A Geochemical Perspective of Red Mountain—An Unmined Volcanogenic Massive Sulfide Deposit in the Alaska Range

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The U.S. Geological Survey (USGS) has investigated the environmental geochemistry of a group of unmined volcanogenic massive sulfide (VMS) deposits in the Bonnifield mining district, Alaska Range, east-central Alaska. The spectacularly colored Red Mountain deposit is the best exposed of these and provides excellent baseline geochemical data for natural environmental impacts of acidic rock drainage, metal dissolution and transport, and acidic salt and metal precipitation from an exposed and undisturbed VMS deposit.

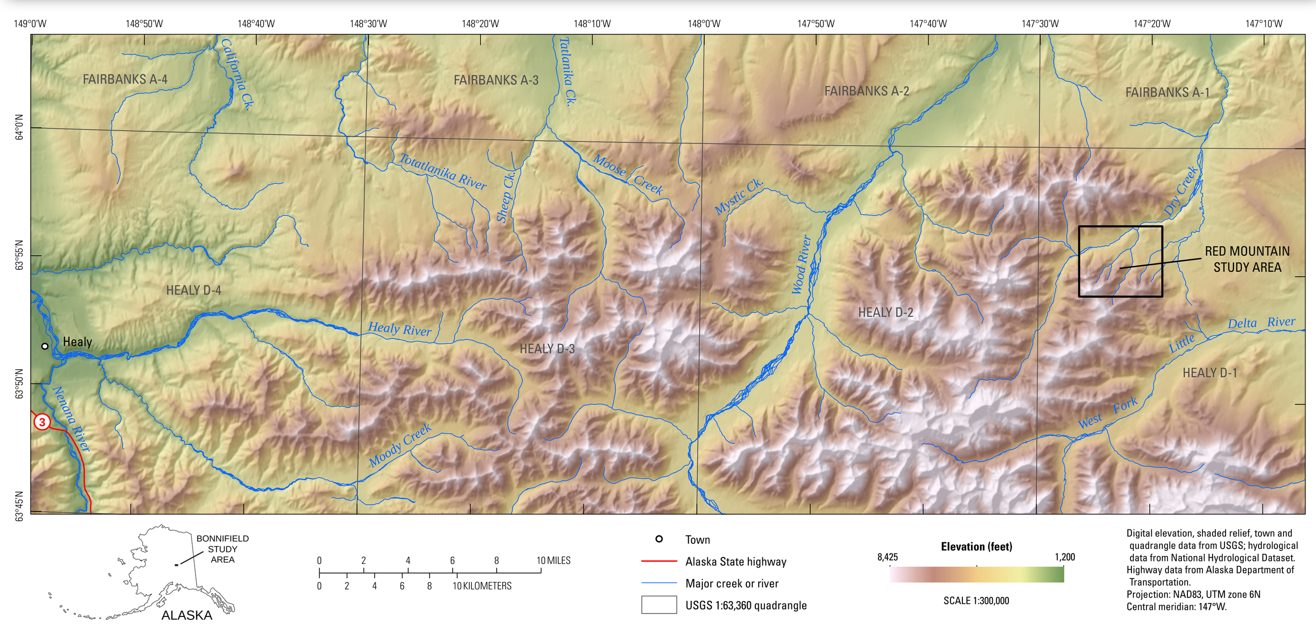
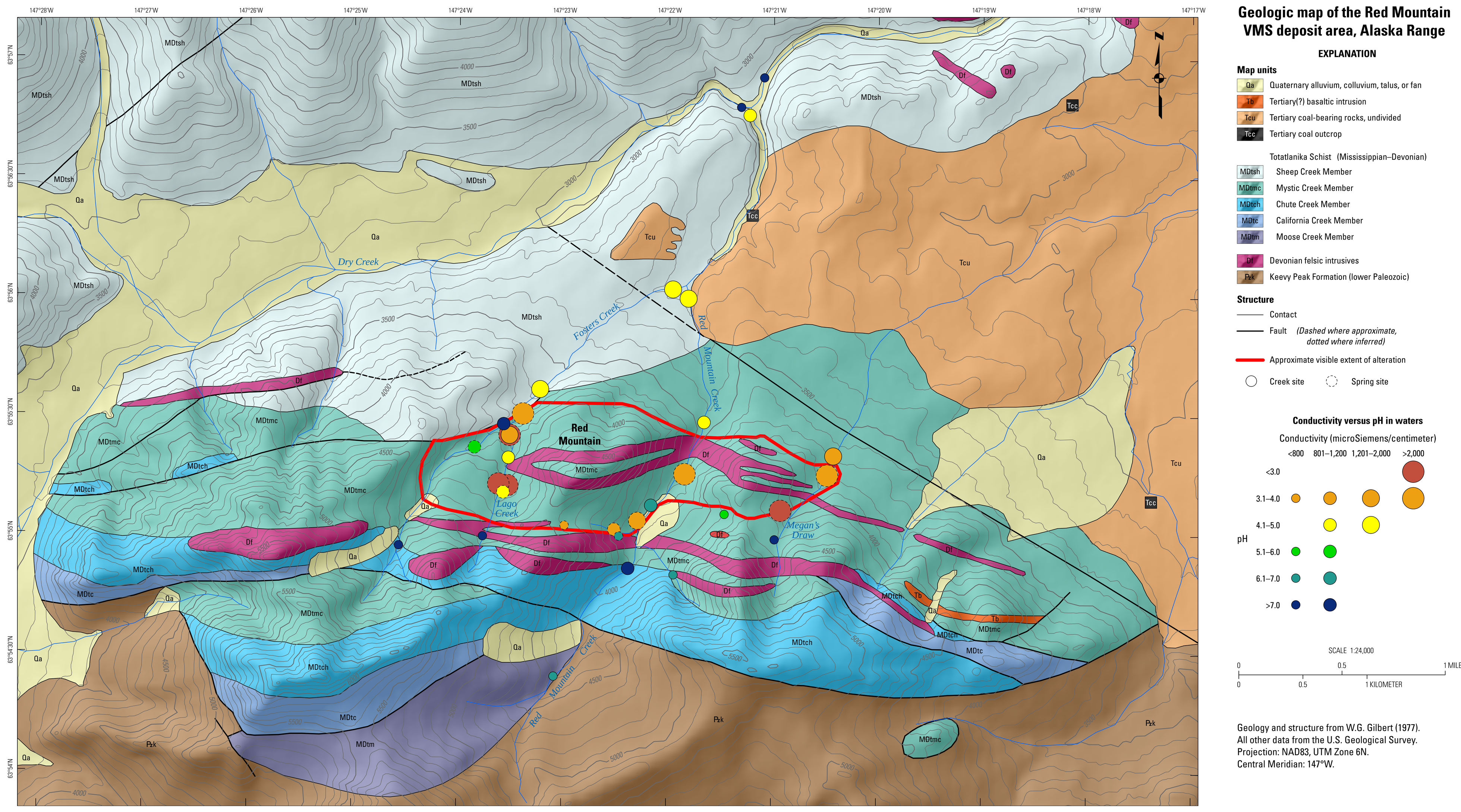


