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THE GEOCHEMISTRY OF HOT SPRING WATERS AT NORRIS GEYSER BASIN, YELLOWSTONE NATIONAL PARK

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ABSTRACT

Relatively dilute alkali-chloride waters at Norris Geyser Basin attain chemical equilibrium with reservoir rocks underground in a series of reservoirs at temperatures ranging from about 200 to 325°C. Reservoirs of acid-sulfate-chloride waters at >190–200°C also exist underground at Norris and there is episodic mixing (usually in the fall) of acid-sulfate-chloride and alkali-chloride waters. The rate of discharge of sulfate by acid-sulfate-chloride water from deep in the system is large, and it is difficult to account for the generation of all of this type of water solely by present-day local oxidation of H_2S that is carried in steam to the Earth's surface at Norris, followed by infiltration of acid-sulfate water back underground where it mixes with chloride-rich water. Additional sulfate may be generated by bacteria (*sulfolobus*) that consume native sulfur and liberate sulfuric acid in shallow underground environments. The source of native sulfur may be old solfataras in the Norris region, formed as a result of volcanic activity that produced silicic domes south of Norris, and that were subsequently covered either by later volcanic flows, or by glacial material deposited on hot ground. Another possibility, supported by $^3He/^4He$ data, is that a component of magmatic gas containing SO_2 is entering parts of the Norris system and reacting with water to form H_2SO_4 and H_2S.

INTRODUCTION

Fournier (1989) presented a general overview of the geochemistry of the thermal waters throughout Yellowstone National Park that categorized the Norris waters within a general model of the hydrothermal system, and White et al. (1988) focused on the geology and thermal activity of Norris Geyser Basin (Norris). Here we briefly outline the geochemical variations in the thermal waters found at Norris, where over 360 samples of thermal waters have been collected and analyzed for major dissolved constituents from about 70 hot springs and geysers over a period of 108 years.

CHEMICAL CHARACTERISTICS OF THERMAL WATERS

Representative chemical analyses of thermal waters at Norris are shown in Table 1. Waters from the hottest (275–323°C, based on silica and Na-K-Ca geothermometry, and on mixing models) and probably deepest reservoir at Norris flow to the surface at the side of Porcelain Terrace at the NE corner of the geyser basin (Figure 1). These waters generally are pH-neutral with relatively high chloride (550–800 mg/kg) and low sulfate (10–50 mg/ kg). As a result of the high reservoir temperature and neutral pH of water, the rate of sinter deposition at the side of Porcelain Terrace is the fastest in Yellowstone. Analysis No. 1, Table 1 is typical of thermal waters issuing along a N-trending zone at the W side of the Terrace.
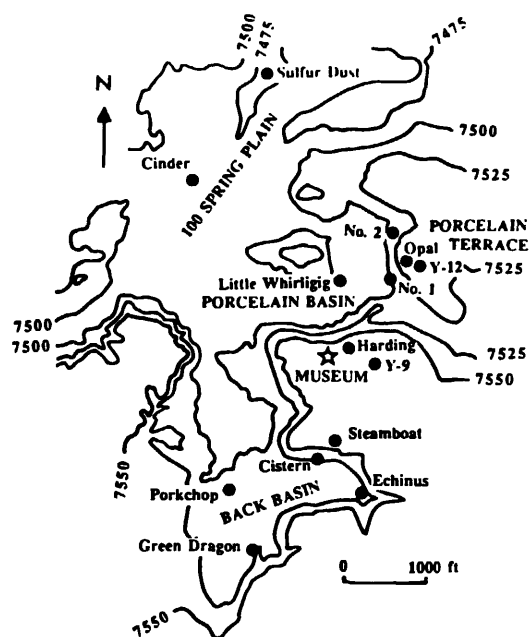
Figure 1. Sketch map of Norris Geyser Basin showing topographic features and locations of selected hot springs and geysers. Contours showing equal altitude at 25-foot intervals are shown in the range 7475 feet to 7550 feet.

A USGS drill hole (Y-12) at the SE end of Porcelain Terrace attained a depth of 331.7 m and a temperature of 238°C (White et al., 1975). Fluid was collected from the bottom of this well using a downhole sampler. The chemical composition of that water is shown in Table 1 (No. 12). The most significant information provided by this sample is the chloride concentration of 528 mg/kg. There was no indication of steam separation before or after the sample was collected, so the measured chloride is probably close to the concentration of chloride in the deep reservoir beneath Norris that supplies water to the springs at Porcelain Terrace. The cation composition reflects reaction of hot water with glass-rich ash-flow tuff within the uncased portion of the drill hole where temperatures range from 190 to 238°C. Most of the sulfate in this water probably dissolved from sulfides in the wall rock when oxygenated water filled the well after drilling was completed.
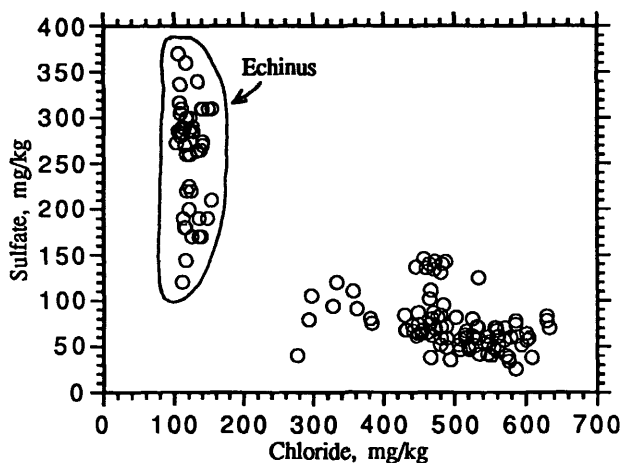
Figure 2. Chloride-sulfate relations exhibited by waters collected at different times from Cistern Spring (circles) and Echinus Geyser (dots within the encircled area).

