Porewater and Hydrothermal Vent Water Inputs to Yellowstone Lake, Wyoming

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Abstract

Geochemical inputs to Yellowstone Lake, Wyoming, come from a variety of sources, including hydrothermal vents, groundwater, rainwater, flux from sediments, and direct runoff. One-third of Yellowstone Lake is directly influenced by hydrothermal activity (hot-water vents and fumaroles). Geothermally heated water percolating through the chamber is highly enriched with carbonate, silicate, chloride, and methane, with some locations additionally rich in iron and sulfide. Vent waters in West Thumb typically contained sub-micromolar concentrations of Fe (iron), while those in Mary Bay and off Stevenson Island contained about 10 µM (micromolar). Water column concentrations of dissolved iron ranged from 250 to 450 nM (nanomolar) in Mary Bay, but were very low in the waters of Southeast Arm, West Thumb, and off Stevenson Island. Porewater and vent water chemistry provided evidence for lake water dilution of vents below the sediment–water interface. Significant fracturing of source water conduits was indicated by extreme differences in porewater profiles from cores less than 5 m apart in the geothermally vigorous West Thumb. Some samples approached theoretical reservoir composition for geothermally active areas of Mary Bay and West Thumb, showing chloride concentrations reaching several mM (millimolar), and, in the case of Mary Bay, extrapolate to the geothermal end member (~20 mM) at a depth of only 2–3 m. These steep concentration gradients support diffusive chloride fluxes across the sediment–water interface three orders of magnitude higher than those in non-venting depositional areas.

Introduction

Yellowstone Lake, Wyoming, is located in the caldera of the largest volcanic eruptions known, which occurred 1.2 million and 650,000 years ago at a mid-continental hot spot, rather than in the more widespread tectonic spreading centers. The Yellowstone hot spot has interacted with the North American plate for millions of years, causing widespread outpourings of basalt. Some of the basaltic melt, or magma, produced by the hot spot accumulates near the base of the plate, where its heat melts the rocks from the Earth's lower crust. As a result, the underlying structure is composed primarily of granite overlain by volcanic silica as opposed to freshly upheaved basalts. Geothermally heated water percolating through the relic chamber is highly enriched in carbonate, silicate, chloride, and methane; some locations are also enriched with iron, manganese, and sulfide. Yellowstone National Park is well known for its steaming geysers, shimmering thermal pools, and bubbling painted mudpots. Some of the greatest characteristics that are not visible are the hydrothermal vents submerged under Yellowstone Lake; hydrothermal activity in the form of springs and fumaroles are described by Remsen et al. (1990) and Marocchi et al. (2001).

The magma chamber encompasses the northern part of Yellowstone Lake, while the Yellowstone River inflow and the southern half of the lake (South and Southeast arms) are outside the caldera. Previous work has shown active hydrothermal venting (geothermal hot springs and fumaroles) in several areas of the lake, which strongly influences the chemical composition of the lake water (Cuhel 1998; Klump et al. 1988). This is also observed in deep-sea hydrothermal vents, where vigorous plumes mix with deep water (Butterfield et al. 1997; Cowen et al. 1986), but the large receiving volume defies budget closure, which is one of the goals of past work in Yellowstone Lake (Aguilar et al. 1999).

Previous investigations of thermal waters from the Norris–Mammoth corridor have used different approaches to identifying sources of hydrothermal fluids. These have included the use of natural isotope tracers (e.g., H, He, Li), elemental abundances (e.g., S, Cl, Na, Ca), and the number of dissolved species present (Fournier 1989; Palmer and Sturchio 1990; Kharaka et al. 1991; Bullen and Kharaka 1992; Fournier et al. 1992; Kharaka et al. 1992, Rye and Truesdell 1992; Sturicho et al. 1992; Lewis et al. 1997). Based on all these studies we can compare recent results with those performed several years ago in order to have a better understanding of the changing environment in the Yellowstone Lake area and other areas in the caldera.

The interactions of the geothermal systems with biology have an important role in understanding the processes of the origins of early life. The high-temperature systems may be relevant to understanding extreme environments on Earth as well as on other planets and moons in our solar system.

Study Area

Sampling sites on Yellowstone Lake. Yellowstone Lake is located in the southeast section of Yellowstone National Park, in an area with frequent tectonic activity. The lake comprises an area of 341 km^2 and it is the largest high-altitude lake in North America. The northwestern area of the lake lies inside the caldera, whereas the southern area as well as South and Southeast arms are located outside the caldera (Figure 1). Several areas have been sampled through the years, but all the collections mentioned in this paper were from 1998. There are areas with evident geothermal activity, such as Mary Bay, Sedge Bay, Steamboat Point, Stevenson Island, and West Thumb. All these areas have been sampled frequently, as have others such as the Yellowstone River inlet (located outside the caldera, Southeast arm) and outlet (inside the caldera).