Figure 1. Map of the central part of the Bonnifield mining district and study area, with the Red Mountain deposit study area identified.



Geology

Figure 2. View of Red Mountain from the air, looking south. Note the extraordinary orange and red staining and lack of vegetation over the deposit.

The Bonnifield mining district includes 26 known volcanogenic massive sulfide (VMS) prospects. These occur in a greenschist-facies assemblage of metavolcanic and metasedimentary rocks in the Yukon-Tanana terrane. Protoliths consist of felsic and mafic volcanic and subvolcanic rocks interfingered with carbonaceous and siliciclastic sediments, indicative of a submarine extensional back-arc-basin setting near the continental margin of the North American craton that was subsequently uplifted and exposed (Dusel-Bacon and others, 2007). See figure 3.

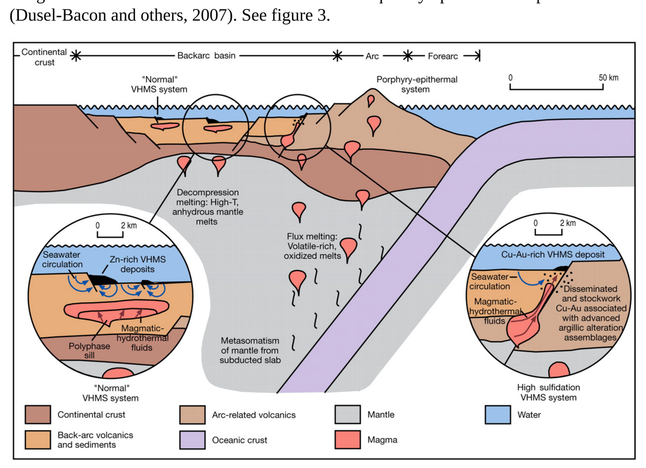


Figure 3. Possible settings of volcanic-hosted massive sulfide (VHMS) deposits in convergent margins. High-T = high temperature. Adapted from Huston and others (2010).

At Red Mountain, several massive sulfide horizons have been identified within the Totatlanika Schist, near the contact between the felsic metavolcanic and carbonaceous rocks of the Mystic Creek Member and the overlying metasedimentary rocks of the Sheep Creek Member (see geologic map). Sulfide minerals such as pyrite, sphalerite, galena, and chalcopyrite were deposited throughout a brown pyritic mudstone or in massive horizons at the base of and within a mottled metarhyolite. Figure 4 shows a mechanism for sulfide deposition by typical "black smoker" plumes in a spreading center.

