

Violation of Common ABA Prediction Rules by Molybdenum-Related Minesites in British Columbia, Canada

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Abstract: In 1993, acid-base accounting (ABA) indicated most of the tailings at a closed molybdenum minesite in British Columbia, Canada, should generate acidic drainage, and some samples were already acidic based on paste pH. On the other hand, detailed geochemical studies and on-site monitoring showed there was no evidence of large-scale acidic drainage at the minesite over decades of weathering, and such acidic drainage was not expected at any point in the future. As a result, the common ABA predictive rules for acidic drainage had an interesting exception.

Available geochemical data were recently compiled for six molybdenum-related minesites and properties in British Columbia, namely Boss Mountain, Brenda, Endako, Highland Valley Copper, Kitsault, and Trout Lake. Similarities and differences were sought out to explain their violations of common prediction rules.

The first key to the puzzle was that these minesites had hidden reservoirs of neutralization potential (NP) that are not detected by standard ABA analyses for NP. These reservoirs reflect the presence of abundant silicate-based minerals like plagioclase and hornblende. The second key to the puzzle was that most drainages from these sites contained aqueous sulphate concentrations well below gypsum saturation, often around 50-500 mg/L. This indicated the rates of sulphide oxidation and acid generation are relatively low at these sites.

As a result, the rates of acid generation at these sites happen to be sufficiently low so that the slowly-dissolving, unmeasured silicate-based NP is able to maintain near-neutral pH on a large scale, but not always on smaller scales. The reason for the depressed oxidation rate is not clear from available information, but could be related to the significant amounts of non-iron-based sulphide minerals. Such a scenario is probably not unique to molybdenum-related minesites, and may be found at other types. Integrated, multifaceted geochemical studies are needed to identify and understand such exceptions and to better predict future aqueous concentrations.

Introduction

Although molybdenum and molybdenum-copper deposits can be thought of as variations on copper-molybdenum and copper deposits, the limited information on environmental geochemistry does not support this. For example, acid-base accounting (ABA), which is frequently used to identify net-acid-generating rock and tailings, has been known to fail for some molybdenum deposits (Morwijk Enterprises Ltd., 1993; Morin and Hutt, 1997). As a result, some molybdenum deposits could have a distinct environmental geochemistry, and one that could consistently violate typical geochemical prediction rules.

To examine in more detail the environmental geochemistry of molybdenum-related deposits, this paper compiles non-confidential information (Morin and Hutt, 2000a). The focus is on the Province of British Columbia in Canada, because this is where an exception is already documented and because open government files and studies were readily available (e.g., Price, 1996; Price et al. 1997 and 1999). Limited additional information from outside British Columbia is used in this paper where available and relevant.

The Government of British Columbia maintains a computer-based database known as Minfile, in which geological and mineralogical (not environmental) information is stored about mineral deposits. This database was searched for those in which molybdenum was a primary target. Of these, some environmental information could be found on the operating/closed minesites of Highland Valley Copper (a combination of several ore bodies including Highmont), Boss Mountain, Brenda, Endako, Kitsault, and on the proposed minesite of Trout Lake (Figure 1).

Ore-Deposit Models

In general, most molybdenum deposits occur as clustered porphyry stocks of quartz monzonite less than 1500 m in diameter (Soregaroli and Sutherland Brown, 1976). Prominent exceptions in British Columbia are Endako and Adanac which are related to larger batholiths. In any case, mineralization typically involves multiple stages of fracturing and veining in the host rock, which varies from deposit to deposit. Potassic alteration (potassium feldspar and/or biotite) is common with molybdenum mineralization, but not unique to it. Sericite and argillic alteration can also be important.

Due to factors such as temperature, pressure, host-rock geochemistry, and proportions of



FIGURE 1. Locations of Six Molybdenum-Related Ore Deposits Discussed Here, in British Columbia, Canada.

various metals, the mineral deposits containing significant amounts of molybdenum can be divided into several categories (Kirkham and Sinclair, 1995). These categories are typically subsets of porphyry deposits, which are relatively large, low- to medium-grade deposits with the hypogene (primary) minerals often related to felsic to intermediate porphyritic intrusions.