Progressing westerly from Porcelain Terrace through Porcelain Basin, and to the NW through 100 Spring Plain (Figure 1) there is a decrease in chloride, an increase in sulfate, and a decrease in pH (e.g., Little Whirligig and Sulfur Dust(Nos. 4 and 5, Table 1). Also, the estimated reservoir temperature decreases to about 200–230°C. Very little sinter deposits in Porcelain Basin and in the 100 Spring Plain because the water that is discharged there has a low pH.

In the Back Basin (Figure 1) the hydrothermal system is chemically and hydrologically complex. There, some waters issue from an acid-sulfate-chloride reservoir at about 195–215°C (e.g., Echinus, Table 1) and others issue from at least two pH-neutral, chloride-rich reservoirs, one at a temperature of about 210–230°C and the other at about 275–310°C. As an example, Porkchop Geyser (No. 7, Table 1) recently has discharged water mainly from a hotter (presumably deeper) neutral-chloride reservoir where dissolved silica concentrations and K/Na ratios are relatively high, while in the past it has discharged from an apparently different (presumably shallower) reservoir where pH-neutral water has reacted with rock at lower temperatures, yielding lower concentrations of dissolved silica and lower K/Na values (No. 6, Table 1). A gradual change in the composition of water discharged by Porkchop Geyser over the period 1960–1990 was documented by Fournier et al. (1991), who showed that the temperature of last water-rock equilibration of the discharged water increased by about 60–70°C during that same period of time, accompanied by an increase in eruptive activity which culminated in a hydrothermal explosion that destroyed the geyser in 1989.

Some springs that were sampled at different times show variable degrees of mixing of the acid-sulfate and neutral-chloride waters. This is most strikingly exhibited by Cistern Spring (Figure 2) that was sampled more than 100 times during a 25-year period. The variations shown in Figure 2 result partly from different amounts of mixing of different waters, and partly from different degrees of steam loss (adiabatic expansion) during upflow (Fournier et al., 1986).

EPISODIC INCREASED BOILING FOLLOWED BY INCREASED MIXING OF SULFATE-RICH AND CHLORIDE-RICH WATERS

Episodically (generally in the fall) there is a hydrothermal "disturbance" that affects waters in all of the Norris basins. The disturbance is characterized by increased turbidity of manyhot springs, increased discharge of water and steam, extreme fluctuations in temperatures of pools, and, in some years, small hydrothermal explosions (White et al., 1988). In addition, underground mixing of alkali-chloride and acid-sulfate-chloride waters apparently coincides with the disturbance. Systematically increasing chloride in waters collected monthly from Cistern Spring in the Back Basin during 1976–1985 showed that there was increased boiling preceding these disturbances. Immediately following the onset of these disturbances decreased chloride and increased sulfate were found (Fournier et al., 1986).

As a second example, one usually neutral-chloride spring at Opal Terrace was sampled on the first day of a disturbance (No. 2, Table 1); its pH was 2.82 and its sulfate concentration was 133 mg/kg. Four days later its pH had increased to 5.36 and its sulfate concentration had dropped to 99 mg/kg (see No. 3, Table 1). The cause of the hydrothermal disturbance is uncertain, but may be related to seasonal fluctuations in the regional groundwater potentiometric surface.

CHEMICAL CHARACTERISTICS AND ORIGIN OF SULFATE-RICH ACID WATERS AT NORRIS

There are two types of sulfate-rich acid waters at Norris. One type is found in topographically high regions where nonoverflowing, boiling pools of low-chloride (<10 mg/kg), sulfate-rich waters originate by oxidation of H_2S to H_2SO_4 where steam and other gases bubble through surficial pools of perched groundwater and condensed steam (e.g., Opal Spring, No. 10, Table 1). The second type generally contains >100 mg/kg chloride (acid-sulfate-chloride waters), and has relatively high rates of discharge, particularly from Echinus during its large geyser eruptions that currently occur almost every hour. The pH of the Echinus waters (3.0–3.5) appears to be buffered by the assemblage kaolinite-muscovite at about 195–215°C (the silica geothermometer temperature range).