Methods

Use of a remotely operated vehicle. The use of a remotely operated vehicle (ROV) is critical for general surveying of and sampling hydrothermal vent systems in Yellowstone Lake (Figure 2). The ROV designer and operator, Dave Lovalvo of Eastern Oceanics, is a former pilot of *DSRV Alvin* (deep sea research

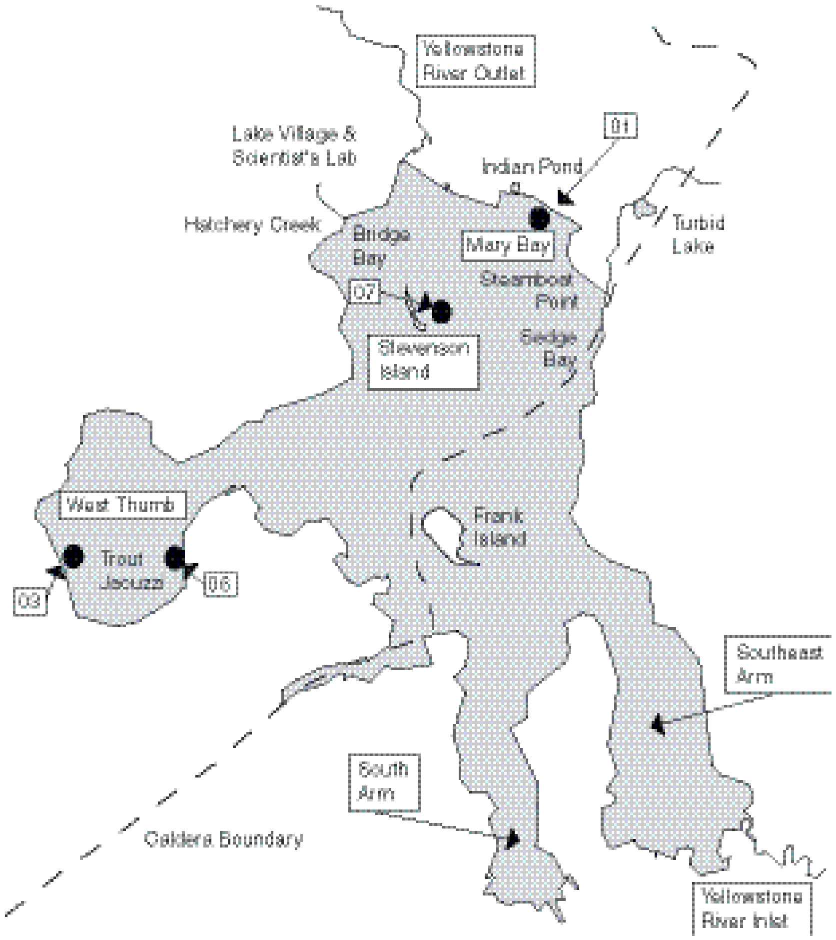


Figure 1. Map of Yellowstone Lake showing selected sampling areas: West Thumb, Mary Bay, Stevenson Island, Southeast Arm, and Yellowstone River inlet and outlet. The rim of the caldera is depicted by the dotted line. Core collection sites are in solid circles, as follows: 01 = Mary Bay 01 core, 03 = West Thumb 03 core, 06 = West Thumb 06 core, and 07 = Stevenson Island 07 core. Map from Marocchi et al. 2001; reproduced by permission.

vessel) and *ROV Jason*, and has produced a practical array of modular instruments for water and solid phase sampling, as well as cameras for still pictures and video (Buchholz et al. 1995; Klump et al. 1992). The areas of interest are hard to sample by conventional means. Visual observations of shimmering surface waters are always important clues to exploring the bottom of the lake. When looking for evidence of vents on the surface waters, we rely on vigorous bubbling that is visible from a distance on a calm day (Figure 3).

Field methods. Vent samples were collected with the ROV on board the *R/V Cutthroat*, using an articulated arm outfitted with a thermistor probe at the end to

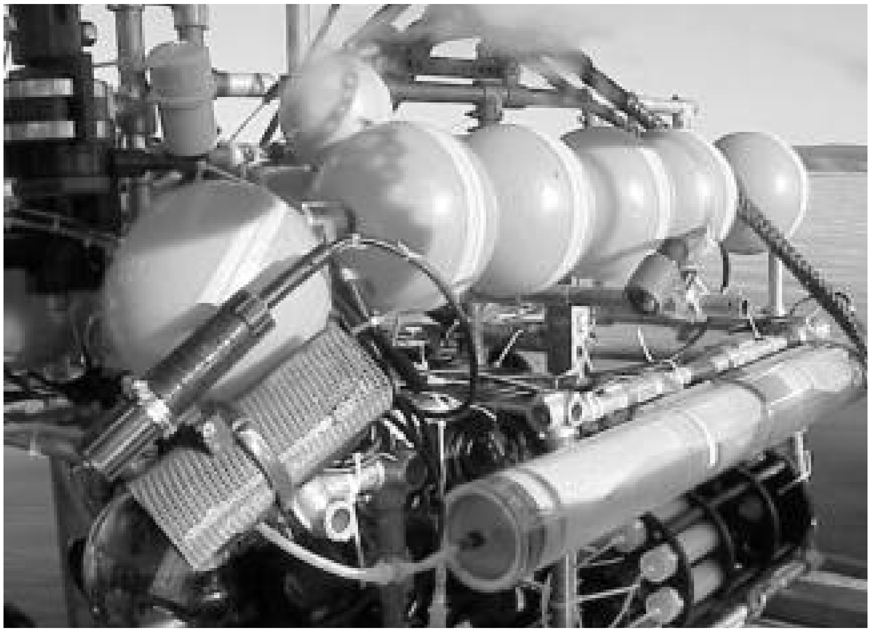


Figure 2. Remotely operated vehicle from Eastern Oceanics used to collect vent and bottom water.

Figure 3. Bubble field on surface waters of Mary Bay. On a calm day they can be seen from a distance. The bubbles are used to find new vent activity in different areas of the lake.

measure the temperature of the water as it was collected. Water was collected into 2-L polycarbonate syringes; samples were then retrieved and put into smaller, all-plastic syringes through a three-way valve. Samples were then transported in a cooler to the laboratory for analysis and preservation.