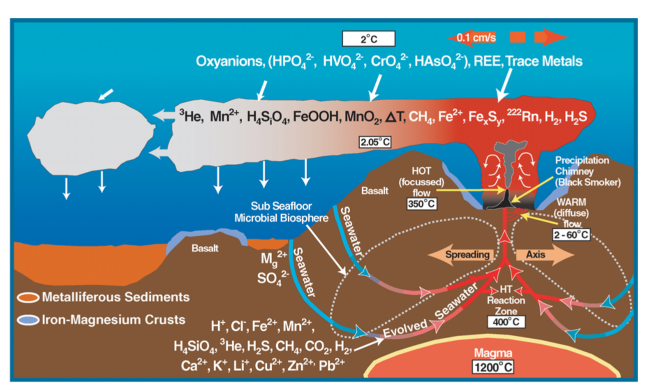


Figure 4. Volcanic heat at spreading center drives hydrothermal circulation and chemical exchange between the ocean crust (brown) and seawater (dark blue). Metal-laden plume drifts on sea current and minerals precipitate into seafloor deposits. HT = high temperature. cm/s = centimeters per second. Image from National Oceanic and Atmospheric Administration (2002).

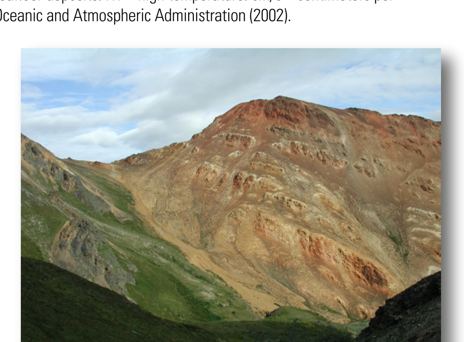


Figure 5. View of Red Mountain from Red Mountain Creek above the deposit. Note the natural transition from vegetation-covered Totatlanika Schist (left) to the completely vegetation-free volcanogenic massive sulfide deposit (right).

Sulfide Geochemistry

The massive to semimassive zinc-, lead-, and silver-rich sulfide horizons at Red Mountain occur within and at the base of an aphanitic (microcrystalline) metarhyolite that has undergone intense primary quartz-sericite-pyrite (QSP) alteration and secondary oxidation of pyrite.

Common sulfides found at the Red Mountain VMS deposit:

Pyrite	(FeS_2)	Chalcopyrite	($CuFeS_2$)
Sphalerite	(ZnS)	Galena	(PbS)

As the deposit became exposed to air and water, supergene processes involving the chemical destruction of pyrite and coincident production of sulfuric acid and various secondary acidic minerals produced strongly acidic groundwater. The acidic groundwater further altered the bedrock creating local clay-rich zones and vuggy (cavitied) silica-rich rocks, and completely destroyed the original rock-forming minerals (figs. 6 and 7).

Examples of pyrite oxidation (from Plumlee, 1999):

$FeS_2 + 3.75O_2 + 0.5H_2O = Fe^{3+} + H^+ + 2SO_4^{2-}$	1 mole acid
$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$	2 moles acid
$FeS_2 + 3.75O_2 + 3.5H_2O = 2SO_4^{2-} + 4H^+ + Fe(OH)_{3(5)}$	4 moles acid
$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	16 moles acid

Figure 6. Dissolution vugs (cavities) in sulfide-rich mottled metarhyolite found on the west end of the deposit between Fosters and Lago Creeks (see geologic map).

Figure 7. Quartz stockwork observed in colluvium. The surrounding rock has been eroded away leaving raised quartz veinlets behind.

Acidic Springs and Runoff

Red Mountain is divided by a dense network of faults and fracture zones (unpublished data), and the deposit is tilted to the north (see geologic map) exposing underlying quartz stockwork veins in the lower (southern) section of the deposit and massive sulfide horizons in the upper (northern) section. A zone of altered rock has formed around and within the deposit, marked by intense red, maroon, orange, and yellow colors and a near-total lack of vegetation (fig. 5). A series of acidic springs, sampled during the study (figs. 8, 10, 18, and 19), were found to be associated with the fault and fracture network suggesting that groundwater flow along fractures is important, if not prevalent. As Red Mountain Creek, Fosters Creek, and Lago Creek bisect and cross the deposit, the waters become acidic and metalliferous, with corresponding increases in conductivity (see geologic map).

Figure 8. Acidic spring east of Red Mountain alongside Red Mountain Creek. This spring has one of the lowest pH values (3.0) and highest specific conductance values (3,400 microSiemens/centimeter) found at the deposit. The sum of rare earth elements dissolved in the spring water is 583,000 parts per billion, more than 100,000 times crustal background levels (fig 27).

Metal Dissolution and Transport

The destrucion of the original rock-forming minerals through QSP alteration has released many of their elemental constituents into the subsurficial and surficial aquatic environments. Figure 9 illustrates how neutral-pH waters from upstream of the deposit are low in metals, whereas acidic waters within and below the deposit approach extreme levels. The primary metal is iron, indicated by the extreme amount of red oxide staining throughout the deposit, but other metals include Al, Cd, Co, Cu, Ni, Mn, Mo, Pb, Zn, and various rare earth elements (figs. 20 and 21). The metals remain dissolved until a change in Eh (oxidation potential) or pH causes them to precipitate. Hence, some metals can remain dissolved in waters flowing beyond the boundary of a VMS deposit (see Element Maps).

