GEOCHEMISTRY AND STABLE ISOTOPES OF ACID MINE DRAINAGE IN THE BELT-STOCKETT AREA, MONTANA[1]

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Abstract. The towns of Belt and Stockett, Montana, as well as several nearby communities, were founded by mining of the Great Falls–Lewistown Coal Field (GFLCF). Extraction of this late Jurassic-aged, high-S coal was mainly by underground room and pillar methods, and ceased by the mid-20th century. The majority of the mine workings are now flooded or partially flooded, and numerous small-volume but severely acidic mine water discharges are present. Water in mines that are partially flooded or freely draining typically has a pH near or below 3, with high Fe and Al concentrations (typically above 100 mg L^{-1}). In contrast, mine water in completely flooded portions of the mine workings is mildly acidic, and has low to moderate concentrations of Fe and other heavy metals. Nonetheless, this water may turn strongly acidic after discharge to the surface, due to oxidation and hydrolysis of Fe^{2+} to hydrous ferric oxide. Stable isotope work (in progress) shows that the mine drains are local meteoric water which has underwent varying degrees of evaporation. Sulfur isotopes show that dissolved sulfate in the acidic mine drains was mainly derived by oxidation of pyrite in the coal itself, whereas sulfate in groundwater in the underlying Madison Limestone aquifer came from leaching of gypsum of probable marine origin. Although the majority of the mine drains are small in volume, their low pH and high metal concentrations create serious water quality problems. Historical efforts to passively treat acid mine drainage in the GFLCF using wetlands, limestone channels, and anoxic drains have been unsuccessful, due to the harsh climate and high acidity of the mine waters. Alternative mitigation concepts are currently being evaluated that focus on source control rather than treatment.

Additional Key Words: coal, sulfur isotopes, oxygen isotopes

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Introduction

The Great Falls-Lewistown Coal Field (GFLCF) is situated in Central Montana, between the cities of Great Falls and Lewistown (Figure 1). The GFLCF was extensively mined in the late 1880's and early 1990's, and contains over 400 abandoned coal mines, most of which were underground operations. Many of these mines are now generating acid mine drainage (AMD), with the larger mine complexes producing the worst water quality problems. To date, the majority of reclamation projects have focused on adit closures, removal of mine dumps, and revegetation. In addition, various passive treatment methods have been attempted, including wetlands, anoxic drains, and limestone channels. Due to the harsh winter climate and high metal and sulfate concentrations of the AMD waters, attempts at passive treatment have been unsuccessful to date (Botsford and Duaime, 2003).

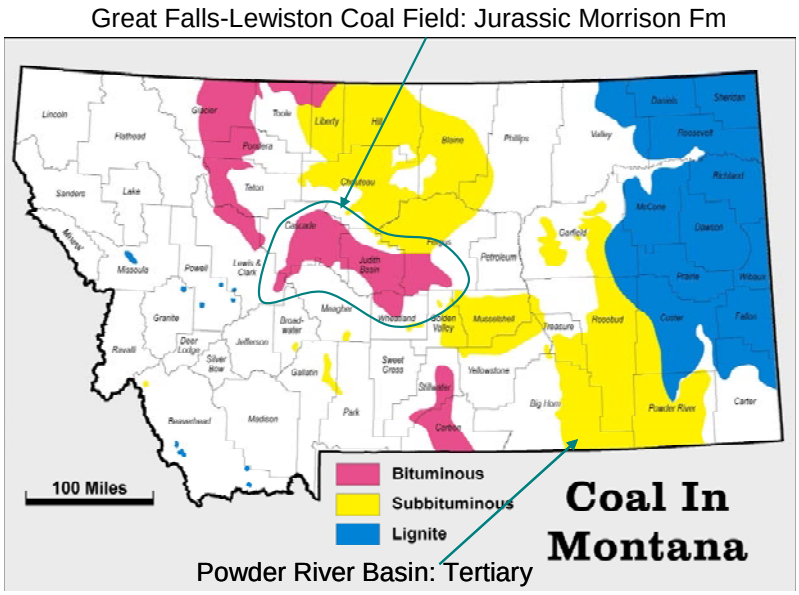

Figure 1. Location of major coal fields in Montana.