Cores were collected from the *Cutthroat* with a 3-inch Benthos gravity corer with cellulose acetate butyrate liners (Figure 4). Sediment was then transported to the laboratory and transferred with a hydraulic extruder to the Jahnke squeezer (Jahnke 1988) to subsequently obtain porewater (Figure 5). Porex inserts (a porous polyethylene rod to "guide" the water through while being pushed out by the action of the piston) were acid-washed and rinsed through many changes of E-Pure water (18-meg ohm/cm resistance) to zero residual chloride. The last rinses with E-Pure water were done in a Coy anaerobic chamber (90% N_2, 10% H_2) with water devoid of oxygen. All parts contacting the sample were acid-washed and those inserted were maintained anaerobically (in sealed serum vials) until the instant of use. The in-line 25-mm filters (0.2-µm pore size) used were ion chromatography-approved ultraclean commercial units (IC Gelman Acrodiscs), and all-polypropylene syringes received the sample. Components for reduced sulfur analysis were prepared in an anaerobic chamber, with dilution blanks, standards, and reagents in serum vials. Samples for trace metals were acidified with trace metal-certified nitric acid and stored in acid-washed polypropylene tubes. The samples for routine chemical analysis were stored at 4°C in polypropylene tubes. Core processing (sectioning, squeezing) was accomplished in a protected part of the National Park Service garage.

Figure 4. Core from West Thumb inside a core liner. Notice the darker sediment water–interface. This core is on the extruder, ready to be transferred into the squeezer liner.

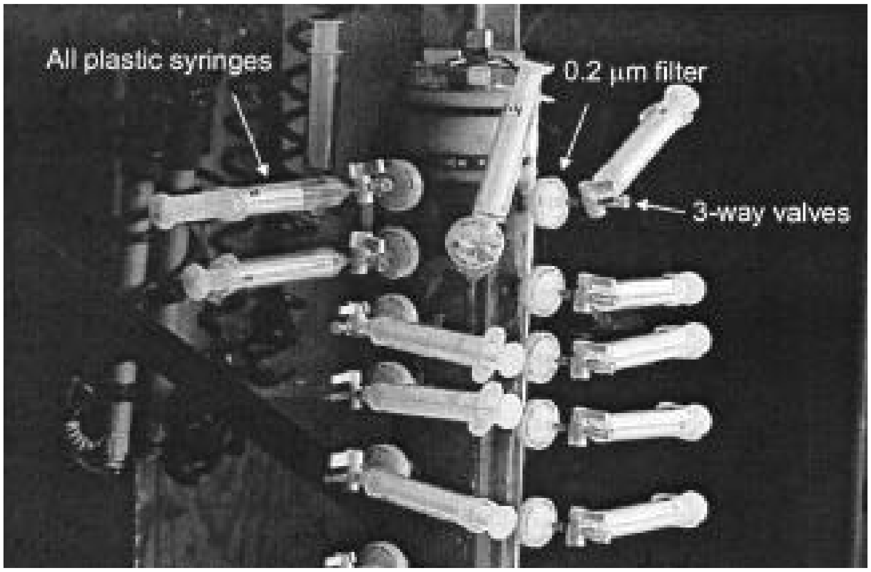


Figure 5. Porewater squeezer used to obtain porewater by applying pressure vertically; the water tends to be forced horizontally ("guided") by the porex inside the sediment at the end of the filter. The picture shows how the squeezer is put together, showing the depth intervals to obtain porewater from different depths in the core.

Chemical analyses. In the laboratory, samples were filtered through 0.2-µm filters (Supor, Nuclepore) and water was aliquotted for the different analyses. Dissolved mineral compounds were measured in the field laboratory by several methods: flow injection analysis (FIA; silicate, SiO_2), ion chromatography (IC: chloride, Cl^-, sulfate, $SO_4^=$), and spectroscopy (ammonium, NH_4^+), all according to standard methods (APHA 1992). Reduced and total iron was also determined in the field by the ferrozine spectrophotometric method of Stookey (1970), with (total iron) and without (reduced iron, FeII) reductant extraction. Total carbon dioxide, $\sum CO_2$, was analyzed by the Teflon–membrane flow injection method of Hall and Aller (1992). Reduced sulfur compounds (hydrogen sulfide, H_2S, thiosulfate, $S_2O_3^=$, sulfite, $SO_3^=$) were quantified by a scaled-up modification of the micro-bore high-performance liquid chromatographic (HPLC) method of Vairavamurthy and Mopper (1990), using dithio-bis-nitropyridine (DTNP) derivatization. The analytical equipment was transported to Yellowstone National Park, where all labile species were analyzed on site within one day of collection and analytical preparation.

Porewater flux was calculated from porewater concentration profiles, and concentration gradients at the sediment–water interface were used to calculate fluxes via Fick's first law of diffusion (Berner 1980): $J = D_S \cdot \phi \cdot dC/dz$, where J is the flux of the different components; D_S is the whole sediment molecular diffusivity corrected for tortuosity (Li and Gregory 1974); ϕ is the porosity at the sediment–water interface; and dC/dz is the slope of the concentration gradient.

Results

Porewater. Since almost a third of Yellowstone Lake is directly influenced by hydrothermal activity, it is important to measure chemical components that can provide a proxy for geothermal activity in the lake. Chloride is an important indicator of geothermal activity, and the Yellowstone River inlet provides a low-chloride concentration (<7 µM). The subsurface deep reservoir containing fluids that feed the thermal basins in Yellowstone National Park is thought to have concentrations of about 20 to 21 mM chloride (Truesdell et al. 1977; Fournier 1989).

