Aqueous geochemistry of the "other" pit lake in Butte, Montana, USA

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Abstract The Continental porphyry Cu-Mo mine, located 2 km east of the famous Berkeley Pit lake of Butte, Montana, contains two small lakes that vary in size depending on mining activity. In contrast to the acidic Berkeley Pit lake, the Continental Pit waters have near-neutral pH and relatively low metal concentrations. The main reason is geological: whereas the Berkeley Pit mined highly-altered granite rich in pyrite with no neutralizing potential, the Continental Pit is mining weakly-altered granite with lower pyrite concentrations and up to 1–2 % hydrothermal calcite. The Continental Pit waters are near equilibrium with a number of carbonate, sulfate, and molybdate minerals.

Keywords neutral mine drainage, trace metals, pit lake, geochemistry, mineral solubility

Introduction

Just east of the famous Berkeley Pit lake in Butte, Montana (Davis and Ashenberg 1989), there is a lesser known active open pit mine, the Continental Pit. The Continental Pit contains a large but low-grade Cu-Mo porphyry deposit (Czehura 2006). Two small water bodies exist on the property, here called the North Pond and the South Pond (Fig. 1). Presently, the elevations of these lakes are maintained at a low level by the Sarsfield pumping well, located near the north shore of the North Pond. Pumping ceased in 2001–2003 after the mine

temporarily shut down in 2000 due to unfavorable economics. Dewatering resumed in 2003 when the mine reopened, and continues to the present day, at a typical rate of 800 to 1200 liters per minute (S. Czehura, pers. commun. March 2013).

During the mine-closure period of 2000–2003, samples of groundwater from the Sarsfield Well as well as samples of surface water from the North Pond (Fig. 2A) were collected monthly by the MBMG. Since 2006, the active mine has been collecting water samples twice a year from several locations on their property,
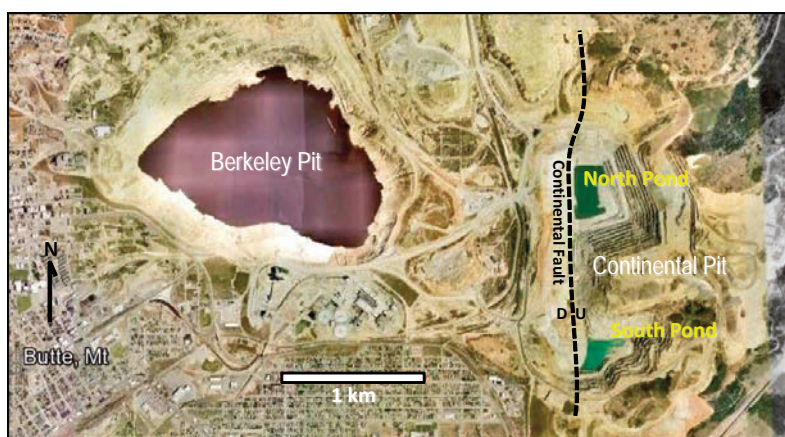
Fig. 1 Google Earth image showing the location of the North and South Ponds in the Continental Pit, with the nearby Berkeley Pit lake for comparison. Image taken July 16, 2002.

including the North and South Ponds, the Sarsfield Well (sampled instead of the North Pond when the latter is dry or frozen), and the Pavilion Seep. The water quality results are sent to the Montana Department of Environmental Quality (MDEQ), and are publically available upon request. The Pavilion Seep is a relatively small volume of acidic groundwater that enters the Continental Pit from a bench on the southeast highwall. At the time of this writing, Pavilion Seep water is collected and pumped to a site outside of the pit where it is mixed with Sarsfield Well water and used in the mill.

Because the active mining company intends to continue open-pit mining for decades, no formal plans for closure of the Continental Pit exist. The final closure scenario may well not include a pit lake. Nonetheless, it is interesting to look at the data in hand to predict the water quality of a hypothetical lake formed from flooding of the Continental Pit, and to compare this result to the nearby Berkeley Pit lake (Fig. 2B).

