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Effect of Ultramafic Intrusions and Associated Mineralized Rocks on the Aqueous Geochemistry of the Tangle Lakes Area, Alaska

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U.S. Department of the Interior U.S. Geological Survey

Cover. Photograph of the Tangle Lakes area, Alaska (U.S. Geological Survey, photograph by Bronwen Wang).

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Conversion Factors

Inch/Pound to SI

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=(1.8×°C)+32

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

 $°C=(°F-32)/1.8$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at $25 °C$).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Effect of Ultramafic Intrusions and Associated Mineralized Rocks on the Aqueous Geochemistry of the Tangle Lakes Area, Alaska

By Bronwen Wang¹, Larry P. Gough¹, Richard B. Wanty¹, Gregory K. Lee¹, James Vohden¹, J. Michael O'Neill¹, and L. Jack Kerin2

Abstract

Stream water was collected at 30 sites within the Tangle Lakes area of the Delta mineral belt in Alaska. Sampling focused on streams near the ultramafic rocks of the Fish Lake intrusive complex south of Eureka Creek and the Tangle Complex area east of Fourteen Mile Lake, as well as on those within the deformed metasedimentary, metavolcanic, and intrusive rocks of the Specimen Creek drainage and drainages east of Eureka Glacier. Major, minor, and trace elements were analyzed in aqueous samples for this reconnaissance aqueous geochemistry effort. The lithologic differences within the study area are reflected in the major-ion chemistry of the water. The dominant major cation in streams draining mafic and ultramafic rocks is Mg^{2+} ; abundant Mg and low Ca in these streams reflect the abundance of Mg-rich minerals in these intrusions. Nickel and Cu are detected in 84 percent and 87 percent of the filtered samples, respectively. Nickel and Cu concentrations ranged from $Ni < 0.4$ to 10.1 micrograms per liter (μ g/L), with a median of 4.2 μ g/L, and Cu <0.5 to $27 \mu g/L$, with a median of 1.2 $\mu g/L$. Trace-element concentrations in water are generally low relative to U.S. Environmental Protection Agency freshwater aquatic-life criteria; however, Cu concentrations exceed the hardness-based criteria for both chronic and acute exposure at some sites. The entire rare earth element (REE) suite is found in samples from the Specimen Creek sites MH5, MH4, and MH6 and, with the exception of Tb and Tm, at site MH14. These samples were all collected within drainages containing or downstream from Tertiary gabbro, diabase, and metagabbro (Trgb) exposures. Chondrite and source rock fractionation profiles for the aqueous samples were light rare earth element depleted, with negative Ce and Eu anomalies, indicating fractionation of the REE during weathering. Fractionation patterns indicate that the REE are primarily in the dissolved, as opposed to colloidal, phase.

Introduction

Since 1991, several companies have explored the Tangle Lakes area, Alaska, for economic mineral deposits. Most of the effort has been focused on the Fish Lake intrusive complex (Bittenbender and others, 2007). Because of the upturn in exploration, drilling, and mineral-resources evaluations in the area, the U.S. Geological Survey (USGS), in collaboration with the Alaska Department of Natural Resources (ADNR), conducted reconnaissance sampling in June 2006 to evaluate the effects of lithology and mineralized rock on the aqueous geochemistry of the region. The primary focus of this study was an aqueous chemical characterization of first-order streams in the headwaters of the Delta River.

Study Area

The study area, located about 30 kilometers (km) westnorthwest of the community of Paxson (fig. 1), is part of the Tangle Lakes area of the Delta mineral belt (Dashevsky and others, 2003) that lies south of the Alaska Range in southcentral Alaska. Eureka Creek bisects the study area and flows east to the Delta River, which in turn drains north through the Alaska Range. The landscape varies from scrub-vegetated hills to high, rugged, barren mountains. Most of the study area is above tree line and the alpine tundra vegetation is composed of herbaceous flowering plants (forbs), herbs, and low shrubs (for example, *Salix*, *Betula*, and *Spirea*). Ground cover is composed of forbs, mosses, and lichens.