Porewater profiles in Figures 6–12 depict distinct sites in Yellowstone Lake, with all cores being collected during the 1998 season. The Mary Bay 01 core (01-MB; shown as open squares in the figures) was taken from a vent field in the bay, and smelled of hydrogen sulfide as we brought it onto the vessel. This core was close to one that melted the plastic core liner (temperature >135°C) moments before. The West Thumb 03 core (03-WT; open circles) was collected near the West Thumb geyser basin. The West Thumb 06 core (06-WT; closed circles) was collected in the West Thumb deep basin. The Stevenson Island 07 core (07-SI; closed squares) was collected from the deep canyon east of the island (refer to locations in Figure 1).

Chloride is a conservative and non-reactive ion that is used as a geothermal tracer. Chloride concentrations in Mary Bay sediments reached 10 mM, the highest concentration measured in porewater (Figure 6). A concentration of about 5 mM was also found in a core from West Thumb; all the other sites measured showed a concentration lower than 1 mM.

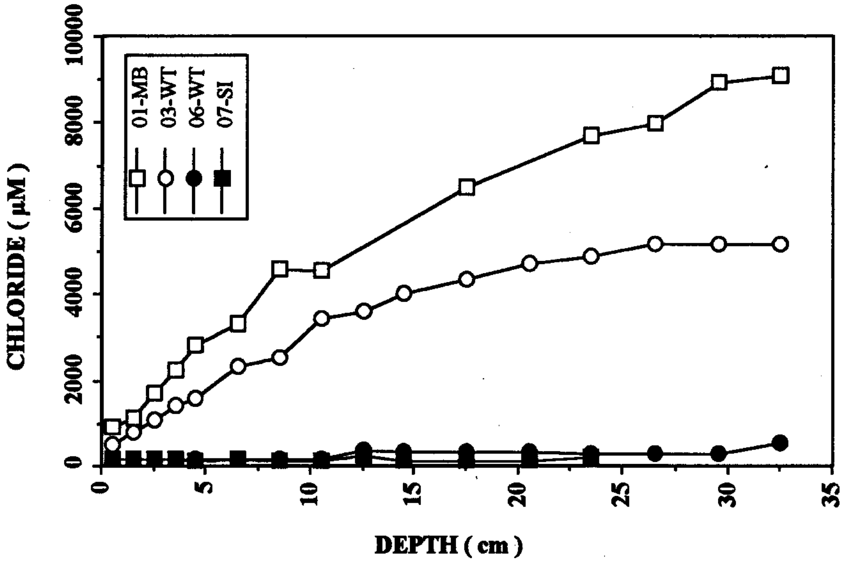


Figure 6. Porewater profile depicting chloride concentration (µM, micromolar) with depth in four different cores from Mary Bay, West Thumb, and Stevenson Island.

Diatoms (algae) require silica to produce frustules (skeletons made of silica). These organisms can settle to the bottom of the lake by different processes; the frustules then begin to undergo dissolution. Evidence of this process is found in the porewater profiles from the sediments from different areas of the lake. Silica is a compound that is non-conservative and biologically reactive. Silicate reflects the diagenetic/dissolution control in the water and sediments, where decomposition takes place without geothermal influence. In addition, vent water seepage into sediments adds additional silicate, and there are some examples of porewater profiles that show this influence. Mary Bay 01 and West Thumb 03 had the highest concentrations, about 2.5 mM SiO_2, whereas non-geothermally influenced cores peaked at 1 mM (Figure 7). Silicate shows a higher concentration than expected from a diagenetically generated profile, showing the influence of vent activity in the area. The values for the Southeast Arm reach a concentration of 750 µM, similar to that of West Thumb 06 and Stevenson Island 07.

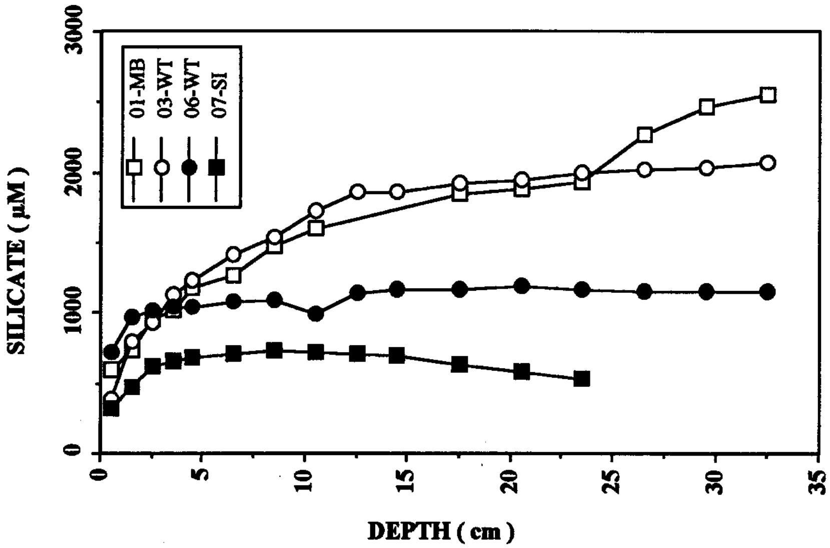


Figure 7. Porewater profile depicting silicate concentration (µM, micromolar) with depth in four different cores from Mary Bay, West Thumb, and Stevenson Island.

Hydrogen sulfide is a compound that we refer to as the “smell of success” since it is a great marker for reducing conditions in sediments as well as vent water. It is a readily distinguishable reduced component that will be present in an area where there is usually little oxygen present. It is also a characteristic of geothermally derived vent waters. Sulfate reduction from bacteria is an important component in the production of this reduced compound. Except for methane, hydrogen sulfide is the most inefficient to produce. Hydrogen sulfide concentration was highest, 550 µM, in Mary Bay 01 (Figure 8). The concentration in the other cores was less than 10 µM, which is significantly lower than that in the active areas. Hydrogen sulfide has been found consistently in Mary Bay.

