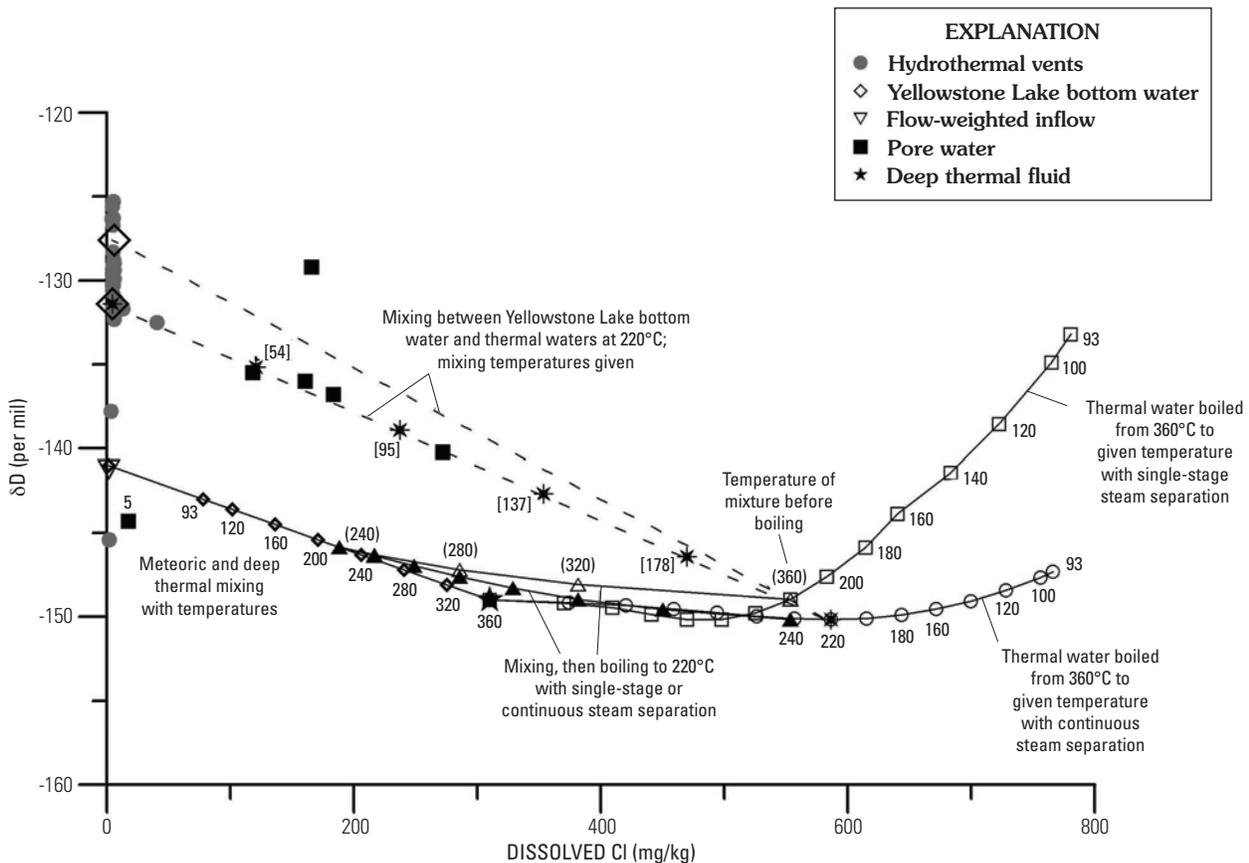
Figure 16. Plot of δD versus dissolved Cl concentrations derived from theoretical calculations and for data from inflow water, lake water, hydrothermal vent fluids, or pore waters in Yellowstone Lake. See text for further discussion. Diagram adapted from Truesdell and others (1977).

the hydrothermal source fluid. The estimated temperature of the boiled hydrothermal source water using pore-water data and Cl-δD relationships is 220°C (fig. 16), within about 60°C of the Na-K geothermometer and within 20°C of the Si geothermometer using amorphous SiO_2. These temperatures are consistent with the observation that vent deposits and the underlying lake sediments are mostly amorphous silica.

