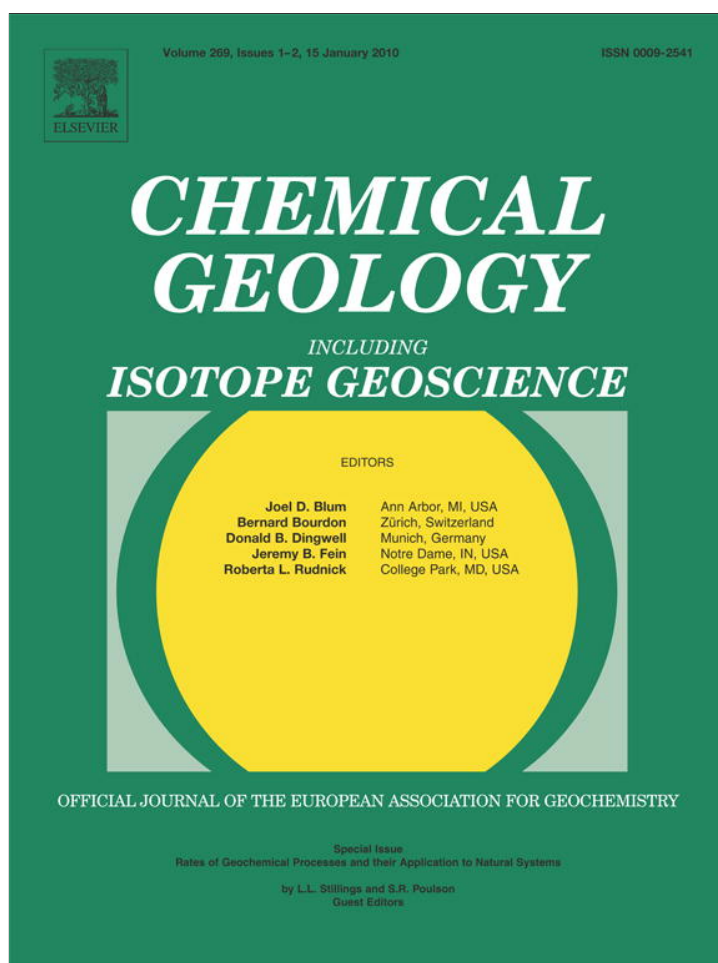


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Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Geochemistry and stable isotope investigation of acid mine drainage associated with abandoned coal mines in central Montana, USA

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ARTICLE INFO

Article history:

Received 14 November 2008

Received in revised 14 April 2009

Accepted 25 May 2009

Keywords:

Acid rock drainage

Geochemistry

Stable isotopes

Coal

Iron oxidation rate

Montana

Diurnal

Diel

ABSTRACT

The Great Falls-Lewistown Coal Field (GFLCF) in central Montana contains over 400 abandoned underground coal mines, many of which are discharging acidic water with serious environmental consequences. Areas of the mines that are completely submerged by groundwater have circum-neutral pH and relatively low concentrations of metals, whereas areas that are only partially flooded or freely draining have acidic pH (<3) and high concentrations of metals. The pH of the mine drains either decreases or increases after discharging to the surface, depending on the initial ratio of acidity (mainly Al and Fe²⁺) to alkalinity (mainly HCO₃⁻). In acidic, Fe-rich waters, oxidation of Fe²⁺ after exposure to air is microbially catalyzed and follows zero-order kinetics, with computed rate constants falling in the range of 0.97 to 1.25 mmol L⁻¹ h⁻¹. In contrast, Fe²⁺ oxidation in near-neutral pH waters appears to be first-order with respect to Fe²⁺ concentration, although insufficient data were collected to constrain the rate law expression. Rates of Fe²⁺ oxidation in the field are dependent on temperature such that lower Fe²⁺ concentrations were measured in down-gradient waters during the day, and higher concentrations at night. Diel cycles in dissolved concentrations of Zn and other trace metals (Mn, Ni) were also noted for down-gradient waters that were net alkaline, but not in the acidic drains.

The coal seams of the GFLCF and overlying Cretaceous sandstones form a perched aquifer that lies ~50 m above the regional water table situated in the underlying Madison Limestone. The δD and δ¹⁸O values of flooded mine waters suggest local derivation from meteoric water that has been partially evaporated in agricultural soils overlying the coal mines. The S and O isotopic composition of dissolved sulfate in the low pH mine drains is consistent with oxidation of biogenic pyrite in coal under aerated conditions. A clear distinction exists between the isotopic composition of sulfate in the acid mine waters and sulfate in the adjacent sedimentary aquifers, making it theoretically possible to determine if acid drainage from the coal mines has leaked into the underlying Madison aquifer.

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1. Introduction

Acid mine drainage (AMD) is a well-documented environmental problem at many active and abandoned mine sites world-wide. The basic problem is simple: exposure of pyrite and other metal-sulfides to weathering under atmospheric conditions produces sulfuric acid, with subsequent mobilization of other toxic substances (metals, metalloids) into groundwater and surface water. The details of the process are complex, however, and involve a large number of gas-exchange, mineral precipitation, surface chemistry, and redox reactions, many of which are catalyzed by microbes (e.g., Nordstrom and Alpers, 1999; Nordstrom, 2003; Blowes et al., 2003; Blodau, 2006; Cravotta, 2008a,b). Although

most active mines have a zero-discharge policy with respect to release of AMD to the environment, this is often not the case for abandoned mines, especially when there is no legally responsible owner. Hence, it is often the case that AMD from abandoned mines is released to down-gradient watersheds with little or no treatment.

An extensive literature exists on characterization and reclamation of AMD from coal deposits in the eastern U.S. (Growitz et al., 1985; Herlihy et al., 1990; Hedin et al., 1994; Cravotta, 2008a,b). In contrast, most studies of AMD in the western U.S. have focused on hard rock metal mining. Sites such as the Berkeley Pit copper mine in Butte, Montana, (Davis and Ashenberg, 1989; Pellicori et al., 2005), the Iron Mountain Cu–Zn mine in California (Edwards et al., 2000; Nordstrom et al., 2000) and the Summitville gold mine in Colorado (Gray et al., 1994) are highly publicized examples of AMD in the western U.S. that continue to pose significant environmental challenges. Comparatively little scientific

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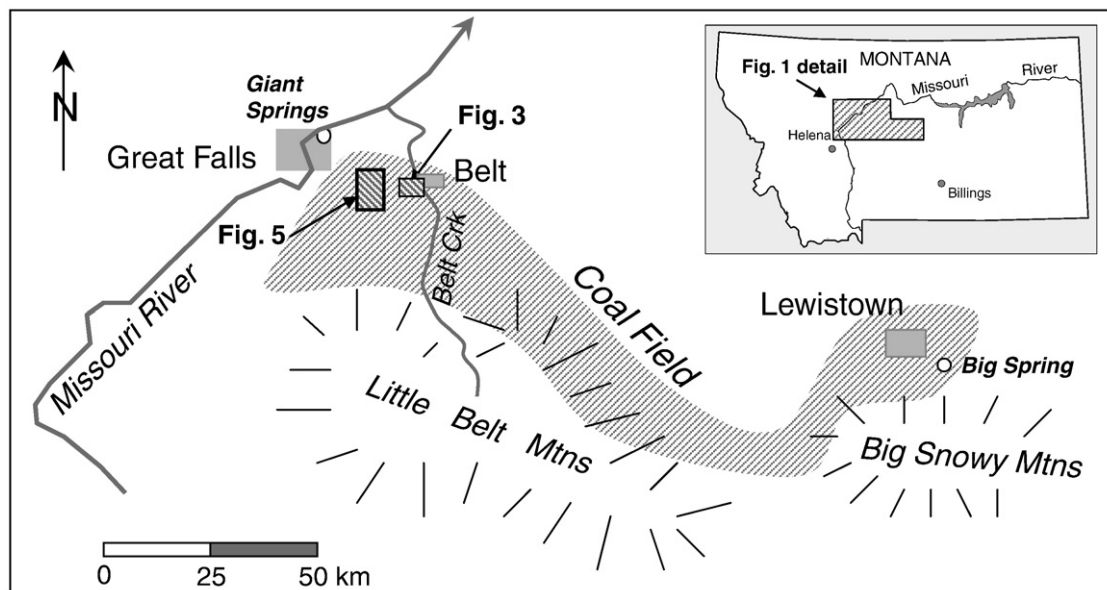


Fig. 1. Generalized location map of the study area.

study has been made on AMD associated with coal in the Rocky Mountain region, despite the fact that many western U.S. states are important producers of coal. This is largely because most of the coal fields actively being mined (e.g., the Powder River Basin of Wyoming–Montana) are low-S coals, and/or are being mined in such a way that major AMD problems have, to date, been avoided (e.g., Davis, 1984; Ferreira et al., 1989). The Great Falls-Lewistown Coal Field (GFLCF) of central Montana, U.S., is an exception to this rule. The purpose of this study is to summarize previous literature on the occurrence of AMD in the GFLCF, to examine spatial and temporal changes in the chemistry of the mine waters after they discharge to the surface and become aerated, and to use stable isotopes to help determine sources of water and dissolved sulfate in the abandoned coal mines, as well as the surrounding sedimentary aquifers.

1.1. Site geology and hydro-stratigraphy

The Great Falls-Lewistown Coal Field (Fig. 1) produced sub-bituminous to bituminous coal from large underground mines in the late 19th and early 20th centuries (Fisher, 1909). The largest mines were located near the western edge of the district near the towns of Belt and Stockett (Figs. 1 and 2), and it is in this region that the most serious environmental problems have occurred. Many of the abandoned mines are producing AMD that contaminates streams and alluvial groundwater (Osborne et al., 1983a, 1987; Karper, 1998). Reclamation of these sites has focused on removal of mine buildings and associated waste, as well as landscaping and revegetation of disturbed soils. Attempts to treat some of the acid mine drainages passively (e.g., open limestone channels, constructed wetlands) have failed due to the high acidity of the waters coupled with extreme cold temperatures in winter (McCurley and Koerth, 1994).