The categories range from the relatively low-molybdenum “porphyry copper” (such as Noranda’s Bell, Granisle, and Gaspé Minesites) to “porphyry copper-molybdenum” (such as Noranda’s Brenda Minesite) to “porphyry molybdenum” (such as Noranda’s Boss Mountain). There is also a less common category known as “porphyry tungsten-molybdenum.” A review of factors like molybdenum content and tonnage do not consistently explain the occurrence or lack of acidic drainage at such sites (Morin and Hutt, 2000a).

Kirkham and Sinclair (1995) explain that associated minerals for porphyry copper, copper-molybdenum, and molybdenum include magnetite, quartz, biotite, potassium feldspar, and clay minerals. They also indicate that pyrite is not associated with porphyry molybdenum, but this must be a generalization because Climax Molybdenum in Colorado, USA, has pyrite and acidic drainage. Therefore, like the factors in the preceding paragraph, the general deposit models do not offer any clear indication of why molybdenum deposits have widely varying environmental geochemistry and why some violate some predictive rules for acidic drainage.

Molybdenum deposits are sometimes divided into fluorine-rich and fluorine-poor, which generally show an inverse correlation with the presence of CO₂ in the original mineralizing fluid (Macdonald et al., 1995). Similarly, Linnen et al. (1995) divide molybdenum deposits into two types: a high-grade, high-temperature, high-tonnage type found in granite, and a fluorine-poor, low-grade low-temperature type found in granodiorite, which is the typical type in British Columbia. Nonetheless, the mineral assemblages formed by alteration in both types are similar and are not unique to molybdenum-related deposits. The presence of CO₂, as well as tonnage and the levels of temperature and pressure, does not seem to correlate with geochemical information like acidic drainage. Therefore, like the factors in the preceding paragraphs, these formational features and associated ore-deposit models apparently do not explain the differences in environmental geochemistry.

Summary of Selected Molybdenum-Related Deposits in British Columbia

The following site summaries are based on information in Morin and Hutt (2000a) and the numerous references therein that provided the detailed information.

Boss Mountain

Between 1965 and 1971, nearly 3.0×10^6 tonnes of ore were mined at Boss Mountain with an average of 0.260% Mo. An additional 3.6×10^6 t with 0.188% Mo was mined from 1974 to 1980. Both underground and open-pit methods were used.

Price (1996) compiled petrographic examinations of various grain sizes of waste rock from the Boss Mountain Minesite. Six samples greater than 19 mm in size were mostly fresh, medium-grained quartz diorite to granodiorite, with a mean modal composition of 70% plagioclase, 15% mafic silicates, 11% quartz, and 2% potassium feldspar. Feldspar was fresh to very mildly sericitized, and mafics were mostly hornblende partly modified to secondary biotite and rare epidote. Carbonate was absent in all samples. Sulphide (pyrite) occurred as

disseminated trace amounts, with most showing partial oxidation to limonite. The rock fragments from 11 to 19 mm in size were similar in composition, but the pyrite was typically partially to completely oxidized. The 0.05-2.0 mm fragments of waste rock were again similar to the coarser fragments, with the individual pyrite grains of 0.02-0.4 mm size showing some weathering to limonite rims.

Drainage chemistry at Boss Mountain is consistently near neutral pH, with typical aqueous concentrations of 100-200 mg/L for sulphate and 2 mg/L for dissolved molybdenum.

Brenda

The Brenda minesite operated from 1970 to 1990, and generated approximately 106×10^6 tonnes of waste rock in four piles and 170×10^6 t of tailings in a single large impoundment. The ore rock averaged 0.169% Cu and 0.043 % Mo over the 20 years of operation. The Brenda ore zone is located in a quartz diorite/granodiorite with most sulphides occurring in veins and fractures. The main sulphides are chalcopyrite and molybdenite with lesser amounts of pyrite and other sulphides.

