ELEVATED ARSENIC IN GROUND WATER, ESTER DOME (ALASKA)

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Abstract

Ester Dome, an upland area near Fairbanks, Alaska, was chosen for a detailed hydrogeochemical study because of the previously reported elevated As in ground water, and the presence of a large set of wells amenable to detailed sampling. Ester Dome lies within the Fairbanks mining district, where gold-bearing quartz veins, typically containing 2-3 volume percent sulfide minerals (arsenopyrite, stibnite, and/or pyrite), have been mined. Ground water at Ester Dome is circumneutral, Ca-HCO$_3$ to Ca-SO$_4$ type, and ranges from dilute (specific conductance of 48 µS/cm) to mineralized (specific conductance as high as 2070 µS/cm). In general, solute concentrations increase down gradient. Redox species indicate that the ground waters range from oxic to sub-oxic (low dissolved oxygen, iron reduction, no sulfate reduction). Waters with the highest Fe concentrations, as high as 10.7 mg/L, are the least oxygenated. Dissolved As concentrations range from < 1 to 1160 µg/L. Arsenic concentrations are not correlated with specific conductance or Fe concentrations, suggesting that neither ground-water residence time nor reductive dissolution of iron oxyhydroxides control the arsenic chemistry. Furthermore, As concentrations do not covary with other oxyanions, HCO$_3$, Mo, F, or U, such that desorption of As from clays or oxides also does not control arsenic mobility. Oxidation of arsenopyrite in the near-surface environment appears to be the primary control of dissolved arsenic in this upland area. Elevated arsenic concentrations are spatially associated with mineralized shear zones and known lode-gold localities. Furthermore, elevated antimony concentrations (as high as 59 µg/L) in some of the waters with high arsenic concentrations is consistent with this interpretation.

Introduction

Elevated As concentrations in drinking water are of international concern due to the potential health risks and widespread distribution. The occurrence of As in sedimentary aquifers in Asia has been the focus of much research because of the documented cases of arsenic poisoning of humans (Smedley and Kinniburgh, 2002). Despite some of the highest reported As concentrations, less attention has focused on elevated As concentrations associated with metallic mineral deposits because many of these occurrences are in more remote regions. As population grows and communities expand into relatively remote areas, arsenic-related problems may arise. Because ground water is the primary source of drinking water in many of these regions, understanding the processes that control As concentrations in ground water is critical.

Ester Dome, located 10 km west of Fairbanks, Alaska (Fig. 1), lies within the Fairbanks mining district and is known to contain ground water with high dissolved As concentrations. In the early 1970s, As concentrations in excess of 1 mg/L in domestic wells were reported (Harrington et al., 1978). The region was once the center of placer gold mining, and small lode mines have been worked on Ester Dome intermittently since the early1900s.

Ester Dome covers approximately 260 km^2, ranges in elevation from 180 to 720 m, and lies within the sub-arctic of interior Alaska. Ester Dome is one of several upland areas surrounding Fairbanks, which were formed by the intrusion of granites and granodiorites into various schistose units. Ester Dome is comprised of metasedimentary and metavolcanic rocks including quartz-muscovite schist, chlorite schist, magnetite-rich biotite schist, amphibolite, quartzite, calcareous schist, and marble (Newberry et al., 1996). The metamorphic units are bounded by four high-angle, northeast trending faults. In addition, Newberry et al. (1996) mapped two low-angle thrust faults on the dome, and other studies have documented numerous smaller-scale faults (Dashevsky et al., 1993; Rogers et al., 1998; Cameron, 2000). The granitoids on Ester Dome are part of the suite of ca. 90 Ma granites and granodiorites in the Fairbanks area, which are spatially and temporally related to gold mineralization (McCoy et al., 1997). On Ester Dome, lode gold deposits generally occur in quartz veins along ductile and brittle shears. The most productive deposit is the Ryan Lode (Fig. 1), which has been mined sporadically since 1912, with the greatest production occurring between 1985 and 1989. The gold is hosted in a deformed quartz vein within a shear zone and is associated with arsenopyrite and subordinate stibnite, pyrite and sulfosalts with an overall sulfide content of > 1 % (McCoy et al., 1999; Cameron, 2000). Within the shear zones, sulfides are usually crushed into finely-ground material. Vein alteration minerals include albite, sericite, ankerite, and carbonaceous material. Scorodite is often present as a weathering phase of arsenopyrite, mainly found as vein coatings, fracture fills, and breccia cement (Metz, 1991; LeLacheur, 1991).