Early geologic investigations in the Rainy Creek area and Amphitheater Mountains were by Rose (1965). Stout (1976) summarized and integrated the geology of the intervening Eureka Creek area with the work by Rose in the north and south. The Nikolai Greenstone (TrN) forms the bulk of the Amphitheater Mountains (fig. 1), whereas to the east and southeast of Eureka Glacier, Paleozoic sedimentary and volcaniclastic rocks (Pzsv), Triassic mafic and ultramafic rocks (Trum), and Mesozoic granitoid intrusions (Mzgr) are

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exposed. Exposures of Nikolai Greenstone, Paleozoic sedimentary and volcaniclastic rocks, and Triassic mafic and ultramafic rocks also occur along the Specimen Creek drainage basin as do gabbro, diabase, and metagabbro (Trgb). The most extensive exposures of the mafic and ultramafic rocks within the study area are found between the Amphitheater Mountains and Eureka Creek. Stout (1976) referred to these exposures as the Fish Lake intrusive complex.

Disseminated chromite in a layered mafic-ultramafic complex and Ni-Cu-platinum group elements (PGE) in differentiated mafic-ultramafic sill occurrences are found within the Fish Lake intrusive complex (fig. 1) (Bittenbender and others, 2007; Mineral Resource Data System: Alaska). Nickel-Cu-PGE, low sulfide gold-quartz veins, disseminated chromite, gold placer, and Cu-skarn mineralized rocks are found in the Specimen Creek watershed (fig. 1) (Bittenbender and others, 2007; U.S. Geological Survey, 2011). The phosphate mineral monazite was found in heavy mineral panned concentrates from the west fork of Specimen Creek (Wang and others, 2008). The monazite family typically contains the rare earth elements (REE) La, Ce, and Nb, as well as minor amounts of other REE (Rosenblum and Fleisher, 1995). Interest in REE mobility in riverine environments has increased in since the 1980s with studies showing REE fractionation and mobility in groundwater, surface water, and thermal springs (Keasler and Loveland, 1982; Cullers and others, 1987; Goldstein and Jacobsen, 1988; Elderfield and others, 1990; Smedley, 1991; Ohlander and others, 1996; Morey and Setterholm, 1997; Banks and others, 1999; Tricca and others, 1999; Johannesson and others, 2000; Eppinger and others, 2007).

Sampling Sites

Sampling focused on streams draining the mafic and ultramafic rocks of both the Fish Lake intrusive complex and the area east of Fourteen Mile Lake, as well as the sedimentary, volcaniclastic, mafic and ultramafic, and intrusive rocks of the Specimen Creek drainage and drainages east of Eureka Glacier. Thirty sites were distributed as follows: (1) along Specimen Creek drainage (six sites), (2) in streams draining the mafic/ultramafic rocks of the Fish Lake intrusive complex (17 sites), (3) drainages in the vicinity of Fourteen Mile Lake (four sites), and (4) drainages east of Eureka Glacier (three sites) (fig. 1). Sampling was performed from June 20 to 25, 2006. Weather conditions varied during sampling (fig. 2). Snow was present both on the slopes and in the drainages at higher elevations (figs. 2*A* and *B*). At lower elevations, snow was present only in patches on the hill slopes (fig. 2*C*). A late season snow storm occurred on June 22, and by June 23, the study area was covered in about 18 inches of snow (fig. 2D). Snow persisted on the ground through the rest of the sampling period.