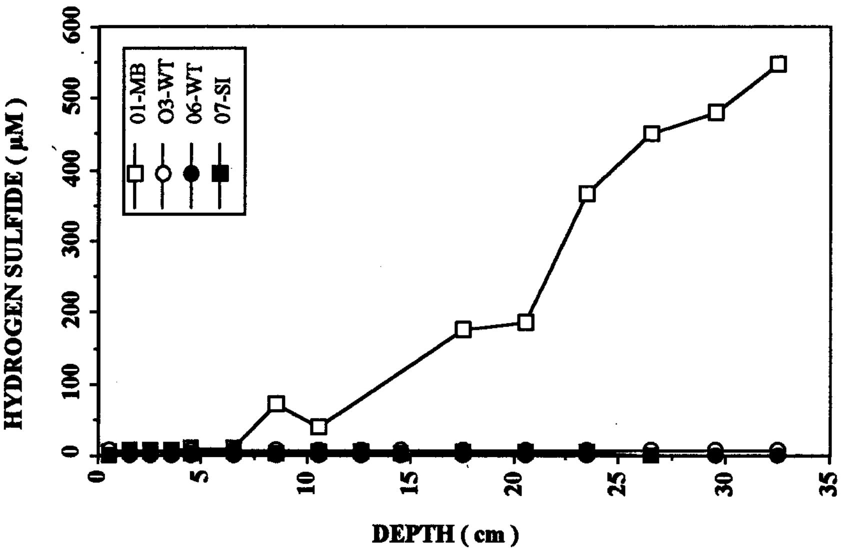


Figure 8. Porewater profile depicting hydrogen sulfide concentration (µM, micromolar) with depth in four different cores from Mary Bay, West Thumb, and Stevenson Island.

Bacterial sulfate reduction is a process of organic matter decomposition, where sulfate is used as an energy source by bacteria, by which sulfate is reduced to hydrogen sulfide. Hence, sulfate reduction tends to decrease with water column depth because less organic matter reaches those sediments. This process occurs in the absence of oxygen. Sulfate was highest, 200 µM, at Stevenson Island, whereas the concentrations in the other cores were less than 80 µM (Figure 9). West Thumb 03 showed a very shallow gradient compared with the gradient from Mary Bay 01.

Reduced iron concentrations were highest in Stevenson Island 07, as well as in West Thumb 06; that core, taken from the deep basin, had a concentration of 37 µM (Figure 10). Iron laminations are found extensively in the West Thumb area. Typically, vent water lacks reduced iron in the effluent, but some areas in the sediment show evidence of iron oxides.

Ammonium is released to porewater from the decomposition of labile organic nitrogen compounds contained within the bulk of the organic matter deposited in sediments (2–4% organic carbon and 0.3–0.5% total nitrogen). Porewater concentrations of ammonium produced by organic matter decomposition can reach 600 µM in the high-deposition areas of the lake (Figure 11). Profiles observed in these locations are consistent with a diagenetic source, but the steep gradient measured in Mary Bay could result in part from geothermally influenced processes.

Though produced by organic matter decomposition, its main source of enrichment is the extraordinarily high concentrations (to 25 mM) in vent reservoir fluids. Carbon dioxide is another indicator of geothermal activity. High con-

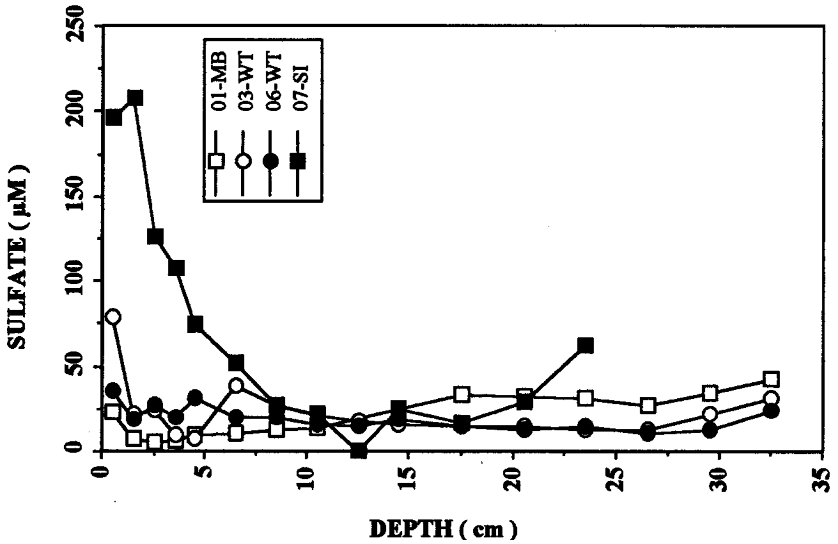


Figure 9. Porewater profile depicting sulfate concentration (µM, micromolar) with depth in four different cores from Mary Bay, West Thumb, and Stevenson Island.