This hydrogeochemical investigation was conducted to determine baseline conditions and to identify processes controlling the variability of As in the ground water in Ester Dome, Alaska. Twelve monitoring wells, located on

or adjacent to Ryan Lode, and 16 domestic wells were sampled quarterly to determine the spatial and temporal variability in water chemistry. Field parameters, major and trace element concentrations, and Fe and As redox species were determined. In addition, geochemical modeling was undertaken to better constrain the hydrogeochemistry of Ester Dome.
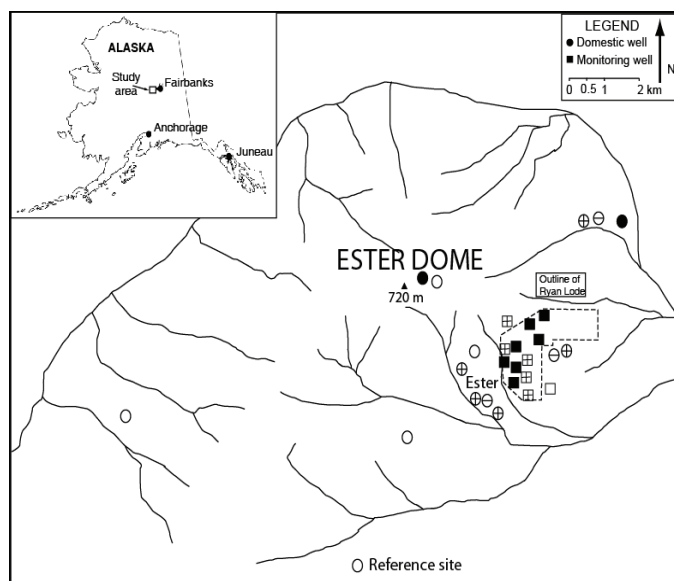
Figure 1. Map of study area with well locations coded by dissolved As concentration: open symbol, <10 μg/L; single divided symbol, 11-50 μg/L; double divided symbol, 51-200 μg/L; and closed symbol, > 200 μg/L. Dashed field outlines Ryan Lode.

Methods

Water samples were collected seasonally from water wells during 2000 and 2001. Before sampling, monitoring wells were purged of three well volumes, and pH, specific conductance and temperature were monitored after each well volume. Domestic wells were sampled using an inert plastic hose connected to the pressure tank intake. Initially, water was allowed to discharge until the pump turned on. As the water continued to discharge, specific conductance and water temperature were monitored until they were stable, usually at a water temperature between 3 and 4°C. On-site measurements of pH, specific conductance, and temperature were obtained. Water samples consisted of (1) an unfiltered, acidified sample preserved with nitric acid for total recoverable cations, (2) one filtered, unacidified sample for anion determinations and alkalinity, (3) a filtered, acidified sample preserved with ultra-pure nitric acid for dissolved cation determinations, and (4) two filtered samples, acidified with ultra-pure hydrochloric acid, for As and Fe redox determinations. Samples were filtered on site using 0.45 μm pore size capsule filters.