The purpose of this paper is to review the geologic setting of the western GFLCF, and the geochemistry of its contained mine waters near the towns of Belt and Stockett (Figure 2). New stable isotope data are presented that place constraints on the sources of water and sulfate in the flooded mine complexes, as well as the underlying groundwater aquifers. Finally, a brief overview of historic AMD treatment projects is presented, along with some ideas for future projects.

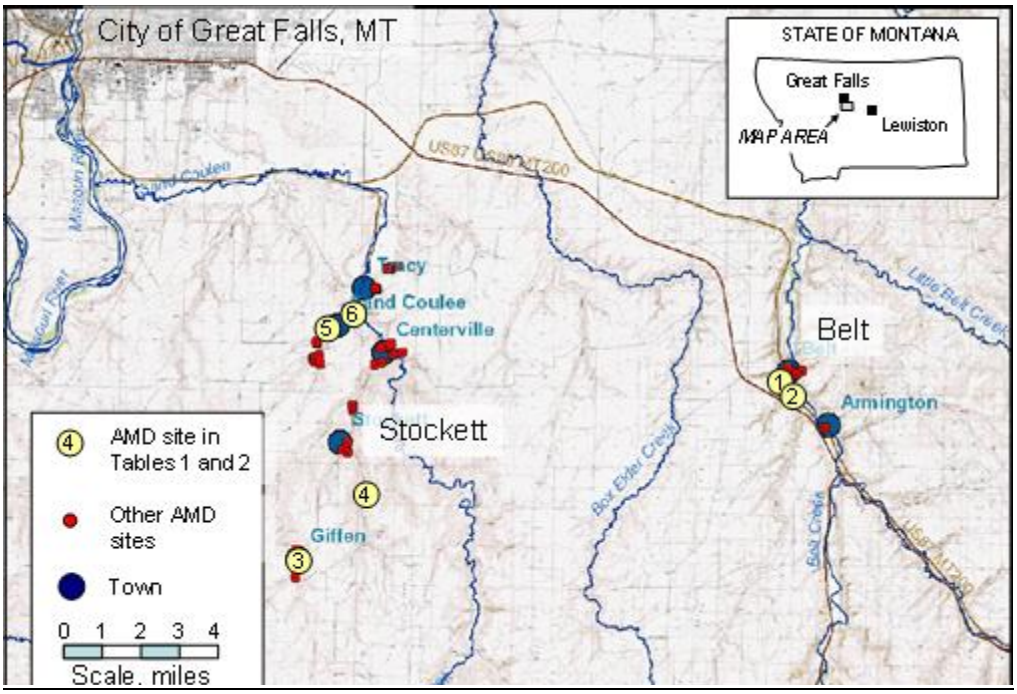

Figure 2. Location map of the western portion of the Great Falls-Lewiston Coal Field. Descriptions: 1 – Anaconda drain; 2 – French Coulee Drain; 3 – Giffen Spring; 4 – Cottonwood No. 6 drain; 5 – Mt. Oregon drain; 6 – Nelson Drain.

Geology and Hydrogeology

Figure 3 is a schematic cross-section showing the main hydro-stratigraphic units in the study area. The coal seams of the GFLCF are located at the top of the Jurassic Morrison Formation – mainly shale and siltstone – and are overlain by sandstone and shale of the Cretaceous Kootenai Formation. Sandstone units within the lower Kootenai are resistant to erosion, and form the backbone of the broad, grassy upland areas in this portion of the Rocky Mountain foothills. These strata, as well as the immediately underlying coal seams, outcrop in deeply incised valleys formed by ephemeral or - in the case of Belt Creek - permanent streams that drain northward towards the Missouri River. Beneath the Morrison Fm., and roughly 50 m below the coal, is the Mississippian Madison Formation, a thick limestone unit that is an important regional source of groundwater. The Madison aquifer feeds two very large natural springs at either end of the coal field named Giant Spring (Great Falls) and Big Spring (Lewiston). In this study, samples of water from Giant Spring were collected for stable isotopic analysis to compare with groundwater samples collected from monitoring wells closer to the coal mines.