Fig. 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–Cretaceous Morrison Formation – mainly shale and siltstone – and are conformably overlain by clastic sediments of the Cretaceous Kootenai Formation (Vuke et al., 2002; Duaiame et al., 2004). Erosion-resistant sandstone units within the Kootenai Fm., including the Cutbank and Sunburst members, form the backbone of the broad, grassy uplands in this portion of the Rocky Mountain foothills. The coal seams crop out in deeply incised valleys formed by ephemeral streams that drain northward towards the Missouri River.

In the vicinity of Belt, the Jurassic Swift and lower Morrison Formations lie unconformably above the Mississippian Madison Group, a ~500 m thick marine limestone consisting of the Mission Canyon and underlying Lodgepole Formations. The Madison aquifer is an important local and regional source of potable groundwater. The Madison feeds two very large natural springs at either end of the GFLCF named Giant Springs and Big Spring (Fig. 1). Giant Springs, one of the largest fresh water springs in the U.S., discharges ~8400 L s⁻¹ of

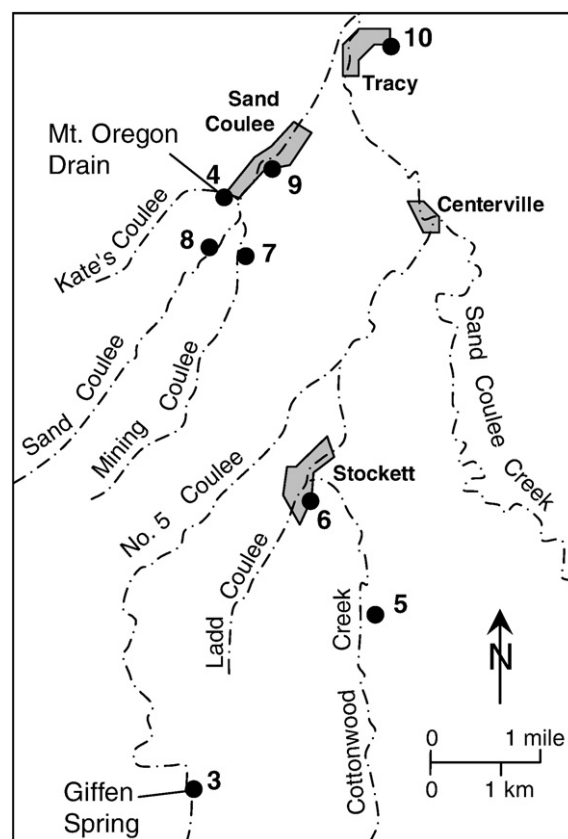


Fig. 2. Location map of the Stockett area. Solid circles show locations of mine drains discussed in this paper (see Table 1 footnotes for location names).

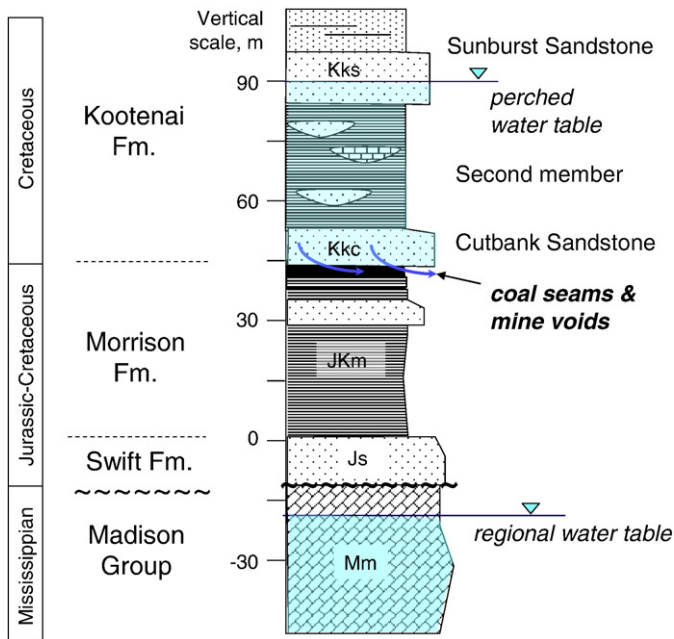


Fig. 3. Simplified section showing major hydro-stratigraphic units in the Belt–Stockett area. Blue shading denotes groundwater. Adapted from Duaiame et al. (2004).

groundwater near the banks of the Missouri River in the city of Great Falls (Davis et al., 2001). The recharge zone for Giant Springs has traditionally been thought to be outcrops of the Madison Group in the Little Belt Mountains, ~50 km south of Great Falls (Fig. 1). However, recent tritium analyses of Giant Springs (Davis et al., 2001; Duaiame et al., 2004) indicate a component of recharge that is relatively young and therefore inferred to be more local. Big Spring, near Lewistown, MT, has an average discharge of 3700 L s^{-1} and is thought to be recharged in the Big Snowy Mountains, ~15 km to the south (Fig. 1).

Near Belt, the coal seams of the GFLCF are located several 10s of meters above the regional water table (Fig. 3). A perched water table of considerable lateral extent overlies the coal seams in permeable sandstone units (Cutbank, Sunburst members) of the Kootenai Fm. This water slowly drains into the underlying mine workings, and serves as the main source of groundwater recharge to the mines (Duaiame et al., 2004). 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 mines have extensive groundwater 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 (Fig. 4). Most of the AMD from the Anaconda Mine exits at the Anaconda drain (Fig. 5A); a lesser amount exits at the French Coulee drain. The combined AMD flows directly to

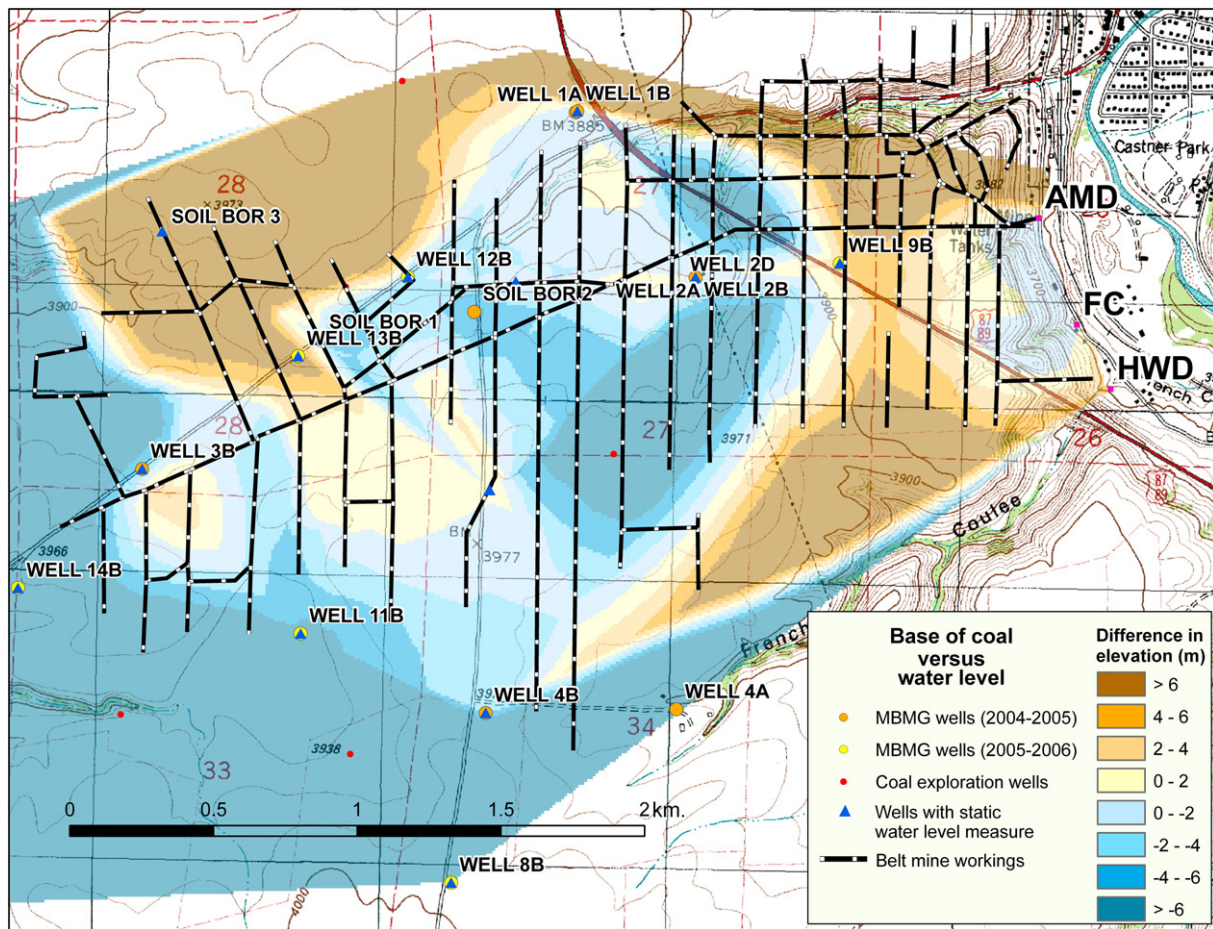


Fig. 4. Map of the major haulage tunnels (black lines) in the Anaconda Coal Mine near Belt. Belt Creek is in the upper right corner of the map, as is the city of Belt. The colors show the relative elevation of the base of coal and the static water level. Shades of blue indicate portions of the coal formation that are partially or completely submerged in water. Shades of yellow and brown are dry. MBMG monitoring well locations and soil borings are also shown. AMD = Anaconda Mine Drain; FC = French Coulee Drain; HWD = Highway Drain.