Analytical methods and results are presented in a USGS data report (Verplanck et al., 2003); thus, only a summary of methods is presented here. Major cations were determined by inductively-coupled plasma atomic-emission spectroscopy (ICP-AES). Minor and trace elements were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS). Concentrations of major anions were determined by ion chromatography using a Dionex 2010i™ ion chromatograph. Alkalinity was determined using an autotitrator and standardized H_2SO_4. Fe(II) redox species and total Fe, in filtered-acidified samples, were determined using a modification of the FerroZine™ colorimetric method (Stookey, 1970). As(III) species were determined by ICP-MS after ion exchange separation of the inorganic As(III) species using SAX (Strong Ion Exchange Resin) and elution with malonate/acetate buffer solution at pH 4.7. Quality-control included replicate samples, field equipment blanks, analyses by alternative methods, USGS standard reference samples, and calculation of charge imbalance. Detailed discussion is presented in Verplanck et al. (2003).

Results and Discussion

Ground water on Ester Dome is circumneutral, with pH ranging from 6.4 to 7.9, and specific conductance of these waters varies from 48 to 2070 μS/cm. Solute content does not correlate with pH variation (Fig. 2A). Overall, redox conditions are oxygenated with some mildly reducing conditions. Field Eh measurements varied from 150 to 460 mV and dissolved oxygen varied from 0.36 to 9.9 mg/L.
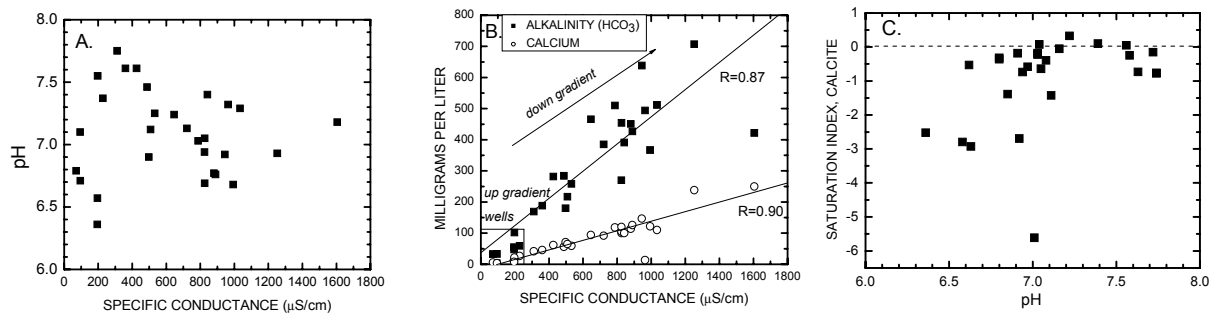
Figure 2. A. Graph displaying poor correlation between pH and specific conductance for groundwater samples. B. Graph displaying strong correlation between carbonate and dissolved calcium concentration with specific conductance. C. Variation in calcite saturation indices with pH.

Most solutes display little variation between sampling events, so to simplify this discussion the mean solute concentrations from each well will be used. Ground water on Ester Dome is $Ca-HCO_3$ to $Ca-SO_4$ type, and the major element compositions are highly variable between wells. Alkalinity and calcium concentrations covary with specific conductance (Fig. 2B), and the most dilute waters tend to be in the up gradient wells on or near the top of the dome. These constituents increase in concentration in the waters from wells along the lower part of the dome. Some major constituents follow this trend (Mg, Na, and K) although others are less well correlated with specific conductance (SO_4, Cl, and Si). When comparing the relative concentrations of SO_4, Cl, and HCO_3, monitoring wells, on or adjacent to Ryan Lode, are not systematically different from domestic wells. The range in absolute concentration of SO_4 in the monitoring wells (11 to 210 mg/L) is also similar to the range in domestic wells (1.4 to 200 mg/L). Comparing the dominant cations (Ca, Mg, Na, and K), the relative concentrations in the monitoring and domestic wells overlap. Dissolved phosphorous concentrations are low, < 0.4 µg/L, and in most wells < 0.04 µg/L.

