

# **PROCESSES GOVERNING ARSENIC GEOCHEMISTRY IN THE THERMAL WATERS OF YELLOWSTONE NATIONAL PARK**

D. Kirk Nordstrom, R. Blaine McCleskey, and James W. Ball  
U.S. Geological Survey  
3215 Marine St., Boulder, CO 80303

## **INTRODUCTION**

Yellowstone National Park, USA, has more than 10,000 thermal features throughout a land area of  $2.2 \times 10^6$  acres (just short of a million hectares). These characteristics make it unique among the world's geothermal areas and, consequently, it has been the subject of numerous geological, geochemical, and ecological studies. Past and current research related to arsenic in the thermal waters of Yellowstone provide insights to our understanding of arsenic geochemistry in geothermal systems.

## **GENERAL TRENDS AND MAIN PROCESSES**

Yellowstone hot springs and geysers tend to have As concentrations in the range of 0.1-4 mg/L with highly variable As[III/(III+V)] ratios from 0 to 1. Most other solutes vary more in concentration than does As and this observation puts responsibility on the analyst to produce highly reliable values for a meaningful interpretation of arsenic geochemistry.

Most interpretations of As in geothermal waters test conservative vs. non-conservative behavior by plotting As concentrations against Cl concentrations. Stauffer and Thompson (1984) showed that when different geyser basins at Yellowstone were plotted in this manner, simple mixing trends could be identified. Many thermal waters mix with cool, dilute meteoric ground waters on their way to the surface and these trends can be distinguished as linear plots with an origin near zero. An updated plot of As vs. Cl determinations in Yellowstone thermal waters is shown in Figure 1 with two symbols illustrating a geographical difference in As/Cl variability. There appears to be a trend of consistently lower As/Cl ratios for Norris and Upper Geyser Basins bounded approximately by the diagonal straight line. Determinations from waters of Ragged Hills, Gibbon, Lower, Midway, Potts, and West Thumb Geyser Basins show much higher variability and a tendency for enriched As/Cl ratios relative to Norris and Upper Geyser Basins. There are, of course, some exceptions to this generalization but mixing trends have been recognized as a major process governing compositional trends in Yellowstone's thermal waters (Fournier and others, 1992).

Mixing trends, of high-concentration thermal waters with dilute meteoric waters, are demonstrated in Figure 2 for Cinder Pool and Cistern Spring. Cistern Spring was recognized by Fournier and others (1986; 1992) as a spring that was subject to mixing caused by climatic or seasonal variations in weather. Most thermal waters from Norris and Upper Geyser Basins tend to lie along the same mixing trends defined by extensions of the Cistern Spring and Cinder Pool mixing lines (Figure 2). The As/Cl relations shown in Figure 2 suggest that these solutes had a similar source (inside the caldera) but that adiabatic cooling (boiling) of the Norris waters effectively increased the solute

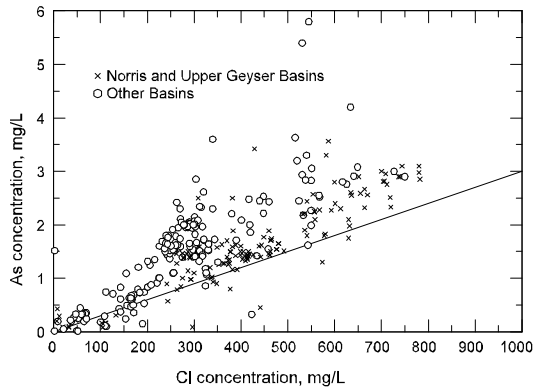


Figure 1. As. vs. Cl concentrations for Yellowstone waters

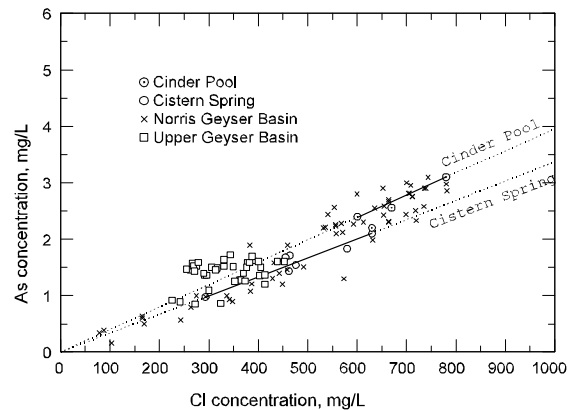


Figure 2. As vs. Cl concentrations for Cinder Pool, Cistern Spring, Norris and Upper Geyser Basins

concentrations along sub-horizontal flow paths. These waters have subsequently mixed with dilute shallow ground waters as they made their way to the surface.