The general composition of Brenda rock is 45-60% An₃₄-An₄₈ plagioclase, 10-30% quartz, 10-20% potassium feldspar, 2-30% hornblende, 1-15% biotite, and <1-2% magnetite and sphene. Minor to rare minerals include carbonate minerals, bornite, specular hematite, sphalerite, galena, pyrrhotite, mackinawite, carrolite, cubanite, ilmenite, rutile, native gold, and secondary sulphides. Other secondary weathering minerals include malachite, azurite, ferrimolybdate, powellite, and tenorite.

Drainage chemistry at Brenda is consistently near neutral pH, with typical aqueous concentrations of less than 500 mg/L sulphate, 2-3 mg/L dissolved molybdenum in the tailings pond, and 5-15 mg/L dissolved molybdenum from the rock piles (Morin and Hutt, 1999a).

Endako

The Endako molybdenum deposit is contained within the Endako Quartz Monzonite, and can be divided into four distinct mineralized zones parallel to strike. From 1965 to 1993, 188×10^6 tonnes of ore had been milled, containing an average of 0.15% MoS₂. Mining continues at this site, but it will be closed shortly.

The Endako Quartz Monzonite on average consists of 35% orthoclase, 30% plagioclase (An₂₀), 30% quartz, 5-10% partially chloritized biotite, with smaller amounts of magnetite, pyrite, apatite, and sphene. There is also some carbonate reported locally. The main secondary minerals, due to historical oxidation, are ferrimolybdate and limonite, with lesser amounts of malachite, pyrolusite, hematite, and powellite. The primary sulphide minerals at Endako are pyrite and molybdenite, and the pyrite in the ore zone is enriched in nickel, manganese, and tin relative to pyrite outside the ore zone. Unlike other molybdenum deposits in British Columbia, argillic alteration is important in the formation of the Endako deposit.

Pit water can attain molybdenum concentrations of 30 mg/L, whereas the tailings impoundment contains around 4 mg/L with higher concentrations of other elements. Aqueous sulphate is around 1500 mg/L in the tailings impoundment, likely indicating gypsum saturation, whereas pit waters are around 500 mg/L sulphate. Molybdenum concentrations of 30 mg/L showed no toxicity or observable effects on early-life-stages of fish.

Highland Valley Copper

This minesite is actually composed of several deposits with variable levels of molybdenum. Mining at the sites began in the 1960's. The Highmont site contains a tailings impoundment with 30.5×10^6 tonnes of tailings containing an average of 0.029% Cu and 0.007% Mo from the mining of several low-grade zones. Subsurface seepage from this impoundment is around $0.03 \text{ m}^3/\text{s}$ with dissolved and total molybdenum concentrations of 7-8 mg/L at pH 7.6 to 8.7 in most seepage during 1999. Other elements include manganese at 0.03-0.38 mg/L and sulphate around 400-500 mg/L in most seepage. The sulphate presumably represents sulphide-mineral oxidation, but combined with calcium around 70-160 mg/L indicates seepage waters are not in equilibrium with gypsum. In turn, this indicated that sulphide-oxidation rates are relatively low, as also noted at Boss Mountain and Brenda.

The ore rock at Highmont was mostly Skeena quartz diorite. Alteration ranged from weak to strong, and affected biotite, hornblende, and feldspars. Molybdenum mineralization showed little correlation with copper mineralization.

Kitsault

A total of 13.5×10^6 tonnes of ore, averaging around 0.2% Mo, was mined at Kitsault in 1968-1972 and 1981-1982. The molybdenite is related to an elliptical stock of diorite to quartz monzonite, which intrudes greywacke and argillite. Some quartz veins also contain base-metal sulphides and Pb-Bi sulphosalts. Hydrothermal alteration varies in intensity and includes sericite, quartz, and orthoclase.