Near Belt, the coal seams of the GFLCF are located several 10's of meters above the regional water table (Fig. 3). Nonetheless, a perched water table of considerable lateral extent exists above the coal seams in permeable sandstone of

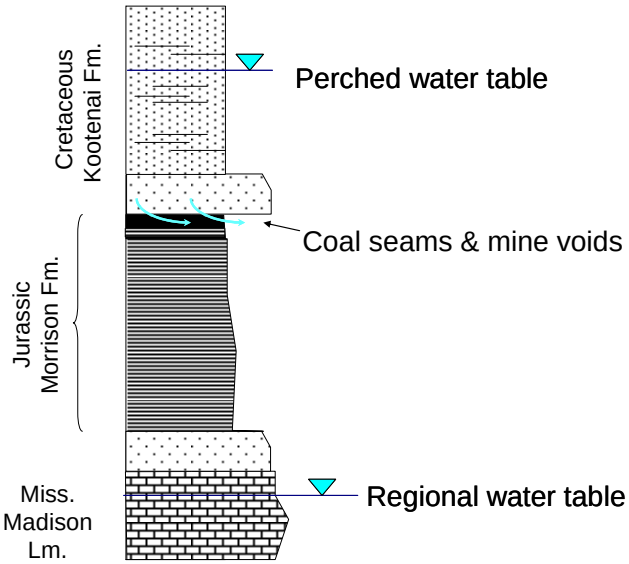

Figure 3. Simplified stratigraphic section showing major hydro-stratigraphic units in the Belt-Stockett area. Blue shading denotes groundwater.

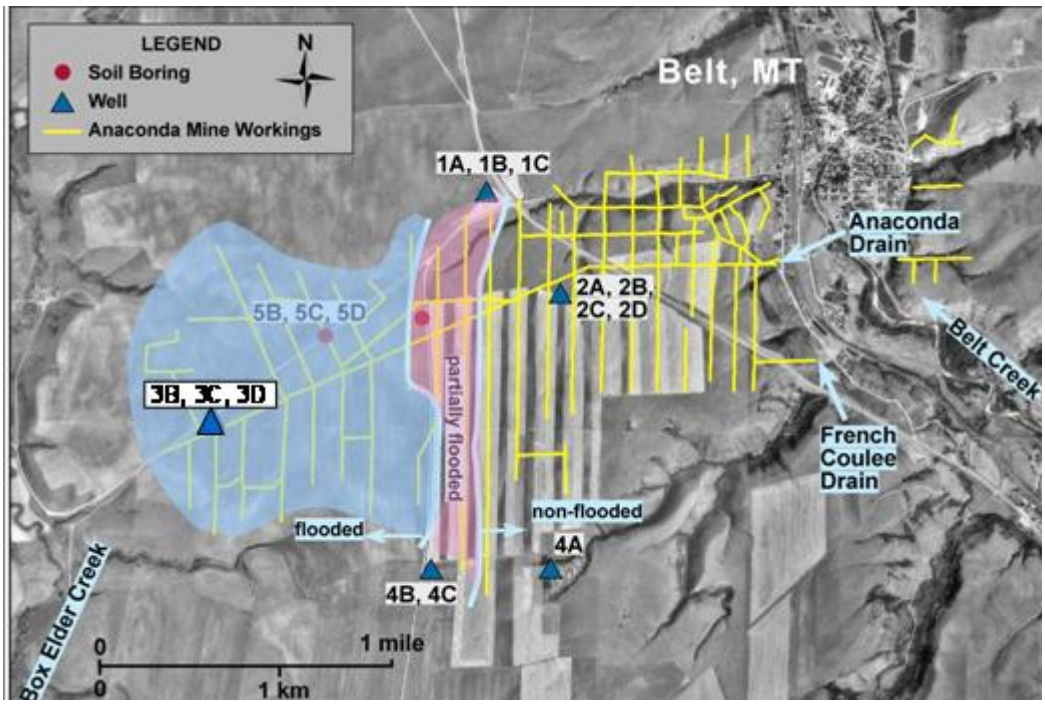

Figure 4. Aerial photo showing the layout of the major underground haulage ways (yellow) used to extract coal at the Anaconda Mine, Belt, MT. The shaded blue region represents mine workings that are now completely flooded, the pink region is partially flooded, and the non-shaded region is freely draining. Also shown are the location of soil sampling sites and groundwater monitoring wells.

the Kootenai Fm. This water slowly drains into the underlying mine workings, and serves as the main source of groundwater recharge to the mines. The mines followed a 1 to 4 m thick coal seam with a shallow, undulatory dip, and for this reason the mine workings are spread laterally over a huge area but have a limited vertical extent. Portions of the mines are now completely flooded with groundwater, other portions are partially flooded, and still others are freely draining to surface discharge points. Some of the larger mining complexes have extensive mine water pools whose elevations are controlled by spill-over points in the underground workings. The Anaconda Coal Mine in Belt is a good example of this pattern (Figure 4). Most of the AMD from the Anaconda Mine exits at the Anaconda drain; a lesser amount exits at the French Coulee drain. The combined AMD flows directly to Belt Creek, with severe contamination of this otherwise high quality trout stream (Figure 5).