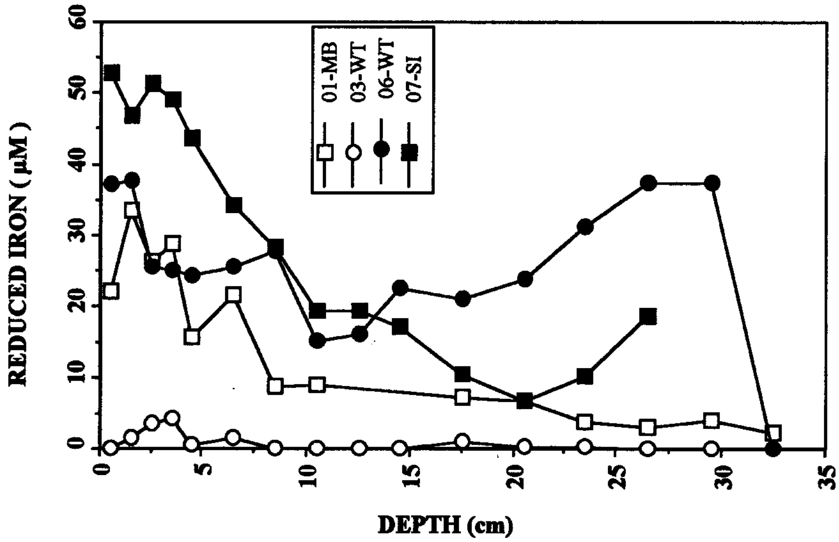


Figure 10. Porewater profile depicting reduced iron concentration (µM, micromolar) with depth in four different cores from Mary Bay, West Thumb, and Stevenson Island.

centrations were measured in the Mary Bay 01 and West Thumb 03 cores (Figure 12), both showing evidence of active geothermal influence, based on the chloride concentration.

Vent water. Vents are very heterogeneous, with temperatures ranging from 20°C to 112°C and pH values from 4 to 8.6, as well as having chemistry that

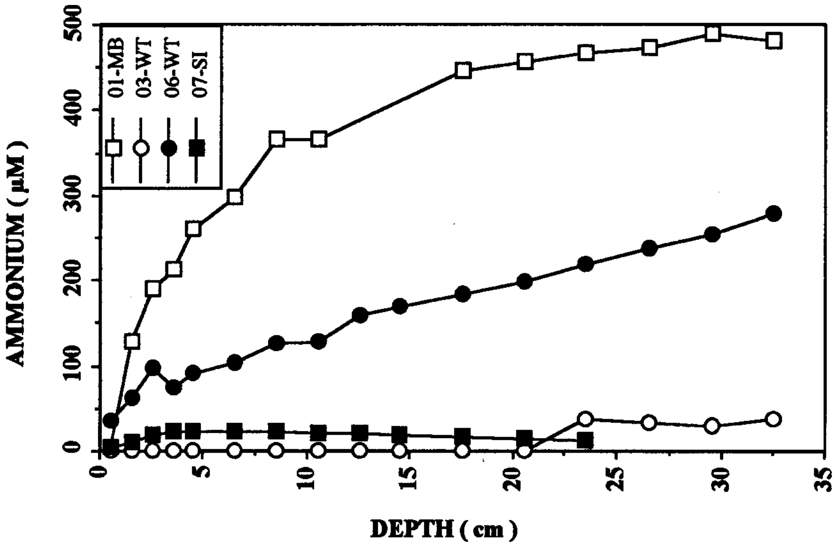


Figure 11. Porewater profile depicting ammonium concentration (µM, micromolar) with depth in four different cores from Mary Bay, West Thumb, and Stevenson Island.

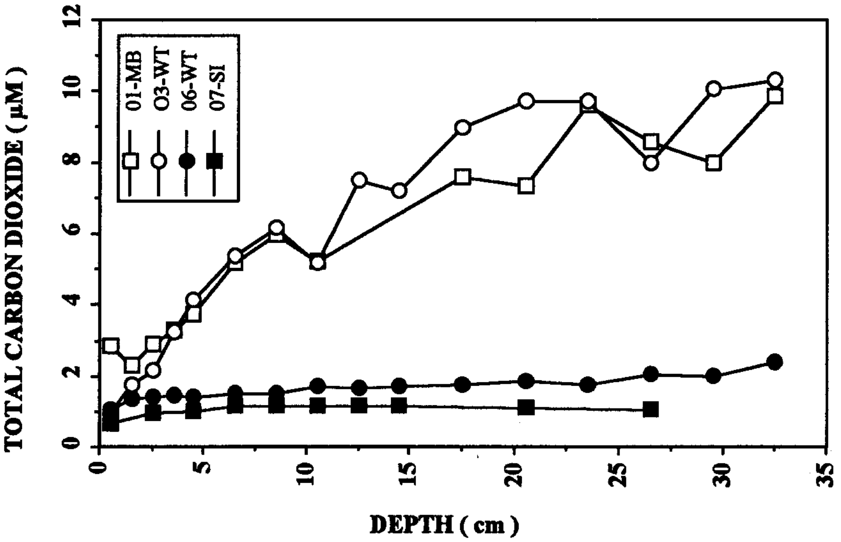
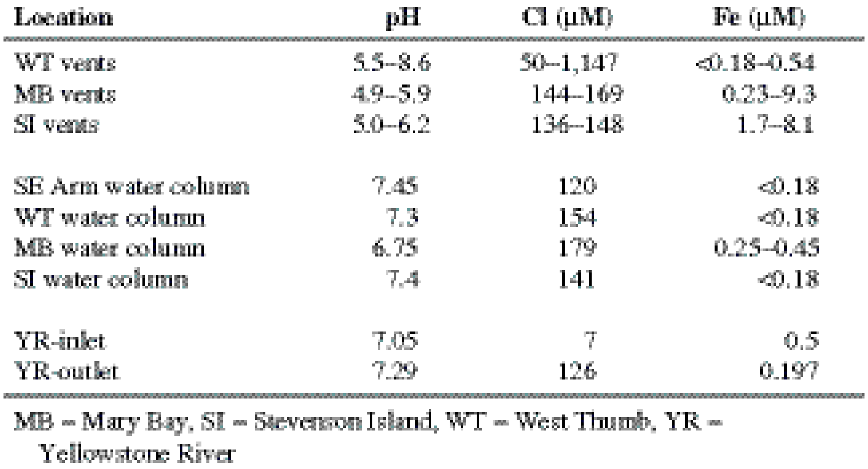


Figure 12. Porewater profile depicting total carbon dioxide concentration (µM, micro - molar) with depth in four different cores from Mary Bay, West Thumb, and Stevenson Island.

varies with location. Chemical differences from vents in different areas have allowed us to group the different characteristics into domains (see Cuhel et al., this volume). Vent waters from West Thumb and Mary Bay showed enrichment in chloride and silicate, although they were highly variable (Table 1). Reduced iron was present in vents from Stevenson Island and Mary Bay, where the reduced species can remain in the water for at least 24 hours (data not shown).