The origin of the relatively high concentrations of sulfate in deep waters flowing from >200°C reservoirs at Norris is uncertain. Studies of sulfur isotopes are underway by others, but to date the results are very preliminary and inconclusive. Oxidation of H_2S at depth using oxygen initially dissolved in meteoric recharge water can account for only about 15 mg/kg dissolved sulfate in deep water. Present-day oxidation at and near the water table of H_2S initially carried in steam, followed by downward percolation may account for some of the sulfate and acidity. However, mass and thermal balance considerations indicate that the large rate of discharge of sulfate in the acid-sulfate-chloride water cannot be accounted for by the above mechanisms alone. Furthermore, the concentration of sulfate in Echinus water ranges widely while there is relatively little change in chloride (e.g. Nos. 8 and 9, Table 1). Figure 2 shows Cl-SO_4 relations for 53 samples from Echinus (all data points located within encircled area) collected from 1884 through 1986, mostly during 1980–1983. Variations in chloride in the Echinus waters are about as expected for different proportions of adiabatic and conductive cooling during upflow, while variations in sulfate are too large to be explained by different degrees of boiling during upflow from a 195–215°C reservoir.

Table 1. Chemical compositions (mg/kg) of selected thermal waters, Norris Geyser Basin

No.	Name	Ref.	Date	°C	pH	SiO$_2$	Na	K	Ca	Mg	Li	Cl	SO$_4$	HCO$_3$
1	S. Base Porc. Terr.	(a)	07/03/75	92	7.00	589	400	93	2.60	0.01	7.18	675	24	60
2	N. Base Porc. Terr.	(b)	09/02/90	88	2.82	520	334	100	1.82	0.21	4.07	527	133	0
3	N. Base Porc. Terr.	(b)	09/06/90	89	5.36	665	400	112	2.82	0.08	5.36	634	99	32
4	Little Whirligig	(c)	09/27/71	91	3.20	420	349	83	2.50	0.50	5.30	607	113	0
5	Sulfur Dust	(d)	09/12/61	50	2.75	280	250	57	4.50	0.15	3.50	427	197	0
6	Porkchop	(d)	09/18/60	72	7.45	435	526	66	6.40	0.50	7.40	860	33	18
7	Porkchop	(e)	06/??/89	92	8.50	741	388	91	3.60	0.06	6.60	687	23	62
8	Echinus	(b)	11/15/81	90	3.14	257	151	45	3.70	0.52	1.00	125	170	0
9	Echinus	(b)	09/15/86		3.06	296	148	52	4.30	0.52	0.75	117	360	0
10	Opal	(d)	09/19/60	90	1.90	168	5	2	0.70		0.05	5	760	0
11	Harding	(c)	06/07/71	93	3.53	325	26	18	0.90	0.25	0.09	2	123	0
12	Y-12	(b)	09/13/69	238	7.86	352	377	21	1.90	0.20	1.43	528	34	79
13	Y-9	(b)	09/16/69	195	8.58	412	268	16	0.80	0.04	0.98	80	43	488

(a) Thompson & Yadav (1979); (b) Unpublished USGS data; (c) Thompson et. al. (1975); (d) Rowe et al. (1973); (e) Kharaka et al. (1990)

One way to pick up sulfate with little change in chloride is for groundwater to come in contact with old native sulfur deposits that may be buried at relatively shallow depths in the cool margins of the Norris system. Sulfur-consuming bacteria (*sulfolobus*) are very effective at generating sulfuric acid using native sulfur and oxygen in the cool margins of hydrothermal systems (Brock, 1978). Native sulfur deposits could have formed in solfataras during early volcanic activity that produced silicic domes south of Norris, and these solfataras could later have been buried, either by younger volcanic flows that partly cover the domes, or by glacial material deposited from melting ice over hot ground.

Yet another mechanism for explaining the chloride-sulfate relations at Norris is by addition of a component of magmatic gas containing SO$_2$ that reacts with water to form H$_2$SO$_4$ and H$_2$S. This latter mechanism is consistent with recent observations that the highest ^{3}He/^{4}He ratios (>8–9 relative to atmospheric concentrations) in Norris waters are found in the acid-sulfate-chloride waters rather than alkaline-chloride waters (B.M. Kennedy, written communication, December 1991).

CONCLUSIONS

At the west side of Porcelain Terrace, Cl-rich and SO$_4$-poor water flows directly to the surface from the deepest and hottest reservoir at Norris (275–325°C). To the west and northwest of Porcelain Terrace, this Cl-rich water becomes progressively more mixed with an acid-sulfate water. A series of stacked reservoirs with different temperatures are present in the Back Basin so that waters of similar chloride content attain chemical equilibrium with rock at a variety of temperatures ranging from about 210 to 300°C before emerging at the Earth's surface. Reservoirs of sulfate-rich waters also exist in the Back Basin region and discharge waters that show relatively large variations in sulfate, but little variation in chloride. Annual mixing of the sulfate- and chloride-rich waters commonly occurs in the fall immediately after a basinwide event characterized by an abnormally high degree of steam discharge (increased boiling).

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