Figure 5. Photographs of Belt Creek taken in November, 2005, looking upstream (left) and downstream (right) of the Anaconda drain. Note the presence of white (aluminum-rich) and orange-red (iron-rich) precipitates.

The coal of the western GFLCF is sub-bituminous B to high volatile bituminous C in grade, and contains an average sulfur content of 4%, locally increasing to values as high as 11% (Silverman and Harris, 1967; Sholes and Daniel, 1992). As an example of the high S content of the coal, the historic Anaconda Coal Mine in Belt processed pyrite balls washed from the mined coal and sent this to the Anaconda smelter in Great Falls to be used as a flux in the copper smelting process (Shurick 1909). The high pyrite content of GFLCF coal is also a major reason for the severity of its associated AMD.

Geochemistry of Mine Drainage

The geochemical characteristics of groundwater and surface mine drains in the Belt-Stockett area were investigated by Osborne et al. (1983, 1987), Doornbos (1989), and Karper (1998). Gammons et al. (2006a) presented a more recent overview of the situation, and also documented changes in the geochemistry of several of the mine waters after they discharged to the surface. Most of the mine drains in the region have strongly acidic pH. Figure 6 shows two examples of

acidic drain water, and Table 1 summarizes some field water quality data. Additional, more detailed water quality data can be found in Karper (1998) and Gammons et al. (2006a). Compared to the majority of the mine drains in the Belt-Stockett area, the Mt. Oregon drain and Giffen Spring are only weakly acidic. The main reason for the differences in pH of the mine waters is the variably saturated nature of the mine workings (Doornbos, 1989; Gammons et al., 2006a). If the workings are completely flooded, then it is much more difficult for oxygen to come into contact with pyrite left in mine pillars and walls. On the other hand, if the mines are partially flooded or freely draining, then O_2 can easily enter the workings, and pyrite oxidation can proceed at a rapid rate (see Figure 7).

Figure 6. Photographs of the Nelson drain (left) and Anaconda drain (right), taken in November, 2005. The deep green color of the Nelson drain is mainly due to abundant growth of algae. The Anaconda drain contains a water quality sonde.

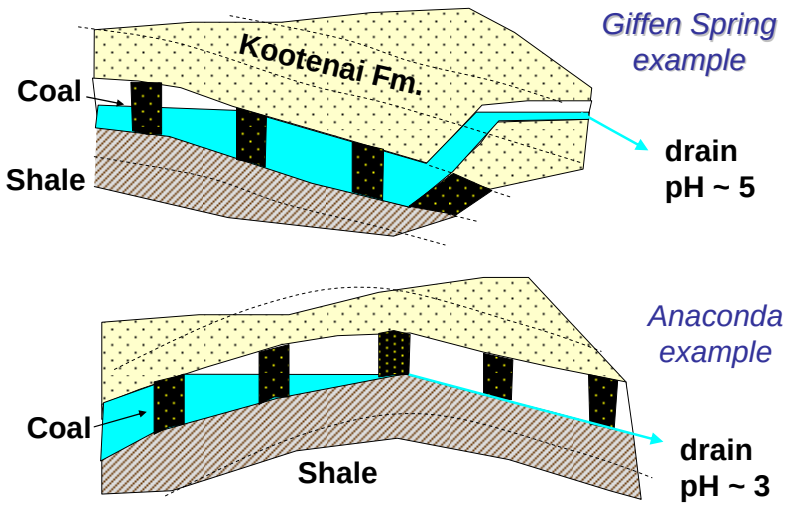

Figure 7. Schematic diagram depicting partially flooded conditions in the abandoned coal mine workings (modified after Gammons et al., 2006a).