Lake water. Lake water collected in a deep vent area (near Stevenson Island) showed chemical enrichment in several constituents—chloride, silicate, sulfate, sodium, etc.—when compared with surface water collected at the Southeast Arm inlet and the Yellowstone River outlet (Table 1). When lake water values were compared with those of vents of the different areas, it becomes evident that, for example, Mary Bay has water that still reflects the hydrothermal composition of the vents.

Table 1. Selected chemistry of Yellowstone National Park vents, Yellowstone River inlet and outlet, and water column values.



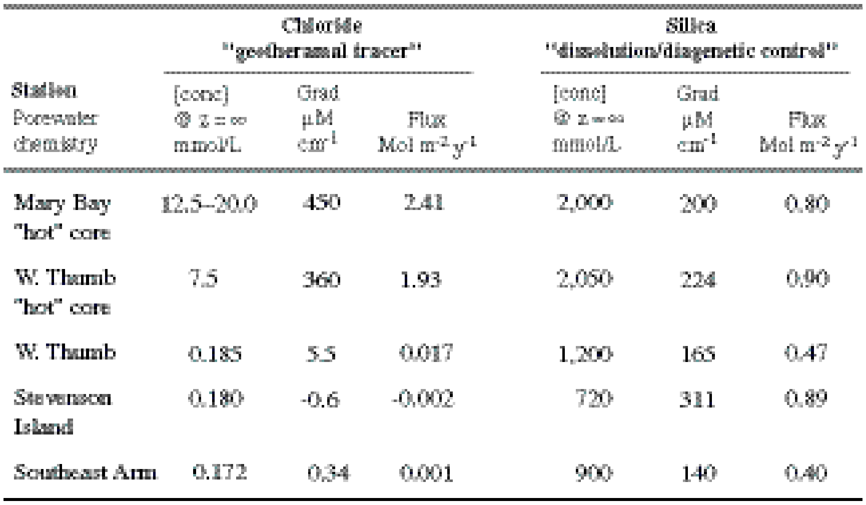
Location	pH	Cl (µM)	Fe (µM)
WT vents	5.5–8.6	50–1,147	<0.18–0.54
MB vents	4.9–5.9	144–169	0.23–9.3
SI vents	5.0–6.2	136–148	1.7–8.1
SE Arm water column	7.45	120	<0.18
WT water column	7.3	154	<0.18
MB water column	6.75	179	0.25–0.45
SI water column	7.4	141	<0.18
YR-inlet	7.05	7	0.5
YR-outlet	7.29	126	0.197

MB = Mary Bay, SI = Stevenson Island, WT = West Thumb, YR = Yellowstone River

There were distinct differences in the composition of hydrothermal vent fluids from different parts of Yellowstone Lake. For example, vents from the West Thumb area were rich in chloride but poor in sulfur compounds, as compared with vents from Stevenson Island which were rich in sulfur but poor in chloride. In contrast, chimney structures from these vents record times that the vent fluids must have been different in composition because they contain precipitates that could not have formed from the vent fluids that currently emanate from these sites; chimney structures from Stevenson Island contain sulfur crystals as well.

Flux from the sediment into the overlying water can be calculated from the porewater chemistry from Mary Bay, West Thumb, and Stevenson Island. Table 2 shows the calculated flux from chloride as the geothermal activity tracer, and silica as the dissolution/diagenetic control in porewater. Chloride flux was highest (two orders of magnitude) from the Mary Bay and West Thumb hot cores; other cores and areas such as Stevenson Island as well as Southeast Arm (which is outside the caldera) do not provide chloride to the receiving lake water. Silica does not show such a dramatic difference, but the same cores have high standing silica concentrations throughout, probably controlled by the solubility of amorphous silica (diatoms) which makes up to ~50% of the sediment mass.

Table 2. Porewater concentrations and flux from cores obtained in Mary Bay, West Thumb, Stevenson Island, and Southeast Arm, showing values for chloride, a “geothermal tracer,” and silica, a “dissolution/diagenetic control” parameter.



Station Porewater chemistry	Chloride "geotheramal tracer"			Silica "dissolution/diagenetic control"		
	[conc] @ $z = \infty$ mmol/L	Grad µM cm^{-1}	Flux Mol m^{-2} y^{-1}	[conc] @ $z = \infty$ mmol/L	Grad µM cm^{-1}	Flux Mol m^{-2} y^{-1}
Mary Bay "hot" core	12.5–20.0	450	2.41	2,000	200	0.80
W. Thumb "hot" core	7.5	360	1.93	2,050	224	0.90
W. Thumb	0.185	5.5	0.017	1,200	165	0.47
Stevenson Island	0.180	-0.6	-0.002	720	311	0.89
Southeast Arm	0.172	0.34	0.001	900	140	0.40

Discussion

Geochemical inputs to Yellowstone Lake come from a variety of sources, namely: hydrothermal vents, groundwater, rainwater, flux from sediments, and direct runoff (including from tributaries). Approximately one-third of the lake is directly influenced by hydrothermal activity through hot-water vents and fumaroles. Surveys of lake water, vent water, and sediment porewater gradients established zones of direct and subsurface inputs of geochemically altered fluids. Vent water intrusion into the surrounding sediments is evident in some of the profiles. In some instances, chloride approaches theoretical reservoir concentrations (20 mM) and the silicate concentration at depth seems greater than that expected from diagenesis alone. Porewater and vent water chemistry provides evidence for lake water dilution of vents below the sediment–water interface.