In general, the higher-elevation wells contain the most dilute water, and the wells at or near the base of Ester Dome have water with the highest specific conductance, thus suggesting that length of flow path is an important variable. The longer the flowpath, the more opportunity for water-rock interaction. Carbonate lithologies are present within the metasedimentary rock sequence and carbonate minerals are part of the alteration assemblage surrounding the mineralized veins on the dome. To investigate the role of mineral dissolution on the evolution of water chemistry, mineral saturation indices (SI) were calculated using the computer program WATEQ4F (Ball and Nordstrom, 1991). Calcite SI values plotted as a function of measured pH show that many waters are near saturation with respect to calcite (Fig. 2C). The five samples with a calcite SI < -2 are the most dilute waters and are from sites that are on top of Ester Dome or on adjacent ridges with little up-gradient catchment area.

The concentration of total dissolved Fe varies from 0.001 to 10.7 mg/L, with the fraction of Fe(II) ranging from 0.01 to 1.0. In samples with total Fe concentrations > 1 mg/L, most is Fe(II). Samples with elevated Fe have relatively low Eh. In addition to field redox determinations, the redox potential was calculated utilizing the iron redox determinations and speciation computed with WATEQ4F. Overall, the range in calculated redox potential utilizing the Fe results, 220 to 440 mV, is similar to that for the measured values 150 to 460 mV and the Eh values for individual samples tend to correlate.

Dissolved As concentrations in ground waters from Ester Dome vary over three orders of magnitude, from < 1 to 1160 µg/L. Most water samples from Ester Dome exceed 10 µg/L, the WHO guideline value and USEPA drinking-water standard. Spatially, sampled wells with <10 µg/L As are widely distributed (Fig. 1). The As concentration of water collected at our reference site, located on a ridge adjacent to Ester Dome, was < 7.0 µg/L for all sampling trips. Two sites on or near the top of Ester Dome had < 6 µg/L As. Another site with a low As concentration lies on the northwest flank of Ester Dome, away from any known mineralization. Sites with slightly elevated (10-50 µg/L) and moderately elevated (50-200 µg/L) dissolved As concentrations are located in the eastern section of Ester Dome near mapped faults and known Au mineralization. Sites with the highest As concentrations (> 200 mg/L) cluster near the Ryan Lode deposit, but a few others are located elsewhere in the study area. One site with elevated As is a domestic well on top of Ester Dome along a mapped fault and adjacent to a lode-Au locality. The site with the highest dissolved arsenic concentration (1160 µg/L) is located along the projection of the Ryan Lode shear zone.

Unlike many major constituents, dissolved As concentrations do not covary with specific conductance (Fig. 3A). Furthermore, dissolved As concentrations do not covary with total dissolved Fe or SO_4 (Fig. 3B). Similar to other redox indicators, the ratio of As(III) to As(V) varies, but in general, the highest As concentrations are

found in ground waters that are dominated by As(V). Dissolved As concentrations are poorly correlated to other oxyanions (HCO_3, Mo, F, and U; Fig. 3C).
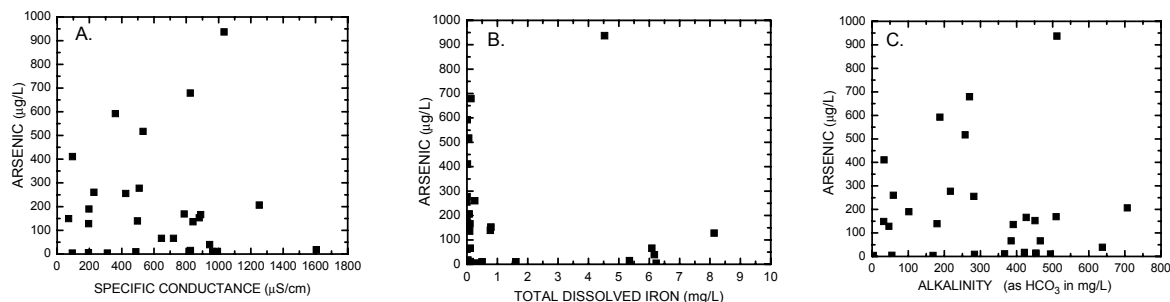
Figure 3. Dissolved As variation of groundwater and (A) specific conductance, (B) Fe, and (C) alkalinity.