In 1994-1996, the U.S. Geological Survey conducted a detailed survey of the water-quality of mine discharges and down-gradient ephemeral streams and wetlands in the GFLCF (Karper, 1998). Each site was visited approximately once a month for two successive years. The majority of the drains had pH in the 2.5 to 3.1 range, with extremely high concentrations of sulfate (up to 16 g L^{-1}), Fe (up to 2000 mg L^{-1}), and Al (up to 1600 mg L^{-1}). Only two mine discharges – Giffen Spring and the Mt. Oregon drain – had average pH values > 4. Average annual discharges of the mine drains monitored in the USGS study ranged from 0.5 to 14 L s^{-1} (Table 1). Whereas most of the drains show marked seasonal variations in flow, others – such as the Anaconda drain – are more constant. Increases in mine discharge correspond to seasonal patterns of snowmelt and extended precipitation events.

Table 1. Water quality data for selected mine drains near Belt and Stockett, MT, collected during field visits in 2004 and 2005. n.a. = not analyzed

	pH	Eh mV	SC µS/cm	Temp °C	Total Fe mg L^{-1}	Fe^{2+} mg L^{-1}	Fe^{3+} mg L^{-1}
Anaconda drain	3.07	650	2340	10.4	215	194	21
French Coulee drain	2.32	500	6315	9.0	1230	n.a.	n.a.
Nelson drain	3.14	638	9600	10.9	1725	1525	200
Cottonwood No. 6	2.53	653	5530	8.5	700	553	147
Giffen Spring	5.78	310	1170	9.4	62	62	< 1
Mt. Oregon drain	4.22	397	2950	11.5	280	274	6

Based on field colorimetric measurements using the FerroZine method, the majority of the dissolved Fe in the mine workings is present in the reduced, ferrous (Fe^{2+}) state, although appreciable amounts of dissolved Fe^{3+} are present in the more acidic mine waters (see Table 1). In the case of the weakly acidic Giffen Spring and Mt. Oregon drains, nearly all of the dissolved iron exiting the subsurface is present as Fe^{2+}.

Gammons et al. (2006a) showed that the pH of the Mt. Oregon drain drops sharply after discharge to the surface. This is attributed to oxidation and hydrolysis of dissolved Fe^{2+} to form secondary ferric precipitates, as shown by the following overall equation:

$$Fe^{2+} + \tfrac{1}{4} O_2 + 5/2H_2O = Fe(OH)_3(s) + 2H^+ \qquad (1)$$

Downstream changes in pH, Eh, and dissolved Fe speciation observed in the field are consistent with this hypothesis (Figure 8). Although oxidation of Fe^{2+} also occurred at Giffen Spring, in the latter case the presence of a high concentration of bicarbonate ion prevented the downgradient waters from becoming strongly acidic (Gammons et al., 2006a).

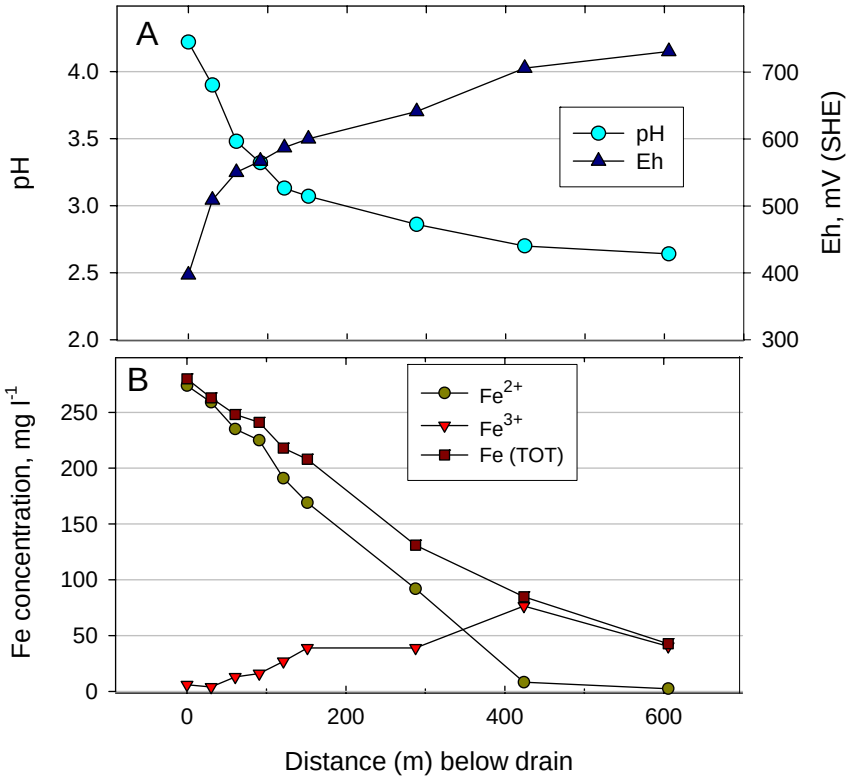

Figure 8. Changes in chemistry of the Mt. Oregon drain after it discharges to the surface (modified from Gammons et al., 2006a).