Reduced sulfur compounds are important components of the vent waters in Mary Bay and Stevenson Island, while in the West Thumb these compounds were usually undetectable. The vent fluids exhibit a highly variable concentration of dissolved minerals in different areas of the lake as well as for different years of sampling. This is shown, for example, in the solid phase from West Thumb (Figure 13), where highly laminated iron–manganese oxide crusts are found in areas that typically do not contain sulfide, methane, or other reduced compounds.

Strong evidence for vent fluid seepage was found in the hot-core porewater measurements of chloride (10 mM), total CO_2 (to 11 mM), and silicate (2.8 mM), all highly enriched in deep reservoir fluids. Some areas of the lake contain high concentrations of sulfide (500 µM) and of iron (50 µM). Because inorganic nitrogen (ammonium) is virtually absent from the water column and vent fluids, diagenetic production of ammonium from organic matter may provide more growth-

Figure 13. Solid phase sample collected from West Thumb. Note the laminations on the surface of alternating manganese and iron oxides.

promoting habitats in surrounding sediments than in aqueous environments.

One of the factors that may have influenced the vent activity throughout the lake was the lake stage or water level, which directly affects the hydrostatic pressure on vent systems. There seemed to be a correlation between high activity in the vents when water levels were low, and low activity when water levels were high. This is one of the factors that will benefit from long-term studies of the different vent areas in the lake.

Comparing data from the inlet of the Yellowstone River (in Southeast Arm) and its outlet (in the northern part of the lake), it is clear that there is a significant hydrothermal influence in the lake (Figure 14). Chloride is virtually absent in the inlet waters. Hence, much higher values of lake water provide strong evidence for an external source of the ion. During three years of piezometer studies to measure the groundwater inputs to the lake, we concluded that the source is not sufficient to explain the lake water enrichment. Chloride, then, contributes another piece of evidence that points to a geothermal influence in the concentration of key components (see Klump et al., this volume). There are also sources and sinks of other elements, but having mentioned just a few we can see that this is a very dynamic geoecosystem, in which different sources of chemicals are found and where microbiology is an important component.

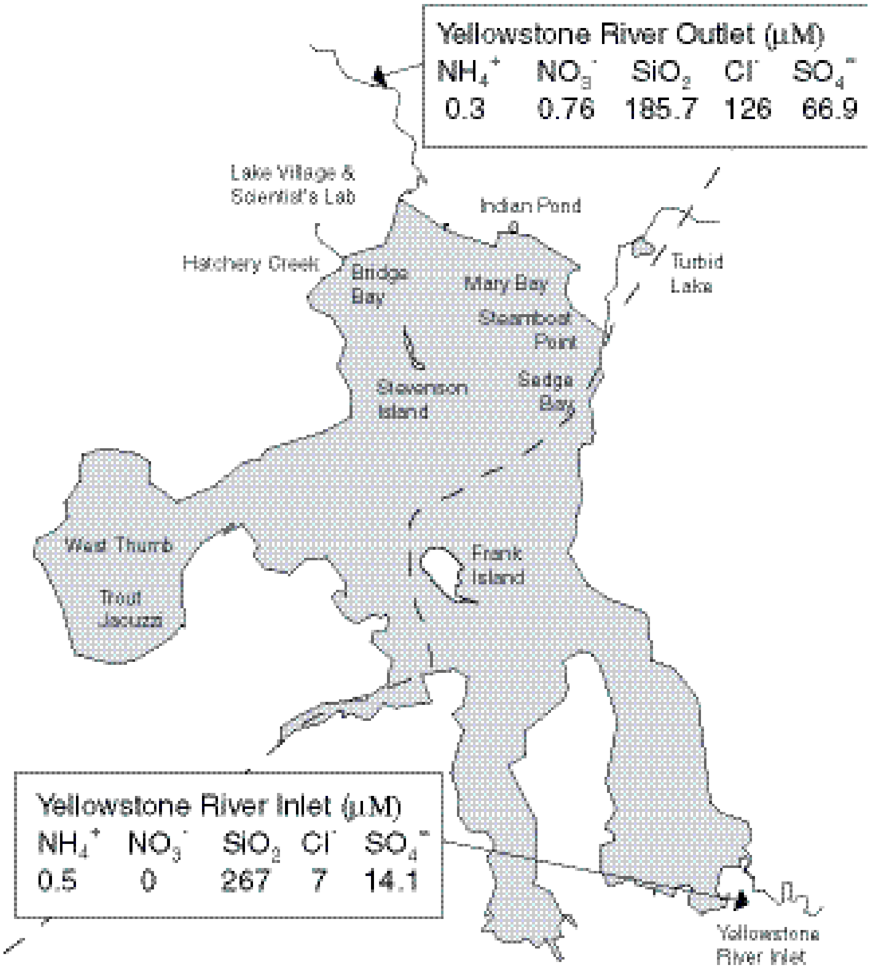


Figure 14. Yellowstone Lake map showing different concentrations of selected compounds and the changes incurred from the source of the water coming into the lake outside the caldera region to the Yellowstone River outlet.

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