Methods

Water chemistry data for the North Pond from 2001 to 2003 were downloaded from the MBMG's Groundwater Information Center website (GWIC 2013). In June of 2003, shortly before dewatering resumed, a vertical profile of field parameters in the North Pond was collected by MBMG from a boat, and water sam-

ples were taken at near-surface and at a depth of 11 m. Additional data for the North Pond, the South Pond, and the Pavilion Seep collected between 2006 and 2012 were provided by MDEQ. All of the water quality analyses were conducted by certified labs following strict quality assurance protocols. In March 2013, the authors sampled the discharges from the Sarsfield Well and the Pavilion Seep. Samples were submitted for chemical analysis, as well as determination of $\delta^{18}O$ and δD of water, $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate, and $\delta^{13}C$ of dissolved inorganic carbon. Results from the March 2013 sampling were not available at the time of this writing, but will be presented at the 2013 IMWA meeting.

Data for each chemical analysis of the North Pond between 2001 and 2003 ($n = 17$) were input into the program Visual Minteq, v. 3.0 (a recent adaptation of the original MINTEQA2 program of Allison *et al.* 1991), and saturation indices (S.I.) were determined for a number of minerals and amorphous solid phases. In this paper, the S.I. values for each solid were adjusted to one metal ion per formula unit. For example, amongst the common secondary Cu minerals, the S.I. value for malachite ($Cu_2CO_3(OH)_2$) was divided by two and the S.I. value for azurite ($Cu_3(CO_3)_2(OH)_2$) was divided by three. This was done so that S.I. values could be more equally compared between a set of minerals that contain a common element of interest. For modeling purposes, dis-
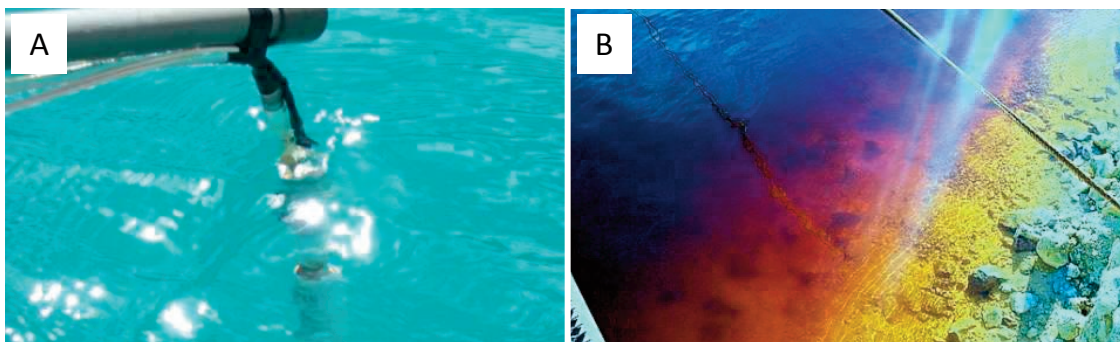
Fig. 2 *Close-up photographs comparing the appearance of water in the North Pond of the Continental Pit (left, with a submersible pump) and the Berkeley Pit lake (right).*

solved Cu and Mn were assumed to be in the +2 valence, Fe was assumed to be +3, and Mo and U were assumed to be +6. These redox assignments are consistent with the presence of > 5 mg/L dissolved oxygen throughout the water column of the lake in June 2003 (see below).

Results

The chemical compositions of the North and South Ponds in the Continental Pit are very similar (see Table 1). Both water bodies have a pH near 7, with a significant amount of bicarbonate alkalinity (> 100 mg/L as $CaCO_3$). The concentrations of most metals of concern, such as Cu and Zn, are quite low when compared to the Berkeley Pit lake, but are nonetheless well above regulatory standards for surface water. However, it is emphasized that these standards are not relevant as long as the mine is in operation. Unlike some pit lakes with neutral or alkaline pH, the concentration of arsenic in both of the Continental ponds is not particularly high (< 10 μg/L). This is not due to a lack of As in the ore body, since the Butte deposits are locally rich in the Cu-As-sulfide minerals enargite and tennantite (Meyer *et al.* 1968). It is possible that As is being adsorbed onto secondary Fe-oxy-hydroxide minerals on weathered bedrock surfaces. In con-

trast to the Berkeley Pit, which has undetectable quantities of dissolved Mo (Table 1), concentrations of Mo in the North Pond are elevated (in the 0.5 to 0.7 mg/L range). This difference is geological, as the Berkeley deposit produced no Mo, whereas molybdenite is an important ore mineral at the Continental deposit (Czehura 2006). Between 2006 and 2012, the Pavilion seep had an average pH of 3.31, and concentrations of dissolved metals and metalloids were much higher than in the North and South Ponds, but still considerably lower than the Berkeley Pit lake (Table 1).