The Montana Bureau of Mines and Geology (MBMG) is currently undergoing a detailed hydrological study of the abandoned Anaconda Coal Mine in Belt. Table 2 presents water quality results for several groundwater monitoring wells in the vicinity of the Anaconda Mine (locations for these sites are shown in Figure 4). While waters from the mine drains are characterized by low pH and highly elevated metal concentrations (Table 1), samples of groundwater from the alluvial aquifers that overlie the mine (sandstones of the Kootenai Fm.) have a neutral pH and low sulfate concentrations, with trace metal concentrations near or below the instrument detection limits. Groundwater from the *flooded* portion of the coal mine (Well 4B) is very similar to that of the overlying alluvial aquifers, with the exception of sulfate which is higher by an order of magnitude. However, the sulfate concentration is still an order of magnitude less than that of the mine drains. In contrast, mine water from *non-flooded* portions of the mine (Well 2B) has poor quality (pH 2.2). Because of the small amount of water in Well 2B, it has not yet been possible to pump out a groundwater sample. However, judging from the very high SC and low pH of water trickling across the bottom of the mine void, it most likely has an overall chemistry that is similar to the drains. This underscores the importance of oxygen ingress into the mine passageways as a prerequisite for rapid pyrite oxidation and generation of mine water with strongly acidic pH.

Table 2. Selected water quality data for groundwater monitoring wells in the vicinity of the Anaconda Coal Mine, Belt. n.a. = not analyzed.

sample	lithology	pH	SC µS/cm	Temp °C	Fe mg L^{-1}	SO_4 mg L^{-1}
Well 3C	Kootenai	7.2	560	14.7	0.45	29
Well 2D	Kootenai	7.5	495	10.9	0.01	15
Well 2B	Coal (void)	1.9	9,500	10.0	n.a.	n.a.
Well 4B	Coal (flooded)	7.0	750	10.5	0.10	184
Well 1A	Madison	7.4	535	10.8	0.01	188
Well 4A	Madison	7.3	885	11.3	0.08	325

Stable Isotope Studies

A stable isotope investigation of groundwater and mine discharges in the Belt-Stockett area is in progress. The purpose of this work is to help delineate sources of water to the flooded mines, and to characterize the isotopic signature of sulfate derived by oxidation of pyrite in the coal beds.

Figure 9 shows the isotopic composition of water from several mine drains in the Belt-Stockett area. Also shown are 4 groundwater wells near Belt and Giant Spring, the latter being a very large natural spring near Great Falls that discharges groundwater from the Madison Fm. The majority of the samples shown in Figure 9 were collected in 2005. The exception is two samples from the Anaconda and French Coulee drains collected in 2003. On this diagram, the average stable isotopic composition of rain and snow is given by the solid line (the so-called "global meteoric water line" of Craig, 1963). Also shown is the local evaporation line (LEL) derived by Gammons et al. (2006b) for evaporated surface water near Butte, Montana. Most precipitation in Montana falls near the global meteoric water line (MWL), with more negative δD and $\delta^{18}O$ values associated with winter snows, and less negative values with summer rains. Once the precipitation reaches the ground – or even before it hits the ground if the lower air mass is dry – evaporation can cause the isotopes to shift away from the MWL on a trajectory with a lower slope. The intersection of the MWL and the LEL gives the isotopic composition of average groundwater recharge. The location of this point of intersection can vary from year to year, depending on changes in climate and precipitation trends.