Two unexpected trends in As enrichment relative to Cl were discovered in this study but their causes are not fully understood. The first trend is seen in the high variability and enrichment in samples from a relatively small area in Ragged Hills. This area has experienced several new eruptions in 1999 and water analyses were obtained shortly thereafter. Some of these analyses fit in quite well with the Norris Geyser Basin mixing trend but a few samples are significantly enriched in As/Cl. The geographic distribution of this enrichment indicates it is coming from one small area where yellow precipitates, possibly amorphous orpiment ( $As_2S_3$ ), occur in small hot spring outflows. An accumulation of As in this area (analogous to sulfur enrichment in areas of  $H_2S$  oxidation) may have caused As enrichment in the near-surface waters. The second enrichment trend is the variation in As at nearly constant Cl for several geysers and springs shown in Figure 3. Although this behavior has not been noted previously for As/Cl relations, Fournier and others (1992) reported a wide range of  $SO_4$  concentrations for Echinus Geyser over a narrow range of Cl concentrations. They did not have a favored hypothesis for this observation but suggested that infiltration of  $H_2SO_4$  formed at or near the surface was insufficient to account for the variation in  $SO_4$  and perhaps oxidation of deeply buried solfataras or residual magmatic  $SO_2$  that disproportionated to  $H_2SO_4$  and  $H_2S$  may account for it. Further research and monitoring of these sites should provide clues to the cause of these arsenic anomalies.

A combination of complex processes can explain the variation in As concentrations in hot springs and geysers. There are two primary end-member waters. The first is hydrothermal fluid leaching rocks at temperatures of 200-350°C and about 400 mg Cl/L before adiabatic or conductive cooling which can be enhanced by increasing  $CO_2$  content. The second is dilute meteoric water of only a few mg Cl/L. The hydrothermal fluids can undergo significant adiabatic cooling causing an increase in Cl to over 700 mg/L and in As to over 3 mg/L. This “evaporated” water can then mix with dilute meteoric water. There are indications in the Yellowstone geothermal data that local As enrichment might be caused by accumulation at or near the surface through arsenic sulfide precipitation and it might occur

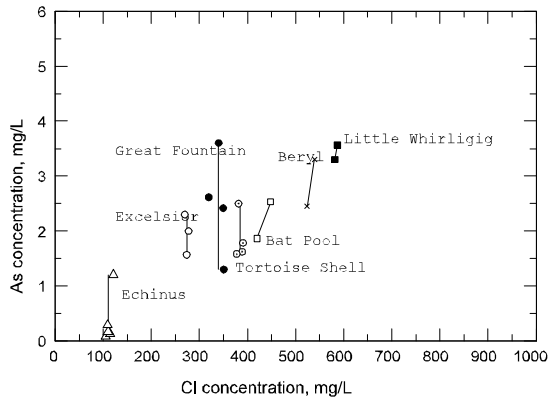


Figure 3. As vs. Cl concentrations for selected waters in certain

types of hot springs and geysers without the accumulation by precipitation. Finally, any of these types of evolved waters can mix to varying degrees.