Because dissolved As concentrations do not correlate with specific conductance, either the source of As is not evenly distributed throughout Ester Dome, or other processes control the concentration of As in ground water. Redox state of ground water has been shown to be a primary control of As, but depending on the hydrogeochemical environment, elevated As concentrations are found in either oxygenated or reduced waters. In these circumneutral waters, dissolved Fe concentration is strongly controlled by redox conditions with the highest dissolved Fe concentrations were determined to be in the least oxygenated waters and, in these waters, Fe(II) is the dominant species. In contrast, elevated dissolved As concentrations were not found in the more reduced waters, suggesting that reductive dissolution of Fe is not the dominant process controlling the dissolved As concentration.

In oxygenated ground water, two geochemical processes have been proposed to account for elevated As concentrations. In mineralized and mined areas, oxidation of arsenopyrite or arsenian pyrite is a primary source of As (for example: Williams et al., 1996; Boyle et al., 1998). Gold mineralization hosted by metasedimentary rocks in the Fairbanks mining district is intimately associated with arsenopyrite- and stibnite-bearing quartz veins, and such veins on Ester Dome are within shear zones cutting the upland at Ryan Lode and elsewhere. The arsenopyrite is fine-grained due to deformation along the shears, providing a large surface area available for oxidation. Previous studies in the area also have proposed that oxidation of arsenopyrite is the primary source of dissolved As (Hawkins et al., 1982). Many of the wells contain measurable dissolved Sb, as high as 59 µg/L, which is consistent with the interpretation that oxidation of sulfides from the gold-bearing quartz veins contributes to the chemistry of these ground waters.

A second process that has been proposed for elevated As concentrations in oxygenated ground waters is desorption of As from Fe and manganese oxides or clays (Smedley et al., 2002). The ground waters described in Smedley et al. (2002) typically have pH values between 7 and 9 and the dissolved As concentration should correlate with other anion and oxyanion elements (B, F, HCO_3, Mo, and V). At pH values between 8 and 9, As and other oxyanions are released from Fe and Mn oxides by desorption (Smedley et al., 2002). Our data suggest that desorption is not a significant process at Ester Dome because the highest measured pH was 7.9 and dissolved As concentrations do not correlate with other anions and oxyanions. Furthermore, comparison between As concentration in filtered and unfiltered samples shows that, for some wells, the unfiltered samples have substantially higher concentrations suggesting that As is still strongly associated with the solid phase.

Many of the samples with elevated As concentrations are from wells within a few hundred meters of the Ryan Lode deposit. It is difficult to determine what fraction of the mobilized As is from natural weathering of mineralized rock and what fraction results from increased surface exposures due to mining disturbances. Two wells upstream from the mine property have dissolved As concentrations as high as 387 and 161 µg/L. The range in dissolved As concentrations in monitoring wells on the mine site is 9.2 to 845 µg/L, with a mean value of 272 µg/L. The highest concentration of dissolved As, 1160 µg/L, occurred in a well at the base of Ester Dome along the projection of the Ryan Lode shear zone.

Conclusions

The focus of this hydrogeochemical investigation was to determine baseline conditions in an area of naturally-high, ground-water As concentrations and to identify processes controlling the variability of As in the ground water in the Ester Dome flow net. Oxidation of arsenopyrite in sheared gold-bearing quartz veins is the primary source of elevated As concentrations in ground water at Ester Dome. Measurable dissolved Sb in many samples

is consistent with this interpretation. Reduction of iron oxides is not responsible for the elevated As because these waters are oxygenated and the dissolved As concentration does not correlate with Fe variations. Furthermore, desorption of As from iron or manganese oxides or clays is also not responsible for the elevated As because of the lack of correlation with other oxyanions that should behave similarly. Determining the fractional contribution of dissolved As from mining activity was beyond the scope of this study. Some wells up gradient from mining disturbances had elevated As, as high as 161 and 387 µg/L, documenting an elevated lithologic baseline of dissolved As in this area.

Acknowledgements

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