In Figure 9, the sample that plots the closest to the global MWL is Giant Spring. Most of the groundwater in the Madison Limestone is recharged from snowmelt and Spring rains in mountain ranges to the south of the study area. The mine drain samples collected in 2005 plot in an elongated cluster that is offset from Giant Spring with a slope that is similar to the evaporation line of Gammons et al. (2006b). This suggests that some of the mine drain waters (especially the so-called "Highway Drain") are partially evaporated. Samples collected in 2003 plot somewhat off the trend of the 2005 samples. This may reflect differences in climate between the two sampling years, with 2003 having a colder winter with more snow.

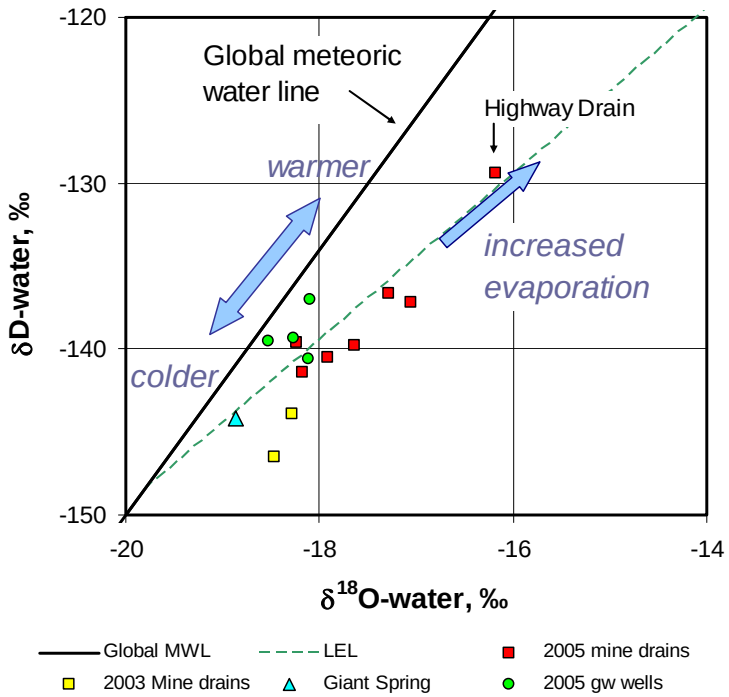

Figure 9. Stable isotopic composition of water from mine drains and groundwater wells and springs in the Belt-Stockett area.

Figure 10 summarizes the isotopic composition of dissolved sulfate in groundwater and mine drains in the Belt-Stockett area. Sulfate in the highly acidic mine drains (which include the Anaconda, French Coulee, Giffen, Nelson, Mt. Oregon, and Cottonwood No. 6 drains) is isotopically "light" with respect to both O and S, meaning that it is enriched in the lighter ^{16}O and ^{32}S isotopes relative to the seawater isotopic standard. This causes the $\delta^{18}O$ and $\delta^{34}S$ values – expressed in parts per thousand, or "per mil" – to be strongly negative. In contrast, groundwater in the underlying Madison Limestone (which includes Well 1A and Giant Spring) contains sulfate that is isotopically "heavy" (enriched in ^{18}O and ^{34}S).

The clear separation in $\delta^{18}O$ and $\delta^{34}S$ of the mine drains as opposed to the Madison Fm. groundwater makes it possible to use stable isotopes to determine whether or not acid mine drainage in the GFLCF is leaking vertically into the underlying Madison Limestone. Given the importance of the Madison as a groundwater aquifer, this would be an undesirable circumstance. Our preliminary data suggest that some small-scale leakage of AMD into the Madison may indeed have occurred, for example in the vicinity of Well 4A. This well was screened in the Madison Limestone, but contains isotopically light sulfate, possibly due to mixing with AMD from the Anaconda Coal Mine. Additional sampling and isotopic analysis are needed to follow up these preliminary results.