Sites MH01 through MH06 are located in the Specimen Creek drainage (fig.1). Sites MH01 and MH05 are on the west fork of Specimen Creek with site MH01 upstream of MH05. Iron staining is evident on the slopes above site MH01 (fig. 2*A*). An inactive placer mine (activity predates 1965, Bittenbender and others, 2007) lies between MH01 and MH05 (fig.1). Au, Ag, and PGE were the primary commodities with ancillary Cu, Ni, and Zn (Bittenbender and others, 2007; U.S. Geological Survey, 2013) from this inactive operation. In addition, Ni-Cu-PGE in differentiated mafic-ultramafic sill, low sulfide gold-quartz vein, chromite disseminated in mafic/ ultramafic rock occurrences and a copper skarn prospect are found to the west of MH01 (fig. 1). MH02 and MH03 are sequential sites on the east fork of Specimen Creek, with site MH02 upstream of MH03. Copper skarn Ni-Cu-PGE and chromite disseminated occurrences occur on a ridge south of site MH02 (fig. 1). Site MH04 is located on Specimen Creek below the confluence of Specimen Creek's east and west forks (note that this places site MH05 on the west fork Specimen Creek upstream of MH04). MH06 is the most downstream site on Specimen Creek and is upstream of the confluence with Eureka Creek. The Specimen Creek sites are the only sequence of sites collected from upstream to downstream on a single drainage in this study.

Sites MH07–MH13, MH15–MH18, MH20, MH23–24, and MH26–MH28 are located on streams draining the mafic/ ultramafic rocks of the Fish Lake intrusive complex. Sites MH07, MH08, and MH09 are located in the vicinity of known chromite mineralized rock. Sites MH07 and MH08 are located near a scarp with visible iron staining. Site MH24 is located on a stream which drains Nikolai Greenstone rather than the mafic and ultramafic rocks of the Fish Lake intrusive complex. Sites MH14, MH21–MH22, and MH25 are located on streams draining the intrusive and surficial deposits near Fourteen Mile Lake; sites MH19, MH29, and MH 30 are on streams draining the area east of Eureka Glacier.

Sample Collection and Methods

Sample collection and analysis is briefly described here; details of sampling, quality assurance samples, and methods of analysis are published in Wang and others (2008). Water samples were collected as stream depth- and width-integrated composite samples. Samples collected for major, minor, and trace-element analyses were filtered through a 0.45 μ m syringe-end filter. Samples for cation analyses were stabilized with ultra-high-purity HNO_3 ; samples for anion $(SO_4^{2-}, Cl^-,$ F, NO₃) analyses were filtered but not acidified. Alkalinity samples were either filtered and not acidified or unfiltered and not acidified. Cation concentrations were determined by inductively coupled plasma-mass spectrometry (ICP-MS), and major anions were determined by ion chromatography (IC) (Lamothe and others, 2002; Theodorakos, 2002). Alkalinity was determined using a preset endpoint (pH 4.5) autotitration system (Theodorakos, 2002). Water conductivity, pH, and temperature were measured in the field using standard pH and conductivity meters and submersible thermometers. Stream

Figure 2. Site photographs illustrating spatial and temporal variability during stream-water sampling in the Tangle Lakes area, Alaska, during June 2006. Sampling condition at high elevation sites on June 20—(*A*) site MH01 and (*B*) site MH02. Sampling conditions at low elevation sites on June 21—(*C*) MH10. Sampling conditions at lower elevation sites on June 22—(*D*) MH15 and June 23 (*E*) MH13. See figure 1 for site locations. (U.S. Geological Survey photographs by Bronwen Wang (*A*–*D*) and Jim Vohden (*E*).)

discharge was measured using the cross-sectional area of the stream and velocity determined by a hand-held flow meter.

Data Handling

For those elements where at least 75 percent of the data are above the analytical detection limit, the Kaplan-Meier method for censored data, that is data with values less than the detection limit of the analytical method, is used to calculate the median concentration and interquartile range (the difference between the $75th$ and $25th$ quartiles) (Helsel, 2005). To compare stream water metal concentrations with the U.S. Environmental Protection Agency's (EPA) aquatic life criteria, hardness must be considered for Cd, Cr, Cu, Ni, and Zn. Hardness was calculated as the sum of the Ca^{2+} and Mg^{2+} concentrations in the $0.45 \mu m$ filtered sample and expressed as milligrams of CaCO₃ per liter (Greenberg and others, 1985).