The main body of igneous rock is medium grained and consists mostly of euhedral to subhedral phenocrysts of plagioclase (An_{25-30}), potassium feldspar, hornblende and biotite. Pyrrhotite and pyrite are present at levels locally exceeding 0.4% and 1.6%, respectively. Other areas of the deposit include quartz diorite with sparse phenocrysts of plagioclase, fine-grained secondary biotite replacing hornblende, and large potassium-feldspar crystals.

Price (1996) compiled petrographic examinations of various grain sizes of waste rock from the Kitsault Minesite. The waste rock could be divided into three groups. The first was fine-grained quartzo-feldspathic rock of meta-sedimentary or possibly meta-tuffaceous rock. Mean modal composition of this group is 42% quartz, 23% plagioclase, 6% potassium feldspar, 10% biotite, 10% sericite, 6% carbonate, and 2% pyrite. Pyrite was randomly disseminated or present as fracture-related strings of subhedral grains, 10-500 μm in size.

A second group of waste-rock samples was distinctly different, leucocratic, potassium-rich intrusive rock. Mean modal composition is 38% quartz, 51% potassium feldspar, 3% plagioclase, 9% sericite, and 2.5% biotite. Carbonate and sulphides were rare, with pyrite occurring as sparse disseminations that were mildly to strongly altered to limonite. The notably low plagioclase in this group is distinctly different from the first group and from plagioclase levels in the other deposits discussed in this chapter. Finer-grained fragments (11-19 mm) were similar in composition and appearance to the coarser fragments (>19 mm), except for more plagioclase (15%) at the expense of potassium feldspar.

A third set was felsic intrusives of porphyritic quartz monzonite to granitic composition. The mean modal composition of the quartz monzonite was 51% potassium feldspar, 32% plagioclase, 13% quartz, and 4% biotite. The granitic rock has a mean modal composition of 67% potassium feldspar, 16% quartz, 13% plagioclase, and 3% biotite. Many samples had

abundant quartz veining (not included in the preceding modal compositions). Carbonate was typically absent, but reached 3% in a few samples. Sulphide was predominantly fresh disseminated pyrite in subhedral grains of 0.02-0.5 mm size. Compared to fragments > 19 mm in size, the smaller 11-19 mm fragments were similar in composition and appearance, except some samples showed substantial alteration to sericite.

Drainage chemistry at Kitsault is predominantly near neutral pH. However, one rock unit outcropping locally in the pit releases acidic drainage.

Trout Lake

The Trout Lake molybdenum deposit is located in southeastern British Columbia, and contains an estimated 49×10^6 tonnes of ore grading 0.19% MoS_2 at 0.10% cutoff. The ore-bearing Trout Lake Stock is a late Cretaceous granodiorite-tonalite intrusion, with the granodiorite containing 40% plagioclase, 40% quartz, 10% potassium feldspar, 10% biotite, and rare hornblende. The four major types of alteration are: skarn and calc-silicate, potassic, quartz-feldspar-muscovite, and muscovite-ankerite. Mineralization occurs in quartz veins that can also contain pyrite, pyrrhotite, and chalcopyrite.

The site contains one adit, extending approximately 1.7 km through the deposit. There were approximately 170 small waste-rock and ore piles around the site, with many showing significant surficial oxidation. Some of the rock is net acid generating based on acid-base accounting. However, drainage waters have pH around 7-8 and aqueous sulphate concentrations are less than 100 mg/L. As a result, Trout Lake is reportedly similar to Boss Mountain and thus should not generate acidic drainage.

Violation of ABA Predictive Rules

In a general sense, most minesites around the world follow most predictive rules (Morin and Hutt, 1997; Hutt and Morin, 2000; Morin and Hutt, 2000b). For example, if acid-generating sulphide exceeds available neutralization potential, there will eventually be acidic drainage in most cases. However, for some molybdenum deposits like Boss Mountain, ABA data has indicated there should be widespread acidic drainage, but none is found (Morwijk Enterprises Ltd., 1993). Therefore, a closer look at ABA data for the six relevant sites in this paper is justified.