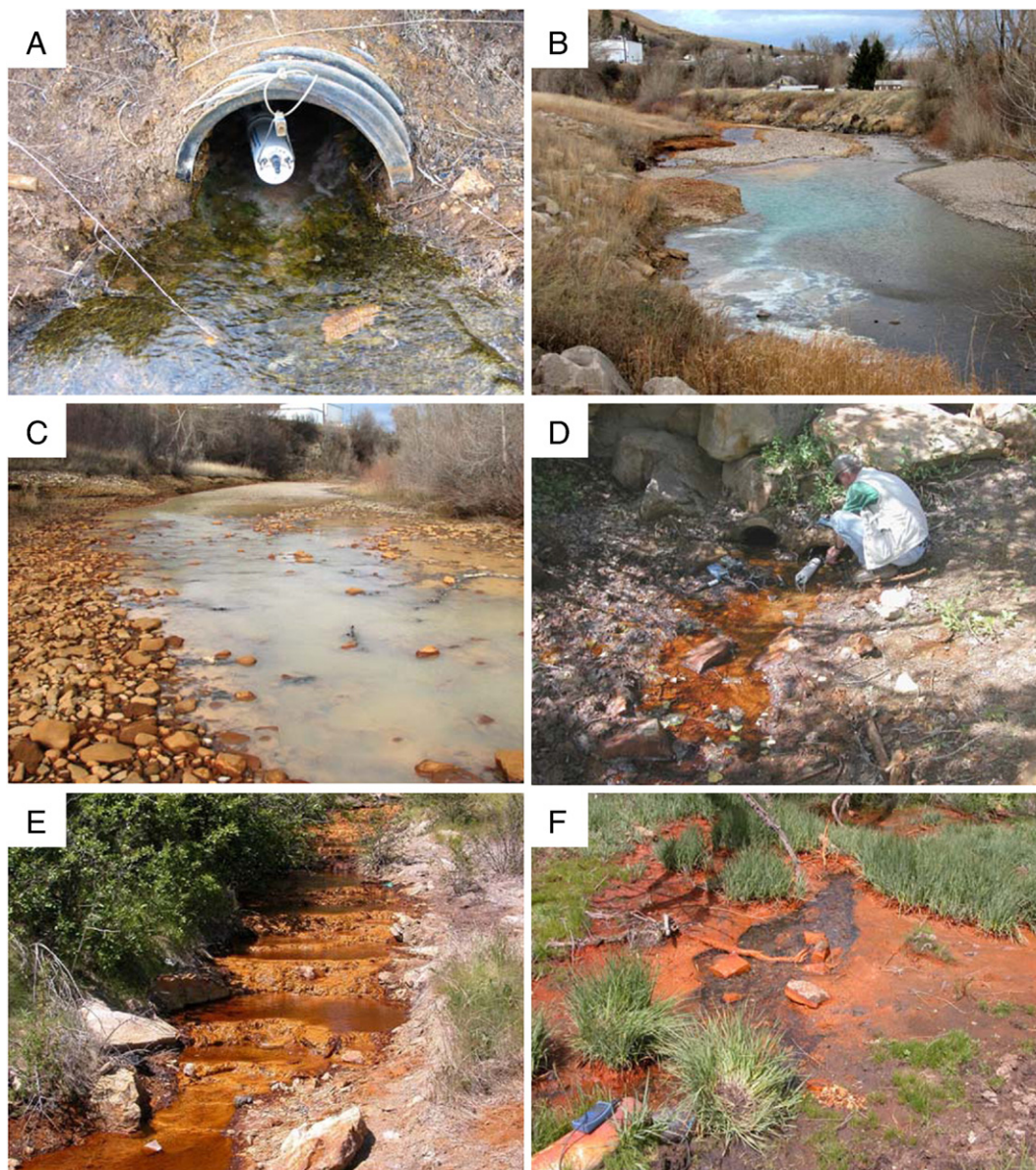


Fig. 5. Photographs of the study area. A) Anaconda drain with datasonde (Nov-04); B) White aluminous precipitates (foreground) and red ochre precipitates (upper left) at confluence of the Anaconda drain (entering from left) and Belt Creek (Nov-04); C) Belt Creek 100 m below the confluence with the Anaconda drain (Nov-04); D) Mt. Oregon drain (June-04); E) Ferric hydroxide terraces in Kate's Coulee (June-04); F) The main mine discharge at Giffen Spring (June-04).

Belt Creek, with severe contamination of this otherwise high quality water (Fig. 5B and C) (Reiten et al., 2006).

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.

2. Methods

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.

Further details on methodology are given in Karper (1998). Results from the USGS study are used below to discuss general trends in the chemistry of AMD discharges in the GFLCF. Several of the same mine discharges sampled by Karper (1998) were visited during 2005–2006 to collect samples for $\text{Fe}^{2+}/\text{Fe}^{3+}$ speciation and stable isotope analysis (see below).

The Montana Bureau of Mines and Geology (MBMG) is currently undertaking a hydrological study of the abandoned Anaconda Coal Mine in the town of Belt. Several dozen PVC groundwater monitoring wells have been installed to depths up to 236 m. Selected results from this ongoing study are included in this paper. Groundwater samples for water quality and/or stable isotope analysis were obtained after pumping at least three well volumes, during which time field parameters including pH, water temperature, specific conductance (SC), dissolved oxygen (DO), and redox potential (Eh) were continuously monitored using a freshly-calibrated Hydrolab datasonde. Filtration was accomplished on-site using disposable 0.45 μm in-line filters. Separate samples were collected for alkalinity and

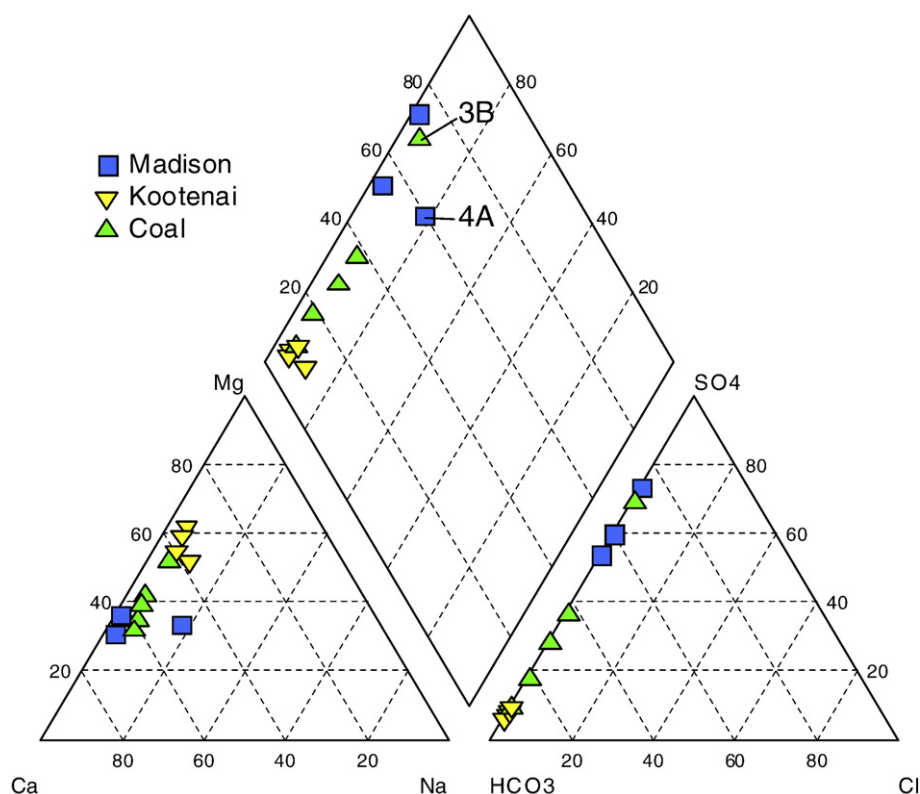


Fig. 6. Piper diagram for groundwater samples from monitoring wells near the Anaconda Coal Mine. The diagram is based on mg L⁻¹ units.

laboratory pH (raw, unacidified), anions (filtered, unacidified), and major/trace metals (filtered, acidified to pH < 2 with HNO₃). The samples were analyzed at the MBMG laboratory in Butte, Montana, and all of the analytical data are stored electronically at GWIC (2008). Additional information on well completion and sampling/analytical methods can be found in Duime et al. (2004).

To investigate changes in the chemistry of AMD waters below their respective point-source discharges, synoptic and diel surface-water samples were collected at Giffen Spring and Kate's Coulee during June, 2004. Field parameters were measured on site with a Hydrolab Minisonde MS-5 and hand-held WTW or Orion multimeters. Eh measurements were corrected to the Standard Hydrogen Electrode by calibration with ZoBells solution. Alkalinity was determined in the field by pH titration. Water samples were collected in 60 mL high density polyethylene (HDPE) bottles and preserved with 0.6 mL conc. trace metal grade HNO₃. Parallel samples were collected for total metals (unfiltered) and dissolved metals (filtered in the field to 0.2 μm using a plastic syringe and disposable PES syringe filters). No attempt was made in this study to quantify the abundance of colloidal metal particles with diameters less than the filters used in the field. Filtered and HCl-preserved samples were analyzed in the field within 12-h of sample collection for Fe²⁺/Fe³⁺ speciation using a portable colorimeter and the Ferrozine procedure (Stookey, 1970). Filtered and HNO₃-preserved water samples were analyzed for a suite of major and trace metals by conventional ICP-AES analysis (EPA Method 200.7).

Filtered samples for isotopic analysis of water were collected in a 10 mL glass vial with no head space. Preparation of samples for isotopic analysis of dissolved sulfate followed the procedures of Carmody et al. (1998). Sulfate was extracted as BaSO₄ by addition of BaCl₂ to a filtered water sample with pH adjusted to < 3 to prevent formation of BaCO₃. Stable isotope analyses were performed at the University of Nevada-Reno using a Micromass IsoPrime stable isotope ratio mass spectrometer (IRMS). Water-δ¹⁸O analyses were performed using a Micromass MultiPrep device interfaced to a dual inlet and the IRMS, and all other isotope analyses were performed using a

Eurovector elemental analyzer interfaced to the IRMS. Isotope values are reported in the usual δ notation in units of ‰ (per mil, or parts per thousand), versus VCDT for sulfur and versus VSMOW for oxygen and hydrogen. Sample preparation followed the method of Epstein and Mayeda (1953) for δ¹⁸O_{water}, Morrison et al. (2001) for δD_{water}, Giesemann et al. (1994) for δ³⁴S_{sulfate}, and Kornexl et al. (1999) for δ¹⁸O_{sulfate}. Analytical uncertainties are ± 0.2‰ for δ³⁴S_{sulfate}, ± 0.4‰ for δ¹⁸O_{sulfate}, ± 0.1‰ for δ¹⁸O_{water}, and ± 1‰ for δD_{water}.