Instantaneous loads were calculated after Kimball and others (2004):

$$
Ma=CaQa,
$$
 (1)

where

REEs are normalized to chondrite (Goldstein and Jacobsen, 1988; McLennan, 1989) to account for the inherent difference in abundance of the individual elements in the lanthanide series. Selected samples (see discussion) were also normalized to the REE available for unit Trgb in the Tangle Lakes area

(Bittenbender and others, 2003). Fractionation of REEs in a given sample is determined by the normalized (La/Yb) ratio:

$$
(La/Yb)_{n} = (La/Yb)_{\text{sample}} / (La/Yb)_{\text{normalizing component}}, \qquad (2)
$$

where the normalizing component was either chondrite or the Trgb unit. (La/Yb) ^{>1} indicates light rare earth element $(LREE)$ enrichment, $(La/Yb)_n$ ⁻¹ indicates LREE depletion, and (La/Yb) _n \cong 1 indicates little REE fractionation in the sample relative to the normalizing component. Ce and Eu are more redox active than the other REE, and the redox behavior of these elements can lead to either positive or negative anomalies (Banks and others, 1999), depending on environmental conditions. Ce and Eu anomalies typically are expressed as Ce^* and Eu/Eu^{*}, given by $Ce^* = 3Ce_n/(2La_n + Nd_n)$ and

 $Eu/Eu^* = Eu_n/(Sm_n \times Gd_n)^{0.5}$, respectively, where the subscript "n" denotes the chondrite or Trgb normalized concentration (Goldstein and Jacobsen, 1988; Elderfield and others, 1990). Again, values less than and greater than unity are called negative and positive anomalies, respectively.

Results and Discussion

The pH and conductivity of the streams range from near neutral to alkaline (pH 6.8 to 8.1, where pH 7 is neutral) and from 18.5 to 258 microsiemens per centimeter $(\mu S/cm)$, respectively (table 1). The highest conductivity values are from the west fork of Specimen Creek at sites MH01 and MH05 (conductivity 224 and 258 μ S/cm, respectively) and at

Table 1. Summary statistics for field parameters (conductivity, pH, and water temperature) and major, minor, and trace element chemistry in filtered (0.45 micrometer, μ m) and unfiltered water samples from the Tangle Lakes area, Alaska.

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Table 1. Summary statistics for field parameters (conductivity, pH, and water temperature) and major, minor, and trace element chemistry in filtered (0.45 micrometer, μ m) and unfiltered water samples from the Tangle Lakes area, Alaska.—Continued

[LLD, lower limit of determination; min, minimum;, max, maximum; IQR, interquartile range; – not calculated censored value exceeded 25 percent; °C, Celsius; µS/cm, microsiemens per centimeter; mg/l, milligrams per liter; µg/L, micrograms per liter; NA, not applicable;*, Theodorakos, P.M., 2002]

Table 1. Summary statistics for field parameters (conductivity, pH, and water temperature) and major, minor, and trace element chemistry in filtered (0.45 micrometer, µm) and unfiltered water samples from the Tangle Lakes area, Alaska.—Continued

sites MH07 and MH08 on the knob where the vertical angle bench mark (VABM) "Wild" is set (hereafter called Wild Knob) (151 and 159 μ S/cm, respectively).