Fig. 3 summarizes long-term trends in the concentrations of Cd, Cu and Zn in the North Pond as well as Sarsfield Well between 2001 and 2012. During the period of mine closure (2001–2003), concentrations of these metals steadily increased. The North Pond was seasonally stratified during this time (Fig. 4), with a chemocline situated at a depth of 4.2 m in June 2003. A single water sample collected at 11 m depth had slightly lower pH and significantly higher concentrations of Cd, Cu and Zn compared to a near-surface sample (Table 1). Dissolved oxygen concentrations were > 5 mg/L at all depths, which is in contrast to the Berkeley Pit lake, which typically has undetectable DO concentrations below the top 1–3 m (Pellicori *et al.* 2005). Although the moni-
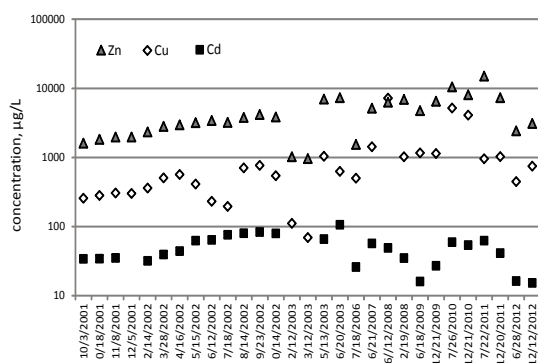
Fig. 3 *Concentrations of Cu, Cd, and Zn in the North Pond from 2001 through 2003 (GWIC 2013) and from 2006 through 2012 (MDEQ 2013). Some of the latter data are from the Sarsfield Well.*
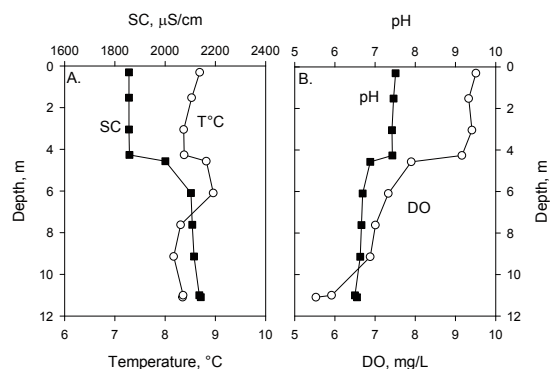
Fig. 4 *Vertical profiles in water temperature, specific conductance (SC), pH, and dissolved oxygen (DO) for the North Pond of the Continental Pit, collected on June 12, 2003.*

Location	pH	SC[1]	Ca	Mg	Na	K	SO_4^{2-}	Cl^-	F^-	HCO_3^-	NO_3-N	PO_4-P
CP-N surface[2]	7.34	2050	433	37	38	10	1241	9.1	3.3	146	1.3	<0.5
CP-N surface[3]	7.05		502	43	36	8	1310	8.9	4.2	123	0.6	0.04
CP-N 11 m[4]	6.55	2140	477	46	41	11	1440	8.6	4.3	92	1.7	<0.5
CP-S surface[5]	7.33	1860	397	38	32	6.1	1070	8.9	4.1	115	0.23	0.08
Pavilion [6]	3.31	2360	225	86	24	4.6	2060	5.3	4.7	< 1	0.57	0.14
BPit surface[7]	2.75	7340	475	534	74	9.6	8170	<50	30	< 1	<5	<5
BPit 210 m[7]	2.53	8160	442	515	74	7.6	9090	<50	30	< 1	<5	<5