3. Results and discussion

3.1. Geochemistry of mine seepage waters

Selected water quality results from the earlier USGS study (Karper, 1998) for mine water discharges in the GFLCF are summarized in Table 1. 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 2 g L⁻¹), and Al (up to 1.6 g L⁻¹). Only two mine discharges – Giffen Spring and the Mt. Oregon drain – had average pH values > 4. As discussed below, a major factor to explain the differences in pH of the mine waters is the variably saturated nature of the mine workings (Osborne et al., 1987; Doornbos, 1989). Pyrite oxidation in mine workings that are completely flooded is limited by availability of oxygen, whereas there is no O₂ limitation in mines that are partially flooded or freely draining.

The concentrations of Fe in the GFLCF mine drains are in most cases greater than those of the common ions (Ca²⁺, Mg²⁺, Na⁺, K⁺), and therefore these waters are best classified as Fe–SO₄ or Fe–Al–SO₄ waters. The dominant dissolved metals in the GFLCF mine seeps, in order of average abundance (computed from data in Karper, 1998), are Fe (620 mg L⁻¹) > Al (430 mg L⁻¹) > Zn (19 mg L⁻¹) > Ni (4.2 mg L⁻¹) > Mn (2.7 mg L⁻¹) > Co (2.4 mg L⁻¹) > Cu (140 μg L⁻¹) > Cr (120 μg L⁻¹) > Cd (65 μg L⁻¹). Aside from somewhat lower Mn abundances, this sequence is similar to what has been documented from Pennsylvania coal mine discharges (Cravotta, 2008a).

Table 1
Selected water quality parameters for mine discharges in the Great Falls-Lewiston Coal Field, Montana.

Site	1	2	3	4	5	6	7	8	9	10
pH, s.u.	2.9	2.9	4.9	4.2	2.6	2.5	2.6	3.1	2.6	2.9
Max	3	3	5.8	4.7	2.8	2.8	3	3.4	3	3.1
Min	2.8	2.8	3.7	4.0	2.5	2.2	2.4	2.9	2.3	2.4
Q, l s ⁻¹	6.2	6.2	13.9	1.98	1.42	0.57	0.57	0.85	0.85	2.55
Max	8.2	8.2	15.6	5.10	4.25	2.83	1.13	3.12	2.27	17.3
Min	4.2	4.2	10.8	0.57	0.57	0.03	0.28	0.00	0.25	0.85
Temp, °C	12.3	12.3	9.2	11.4	9.6	11.7	9.6	11.1	11.6	10.7
Max	18.5	18.5	11	15	11.5	26	14.5	23	17.5	11.5
Min	6.5	6.5	8.5	10	6	0	7.5	7.5	5.5	8.5
SC, mS cm ⁻¹	2.38	2.38	1.16	2.83	5.79	8.92	7.31	3.29	7.80	1.62
Max	2.46	2.46	1.4	3.01	6.02	10.8	7.62	3.48	8.98	2.36
Min	2.28	2.28	0.982	2.69	5.57	6.47	6.68	3.1	6.81	1.41
Acidity ^a	1.05	3.65	0.22	1.50	4.10	10.0	7.5	2.05	8.40	0.30
Max	1.25	6.00	0.48	1.65	4.35	13.5	8.0	2.20	10.0	0.65
Min	0.90	1.10	0.03	1.35	3.70	5.0	7.0	1.75	7.0	0.21
Acidity load ^b	565	447	258	257	502	489	367	150	617	65
Fe ²⁺ , mg L ⁻¹	194	n.a.	69	275	553	n.a.	n.a.	n.a.	1525	n.a.
Fe ³⁺ , mg L ⁻¹	21	n.a.	<1	<5	147	n.a.	n.a.	n.a.	200	n.a.

Italicized values are averages of monthly measurements collected by the U.S. Geol. Survey during the period July, 1994 to Sept., 1996. All results from Karper (1998) except the Fe(II)/Fe(III) speciation data, which were determined on samples collected in this study in 2005.

^a Acidity units are g CaCO₃ L⁻¹.

^b Based on a 3-year average acidity and flow; acidity load units are kg CaCO₃ day⁻¹. Site descriptions (see Figs. 2 and 4 for locations): 1 – Anaconda drain; 2 – French Coulee drain; 3 – Giffen Spring; 4 – Mt. Oregon drain; 5 – Cottonwood Mine no. 6 drain; 6 – Cottonwood Mine no. 2 drain; 7 – unnamed drain in Mining Coulee; 8 – unnamed drain in Sand Coulee; 9 – Nelson Mine drain; 10 – Pipe Spring at Tracy.

The majority of the dissolved Fe in the mine drains was ferrous (Fe²⁺), although Fe³⁺ was also present in the more acidic waters (Table 1). In the higher pH Giffen Spring and Mt. Oregon drains, essentially all of the dissolved iron exiting the subsurface was ferrous. Average dissolved As concentrations in most of the GFLCF mine seeps were below 10 µg L⁻¹, with the exception of the Nelson drain (54 µg L⁻¹), the Mt. Oregon drain (14 µg L⁻¹), and the French Coulee drain (19 µg L⁻¹). Dissolved Se concentrations were all below the limit of detection (1 to 5 µg L⁻¹). Low As and Se concentrations are also typical of coal mine drainage in the eastern U.S., and most likely reflect the strong affinity of these metalloids to adsorb onto secondary Fe oxy-hydroxides in acidic waters (Cravotta, 2008a,b).

Acidity values based on titrations performed in the laboratory (Table 1, Karper, 1998) were quite high, ranging from 0.3 to 10.0 g L⁻¹ CaCO_{3,eq}. The titrated values are slightly higher (8.4% on average) than acidity values calculated from the published analytical data of Karper (1998) using the following formula (Kirby and Cravotta, 2005):

$$\text{acidity}(\text{mgCaCO}_3\text{L}^{-1}) = 50 * (1000 * 10^{-\text{pH}} + 2 * [\text{Fe}] / 55.85 + 2 * [\text{Mn}] / 54.94 + 3 * [\text{Al}] / 26.98) \quad (1)$$

where the brackets [] denote concentration in mg L⁻¹. This discrepancy is attributed to the presence of HSO₄⁻ acidity for many of the GFLCF mine seeps with pH < 3, as well as the fact that some dissolved Fe was present as Fe³⁺ in the mine seeps (Table 1), whereas Eq. (1) assumes all Fe is present as Fe²⁺. Because the average discharge volumes were small (0.57 to 13.9 L s⁻¹, Table 1), the average acidity loads were all less than 1 × 10³ kg CaCO₃ day⁻¹. Whereas most of the drains showed marked seasonal variations in flow, others – such as the Anaconda drain – were more constant. Increases in mine discharge correlate to seasonal patterns of snowmelt and extended precipitation events (Karper, 1998; Duaique et al., 2004).

3.2. Geochemistry of groundwater at the Anaconda Coal Mine

Table 2 and Fig. 6 summarize water quality results for groundwater monitoring wells in the vicinity of the Anaconda Coal Mine. Locations for these sites are shown in Fig. 4 (note that A, B, C, and D for a given well number have nearly the same map location). Samples from the Kootenai Fm. (Cutbank and Sunburst members) are Mg–Ca–HCO₃ waters with neutral pH and relatively low sulfate concentrations (15

to 32 mg L⁻¹), and trace metal concentrations near or below the instrument detection limits. Samples from the Madison aquifer (Wells 1A, 2A, 4A) are Ca–Mg–SO₄–HCO₃ waters (Fig. 6) with neutral pH and relatively high SC values. Samples from unmined portions of the coal seam (Wells 8B, 14B, 15B) have a major ion chemistry that is intermediate between that of the overlying Kootenai and underlying Madison aquifers (Fig. 6). Groundwater in the flooded portions of the coal mine (Wells 3B, 4B) is characterized by higher concentrations of dissolved sulfate, but still quite low concentrations of metals, with the exception of Well 3B, which contains 34.5 mg L⁻¹ Fe (Table 2). Well 3B may represent submerged mine workings that have received AMD from tunnels to the south where the coal bed is exposed to air (Fig. 4). To date, it has not been possible to obtain a water sample from any of the wells drilled into the non-flooded portions of the mine complex (e.g., Wells 1B, 2B, 9B, 13B). However, at Well 2B it was possible to lower a datasonde into a shallow pool of water on the mine floor. This water had a pH of 1.9 and an SC of 9.5 mS cm⁻¹, indicating severe AMD conditions. Not surprisingly, oxygen ingress into the mine passageways is a prerequisite for rapid pyrite oxidation and generation of mine water with strongly acidic pH.

3.3. Downgradient changes in chemistry of surface AMD water

This section examines changes in the chemistry of the mine drain waters after they emerge at the surface, become aerated, and move off-site. The Mt Oregon drain and Giffen Spring were selected for detailed examination because they show very different geochemical behavior upon reaction with the atmosphere.

3.3.1. Mt. Oregon drain

The Mt. Oregon drain is located near the town of Sand Coulee, in an ephemeral side drainage known as Kate's Coulee (Fig. 2). AMD from the drain emerges from a pipe at the base of a sandstone outcrop (Fig. 5D). On the date visited (June 16, 2004) this water had a pH of 4.2, a flow of 0.8 L s⁻¹, and a dissolved Fe concentration of 275 mg L⁻¹. The emerging water was devoid of dissolved oxygen (DO), and all dissolved Fe was ferrous. Below the drainpipe, the mine discharge flowed down Kate's Coulee in a series of ferric oxide-stained terraces (Fig. 5E) before joining the larger streambed of Sand Coulee. Sand Coulee above Kate's Coulee was dry, and the red-stained mine water passed through the village of Sand Coulee undiluted before soaking

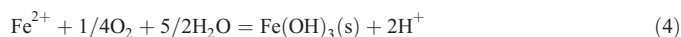
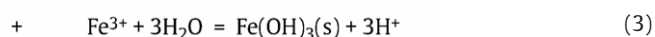
Table 2
Selected water quality data for groundwater wells in the vicinity of the Anaconda Coal Mine.