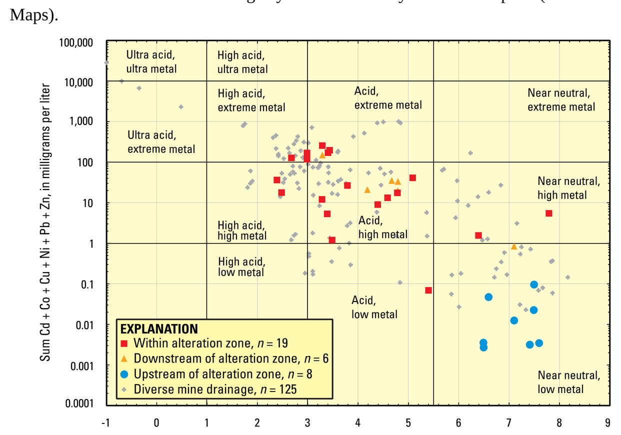


Figure 9. Ficklin diagram of pH versus the dissolved metals Cd + Co + Cu + Ni + Pb + Zn from filtered and acidified water samples. Mine drainage waters are from diverse mineral deposit types worldwide, for purposes of comparison. Diagram from Eppinger and others (2007).

Figure 10. Acidic spring west of Red Mountain alongside Lago Creek. The bright salmon-colored precipitate was identified by x-ray-diffraction analysis as dominantly schwertmannite, a mineral that commonly forms in iron-rich, acid sulfate waters in the pH range of 2–4. Note black liverwort, a possible acidophile or metallophile (Gough and others, 2006), growing in the splash zone on the right side of the creek.

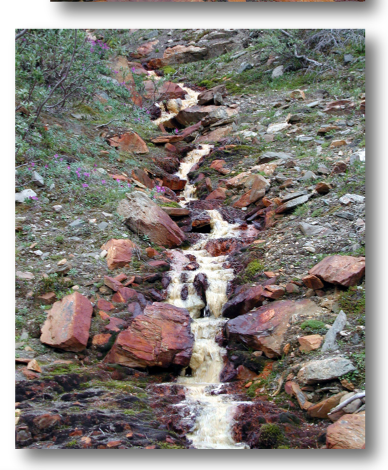


Figure 11. Fosters Creek just above the confluence with Lago Creek. The flowing water is clear; the white color is caused by aluminum-oxyhydroxide precipitates coating the creekbed.

Figure 12. Iron-oxide-cemented pool on Lago Creek. Ferricrete underlies and cements all alluvium. Note milky appearance of water due to actively precipitating aluminum floc.

Metal Oxide Precipitation

When a pH change occurs in acidic runoff, the dissolved metals can start to precipitate. Figure 13 shows a vivid example of this process. Here, water from the same acidic spring shown in figure 8 (top half of channel in figure 13) mixes with water from Red Mountain Creek (bottom half of channel in figure 13). The spring water, at a pH of 3.0, has a load of dissolved iron and is actively precipitating iron (orange colors), while the creek water, at a pH of roughly 5, has previously lost all iron and is precipitating only aluminum (white colors). As the two waters mix, the pH rises in the spring water and drops in the creek water, causing a reaction front.

Iron precipitates throughout the deposit and down all creeks draining the deposit in the form of "ferricrete" and underlies and cements all alluvium to a depth of several meters (figs. 8, 12, and 14). Aluminum-oxyhydroxide-floc precipitates cause a milky appearance in flowing water and collect in calm water and pools in a white, gel-like coating that breaks apart when disturbed (figs. 11, 12, 13, and 15).

Figure 13. Mixing of low-pH water from the acidic spring (upper half of channel) with higher pH water of Red Mountain Creek (lower half of channel). Changes in pH trigger precipitation of iron oxides from the springwater and aluminum-oxyhydroxide minerals from the creekwater.

Figure 14. Supergene vuggy silica float (rock fragments) from a scree pile shed from the west side of Red Mountain. Precipitating iron-oxide cements the rock fragments together with "ferricrete."

Figure 15. Aluminum-oxyhydroxide-floc precipitate. The floc has a gel-like appearance but breaks apart when disturbed

Acid Salts

In protected areas, secondary dissolved minerals precipitate as acidic salts (fig. 16). These highly soluble efflorescent sulfate salts temporarily sequester iron, other metals, and acidity. Dissolution of these salts during precipitation events, or by snowmelt, can cause a pulse of acidity and dissolved metals into the surface-water environment. Soluble accessory metals include Fe, Al, Mg, Mn, Cd, Co, Cu, Ni, Mo, Pb, Zn, and the rare earth elements. A variety of accessory mineral salts have been identified at Red Mountain, all of which are products of pyrite dissolution and coincident acid rock drainage.