Our final calculations assess the fraction of hydrothermal source fluid that is in the water column of Yellowstone Lake and estimate the flow of water from hydrothermal vents into the lake. The calculations are done using Cl concentrations. Cl and other element concentrations in the water column of Southeast Arm, West Thumb, near Stevenson Island, and Mary Bay differ because of variable inputs of hydrothermal source fluid (table 2). Using a predicted concentration of 16 mM Cl in the hydrothermal end member, the percentage of hydrothermal source fluid in the bottom water (>15m depth) of Yellowstone Lake is lowest in Southeast Arm (0.74$\pm$0.04 percent) and it increases from near Stevenson Island (0.87$\pm$0.01 percent) and West Thumb (0.95$\pm$0.04 percent) to the highest values in the deep hole of Mary Bay (1.04$\pm$0.01 percent). The flow of water from hydrothermal vents is estimated by rearranging equation 2, assuming that $J = 0$ for a conservative element such as Cl, ΣQin = 0.67 to 3.6 km^3/yr (table 1), ΣQin = 9 to 15 µM Cl, $Qout$ = 1.19 km^3/yr (table 1), $Cout$ = 130 µM Cl, $Cvent$ = 16 mM Cl, ground-water contributions are negligible, and solving for $Qvent$. This calculation indicates that the flow of hydrothermal source fluid to the lake is 0.006 to 0.009 km^3 of water per year or about 8 x 10^9 kg of water per year. Although the flow rate of hydrothermal source water to the lake is small compared to the flow rate of water from streams, the flux or loading of elements to the lake from sublacustrine vents is very significant because of the high concentrations of Cl and other elements in the hydrothermal source water.

Using the same procedure, we also estimate the flux of hydrothermal water in terms of the deep thermal reservoir fluid. This fluid has a predicted Cl concentration of 8.7 mM. Substituting that concentration into equation 2 and using the same parameters for inflow and outflow water yields a discharge from the deep thermal reservoir of 0.01 to 0.02 km^3 of water per year or about 1.5 x 10^{10} kg of water per year. Studies of Cl in streams indicate that in 1999 there was a total flux of deep thermal water of about 16 x 10^{10} kg/yr from all thermal areas in the Park (Friedman and Norton, 2000, this volume). This means that, according to this estimate, sublacustrine vents in Yellowstone Lake account for ~10 percent of the total flux of deep thermal reservoir water in the Park. This estimate is very similar to that of Fournier and others (1976) based on Cl content at the lake outflow at Fishing Bridge in 1972. Because we estimate that 41 million kg/d of deep hydrothermal fluid flows into the lake and recent studies have revealed the presence of numerous hydrothermal features on the lake bottom (Morgan and others, 1999; Shanks and others, 1999), Yellowstone Lake should now be considered one of the most important thermal basins in the Park.

Summary

Mass-balance calculations and comparisons of concentrations of elements in inflowing surface water and in the water column indicate that Yellowstone Lake is enriched in a suite of elements, most of which are also enriched in subaerial geyser waters. Relationships between the concentrations of Cl and many elements in both lake water and hydrothermal vent fluids indicate that mixing of end-member solutions is occurring. Yellowstone Lake appears to be a slightly evaporated mixture of inflowing stream water and hydrothermal fluids.

The chemical composition of lake and hydrothermal water is dominated by Na and HCO_3. Although lake water is nearly neutral, most of the vent fluids are acidic. This acidity is due mainly to dissolution of CO_2, a volatile gas associated with ascending hydrothermal fluids. Vent fluids in Mary Bay and near Stevenson Island have a larger component of SO_4 than do some vent fluids from West Thumb. This observation indicates that dissolution and oxidation of H_2S are important processes in the Mary Bay and Stevenson Island vent water. Although sulfide-oxidation processes contribute to acidity, dissolution of CO_2 dominates the pH of vent fluids in Mary Bay and near Stevenson Island.