### ARSENIC (III/V) REDOX CHEMISTRY

Deep geothermal waters should be reduced and contain only As(III). Oxidation would occur upon ascension of the fluid and mixing with shallow oxidizing ground waters and the potential for conversion to As(V) exists depending on the rate of oxidation relative to the fluid flow rate. Further potential for oxidation to As(V) would exist when the hot spring or geyser discharges on the surface and mixes with atmospheric oxygen. The available data indicate that both reduction and oxidation are important and cause the As(III)/As(total) ratios to vary over a wide range. Figure 4 illustrates the decrease in As(III) during overflow from a discharging thermal water. Arsenic oxidation is rapid in the overflows and seems to be related to the disappearance of H<sub>2</sub>S, a reducing agent. Figure 5 is a frequency diagram for the ratio of As(III)/As(total) from 151 samples collected at Yellowstone National Park, including hot springs, geysers, drainage waters, and river water samples. A distinct bimodal distribution appears in these data reflecting the tendency of the As to be either fully reduced or fully oxidized. Hot springs are dominated by As(III) species and drainages are dominated by As(V). Arsenite oxidation rates in these thermal waters are very rapid considering the fast flow velocities of the overflows, especially when compared to known inorganic oxidation rates (Cherry and others, 1979; Eary and Schramke, 1990). Another example is offered by unpublished data from a bubbling fissure in One Hundred Springs Plain (Norris Geyser Basin) that feeds an adjacent pool with nearly identical chemistry. The bubbling fissure has 86% As(III) whereas the pool has only 6% As(III). These rapid oxidation rates must be microbially catalyzed. Bacteria have been found at Yellowstone that oxidize arsenite to arsenate and research is underway to identify them and their mechanism of oxidation, i.e. whether it is autotrophic metabolism or detoxification (Mielke and others, 2000).

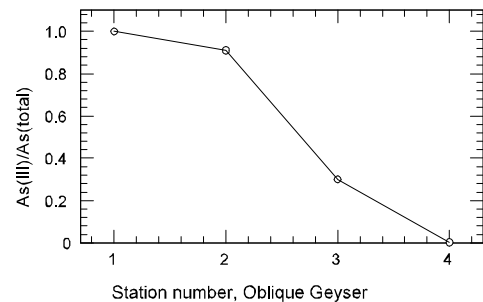
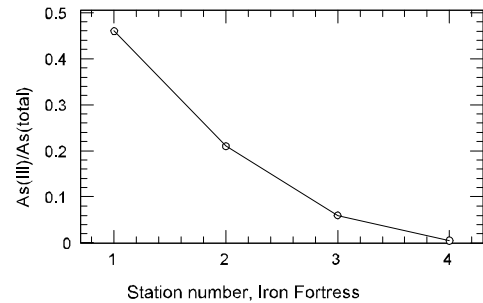
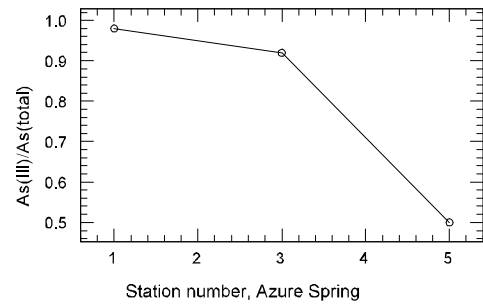


Figure 4. Decrease in As(III)/As(T) for 3 hot spring overflows.

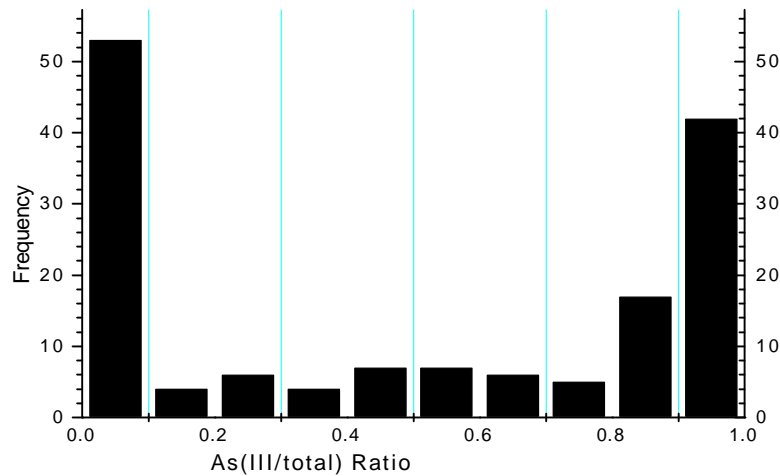


Figure 5. Frequency of As(III/total) in Yellowstone waters.

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