	Al	As	Cd	Cu	Fe	Mn	Mo	Ni	Si	Sr	U	Zn
CP-N surface[2]	0.98	0.001	0.05	0.43	0.05	3.1	0.69	0.031	5.5	4.07	0.29	3.14
CP-N surface[3]	1.01	0.005	0.04	1.61	4.0	5.5	n/a	0.043	9.3	2.94	n/a	6.46
CP-N 11 m[4]	0.18	<.005	0.17	3.71	0.04	5.5	0.55	0.039	5.4	5.27	0.22	8.92
CP-S surface[5]	0.24	0.003	0.06	1.05	0.23	8.6	n/a	0.047	8.7	1.75	n/a	6.76
Pavilion [6]	41	0.02	0.43	58.6	76.7	22	n/a	0.15	28	0.66	n/a	46.2
BPit surface[7]	275	0.135	2.26	79	564	261	<0.02	2.4	38	1.55	1.97	627
BPit 210 m[7]	268	0.097	2.27	153	1007	248	<0.02	1.6	36	1.43	1.45	638

[1]Specific conductance in μS/cm; n/a = not analyzed; [2]Continental Pit North Pond, average of 17 samples collected in 2001–2003 (GWIC 2013); [3]Continental Pit North Pond or Sarsfield pumping well, average of 11 samples collected in 2005–2012 (MDEQ 2013); [4]Lake sample collected at depth of 11 m (GWIC 2013); [5]Continental Pit South Pond, average of 10 samples collected between 2005 and 2012 (MDEQ 2013); [6]Pavilion Seep, average of 11 samples collected between 2005 and 2012 (MDEQ 2013); [7]Berkeley Pit lake samples collected on Nov. 6, 2007 (GWIC 2013).

Table 1 *Chemical composition of selected water bodies of interest in the vicinity of the Continental Pit; Solute concentrations are in mg/L.*

toring data became more scattered after resumption of mining operations in 2003, average values for most water quality parameters in the North Pond from 2001–2003 are similar to those from 2006–2012, suggesting that water quality trends have been fairly stable in the last decade.

Based on the computed saturation indices (Fig. 5), water in the North Pond in 2001–2003 was close to equilibrium with gypsum ($CaSO_4\cdot2H_2O$) and fluorite (CaF_2), as well as a number of carbonate minerals, including calcite, dolomite, smithsonite ($ZnCO_3$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$), and rhodochrosite ($MnCO_3$). On average, the lake waters were undersaturated with otavite ($CdCO_3$). It is possible that Cd resides as an impurity in calcite or another carbonate phase. A large number of Cu(II) minerals were also near equilibrium, including malachite ($Cu_2CO_3(OH)_2$), azurite ($Cu_3(CO_3)_2(OH)_2$), antlerite ($Cu_3(SO_4)(OH)_4$),

brochantite ($Cu_4SO_4(OH)_6$), langite ($Cu_4SO_4(OH)_6\cdot2H_2O$), and possibly atacamite ($Cu_2Cl(OH)_3$). Both the North and South Ponds have a distinctive greenish blue color (Fig. 1, Fig. 2A), which could be partly caused by precipitation of one or more of these sparingly soluble secondary copper minerals. It is significant that metal concentrations in the North Pond appear to be controlled by mineral solubility limits, as this means that the concentrations of elements such as Cd, Cu, Mn, and Zn cannot increase without a simultaneous decrease in pH as well as bicarbonate concentration. Amongst the various silica polymorphs, the lake waters were closest to equilibrium with chalcedony (micro-crystalline quartz). Finally, it is interesting that the lake waters were found to be near equilibrium or supersaturated with several molybdate minerals, including $CaMoO_4$, $CdMoO_4$, $CuMoO_4$, and $ZnMoO_4$.
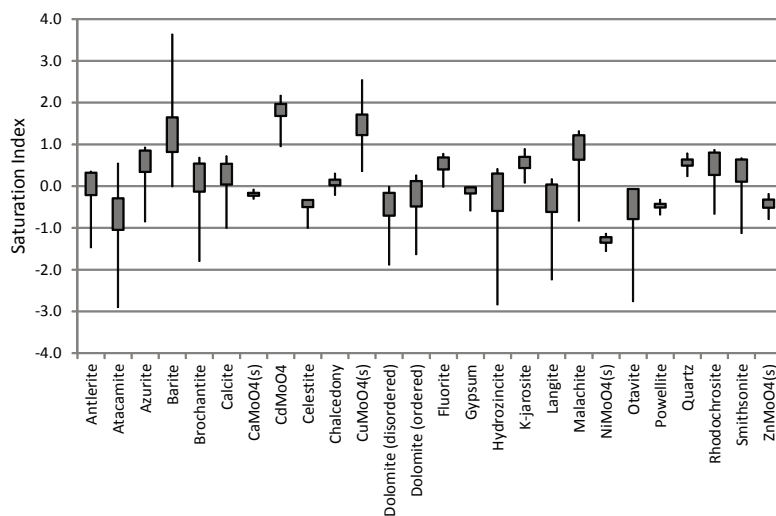
Fig. 5 *Saturation indices of various minerals based on 17 chemical analyses of the North Pond of the Continental Pit. Rectangles represent one standard deviation. Lines show total range.*