Well	Aquifer	T.D. ^a m	Date	pH	SC mS/cm	Temp °C	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Fe mg/L	Mn mg/L	HCO ₃ mg/L	SO ₄ mg/L	Cl mg/L	As ⁵ µg/L	Co µg/L	Ni µg/L	Zn µg/L
2C	Sunburst	24.4	8/05	7.4	0.50	16.1	44	50	7.1	2.0	0.02	0.01	307	19	1.2	<1	<2	<2	6
3C	Sunburst	48.4	8/05	7.2	0.56	14.7	56	47	18	5.1	0.45	0.10	413	29	2.1	8	<2	11	20
8C	Sunburst	31.1	8/06	7.1	0.61	n.a.	53	45	9.0	1.7	0.40	0.08	387	32	1.7	1	<2	<2	6
2D	Cutbank	93.2	8/05	7.5	0.49	10.9	45	45	6.9	1.3	0.01	0.01	303	15	1.4	1	<2	<2	38
2B	Coal (void)	n.a.	8/05	1.9	9.50	10.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3B	Coal (flooded)	85.9	8/05	6.7	0.70	9.6	87	37	9.6	3.5	34.5	0.2	165	301	3.3	<1	10	21	53
4B	Coal (flooded)	86.5	8/05	7.0	0.75	10.5	128	40	17	6.7	0.10	0.58	400	184	3.9	4	3.1	13	23
8B	Coal (flooded)	92.0	12/05	7.6	0.57	16.0	54	40	7.8	1.7	0.26	0.10	363	29	2.1	2	<2	<2	16
14B	Coal (flooded)	82.8	7/06	7.0	0.54	10.7	73	26	9.3	3.3	0.17	0.13	295	92	2.1	<1	<2	<2	36
15B	Coal (flooded)	78.6	8/06	6.9	0.64	16.0	57	27	5.6	1.6	0.02	0.03	285	48	2.3	<1	<2	3	22
1A	Madison	204	8/05	7.4	0.53	10.8	93	26	4.2	1.4	0.01	<0.01	203	188	1.0	<1	<2	<2	22
2A	Madison	224	11/05	7.4	1.07	13.1	197	70	5.5	2.1	0.22	0.24	264	586	<5	5	28	75	
4A	Madison	236	8/05	7.3	0.88	11.3	91	38	3.8	2.3	0.08	0.07	273	325	<5	2	3	11	

n.a. = not available. All data from GWIC (2008). Refer to Fig. 4 for well locations (note: A, B, C, D for a given well number are at the same location).
^a T.D. = total depth of well. All wells include a perforated screen 1 to 10 m in length at the bottom.

into the gravel streambed. A number of changes in water quality were observed with distance downstream (Fig. 7), including: 1) an increase in water temperature; 2) an increase in specific conductance (SC); 3) a steady drop in pH from 4.2 to 2.6; 4) a decrease in total Fe concentration; 5) an increase in the Fe³⁺/Fe²⁺ ratio; and 6) an increase in Eh. Judging from longitudinal trends in the major cations and anions (Ca, Mg, Na, SO₄), the slight increase in SC was probably a result of evapo-concentration. The sampling date was quite hot (T > 35 °C), and the mine water was moving very slowly through Kate's Coulee, pooling up in each of the Fe oxide-stained terraces (Fig. 5E). Based on an SC tracer test using a slug of NaCl, the water took 1.5 h to travel the first 150 m below the mouth of the drain.

The observed changes in pH, Eh, Fe concentration and Fe³⁺/Fe²⁺ ratio (Fig. 7) in Kate's Coulee are explained by oxidation of Fe²⁺ to Fe³⁺, followed by precipitation of ferric oxy-hydroxide, which is a net acid-producing reaction:



Despite a marked decrease in pH, over 80% of the initial dissolved Fe precipitated by the time the drain water soaked into the ground in Sand Coulee, 700 m below the drain opening (Fig. 7). There was a notable decrease in the amount of secondary Fe minerals at this location in Sand Coulee. Apparently, the ochreous precipitates that create an impermeable liner in the creek further upstream were no longer forming at this location due to the fact that the Fe oxidation and hydrolysis reactions had already progressed to a quasi-equilibrium state. Supporting evidence for this idea is given in Fig. 7D, which shows that the saturation indices for all forms of ferric oxy-hydroxide were near or below zero by the time the water reached the furthest downstream sampling location. Previous workers (e.g., Osborne et al., 1983a) have documented AMD contamination of shallow alluvial aquifers occupying the valley floors in the Stockett area, and the present study illustrates why this may be the case. The majority of the local population relies instead on deep groundwater wells completed in the Madison aquifer.

The rate of Fe²⁺ oxidation below the Mt. Oregon drain was calculated by dividing the change in Fe²⁺ concentration between the outlet of the drain and a sampling station 150 m downstream by the estimated travel time of 1.5 h. The resultant rate was 0.97 mmol L⁻¹ h⁻¹ at ~08:00 when water temperature was 11 to 12 °C, and 1.25 mmol L⁻¹ h⁻¹ at ~13:00 when water temperature at the downstream station had increased to 21.3 °C. The linear decrease in Fe²⁺ concentration with distance downstream (Fig. 7) suggests a reaction rate that was zero-order with respect to Fe²⁺. As discussed by Nordstrom (2003), microbial iron oxidation is often zero-order in acidic waters that initially contain very high concentrations of Fe²⁺. Rates determined in the field from studies at other sites (summarized in Nordstrom, 2003) fall in the range of 0.6 to 5 mmol L⁻¹ h⁻¹, in broad agreement with the present results. The temperature dependence for the rate of Fe²⁺ oxidation in Kate's Coulee was somewhat weaker than results reported in the literature. For example, Wakao and Shiota (1982) showed that an increase in water temperature from 9 to 23 °C resulted in a doubling of their measured Fe²⁺ oxidation rates. Because of the weak temperature dependence on Fe²⁺ oxidation rates, diel variations in the concentration and speciation of Fe in Kate's Coulee were minimal (data not shown).

3.3.2. Giffen Spring

Giffen Spring is a large AMD discharge near the headwaters of Coulee No. 5, an ephemeral tributary of Sand Coulee (Fig. 2). Of the various mine waters in Table 1, Giffen Spring typically has the highest discharge, the highest pH, and the lowest metal concentrations. These conditions – along with information on the orientation of the

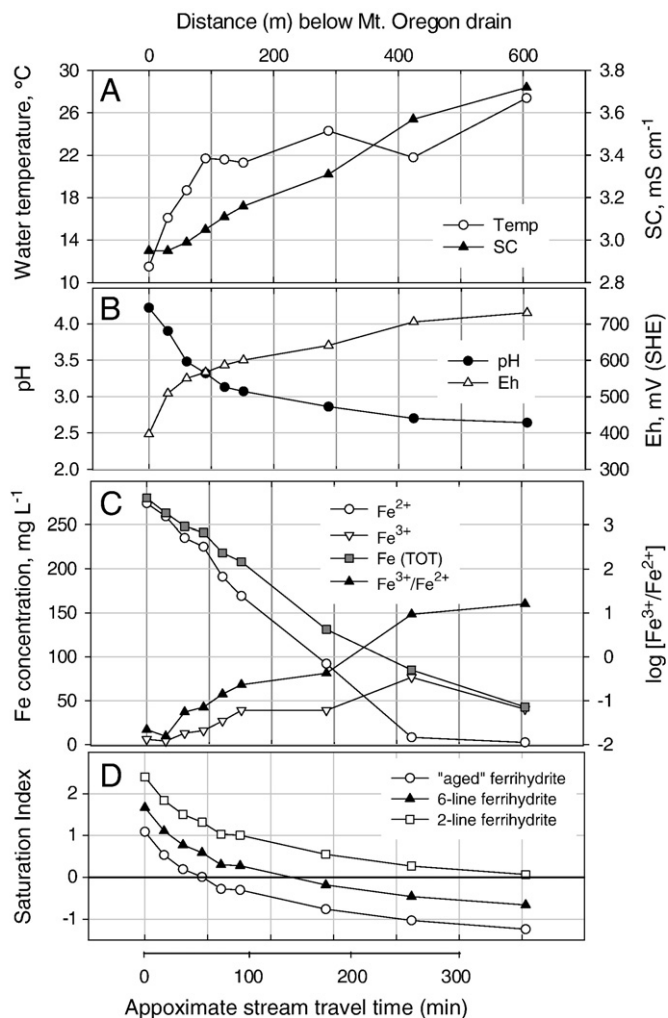


Fig. 7. Changes in chemistry of the Mt. Oregon Drain water with distance below the collapsed adit discharge point. A – changes in water temperature and specific conductance (SC); B – changes in pH and Eh; C – changes in Fe²⁺, Fe³⁺, total dissolved Fe, and Fe³⁺/Fe²⁺ ratio; D – changes in the saturation index for selected ferric oxyhydroxide phases. The bottom x-axis is approximate stream travel time in minutes based on a tracer test.

underground workings with respect to the land surface – have prompted previous workers (Doornbos, 1989; Osborne et al., 1983a) to hypothesize that the mine workings which Giffen Spring drains are completely flooded, thus curtailing the rate of pyrite oxidation. Despite the relatively benign pH values, the total acidity load (mostly as dissolved Fe²⁺) from this spring is considerable (Table 1), and the drainage below Giffen Spring is heavily laden with ferric oxyhydroxide (Fig. 5F).

The Giffen Spring/Coulee No. 5 site was visited on June 14 to 15, 2004. The purpose was to examine downstream changes in chemistry and to collect a set of diel samples at two locations. Over the monitoring period, the main Giffen Spring discharge had a constant pH of 5.7, a constant discharge of roughly 4 L s⁻¹, and a constant dissolved Fe concentration (all ferrous) of 62 mg L⁻¹. These parameters fall within the range reported by the USGS during 1994–1996 (Karper, 1998). The main flow at Giffen Spring issues from a PVC drainpipe (lower left corner of Fig. 5F), and is joined by a small amount (<1 L s⁻¹) of non-acidic groundwater seepage at the head of a small natural wetland dominated by cattails and sedges. The combined flow from Giffen Spring and the smaller adjacent groundwater seeps were the only surface waters in Coulee No. 5 in June 2004.

