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Ammonium in thermal waters of Yellowstone National Park: Processes affecting speciation and isotope fractionation

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Abstract

Dissolved inorganic nitrogen, largely in reduced form ($NH_4(T) \approx NH^+_{4(aq)} + NH^o_{3(aq)}$), has been documented in thermal waters throughout Yellowstone National Park, with concentrations ranging from a few micromolar along the Firehole River to millimolar concentrations at Washburn Hot Springs. Indirect evidence from rock nitrogen analyses and previous work on organic compounds associated with Washburn Hot Springs and the Mirror Plateau indicate multiple sources for thermal water $NH_4(T)$, including Mesozoic marine sedimentary rocks, Eocene lacustrine deposits, and glacial deposits. A positive correlation between $NH_4(T)$ concentration and $\delta^{18}O$ of thermal water indicates that boiling is an important mechanism for increasing concentrations of $NH_4(T)$ and other solutes in some areas. The isotopic composition of dissolved $NH_4(T)$ is highly variable ($\delta^{15}N = -6‰$ to $+30‰$) and is positively correlated with pH values. In comparison to likely $\delta^{15}N$ values of nitrogen source materials ($+1‰$ to $+7‰$), high $\delta^{15}N$ values in hot springs with pH >5 are attributed to isotope fractionation associated with $NH^o_{3(aq)}$ loss by volatilization. $NH_4(T)$ in springs with low pH typically is relatively unfractionated, except for some acid springs with negative $\delta^{15}N$ values that are attributed to $NH^o_{3(g)}$ condensation. $NH_4(T)$ concentration and isotopic variations were evident spatially (between springs) and temporally (in individual springs). These variations are likely to be reflected in biomass and sediments associated with the hot springs and outflows. Elevated $NH_4(T)$ concentrations can persist for 10s to 1000s of meters in surface waters draining hot spring areas before being completely assimilated or oxidized.
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1. INTRODUCTION

Nitrogen associated with geothermal systems occurs predominantly as gaseous species dinitrogen (N_2) and ammonia ($NH_{3(g)}$), and as aqueous ammonia ($NH^o_{3(aq)}$) and ammonium ion ($NH^+_{4(aq)}$). These N species have been attributed to atmospheric, mantle and sedimentary sources (Sano et al., 1998, 2001; Fischer et al., 2002, 2009; Clor et al., 2005). Aqueous “ammonium” in natural waters commonly is reported as NH_4^+, although what is measured by ion chromatography and colorimetry is the sum of dissolved species (e.g., $NH^+_{4(aq)}$, $NH^o_{3(aq)}$, and $NH_4SO^-_{4(aq)}$), expressed here as $NH_4(T)$. $NH_4(T)$ concentrations in hot springs at Yellowstone and elsewhere are highly variable. Unusually high $NH_4(T)$ concentrations (28–57 mM $NH_4(T)$) in thermal waters at Pisciarelli, Italy, were attributed to magma degassing at depth in combination with metamorphic reactions with the carbonate basement rock (Valentino et al., 1999). Similarly, elevated $NH_4(T)$ concentrations (0.9–16 mM $NH_4(T)$) in thermal waters of the Mount Amiata area of central Italy were thought to derive from Mesozoic carbonate rocks based on correlations with both B and Cl,

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suggesting a marine origin (Minissale et al., 1997). Notably elevated aqueous NH_4(T) concentrations have also been reported for thermal waters in the northern California Coast Range (0.7–13 mM NH_4(T)) (Roberson and Whitehead, 1961) and Ketetahi Hot Springs, New Zealand (1.8–20 mM NH_4(T)) (Moore and Brock, 1981). Similarly elevated NH_4(T) concentrations (15–63 mM NH_4(T)) have been reported previously for thermal waters associated with the Washburn Hot Springs complex, Yellowstone National Park (Thompson et al., 1975, 1996; Gooch and Whitfield, 1888; Ball et al., 1998).

Nitrogen in some Yellowstone thermal waters is likely to share the same organic-rich source rocks with hydrocarbons that occur sporadically in the Yellowstone region. Allen, 1935) first proposed that elevated CH_4 (13.2%), C_2H_6 (1.15%) and NH_4(T) concentration (893 mg kg^{-1}) at Washburn Hot Springs was derived from distillation of underlying sediments. Isotopic data from C1 to C4 alkanes indicated that light hydrocarbon gases from Upper Geyser Basin, West Thumb and Mud Volcano originated from thermal alteration of sedimentary organic matter (Des Marais et al., 1981). Isotope ratios of C and H of CH_4 at Calcite Springs and Joseph's Coat Springs indicated a mixture of a volcanic source and thermogenic CH_4, thought to result from pyrolysis of buried sedimentary organic matter (Lorenson and Kvenvolden, 1993).