Discussion

The data presented above show a stark contrast between the highly acidic and metal-rich Berkeley Pit lake and the nearby Continental Pit lakes which have neutral pH and relatively low metal concentrations. The main reason for this difference is geological. The two open pit mines are separated by the Continental Fault (Fig. 1), a large normal fault with > 1 km of vertical displacement (Czehura 2006; Rusk *et al.* 2008), down-dropped to the west. The Berkeley deposit is rich in pyrite (> 5 wt %) with highly altered granitic bedrock (all feldspar and mafic minerals converted to muscovite as well as clay + quartz) that has no acid-neutralizing potential. In contrast, the Continental deposit, which represents a deeper and more peripheral mineral assemblage within the Butte District, contains weakly-altered granite wall-rock (fresh feldspars with abundant primary and secondary biotite) with lower pyrite content (1 to 2 wt %) and a small but significant quantity of hydrothermal calcite. The latter occurs as thin veins and disseminations throughout the ore body (Newbrough and Gammons 2002; Lamsma 2012). In addition, whereas the Berkeley Pit is surrounded and underlain by 1000's of km of underground mine workings (Duaime *et al.* 2004; Gammons *et al.* 2009), very few underground workings extend into the Continental Pit area. Thus, the hydrology of groundwater flow is dominated by open or backfilled/collapsed voids in the vicinity of the Berkeley Pit, as opposed to fractured bedrock in the vicinity of the Continental Pit.

Newbrough and Gammons (2002) used long-term humidity cell tests to compare leachate from crushed bedrock exposed in the Berkeley and Continental Pits, and found very similar water chemistry results to the data presented in this paper. However, Newbrough and Gammons observed that calcite was being dissolved from the crushed Continental Pit samples faster than pyrite was oxidized. Extrapolation of these results suggested that the Continental Pit leachates could become acidic at a future time, when the neutralizing potential was completely depleted. Due to the small number of samples in the Newbrough and Gammons study, and the inherent difficulty of scaling humidity cell tests to field settings, it is difficult to say if or when the small ponds in the Continental Pit might become acidic. The Pavilion Seep shows that some acidic drainage already exists in the Continental Pit, although the volume of this acidic water is presently much less than the pH-neutral, alkaline water that resides in the ponds, or that is being pumped from the Sarsfield Well. Over time,

these conditions could change with continued weathering of the ore body.

Conclusions

The Continental Pit contains two small lakes that have near neutral pH and relatively low metal concentrations compared to the Berkeley Pit lake, which is highly acidic. Mining activity is expected to continue for decades, and closure plans for the Continental Pit may not include a pit lake. Based on Visual Minteq modeling, the existing ponds in the Continental Pit are close to equilibrium saturation with a number of carbonate, sulfate, and molybdate minerals. For metals whose solubility is limited by carbonate minerals (*e.g.* Zn, Cu), dissolved concentrations can only increase if pH or HCO_3^- concentrations decrease. No clear trend in this direction is apparent from the past 10 years of water quality monitoring. Some acid mine drainage does exist within the boundaries of the Continental Pit, and it is possible that the volume as well as severity of this AMD could increase in the future with continued weathering of the ore body. Nonetheless, the weight of evidence presented in this paper suggests that any hypothetical pit lake formed by flooding of the Continental Pit would have substantially different chemistry than that of the Berkeley Pit lake, with higher pH and lower dissolved metal concentrations.

Acknowledgements

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