Figure 16. Detail of acid salt precipitates under a protected ledge.

Self-Mitigation

The waters of Red Mountain Creek remain acidic (pH ≈4.2) and metalliferous from the alteration zone (AZ) to the confluence with Dry Creek 1.5 miles (2.5 km) downstream. By contrast, the waters of Dry Creek are near-neutral pH, alkaline, and relatively nonmetalliferous due to it being a relatively large, turbid, glacial-flour-rich creek that drains rocks with acid-consuming capability (Martin and Whitfield, 1983).

Red to orange staining is evident on alluvium from the AZ down Red Mountain Creek and for about 1 mile (1.5 km) down Dry Creek, but beyond this only weaker hues exist for about another 0.5 mile (0.8 km) (fig. 17). The only geochemical signature of Red Mountain that persists beyond the confluence is slightly anomalous zinc in sediments, and cerium and lanthanum in waters. Thus, the hydrogeochemical and visual indicators are that the Red Mountain VMS deposit appears to be largely self-mitigating within a few miles downstream of the deposit, due largely to dilution by the much larger Dry Creek.

Figure 17. Iron-oxide-stained alluvium on Dry Creek, approximately 0.5 mile downstream of confluence with Red Mountain Creek. Circum-neutral pH of Dry Creek, combined with acid-consuming rock flour in the water, causes final iron load to precipitate as red staining on rocks.

Biology

Almost no vegetation covers the AZ, nor grows within or adjacent to creeks crossing the Red Mountain VMS deposit (figs. 2 and 5) due to the acid generation and mobility of metals into the surface environment. However, creeks, springs, and seeps within the AZ or in areas affected by acidic groundwaters are inhabited by an unusual community of bryophytes (liverworts and mosses). *Gymnocolea inflata*, a black and green bryophyte, grows in areas of standing or flowing water, and the mosses *Polytrichum commune* and *P. juniperinum* grow above the water or in the splash zone (figs. 8, 10, 18, and 19). Analyzed brypohyte vegetation from areas that receive metal-laden spray indicates high levels of metals such as As, Cd, Cu, Fe, Hg, Pb, and Zn. It is unknown whether the Red Mountain bryophyte assemblage is acidophilic or requires high concentrations of dissolved metals, and there are no reports in current literature of similar observations (Gough and others, 2006).

Downstream of the AZ, diamondleaf willow (*Salix pulchra* and *S. glauca*) dominates creekside vegetation and is known to be an important food source for moose, hare, and ptarmigan. Where the tree-root mass is located in creek sediment instead of soil, the willows have much higher levels of major and trace elements (Al, As, Cd, Cr, Fe, Al, and Pb), and levels of cadmium are orders of magnitude above levels found to be toxic to ptarmigan (Gough and others, 2006). It is unknown what toxicity this represents to local fauna.

Figure 18. Mixing zone below clear acidic spring on Lago Creek visible on left edge of photo. Green and black liverwort *Gymnocolea inflata* lines the left bank splash zone.

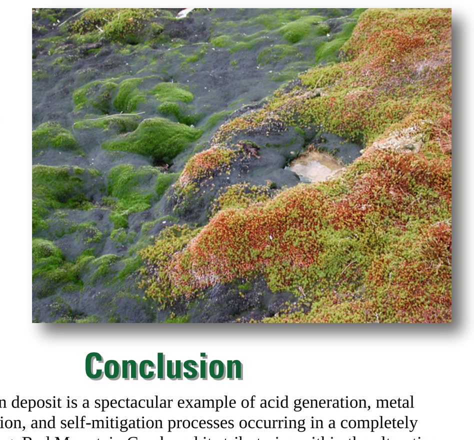


Figure 19. Detail of highly acidic spring on Megan's Draw with *Gymnocolea inflata* (black and green liverwort on left), and a mix of *Polytrichum commune* and *P. juniperinum* (pinkish and light green moss on right). The muddy water-filled depression is a moose footprint.

Conclusion

The Red Mountain deposit is a spectacular example of acid generation, metal leaching, metal precipitation, and self-mitigation processes occurring in a completely natural, undisturbed setting. Red Mountain Creek and its tributaries within the alteration zone do not and probably never have supported significant aquatic life, except perhaps those organisms that have adapted to the extreme environment of low pH and very metalliferous conditions. Any future mining attempts will need to thoroughly account for the deposit's acid-generating and metal-liberating potential as part of mine feasability.