The N isotope ratios of NH_4(T) might be useful for determining sources of N in hot springs, but this approach has not been reported widely. In addition to possibly preserving source characteristics, NH_4(T) is subject to isotopic fractionation associated with dissolution, sorption, speciation, degassing, and oxidation in the subsurface or following spring discharge. The magnitudes of these isotope effects can be functions of temperature and pH, which vary throughout the Yellowstone thermal system. The N isotopic composition of organisms and sediments in hot spring pools and outlet streams can be useful in studies of N uptake and biological cycling (Estep and Macko, 1984; Havig et al., 2011), but the isotope effects of biological processes could be complicated by spatial or temporal variation of inorganic processes affecting N speciation and isotopic composition in the hydrothermal fluids.

The objectives of this study were to document regional patterns of NH_4(T) concentrations and isotopic compositions in Yellowstone hot springs and to interpret the geochemical processes that affect NH_4(T) concentration, speciation, and isotopic composition.

2. METHODS

2.1. Sample collection

Spring waters for this study were collected between June, 2001, and September, 2008. Thermal features were sampled in regions throughout the park, including the Lower, Midway, and Norris Geyser Basins, Mammoth Hot Springs, Washburn Hot Springs, Crater Hills, Mud Volcano, and West Thumb (Fig. 1). Sample locations are documented in a series of U.S. Geological Survey Open-File Reports (Ball et al., 2002, 2007, 2010; McCleskey et al., 2004). Water samples were collected directly from springs and geysers as close as possible to the source of discharge. Sample tubing was positioned by hand in smaller springs, and with the aid of an insulated stainless steel container attached to the end of an extendable aluminum pole in larger springs. In some cases (e.g., Steamboat Geyser), water was sampled from the source using the insulated stainless steel container. Temperature and conductivity were measured with probes placed as close as possible to the source. The pH and redox potential (electrical potential uncorrected for the reference electrode) were measured using a circulating flow cell attached to a peristaltic pump fitted with medical-grade silicone tubing. Samples for analysis of major cations, anions, trace metals, alkalinity and nitrogen species were filtered by pumping from the source with a portable peristaltic pump fitted with medical-grade silicone tubing through a 142 mm diameter plastic filter holder with a 0.1 μm mixed-cellulose–ester membrane filter. Samples for water isotopes (δ^2H and δ^{18}O) generally were collected through the 0.1 μm filter, but were collected using a 0.45 μm cartridge filter when high concentrations of particulate matter impeded filtration.

Samples for analysis of nitrogen species were transported and stored at 4 °C to minimize potential for biological transformations. In addition, splits for NH_4(T) concentration and isotopic analysis were preserved at $pH < 2$ by adding 1:9 H_2SO_4 to prevent volatilization or oxidation (Smith, 1998).

Suspended sediments for C, N and isotopic analysis were obtained from Bathtub Spring and *Mocha Facial* in Norris Geyser Basin (italics indicate an informal feature name), an unnamed spring near Calcite Hot Springs, and Sulphur Caldron in the Mud Volcano thermal area, and four features from Washburn Hot Springs. The sediments were removed from filter membranes following the collection of water samples. Suspended sediments generally consisted of fine-grained particles (<62.5 μm). Features from Washburn Hot Springs had mixed sediment grain sizes that were separated by sieving and density difference into sand (62.5 μm to 2 mm), silt (3.9–62.5 μm) and clay-sized (<3.9 μm) fractions.

Rock samples were collected from outcrops in the vicinity of Mammoth Hot Springs and from archived drill cores collected by the U.S. Geological Survey between 1967 and 1968 (White et al., 1975).

2.2. Chemical analysis

Analytical methods and data for major cations, anions, trace elements, and alkalinity are summarized elsewhere (Ball et al., 2002, 2007, 2010; McCleskey et al., 2004). Serial dilutions were analyzed for NH_4(T) using ion chromatography (Dionex 300; CS12A IonPac column and 15 mN H_2SO_4 eluent; 2% RSD; detection limit 17 μM NH_4(T)) (Smith et al., 2006). Lower concentration samples (<70 μM) were also analyzed by spectrophotometry (Alpchem RFA-300; 3% RSD; detection limit 5 μM NH_4(T)) (Antweiler et al., 1996). Acceptable NH_4(T) values acquired using ion chromatography were compared with values from the same sample acquired using spectrophotometry to