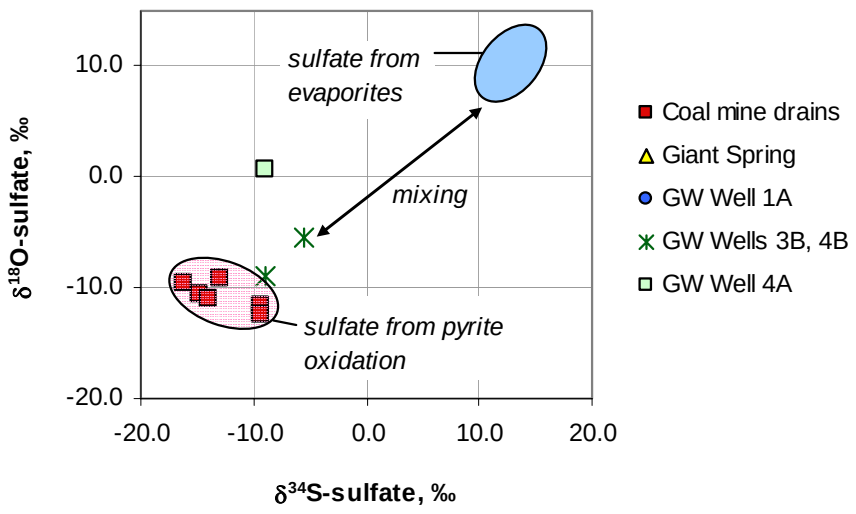

Figure 10. Stable isotopic composition of sulfate from groundwater and acid mine drainage in the Belt-Stockett area.

AMD Treatment and Control

Many of the AMD waters in the GFLCF pass through populated areas such as the towns of Belt, Stockett, and Sand Coulee, and are easily accessible by animals and humans. Because AMD has been occurring since at least the early 1900's (Shurick, 1909), time alone will not solve the problem for many centuries. Despite the longevity and severity of this AMD, relatively little reclamation has been done to date, mainly because there is no long-term source of funding to operate and maintain AMD treatment facilities. Treatment has been attempted at a modest scale using passive methods, only to end in disappointing results. Technologies that were tested but failed include aerobic and anaerobic constructed wetlands, limestone channels, and anoxic limestone drains (McArthur, 1970; McCurley and Koerth, 1994). In most cases, the treatment designs failed due to the very high concentrations and loads of acidity, metals and sulfate of the AMD waters. For example, Figure 11 shows a limestone channel that was constructed to passively treat mine discharge from the Cottonwood No. 6 drain. When this site was visited in November 2005, there was virtually no difference in pH of the mine water between the inlet and outlet of the channel. This is due to the formation of secondary mineral precipitates (gypsum, hydrous metal oxide) that effectively armor the reactive limestone and prevent direct contact between the $CaCO_3$ and the AMD. Another negative factor is Montana's harsh winters. Copious quantities of metal-rich precipitate accumulate in the winter months when vegetation is frozen, and these metalliferous precipitates inhibit regrowth of vegetation during the next growing season.

Figure 11. Results of AMD mitigation efforts. Left – Failed limestone channel at the Cottonwood No. 6 drain. The limestone gravel in the channel has been completely coated with gypsum and hydrous metal oxide [Nov., 2005]. Right – Mine water seepage (brown, devegetated area in center) subbing up behind a house near Stockett [Nov., 2005]. This seepage appeared after one of the main adit seeps in the area was plugged.

Construction and long-term operation of water treatment plants would be very costly and at present exceeds the financial ability of the State of Montana. In lieu of passive or chemical treatment, the most promising mitigation approach involves some form of AMD *source control*. Due to the large extent of the mine workings (approximately 13 km^2 for the Anaconda Mine at Belt, approximately 46 km^2 for the complex of mines at Stockett and Sand Coulee), solutions such as grouting of fractures to reduce the migration of water into the underground workings are impractical. In addition, experience shows that simply plugging the points of discharge from adits and drains merely results in diffuse AMD seepage on surrounding hillsides (Figure 11). A short-term pilot program in the mid-1980's to reduce the infiltration of meteoric water from the overlying crop lands to the mine workings showed some potential but could not be sustained due to the lack of the necessary funding and administrative infrastructure. An alternative idea (described by Osborne et al., 1987) is to install a series of drain wells into the Kootenai Fm. which would route the shallow, clean groundwater overlying the coal-bearing strata by gravity into the underlying Morrison Fm. If successful, this could cut off the primary source of recharge into the coal beds, with a resultant decrease in adit seepage. However, in some cases, it may be more practical to take the opposite approach and completely flood the mine workings – which have extensive horizontal but limited vertical extent – by plugging the existing adit drains, or installing grout curtains in portions of the interior of the mines. Although this would not prevent mine drainage entirely, the quality of the water exiting the subsurface would likely improve, due to reduction of oxygen

infiltration rates into the coal-bearing strata (see discussion of Case Studies above). The relative merits of these various alternatives are still being evaluated.

Acknowledgements

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