Element Concentration Boxplots

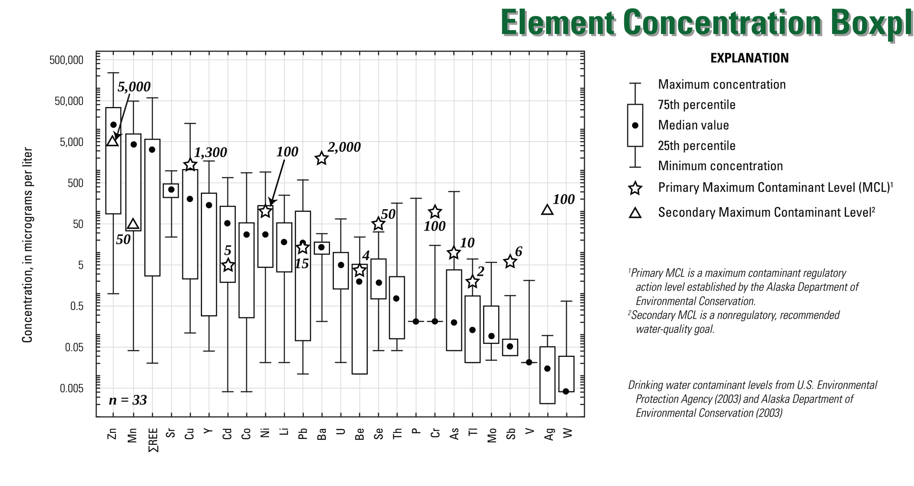


Figure 20. Boxplots of trace cations and sum of rare earth elements (ΣREE). Elements Cu, Cd, Ni, Pb, Be, As, and Tl naturally exceed the Environmental Protection Agency's drinking water primary MCL. Median levels of zinc and manganese exceed the secondary MCL. See Element Maps for maps of Zn, ΣREE, Cu, Cd, and Pb. Data from Eppinger and others (2007).

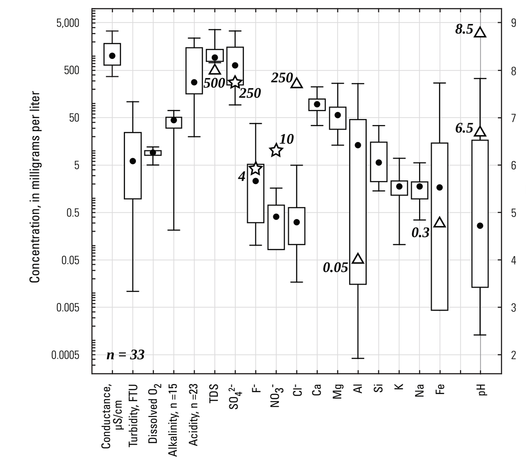


Figure 21. Boxplots of field measurements, anions, major cations, and pH. Sulfate, F^-, and NO_3^- naturally exceed Environmental Protection Agency's drinking water primary MCL. Medians of total dissolved solids (TDS), Al, Fe, and pH exceed the secondary MCL. FTU = formazine turbidity units. µS/cm = microSiemens per centimeter. Data from Eppinger and others (2007).

Element Maps

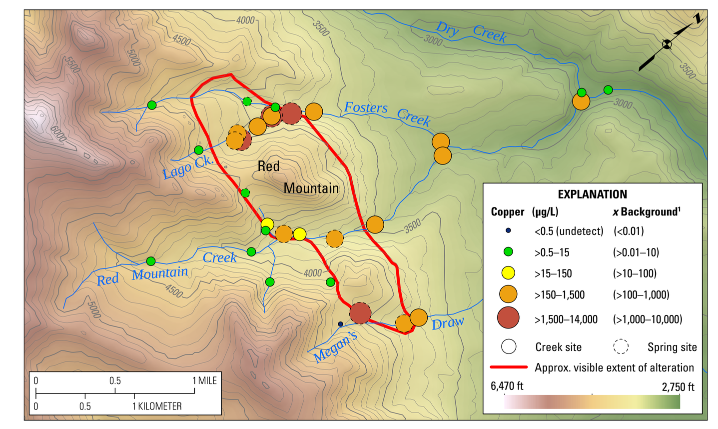


Figure 22. Copper in water samples. Copper exceeds global background levels by up to 1,000× in stream waters, but from 100–10,000× in springs within the alteration zone. Copper is greatly mitigated in waters of Red Mountain Creek by mixing with Dry Creek. µg/L = micrograms per liter.

[1]Crustal background 1.5 µg/L (Martin and Whitfield,1983).

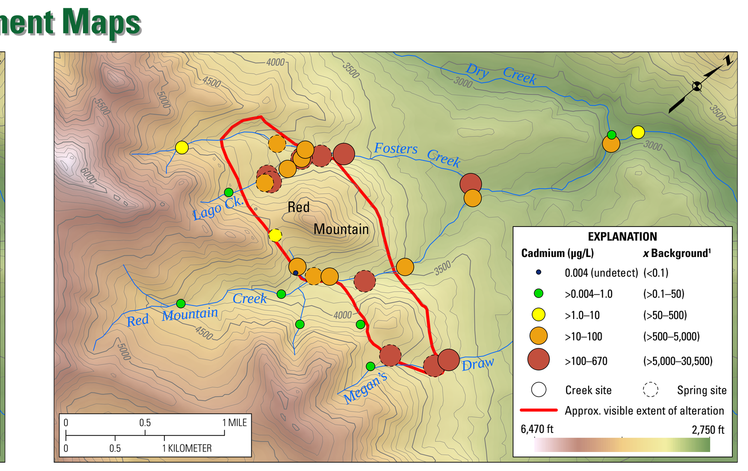


Figure 23. Cadmium in water samples. Waters flowing across the alteration zone (AZ) immediately exceed global crustal background levels by 500×, increasing to >5,000× below the AZ. Most springs within the AZ exceed background by >5,000×. Cadmium is somewhat mitigated in waters after Red Mountain Creek joins Dry Creek. µg/L = micrograms per liter.