Variable mixing or dilution of end members occurs throughout the lake. Once dilution is taken into account, almost all of the elements show little variation in their Cl-normalized concentrations as a function of depth within the water column or as a function of location in the lake. The notable exceptions are Fe and Mn, for which large enrichments are observed in some vent fluids relative to lake water, especially those in Mary Bay and near Stevenson Island. These enrichments in hydrothermal vent fluids translate into enrichments in the bottom water near Stevenson Island and in Mary Bay. The Cl content of the hydrothermal source fluid to the lake is about 16 mM (570 mg/kg). This value was determined by using the Cl and δD contents of pore water, lake water, and hydrothermal vent water in the lake, following Truesdell and others (1977), with modifications to account for conditions at the bottom of the lake and mixing between lake water and hydrothermal source water. We estimate that the final boiling temperature of the hydrothermal source fluid is 220°C, within the temperature range estimated for intermediate reservoirs of hydrothermal source fluids for geyser basins in the Park. We interpret this to indicate that deep thermal reservoir fluid boils with steam loss from about 360°C to 220°C during ascent, and then it mixes with cold ambient lake water. The concentrations of selected elements in the hydrothermal source fluid were calculated from the linear relationships between Cl and elements in lake water and hydrothermal vent fluids, assuming that the Cl concentration of the hydrothermal source fluid is 16 mM. The predicted concentrations of many elements are consistent with concentrations in subaerial geyser fluids. The geochemistry of Yellowstone Lake indicates that it is a mixture of about one percent hydrothermal source fluid

Table 4. Comparisons of predicted chemical compositions of boiled geothermal source fluid to Yellowstone Lake water (YL) and deep thermal reservoir fluid with measured compositions of subaerial geothermal waters in Norris Geyser Basin (Porkchop, Echinus, and Green Dragon) and West Thumb Geyser Basin (Black Pool and Vandalized Pool).

[Note change in units compared to table 2. n.d., not determined]

Parameter, element, or species	Units	Predicted composition of geothermal source fluid to YL[a]	Predicted composition of deep thermal reservoir fluid[a]	Porkchop July 1999	Black Pool Sept. 1998	Black Pool July 1999	Vandalized Pool Sept. 1998	Echinus July 1999	Green Dragon July 1999
temp.	°C	220	360	57	n.d.	72.3	n.d.	68.8	79.9
pH		n.d.	n.d.	6.6	8.2	7.9	8.2	3.2	2.6
Cl	mM	16	8.7	17	8.5	8.5	8.7	4.2	9.3
SiO_2	mM	16	8.7	6.8	6.0	4.8	5.3	4.5	7.8
B	μM	920	500	860	n.d.	320	n.d.	240	500
Li	μM	950	510	1,400	620	560	520	160	890
Na	mM	37	20	17	16	18	16	7.5	9.7
K	μM	1,000	570	1,460	490	500	310	1,330	1,170
Rb	μM	7.4	4.0	5.7	1.8	2.3	1.2	4.1	4.6
Cs	μM	9.0	4.8	4.4	1.8	2.3	0.60	0.61	2.3
Mg	μM	n.d.	n.d.	0	0	0	0.4	21	13
Ca	μM	n.d.	n.d.	130	19	22	17	120	100
Sr	nM	n.d.	n.d.	150	21	23	18	84	130
Ba	nM	n.d.	n.d.	76	0	0	0	420	240
As	μM	32	20	41	21	32	21	3.9	23
Ge	μM	1.6	1.0	0.55	0.44	0.74	0.44	0.14	0.34
Mo	μM	4.6	2.8	2.9	0.93	1.1	1.0	0.06	0.33
Sb	μM	1.7	1.1	1.2	0.82	0.82	0.82	0.007	0.046
W	μM	5.5	3.4	0.87	1.3	2.1	1.4	0.01	0.27
HCO_3[b]	mM	13	n.d.	0.12	7.0	9.0	7.0	0	0
SO_4	mM	5.1	n.d.	0.33	0.41	0.47	0.49	2.7	1.6

[a] Predictive calculations discussed in text.