This flow passed through the Fe-stained wetland and stream channel before soaking back into the ground roughly 1.5 km below the headwater springs. Based on a NaCl tracer test, it took approximately 5.5 h for the water to travel the first 420 m below the Giffen Spring.

Despite having a weakly acidic pH, the combined flow from Giffen Spring and the adjacent seeps had appreciable alkalinity, averaging 1.5 meq L⁻¹ (75 mg L⁻¹ CaCO_{3,eq}). This compares with a calculated acidity of 1.8 meq L⁻¹ for the same water, based on the assumption that all dissolved Fe was Fe²⁺ and that each mole of Fe²⁺ releases 2 mol of acidity after oxidation and hydrolysis (reaction (4)). The fact that the down-gradient waters did not become acidic after near total precipitation of dissolved Fe implies some additional contributions of alkalinity, either from discharging fresh groundwater or alkalinity-generating biological reactions within the wetland.

Unlike the previous example for Kate's Coulee, dissolved Fe²⁺ concentrations in Coulee No. 5 decreased logarithmically (not linearly) with distance downstream (Fig. 8B), implying a first order dependence of the reaction rate on Fe²⁺ concentration. The field data were initially evaluated based on the following simple first-order rate expression:

$$\frac{d\{\text{Fe}^{2+}\}}{dt} = -k_+ \{\text{Fe}^{2+}\} \quad (5)$$

where the brackets {} denote molal concentrations. Values of k₊ were calculated for each sampled location in the top 420 m of Coulee No. 5 based on the observed decrease in Fe²⁺ concentration in each stream segment and a constant water velocity of 76 m h⁻¹ (from the NaCl tracer). The results were then averaged to obtain a single value of k₊ for the entire study reach. The values of k₊ so obtained ranged from 1.7 ± 0.3 × 10⁻⁴ s⁻¹ in the morning when the average water temperature was 7.5 °C to 2.0 ± 0.3 × 10⁻⁴ s⁻¹ in the afternoon when the water had warmed to 14.1 °C.

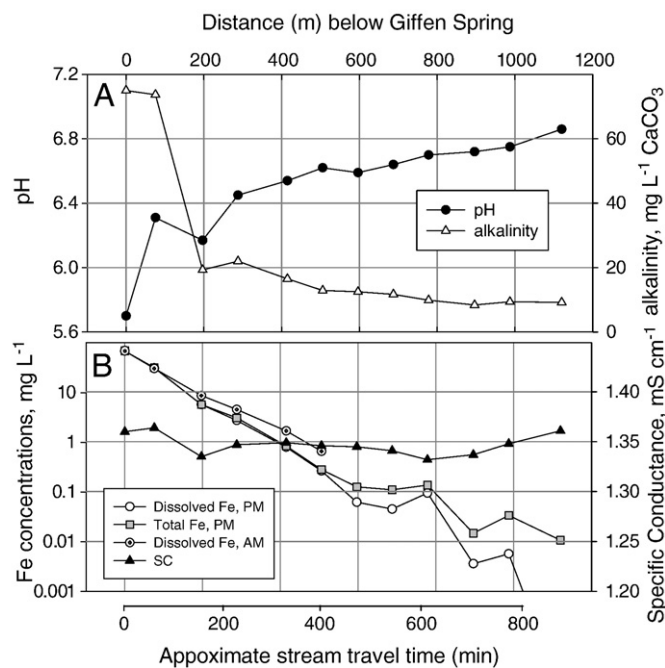


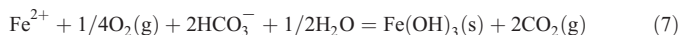
Fig. 8. Changes in chemistry of Coulee No. 5 water with distance below Giffen Spring. A – pH and alkalinity; B – dissolved and total Fe concentration and specific conductance (SC) measured in the afternoon (PM), and dissolved Fe concentration in the morning (AM). The bottom x-axis is approximate stream travel time in minutes based on a tracer test.

Based on a regression of published experimental data, Langmuir (1997) proposed a more complicated rate law expression for abiotic Fe²⁺ oxidation at pH > 4:

$$\frac{d\{\text{Fe}^{2+}\}}{dt} = -k_+ \frac{\{\text{Fe}^{2+}\}}{\{\text{H}^+\}^2} p_{\text{O}_2} \quad (6)$$

Values of k₊ for Eq. (6) were calculated for Coulee No. 5 as above, with the assumption of air-saturated pO₂ (0.19 bars at the field area elevation) and using the average pH value for each stream segment. The k₊ values so obtained ranged from 1.2 ± 1.0 × 10⁻¹¹ molal² bar⁻¹ day⁻¹ in the morning to 2.2 ± 1.9 × 10⁻¹¹ molal² bar⁻¹ day⁻¹ in the afternoon. The large standard deviations indicate problems in either the data interpretation (e.g., an incorrect rate expression) or in the quality and/or quantity of data (e.g., insufficient field data over a range of pH and pO₂). Nonetheless, it is interesting to note that the rate constants obtained in this study based on Eq. (6) are in close agreement with the value of 1.2 × 10⁻¹¹ molal² bar⁻¹ day⁻¹ reported by Langmuir (1997). The fact that the rate constants from the field study are in reasonable agreement with abiotic laboratory rate constants suggests that the oxidation of Fe in Coulee No. 5 was only weakly catalyzed by bacteria. Based on the rather limited field data of this study, the activation energy for the rate-limiting step in the Fe-oxidation process was computed to be 61 kJ mol⁻¹, which compares to a value of 96 kJ mol⁻¹ reported by Langmuir (1997).

As shown in Fig. 8A, the alkalinity of the surface water below Giffen Spring steadily decreased with distance downstream. This is explained by the consumption of HCO₃⁻ by the acid released during the oxidation and hydrolysis of Fe²⁺, as shown by the following overall reaction:



The synoptic data (Fig. 8B) show that essentially all of the dissolved Fe in Coulee 5 was removed by the time the water soaked back into the ground, 1.5 km below the spring. Field measurements showed that all of the dissolved Fe was present as Fe²⁺ at all locations at all times. This

means that the rate of hydrolysis and precipitation of Fe³⁺ to Fe(OH)₃ (s) (Eq. (3)) must have been similar to – or faster than – the rate of oxidation of Fe²⁺ to Fe³⁺ (Eq. (2)). The difference between dissolved (filtered to 0.2 μm) and total Fe concentrations in the lower reaches of the surface flow (Fig. 8B) indicates the presence of suspended particles of ferric oxy-hydroxide, which are notoriously slow to settle out of water.

Interestingly, as the alkalinity of the water in Coulee 5 decreased with distance downstream, the pH of the water increased (Fig. 8A). The reason is that the water discharging at Giffen Spring had a very high concentration of dissolved CO₂ (i.e., H₂CO₃). Using the geochemical modeling program Visual Minteq (Allison et al., 1991), the calculated pCO₂ of this water was 0.12 bars, which compares with an equilibrium pCO₂ of roughly 0.0003 bars for air-saturated water at 1000 m elevation. The most likely explanation for the high CO₂ partial pressure is mixing of AMD water with near-neutral pH, high-alkalinity water somewhere in the submerged mine workings. After reaching the land surface, the excess dissolved CO₂ diffused back into the atmosphere faster than the rate of release of H⁺ from the oxidation and hydrolysis of Fe²⁺, resulting in an overall increase in pH.

3.4. Diel changes in drainage water chemistry below Giffen Spring

Whereas the preceding section summarized spatial (synoptic) changes in chemistry of the surface AMD waters at more or less the same time of day, the following section describes temporal changes in chemistry at a single location over a 24-h period. Fig. 9 summarizes diel changes in pH, water temperature, and the dissolved concentrations of Fe, Mn, Zn, Ni and Co in Coulee No. 5, at a location roughly 500 m below Giffen Spring. The pH averaged 6.5 ± 0.15 over the 24-h period, and showed no clear diel trend (Fig. 9). In contrast, a large 24-h cycle in Fe concentration was noted, with nearly an order of magnitude higher concentrations at night as opposed to the day (Fig. 9). This is attributed to the aforementioned slower rate of oxidation and hydrolysis of Fe²⁺ to ferric oxy-hydroxide in cold vs. warm water. This idea has previously been proposed to explain large

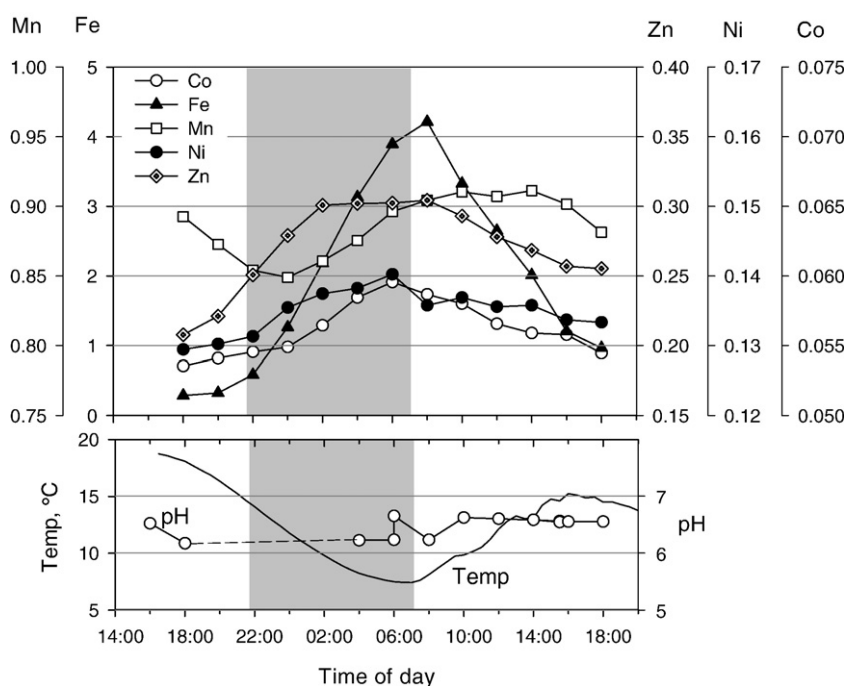


Fig. 9. Diel changes in the dissolved concentration (mg L⁻¹) of Fe, Mn, Zn, Ni and Co in Coulee No. 5, at a point roughly 500 m below Giffen Spring. The lower panel shows changes in water temperature and pH for the same time period. Shaded region denotes night-time hours.