[1]Crustal background 0.02 µg/L (Martin and Whitfield,1983).

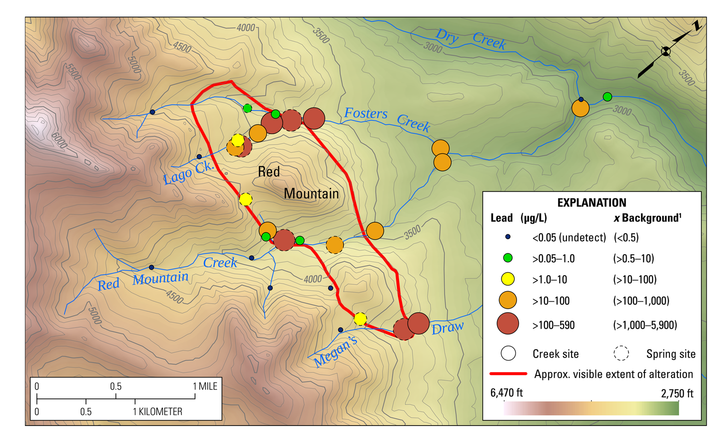


Figure 24. Lead in water samples. Lead is undetected in creek waters above the alteration zone (AZ), but exceeds 1,000× global crustal background on Lago Creek and Megan's Draw after passing through the AZ. Mixing of Red Mountain Creek and Dry Creek mitigates most lead. µg/L = micrograms per liter.

[1]Crustal background 0.1µg/L (Martin and Whitfield,1983).

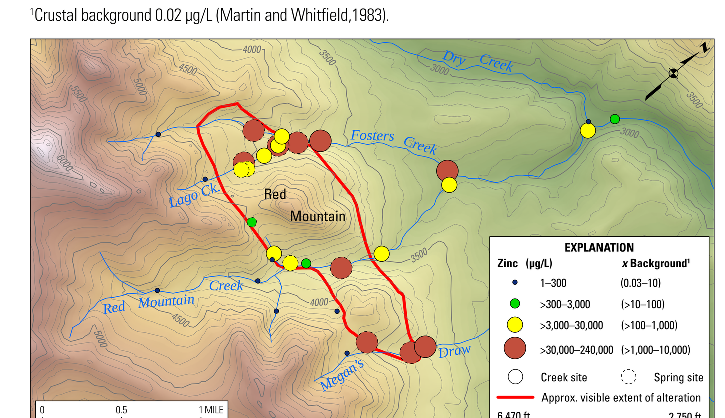


Figure 25. Zinc in water samples. Zinc is high (>1,000× global crustal background) on all creeks except Red Mountain Creek where only the acidic spring east of Red Mountain has zinc higher than 100× background. Zinc is mitigated somewhat after Red Mountain Creek mixes with Dry Creek. µg/L = micrograms per liter.

[1]Crustal background 30 µg/L (Martin and Whitfield, 1983).

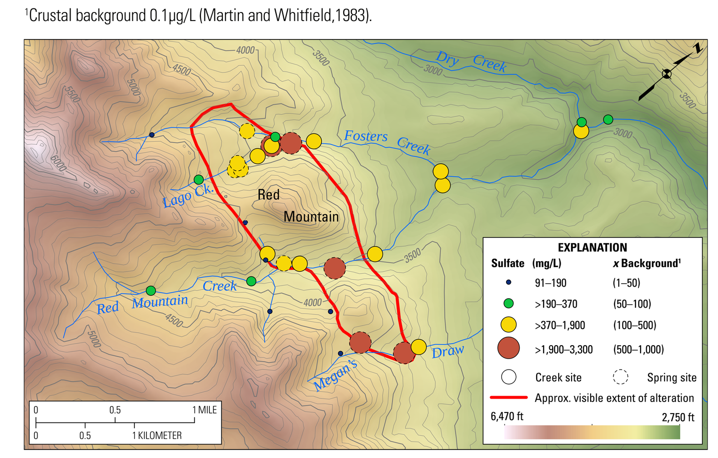


Figure 26. Sulfate in water samples. High sulfate occurs in creek water flowing across the alteration zone (100–500× global crustal background), but sulfate in most acidic springs in lower section of deposit exceeds background by 500–1,000×. Sulfate is mitigated by mixing with Dry Creek. mg/L = milligrams per liter.