[b] Calculated by charge balance.

and 99 percent inflowing surface water. Mass-balance calculations suggest that the flow of hydrothermal source fluid into the lake is about 0.008 km^3/yr, which accounts for about 10 percent of the total flux of deep thermal fluid in the Park. Thus, Yellowstone Lake is one of the most important thermal basins in the Park.

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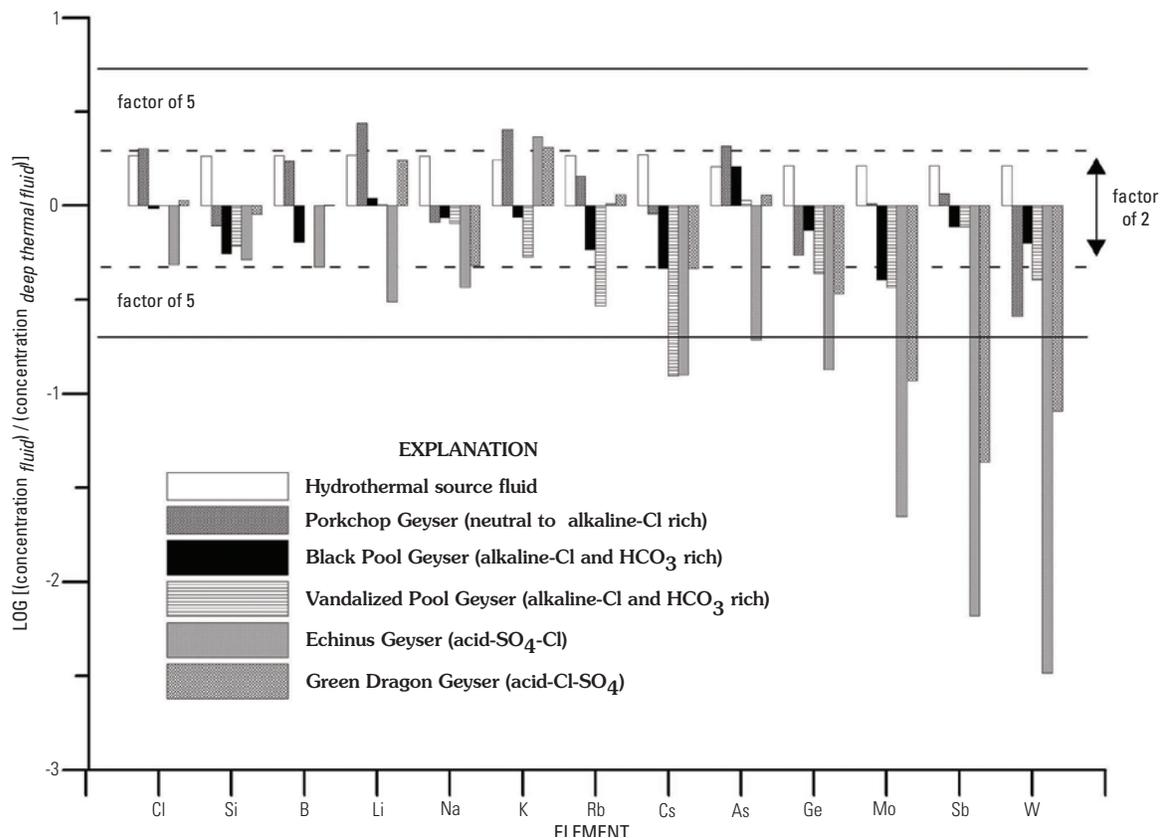
Figure 17.   Concentrations of elements in the predicted hydrothermal source fluid to Yellowstone Lake and in subaerial geysers (Porkchop, Black Pool, Vandalized Pool, Echinus, and Green Dragon) relative to predicted concentrations in the deep thermal fluid in Yellowstone National Park. When the ratio equals 0 on this log plot, the concentrations are the same. Ratios greater than 0 indicate enrichment relative to deep thermal water; ratios less than 0 indicate depletions relative to deep thermal water. Lines are drawn to represent concentrations within factors of 2 or 5 of each other.

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