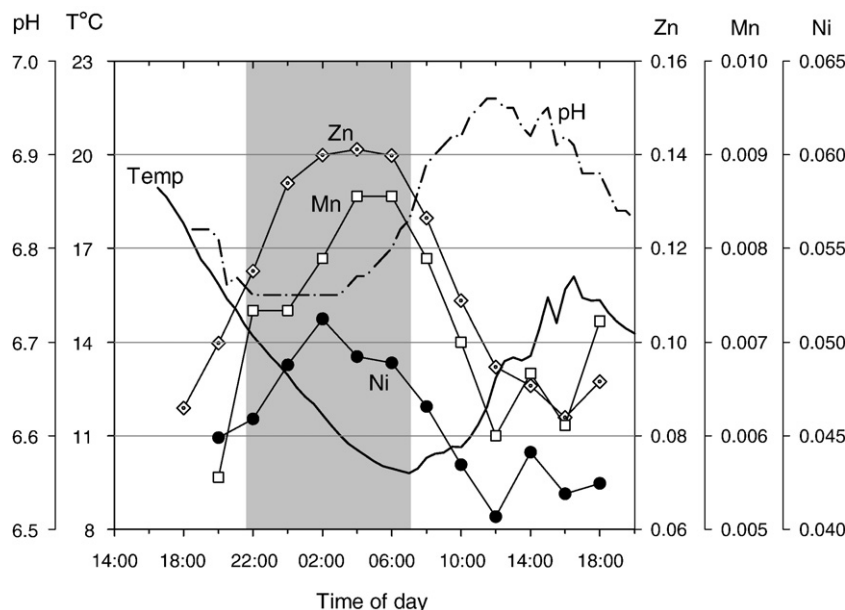


Fig. 10. Diel changes in pH, water temperature, and the dissolved concentrations (mg L^{-1}) of Zn, Mn, and Ni in Coulee No. 5, at a point roughly 1200 m below Giffen Spring. Shaded region denotes night-time hours.

night-time increases in dissolved Fe^{2+} concentrations at near-neutral pH conditions in a stream receiving AMD inputs from an abandoned metal-sulfide mine (Gammons et al., 2005), and in a volcanically-acidified river in Patagonia, Argentina (Parker et al., 2008).

At the 500 m monitoring station in Coulee No. 5, concentrations of other dissolved metals, such as Co, Ni, Zn, and to a lesser extent Mn, tracked closely with Fe, but showed less of a diel swing (Fig. 9). Given the elevated pH of the stream water at this location, it is likely that these trace metals adsorbed onto the ferric oxy-hydroxide particles as they formed. Since the ferric particles formed at a greater rate during the day, the other trace metals also showed a decrease in concentration during the day (see also Gammons et al., 2005; Parker et al., 2008). Robust diel cycles in dissolved trace metal concentrations were also noted at a monitoring station further downstream, below the zone of active Fe precipitation, approximately 1200 m below Giffen Spring (Fig. 10). Again, concentrations of dissolved Mn, Zn, and Ni increased at night and decreased during the day. Because dissolved Fe concentrations were below detection at this location the diel cycles cannot be explained by sorption onto freshly forming ferric oxy-hydroxide particles. Instead, the cycles may have been caused by reversible pH- and temperature-dependent sorption onto hydrous metal oxides stored on the stream bed (see also Brick and Moore, 1996; Nimick et al., 2003; Gammons et al., 2005). Adsorption of metal cations such as Zn^{2+} , Mn^{2+} , and Ni^{2+} onto metal oxides increases with increase in both pH and temperature (Nimick et al., 2003), and both of these variables showed a large diel cycle at the downstream location (Fig. 10). Although these diel relationships are well documented in the literature for streams draining metal mines, the authors are aware of only one other study of diel cycling in streams receiving AMD from coal mines (Smiley, 1997).

3.5. Stable isotopic evidence for origins of water and sulfate

Fig. 11 shows the isotopic composition of water from mine drains in the Belt–Stockett area, as well as numerous groundwater monitoring wells near Belt, the Belt municipal water well (completed in the Madison Limestone aquifer), Giant Springs, and Big Spring. Also shown are the global meteoric water line (MWL) based on worldwide precipitation (Rozanski et al., 1993), the local evaporation line (LEL) for Butte, Montana (Gammons et al., 2006), and isotopic data for

water samples from 20 wells and springs across Montana from the Madison aquifer (Plummer et al., 1990). The majority of the wells and springs from the Madison aquifer plot near the global MWL, indicating minimal evaporation prior to recharge. Two exceptions in the database of Plummer et al. (1990) come from a location that is on a different inferred groundwater flow path to that of the GFLCF area. In the present study, the only Madison aquifer sample that showed possible evidence of evaporation was from monitoring well 4A.

In contrast to the Madison aquifer samples, the majority of the AMD waters as well as several of the groundwater samples from the flooded coal seams and overlying Kootenai Formation have δD and $\delta^{18}\text{O}$ values that indicate moderate evaporation. In particular, the Anaconda, French Coulee, and Highway drain samples near the town

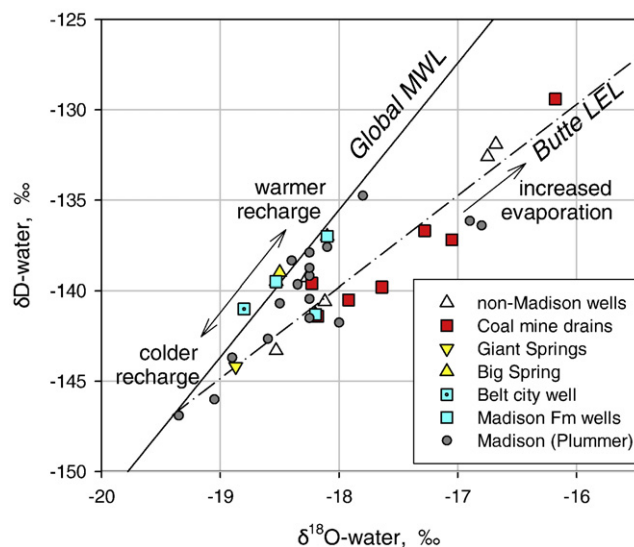


Fig. 11. Stable isotopic composition of water from mine drains and groundwater wells and springs in the Belt–Stockett area. The global meteoric water line (MWL) of Rozanski et al. (1993) and the local evaporation line (LEL) from Butte, Montana (Gammons et al., 2006) are shown for reference. Also shown are isotopic compositions of Madison Lm. groundwater (Plummer et al., 1990) from 20 springs and wells in Montana.

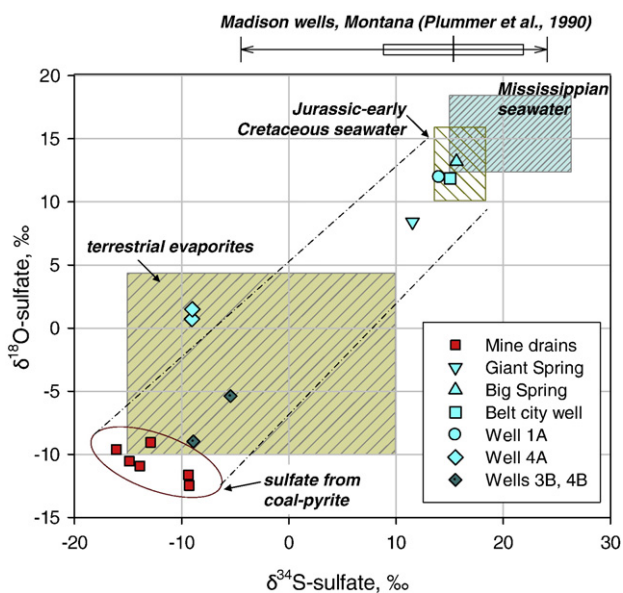


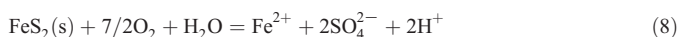
Fig. 12. Stable isotopic composition of sulfate from groundwater and acid mine drainage in the Belt–Stockett area. Data points in light blue are all from groundwater wells or springs in the Madison Limestone. Dark green diamonds are groundwaters associated with coal seams in non-oxidized portions of the Anaconda Mine workings. The two smaller boxes shows the approximate limits of the stable isotopic composition of sea water sulfate during the Mississippian and Jurassic-to-early Cretaceous time periods (Claypool et al., 1980). The larger box is the approximate range of sulfate in terrestrial evaporites (Clark and Fritz, 1997). Data at the top show the range and mean values of $\delta^{34}\text{S}$ for 20 sulfate samples from Madison Limestone springs and groundwater wells in Montana (Plummer et al., 1990).

of Belt diverge from the MWL and follow the LEL. This implies that groundwater in the coal was recharged locally from partially evaporated snowmelt and rain (see also Duaine et al., 2004). This region has a semi-arid climate, and the land is mainly used for production of cereal grains, hay, and alfalfa. Although plant transpiration does not fractionate stable isotopes of water (Clark and Fritz, 1997), direct evaporation of soil moisture would shift the water isotopes to the right along the LEL (Fig. 11). Later rain or snowmelt events would then mix, leading to non-evaporated meteoric water with evaporated soil water, leading to the spread of data shown in Fig. 11.