The Specimen Creek and Wild Knob sites differ markedly in their major ion compositions. Bicarbonate dominates the major anion composition of Wild Knob samples (91 percent to 92 percent of the anionic charge), and Mg^{2+} dominates the major cation composition (81 percent of the cationic charge). In the Specimen Creek samples, SO_4^2 -either contributes substantially to or dominates the anionic charge (42 percent and 64 percent for site MH01 and MH05, respectively), and $Ca²⁺$ dominates the cationic charge (53 percent and 61 percent for site MH01 and MH05, respectively). These sites illustrate a broader trend in the major ion composition of the various sampling locations. Generally, the major cation and anion compositions in samples from the Fish Lake intrusive complex and Fourteen Mile Lake are dominated by Mg²⁺ and HCO_3 , respectively (fig. 3). The primacy of cationic Mg^{2+}

Figure 3. Piper diagram showing proportion of major elements for each filtered water sample from the Tangle Lakes area, Alaska, grouped by geographic area.

in these waters reflects the presence of the mafic and ultramafic rocks in these drainages. In contrast, samples from the Specimen Creek drainage and East Eureka Glacier drainage have major ion compositions in which the cations are either dominated by Ca^{2+} or are an approximately equal mixture of Ca^{2+} and Mg²⁺, and the anions are dominated by SO_4^2 ⁻ or an equal mixture of SO_4^{2-} and HCO_3^- (fig. 3).

The minor and trace elements Al, Ba, Cu, Ni, Rb, and Sr are detected in at least 75 percent of the $0.45 \mu m$ filtered samples from the study area (table 1). The concentrations of these elements range from Al<2 to 161 μ g/L, with a median of 9.7 μ g/L; Ba<0.2 to 36 μ g/L, with a median of 3.9 μ g/L; Cu < 0.5 to 27 μ g/L, with a median of 1.2 μ g/L; Ni< 0.4 to 10.1μ g/L, with a median of 4.2 μ g/L; Rb 0.07 to 3.11 μ g/L, with a median of $0.26 \mu g/L$; and Sr 2.8 to 166 $\mu g/L$, with a median of 11.3 μ g/L. Other frequently detected elements are Co (0.02 to 2.24 µg/L, with 69 percent detection), Sc (0.6 to 2.1 μ g/L, with 62 percent detection), and Zn (<0.5 to 7.9 μ g/L, with 62 percent detection) (table 1). In addition to Cu, Ni, and Zn, elements that are both of regulatory concern and commonly associated with mineralized rock are As, Cd, Cr, and Pb. Concentrations range from <1 to 79 μ g/L for As, <0.02 for 0.1 μ g/L for Cd, and<1 to 2.4 μ g/Cr (table 1). Elevated Pb $(11.4 \mu g/L)$ was detected in a sample from site MH20; however, sample contamination is suspected in this sample (Wang and others, 2008). Relatively similar concentrations of Ni were found in each of the focus areas except Eureka Glacier (fig. 4*A*), whereas the highest concentrations for Cu, Co, Cd, and Zn were found in Specimen Creek (fig. 4*B–E*) and the highest concentrations of As, Sb, and Cr were found at sites MH07and MH08 on Wild Knob (fig. 4*F–H*). The presence of Cr in samples from sites MH07 and MH08 likely reflects close interaction of the aqueous system with the disseminated chromite occurrences in the area (fig. 1). Site MH19 also has elevated concentrations of Cr, as well as As and Sb, relative to the rest of the sites. Only Ni-Cu-PGE mineralized rock has been reported in the vicinity of MH19, but the aqueous signature suggests that chromite mineralized rock may be present in the vicinity of site MH19.

Arsenic, Cd, Cr, Cu, Ni, and Zn have freshwater aquaticlife criteria established by EPA (U.S. Environmental Protection Agency, 1986, 2001). These criteria are the Criterion Continuous Concentration (CCC) and Criterion Maximum Concentration (CMC). The CCC is the highest concentration

of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect, and the CMC is the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect for freshwater aquatic organisms. For Cd, Cr^{+3} , Ni, and Zn the criteria are hardness dependent. For Cu, the EPA has adopted a criterion based on a biotic ligand model that accounts for both the hardness and the dissolved organic carbon content (U.S. Environmental Protection Agency, 2007). Dissolved organic carbon concentrations are not available for this dataset so the older, hardness-based criteria (U.S. Environmental Protection Agency, 1986) are used for comparative purposes. The hardness of the waters in the study area encompasses a wide range (4 to 120 micrograms per liter, mg/L, as $CaCO₃$) Arsenic concentrations are below both the CCC and CMC for all sites, as are Cd, Cr, Ni, and Zn concentrations compared to their respective hardness adjusted CCC and CMC values. Cu, however, exceeded both the hardness based CCC and CMC at sites MH05, MH04, and MH06 on Specimen Creek and at site MH14 near Fourteen Mile Lake (fig. 5).