[1]Crustal background 3.7 µg/L (Rose and others, 1979).

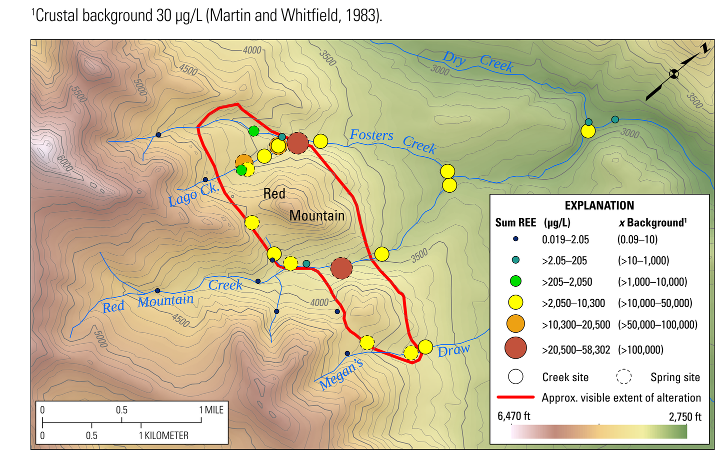


Figure 27. Sum of rare earth elements (REE) (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb) in water samples. The highest REE sampled in acidic springs exceeds global crustal background by >100,000×. REE elements are mobilized by acidic groundwater dissolving accessory minerals, including fluocerite, in the felsic Mystic Creek Member of the Totatlanika Schist, not from the deposit itself. µg/L = micrograms per liter.

[1]Crustal background 0.205 µg/L (Martin and Whitfield,1983).

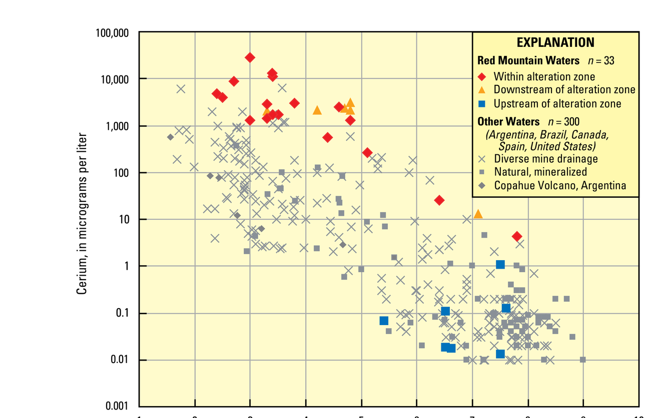


Figure 28. Cerium in Red Mountain filtered and acidified water compared to cerium from mine drainage and mineralized water from diverse deposit types from the United States, Canada, Brazil, and Spain. Rare earth element concentrations in waters from Red Mountain are exceedingly high. Data from Eppinger and others (2007).

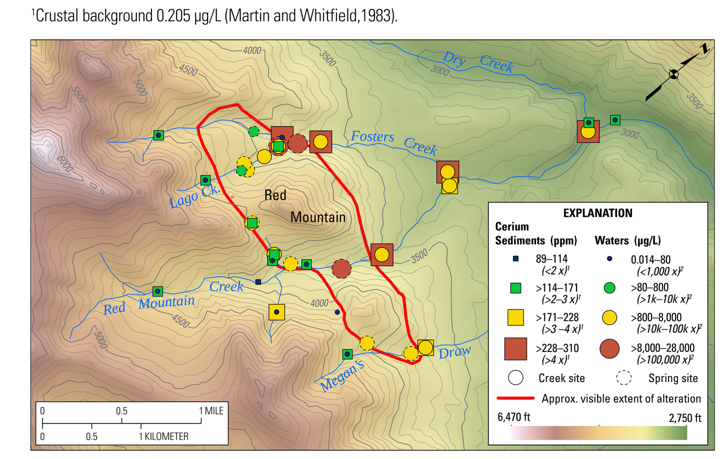


Figure 29. Cerium in water and stream sediment samples. Anomalously high cerium from acidic spring water exceeds global crustal background >100,000×. pH rise due to mixing waters causes cerium to precipitate in creek sediment, which remains high (>4× background) until confluence with Dry Creek. µg/L = micrograms per liter. ppm = parts per million.

[1]Crustal background 57 ppm (Rose and others, 1979).
[2]Crustal background 0.08 µg/L (Martin and Whitfield, 1983).

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All photographs by Robert G. Eppinger except figure 19, by Larry P. Gough.

Suggested Citation:

Giles, S.A., and Eppinger, R.G., 2014, A geochemical perspective of Red Mountain—An unmined volcanogenic massive sulfide deposit in the Alaska Range: U.S. Geological Survey Open-File Report 2014–1037, 1 plate *http://dx.doi.org/10.3133/ofr20141037.*

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ISSN 2331-1258 (online)
http://dx.doi.org/10.3133/ofr20141037