The $\delta^{34}\text{S}$ of sulfate-S from mine drains in the Belt–Stockett area ranged from -16.1 to -9.3‰ , with a mean value of -12.7‰ (Fig. 12). Given their distinct chemistry, it is reasonable to assume that most of the sulfate in these waters was derived through oxidation of pyrite in the coal. Two samples of pyrite in coal from drill cuttings near Belt gave $\delta^{34}\text{S} = -19.6$ and -27.2‰ (Table 3). While the latter values fall outside the range of the $\delta^{34}\text{S}$ -sulfate results from the mine drains, it is also known that the $\delta^{34}\text{S}$ composition of pyrite in coal can vary over a huge range within a single coal field (e.g., -10.3 to $+24.2\text{‰}$, Smith and Batts, 1974; -52.6 to $+34.6\text{‰}$, Hackley and Anderson, 1986). The incorporation of S into high-S coals involves a number of syngenetic and epigenetic processes, including biological assimilation of dissolved sulfate by coal-forming plants, bacterial sulfate reduction, and assimilation of biogenic H_2S into organic material (Spiker et al., 1994). Bacterial sulfate reduction, in particular, is known to cause extreme fractionation in S-isotopes (Canfield, 2001). The fact that the mine waters and pyrite samples in this study are strongly depleted in ^{34}S suggests that bacterial sulfate reduction played an important role in formation of the high-S coals of the GFLCF.

Sulfate from most of the Madison aquifer springs and wells is consistent with derivation from marine evaporites of Mississippian age (well 4A is an exception and, is discussed below). In contrast, the isotopic composition of sulfate from non-acidic groundwater in completely flooded coal beds (wells 3B and 4B) suggests derivation from terrestrial sulfate minerals (Fig. 12). The observed spread in $\delta^{34}\text{S}$ -sulfate and $\delta^{18}\text{O}$ -sulfate for the mine drain waters (Fig. 12) is perpendicular to what would be expected if the variability was due to mixing with sulfate from a marine source, and such a mixing process would be unexpected in the coal, given its stratigraphic and structural position above the Madison Limestone.

It has been proposed (e.g., Seal, 2003; Balci et al., 2007) that the O-isotopic composition of sulfate places constraints on the biogeochemical conditions extant during oxidation of pyrite. At near-neutral pH, pyrite oxidation involves direct attack of the pyrite surface by molecular O_2 :



In this process there is a high probability that O atoms from atmospheric O_2 would be incorporated into the sulfate molecule. Atmospheric O_2 is isotopically heavy ($\delta^{18}\text{O} \sim 23.5\text{‰}$, Kroopnik and Craig, 1972) and dissolved O_2 in equilibrium with this value has

Table 3
Stable isotope data.

Location	Date sampled	Type	$\delta^{18}\text{O}$ -water	δD -water	$\delta^{34}\text{S}$ -sulfate	$\delta^{18}\text{O}$ -sulfate
Anaconda	11/18/05	Mine seep	-18.2	-140	-9.4	-11.6
Fr. Coulee	11/18/05	Mine seep	-17.9	-141	-9.3	-12.5
Nelson	11/18/05	Mine seep	-17.1	-137	-14.9	-10.5
Giffen	11/18/05	Mine seep	-18.2	-141	-12.9	-9.1
Mt. Oregon	11/18/05	Mine seep	-17.6	-140	-16.1	-9.6
Cottonwood 6	11/18/05	Mine seep	-17.3	-137	-13.9	-10.9
Highway drain	8/3/05	Mine seep	-16.2	-129	n.a.	n.a.
Well 1A	8/3/05	gw-Madison	-18.5	-140	14.0	12.0
Well 4A	8/5/05	gw-Madison	-18.1	-137	-9.0	0.7
"	8/22/06	"	-18.2	-141	-9.0	1.5
Well 3B	8/5/05	gw-coal	-18.1	-141	-8.9	-9.0
Well 4B	8/5/05	gw-coal	-18.3	-139	-5.4	-5.4
Well 8B	8/24/06	gw-coal	-16.8	-133	n.a.	n.a.
Well 15B	8/23/06	gw-coal	-18.5	-143	n.a.	n.a.
Well 8C	8/24/06	gw-Kootenai	-16.7	-132	n.a.	n.a.
Belt City Well		gw-Madison	-18.8	-141	15.0	11.9
Big Spring	10/11/07	gw-Madison	-18.5	-139	15.6	13.2
Giant Spring	11/18/05	gw-Madison	-18.9	-144	11.5	8.4
					$\delta^{34}\text{S}$ -pyrite	
Coal 1	2006	Drill cutting			-27.2	
Coal 2	2006	Drill cutting			-19.6	

All results in ‰.

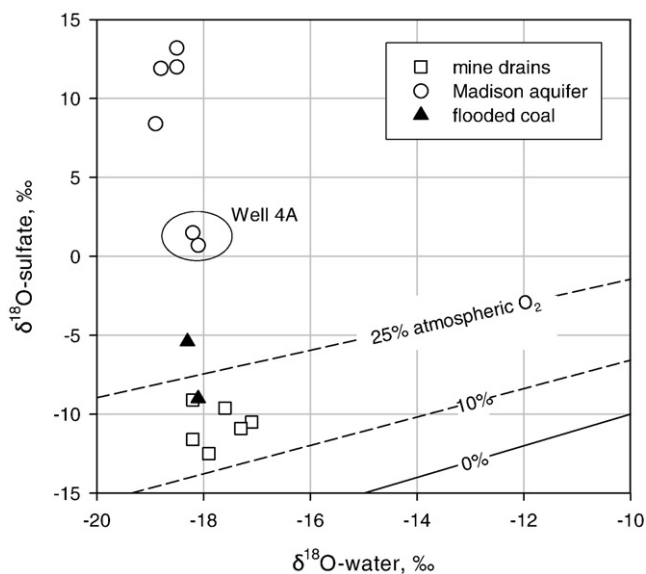
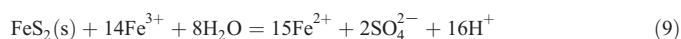


Fig. 13. Stable O isotopes of sulfate and co-existing water. Lines at the bottom show the percentage of O of atmospheric origin incorporated into SO_4 during oxidation of pyrite, assuming local water isotopic values (see text).

$\delta^{18}\text{O} \sim 24.2\%$. Pyrite oxidation can also take place by dissolved ferric iron, but only at relatively low pH where Fe^{3+} is soluble:



If reaction (9) dominates and pyrite oxidation is truly anaerobic, then 100% of the O atoms in the sulfate must come from water, which in the case of Montana is strongly depleted in ^{18}O ($\delta^{18}\text{O} = -17$ to -19% , Table 3). If pH is low and O_2 is present, then some combination of reactions (8) and (9) will apply. Fig. 13 plots $\delta^{18}\text{O}$ -sulfate vs. $\delta^{18}\text{O}$ -water for the samples of interest in this study. All of the mine drains have $\delta^{18}\text{O}$ -sulfate values that correspond to incorporation of between 10 and 25% atmospheric O_2 during pyrite oxidation. This result is consistent with oxidation of pyrite under acidic, aerobic conditions, but cannot be used to discriminate between biotic vs. abiotic oxidation mechanisms (Balci et al., 2007). For comparison, Rose and Cravotta (1998) used the same approach to conclude that both reactions (8) and (9) were important during oxidation of pyrite associated with coal in Pennsylvania.

The clear separation in $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of sulfate in the mine drains as opposed to the Madison groundwater (Figs. 12 and 13) makes it possible to use stable isotopes to determine if AMD from the GFLCF has leaked into the underlying Madison aquifer, potentially contaminating this important regional water supply. Based on trends in specific conductance and sulfate/bicarbonate ratios in domestic water wells, Osborne et al. (1983a,b) concluded that leakage of AMD from coal mines has most likely caused local contamination of the Madison aquifer in the Sand Coulee/Stockett area. The results of this study suggest that localized leakage may also have occurred in the vicinity of Belt, specifically, near Well 4A. This well was screened in the Madison, but contains isotopically light sulfate, possibly due to mixing with AMD from the nearby Anaconda Coal Mine. Additional sampling and isotopic analysis are recommended to delineate the extent of AMD leakage into the Madison aquifer from abandoned mines throughout the GFLCF region.

4. Conclusions

The Great Falls-Lewiston Coal Field (GFLCF) is one of the few documented examples of coal mines in the Western U.S. that produce serious AMD problems. Portions of each mine complex in the GFLCF

that are completely flooded have relatively benign water quality, whereas areas that are partly submerged or completely open to air have strongly acidic water and high dissolved metal concentrations. This underscores the importance of subsurface oxygen ingress in the generation of severe AMD. After discharge to the surface, the pH of the mine drains either increased (Giffen Spring example) or decreased (Mt. Oregon Drain example), depending on the balance of acidity and alkalinity in the water. One mine drain that was net alkaline exhibited diel changes in dissolved Fe, Zn, and other trace metals in down-gradient waters, with concentrations increasing at night and decreasing during the day. These changes are attributed to the temperature-dependence of the rate of oxidation and hydrolysis of Fe^{2+} to $\text{Fe}(\text{OH})_3$ (s), as well as the temperature and pH-dependence of adsorption of divalent metal cations onto freshly formed Fe-oxyhydroxide surfaces. Similar diel patterns likely occur in rivers and streams draining coal-mining regions elsewhere in the world (e.g., Smalley, 1997).

The rate of Fe^{2+} oxidation of mine-drain water after emerging to the surface followed zero-order kinetics in the Fe-rich and strongly acidic waters of Kate's Coulee, but was first-order with respect to Fe^{2+} concentration in the circumneutral pH waters of Coulee No. 5. Rate constants in both cases were similar to previously published data, although the temperature-dependencies (i.e., activation energies) obtained in this study were lower than literature estimates.

Stable O and H isotopic data indicated that perched groundwater in the abandoned coal mines of the GFLCF was recharged locally from overlying agricultural land. Changes in land use that promote storage and evapotranspiration of water in the soil zone could potentially reduce the volume of acidic water discharged from the abandoned mines. The S and O isotopic composition of dissolved sulfate in the acidic, SO_4 -rich mine drains is consistent with a biogenic pyrite source associated with the coal deposits. Sulfate in the AMD waters is isotopically distinct from sulfate in the underlying Madison Limestone aquifer, and limited data presented in this study support the theory that mine drainage may have leaked into the Madison aquifer, as was postulated by earlier workers (Osborne et al., 1983a,b).

Acknowledgements

Funding for this project was provided by EPA-EPSCoR and the Montana Board of Research and Commercialization Technology. We thank Bill Botsford and John Koerth, both of the Montana DEQ, for their assistance. The manuscript was considerably improved by the detailed comments of Lisa Stillings and two anonymous reviewers.

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