Element concentrations in the stream water indicate the amount immediately available for biotic uptake, but the instantaneous load, given as mass per unit time, describes the total mass transported in a stream and, because of differences in discharge rates, is useful for comparing the mass differences among sites (Kimball and others, 2004). Discharge ranges from 0.6 liters per second (L/s) at site MH08 to 566 L/s at site MH04 (fig. 6). Specimen Creek has the three highest discharge rates for the sites sampled, giving rise to the highest elemental loads of Cu, Ni, and Sb for the study area (fig. 7*A*, *B*, and *D*). The highest As loads are found in Specimen Creek and also at sites MH07 and MH19 (fig. 7*C*).

The elemental load increases between sites MH01and MH05 on the west fork of Specimen Creek for Cu, Ni, As, and Sb (fig. 7*A–D*). No surface water input occurs between these two sites, and the increased load reflects a groundwater contribution. Ni and Sb loads increase again between sites MH05 and MH04, reflecting the Ni and Sb contribution from the east fork of Specimen Creek (site MH03 on the east fork above the confluence). In contrast to Ni and Sb, As and Cu loads decreased between sites MH05 and MH04 (fig. 7*A* and *C*). Cu, Ni, As, and Sb loads all decrease between sites MH04 and MH06 (fig. 7*A*–*D*). Load decreases result from elemental loss from the water by physical, chemical, or biological

Figure 4. Distribution of selected element concentrations in micrograms per liter (µg/L) measured in filtered streamwater samples from the Tangle Lakes area, Alaska. Elements shown in *B–E* have their highest concentrations in the Specimen Creek Sites. Specimen Creek sites are given in the downstream sequence with MH01 and MH05 on west fork, MH02 and MH03 on an east fork, MH04 on the main stem below the confluence of the two forks with MH06 on the main stem below MH04. Elements shown in *F–H* have their highest concentrations at sites 7 and 8. *A*, Distribution of Ni concentration; *B*, distribution of Cu concentration; *C*, distribution of Co concentration; *D*, distribution of Cd concentration; *E*, distribution of Zn concentration; *F*, distribution of Sb concentration; *G*, distribution of As concentration; and *H*, distribution of Cr concentration.

Figure 4. Distribution of selected element concentrations in micrograms per liter (µg/L) measured in filtered streamwater samples from the Tangle Lakes area, Alaska. Elements shown in *B–E* have their highest concentrations in the Specimen Creek Sites. Specimen Creek sites are given in the downstream sequence with MH01 and MH05 on west fork, MH02 and MH03 on an east fork, MH04 on the main stem below the confluence of the two forks with MH06 on the main stem below MH04. Elements shown in *F–H* have their highest concentrations at sites 7 and 8. *A*, Distribution of Ni concentration; *B*, distribution of Cu concentration; *C*, distribution of Co concentration; *D*, distribution of Cd concentration; *E*, distribution of Zn concentration; *F*, distribution of Sb concentration; *G*, distribution of As concentration; and *H*, distribution of Cr concentration.—Continued

Figure 5. Ratio of the copper (Cu) concentrations of the 0.45 micrometer (µm) filtered stream-water samples from the Tangle Lakes area, Alaska, to the hardness-adjusted U.S. Environmental Agency aquatic-life criteria. Solid and open bars are the ratio of the Cu concentration, showing the criteria maximum concentration (CMC) and the criterion continuous concentration (CCC), respectively. Values greater than 1 exceed the hardness-adjusted criteria. Specimen Creek sites are given in the downstream sequence with MH01 and MH05 on the west fork, MH02 and MH03 on the east fork, MH04 on the main stem below the confluence of the two forks, and MH06 on the main stem below MH04.

