

3.4.31**Processes governing arsenic geochemistry in thermal waters of Yellowstone National Park**

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Arsenic is commonly high in geothermal waters ranging up to 50 mg/L and has been an environmental problem for waste disposal from geothermal power plants [1]. Geochemical processes controlling dissolved arsenic concentrations have been controversial with advocates for both conservative and non-conservative behavior.

We have made 354 determinations of dissolved As in a variety of Yellowstone thermal waters and overflows, of which 278 have As(III/V) determinations. Combining this data with another 300 determinations previously reported by the USGS provides a useful database for interpretations.

Dilution trends are apparent for the majority of data when As is plotted against Cl., especially for individual springs that have been monitored over time. As/Cl ratios are fairly consistent between thermal basins inside and outside of the caldera boundary indicating either the same source for fluids many kilometers distance or at least the same process and rock types. Areas of dominantly different rock type reflect very different As/Cl ratios.

Anomalously high and low As/Cl ratios also appear predominantly in a specific part of Norris Geyser Basin and are likely related to a structural feature. Evaporating seeps and thermal soils have high As/Cl ratios and orpiment and realgar precipitate in these soils and hot springs. Small stagnate warm pools in this area can be found that precipitate orpiment and have reached orpiment solubility equilibrium as indicated by saturation index calculations based on revised thermodynamic data. In these pools the As/Cl ratio are among the lowest found in the Park, reflecting removal of arsenic.

Arsenic occurs predominantly as As(III) in the discharging thermal water but quickly oxidized to As(V) by microbial catalysis. The oxidation rate is at least 7 orders of magnitude faster than the abiotic rate, it is independent of pH and largely independent of temperature or solution composition. There appears not to be a dominant microbe responsible for the oxidation but a diversity of microbes.

References

- [1] Webster J. B. and Nordstrom D.K.(2003) *Geothermal Arsenic*, in *Arsenic in Ground Water*, A.H. Welch and K.G. Stollenwerk, eds., Kluwer Academic Pub., 101-125.

3.4.32**Distribution and speciation of arsenic in a shallow-water hydrothermal system: Implications for bioavailability**

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The natural input of toxic elements into near-shore marine environments by shallow-water hydrothermal systems has received little attention, despite their global abundance. Shallow-water submarine hot springs near Ambitle Island, Papua New Guinea, are discharging large amounts of arsenic into a coral-reef ecosystem. Although up to 70,000 ppm arsenic are present in hydrothermal precipitates, total arsenic in water and sediments is not a reflection of its bioavailability. Arsenic can be toxic to some organisms, while simultaneously beneficial to microbes, which utilize the different species for metabolic energy. Arsenic bioavailability and toxicity are therefore controlled by a combination of physicochemical and biological processes.

Field research was conducted in November 2003 to determine if the arsenic in water and sediments from hydrothermal vents near Ambitle Island is available for biological processes. Along two transects, beginning at a hydrothermal vent and extending outward beyond the extent of hydrothermal influence, sediment (sea floor) temperature and pH were continuously measured. Temperature decreased from 94°C in the center of the hydrothermal system to 31°C, which is considered ambient while pH increased from 5.8 to 8.2. The extent and influence of the hydrothermal system was much greater than expected. More than 30 m away from the vents, sediment pH and temperature were still above 50°C and below 6.5. Fourteen sediment cores and pore-water profiles down to 100 cm were collected from each transect. Water, sediments and precipitates were also sampled directly from the vent. In addition to field measurements of pH, ORP and alkalinity, water and sediment samples were preserved for laboratory analysis. Arsenic determination was carried out by HPLC-HG-AFS. The primary arsenic were determined by scanning electron microscopy and sequential extraction.

The highest concentrations of arsenic are directly from vent water and consist predominantly of As³⁺, which decreases, and is converted to As⁵⁺, when moving away from the vent. Both arsenic species in pore water typically increases with depth into the sediment, although diffuse discharge away from the main vent causes horizontal variability. None of the methylated species, DMA or MMA were encountered. Arsenic concentrations in sediments ranged from 2 to as high as 1000 ppm, and occurred mostly in iron oxy-hydroxides. Thus the arsenic in the sediment is stable as long as the conditions remain oxygenated and would not be considered bioavailable.