Figure 6. Distribution of discharge in liters per second (L/s) among stream-water sampling sites in the Tangle Lakes area, Alaska. Specimen Creek sites are given in the downstream sequence with MH01 and MH05 on west fork, MH02 and MH03 on an east fork, MH04 on the main stem below the confluence of the two forks with MH06 on the main stem below MH04.

Figure 7. Distribution of selected elemental loads in micrograms per liter (µg/s) among stream-water sampling sites in the Tangle Lakes area, Alaska. *A*, distribution of Cu load; *B*, distribution of Ni load; *C*, distribution of As load; and *D*, distribution of Sb load.

processes (Kimball and others, 2004). Discharge decreases between sites MH04 and MH06 (fig. 6) indicating loss of water and dissolved constituent load to the mixing zone of the shallow groundwater and surface water systems called the hyporheic zone.

All the elements of the REE suite (La to Yb) are detected in samples from Specimen Creek sites MH5, MH4, and MH6 and, with the exception of Tb and Tm, at site MH14 (fig. 8).

The concentrations of the various REE at these sites are within the range found in other rivers (table 2). REE concentration at all other sites were near or below the detection limit for most of the REE elements (Wang and others, 2008).

Figure 8. Rare earth element (REE) concentrations in micrograms per liter (µg/L) for Specimen Creek stream-water sampling sites MH05, MH04, and MH06, and Fourteen Mile Lake site MH014 in the Tangle Lakes area, Alaska. The Specimen Creek sites are listed in the downstream sequence.

Yellow monazite was found in sediment-panned concentrates from the east fork of Specimen Creek (Wang and others, 2008). The monazite mineral family typically contains La, Ce, and Nb, as well other REE (Rosenblum and Fleisher, 1995), and the waters in Specimen Creek reflect the presence of REE bearing minerals. Samples of the Trgb rock unit collected just east of Specimen Creek by the Bureau of Land Management had the highest REE concentration for the lithologies in the study area (Bittenbender and others, 2003). The Trgb unit occurs within the Specimen Creek and the Fourteen Mile Lake drainages. All sites with detectable concentrations across the REE sequence are located within or downstream of mapped

exposures of the Trgb unit (fig. 1).

The distribution of REEs in water and sediment depends on the natural variation in the elemental abundance of the REE suite, the distribution and fractionation characteristics of the geologic material, the varying solubility of REE-containing mineral phases during weathering, and the formation and presence of secondary minerals and colloidal matter (Banks and others, 1999). To account for the inherent difference in abundance of the individual REE elements the concentrations are normalized to chondrite. Chondrite normalized patterns for the Trgb rock samples were LREE enriched ((La/Yb)n range 1.6 to 4.1) with a negative Ce anomaly (Ce* range 0.1 to 0.3) and no to slightly positive Eu anomaly (Eu/Eu* range 1.0 to 1.5) (fig. 9). Samples from Specimen Creek and MH14 are LREE enriched relative to chondrite ((La/Yb)n range 1.2 to 2.0 for the Specimen Creek sites and 1.7 for site MH14) with a negative Ce anomaly (Ce* of 0.4 and 0.8 for Specimen Creek sites and MH14, respectively), and a negative Eu anomaly (Eu/Eu* between 0.5 and 0.8 for Specimen Creek and 0.6 for MH14).

In addition to chondrite, the REE concentrations of Specimen Creek and MH14 samples were also normalized using the range of REE values found in the Trgb unit (fig. 10). The resulting fraction Trgb normalized profiles for the aqueous phase were strongly LREE depleted $((LaYb)_n$ range 0.03 to 0.3) with negative Ce and Eu anomalies.

Table 2. Range of rare earth element (REE) concentrations reported in the literature and in this study for stream-water samples from the Tangle Lakes area, Alaska.

| [REE concentrations in nanograms per liter (ng/L) ; -, no data] | | | |
|---|--|--|--|

1 (1) Goldstein and Jacobsen (1988); (2) Tricca and others (1999); (3) Elderfield and others (1990); (4) Wang and others (2004); (5) Specimen Creek sites MH04, MH05 and MH06, this study; (6) Site MH14, this study.

Figure 9. Chondrite normalized rare earth element (REE) profiles for the Trgb unit, Specimen Creek sites MH05, MH04, and MH06, and for site MH014 in the Tangle Lakes area, Alaska. Data for the Trgb unit from Bittenberg and others (2003). Dashed line indicates gaps in sequence due to concentrations below the detection limit.

Figure 10. Envelope of Trgb normalized rare earth element (REE) patterns for Specimen Creek and site MH14 in the Tangle Lakes area, Alaska. Normalizing concentrations used were the low and high range of Bureau of Land Management's samples (sample numbers10032 and10069, respectively, Bittenburg and others, 2003). Dashed line indicates gaps in sequence due to concentrations below the detection limit in either the aqueous phase (purple) or the Trgb unit (black).

These profiles indicate fractionation of the REE during the weathering of, and transport from, the likely source rock. REE fractionation pattern in rivers can be affected by the presence of colloidal matter. Fractionation between the colloidal and dissolved phase generally produces a flat or light REE enriched profile without a Ce anomaly (or with a slightly negative Ce anomaly) in the colloidal phase and a light REE depleted profile with a strongly negative Ce anomaly in the dissolved phase (Ingri and others, 2000; Wang and others 2004). Our samples were filtered to $0.45 \mu m$, and the light REE pattern observed in the Specimen Creek sites is consistent with dissolved phase fractionation patterns.

Summary

The spatial distribution of major ions in waters of the Tangle Lakes area reflects the dominant lithology in the drainages. Samples collected near the Fish Lake intrusive complex and near Fourteen Mile Lake typically are $Mg-HCO₃$ to Mg-Ca-HCO₃ waters. The dominance of Mg water is consistent with the high-Mg content of the mafic and ultramafic rocks present in these drainages. In contrast, samples from Specimen Creek drainage and Eureka Glacier drainages have major ion compositions where the cations are either dominated by Ca or are approximately equi-mixtures of Ca and Mg, and anions are dominated by SO_4^{2-} or equal mixtures of SO_4^{2-} and HCO_3^- , reflecting the more complex and locally carbonate-rock bearing geology of these areas.

Trace-element concentrations in water are generally low relative to the EPA freshwater aquatic-life criteria; however, the Cu concentration exceeds the EPA hardness-based criteria for acute and chronic exposure at some sites. Cu and Ni are associated with much of the known mineralized rock in the study area and Cu and Ni are detected in water samples from throughout the study area. Concentrations of Cu are highest in the Specimen Creek drainage, whereas Ni was more uniformly distributed throughout the study area. Although Ni concentrations were relatively uniform among the different sampling regions, the largest Ni loads are found along Specimen Creek. Two sites (MH07 and MH08) on Wild Knob have a distinctive aquatic signature with elevated As, Sb, and Cr concentrations. These samples likely reflect the presence of the disseminated chromite mineralized rock of Wild Knob. Site MH19 also has elevated chromite concentrations, along with elevated concentrations of As and Sb. This aqueous signature suggests that undocumented chromite mineralized rock may be present in the vicinity of site MH19.

Site MH05 on Specimen Creek's west fork and the two sites along the main stem (sites MH04 and MH06) had detectable concentrations of the entire suite of REE. Samples from Specimen Creek are LREE enriched relative to chondrite, have negative Ce fractionation, and little to no Eu fractionation. Relative to the likely source rock, the aqueous REE profiles are LREE depleted, with negative Ce and Eu anomalies. This fractionation pattern is consistent with a dissolved, as opposed to colloidal, phase fractionation pattern.

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