Net Neutralization Potential ($\text{NNP} = \text{NP} - \text{AP}$) is calculated by subtracting acid potential based on sulphide or total sulphur (AP) from available neutralization potential (NP). According to standard rules, some net excess of NP, typically set at $\text{NNP} \geq +20$ kg/t of CaCO_3 equivalent, is needed to ensure near-neutral drainage. Similarly, Net Potential Ratio ($\text{NPR} = \text{NP} / \text{AP}$) requires an excess of NP, often to NPR values of 1.5 to 3.0, to ensure near-neutral drainage. All six sites examined here have samples which are theoretically net acid generating as well as samples which are net acid neutralizing (Table 1). However, only Boss Mountain, Kitsault, and Trout Lake have samples that were actually generating net acidity ($\text{pH} < 6$) at the time of analysis. The pervasive non-net-acidity was not caused by the lack of oxidation in fresh samples, because the samples had reportedly been exposed to years of weathering prior to analysis. Nevertheless, site-specific factors like submergence beneath a water table can preclude active acid generation in some samples.

The net-acidic samples at Boss Mountain, Kitsault, and Trout Lake appear to separate these three sites geochemically from Brenda, Endako, and Highland Valley Copper based on acidic paste pH and on some characteristics of bulk (titratable) neutralization potential (NP, Table 1). With NP, Boss Mountain, Kitsault, and Trout Lake have lower values (5th percentile < 10 kg/t). Also, samples with relatively low values of NP below roughly 15 kg/t at Boss Mountain, Kitsault, and Trout Lake have depressed values of paste pH (e.g., Figure 2). On the other hand, low NP values at the other three sites do not show this trend of decreasing pH with decreasing NP (e.g., Figure 3). Additionally, after many years of exposure and weathering, most samples at all six sites still have abundant NP. Therefore, some characteristics of NP at these molybdenum-related sites appear to be related to the observed violation of standard rules.

These observations on NP might suggest that the NP is not being consumed, but this would be wrong because sulphides at these sites are oxidizing and generating acidity based on laboratory kinetic tests and sulphate concentrations in site waters. Therefore, there seems to be a hidden reservoir of NP that maintains near-neutral pH, but is not detected in laboratory NP titrations which typically span no more than 24 hours. This reservoir of NP at Brenda, Endako, and Highland Valley Copper apparently always reacts fast enough to neutralize acidity under site conditions, but reacts too slowly to be fully detected in an NP titration. This reservoir of NP also apparently reacts quickly at Boss Mountain, Kitsault, and Trout Lake to maintain large-scale near-neutral conditions across the minesite, but not fast enough to prevent small-scale net acidity.

At this point, it is worthwhile to examine further the nature of this unmeasured reservoir of NP. Although no inorganic-carbonate data are available for Endako, Highland Valley Copper, and Kitsault, data for the other three sites show that inorganic carbonate (converted to CaNP as kg/t) comprises less than 100% of bulk NP (Boss Mountain, average CaNP = 0.25*NP; Brenda, average CaNP = 0.79*NP; Trout Lake, average CaNP = 0.87*NP). Therefore, some NP, including the undetected reservoir, must occur in a non-carbonate form, and the obvious candidates are the silicate minerals highlighted in the preceding summaries of the minesites.

Based on a review of available geochemical kinetic tests like humidity cells and on-site drainage chemistry, the highest-concentration cation is calcium in small-scale kinetic tests and both calcium and sodium under large-scale field conditions, except for Trout Lake where magnesium replaces sodium as second highest. As a result, the undetected reservoir of NP is likely to be minerals often containing significant levels of calcium and sodium, like plagioclase which contains mixtures of both calcium and sodium.

Also of importance, waters at these sites are below gypsum saturation (usually around 1200-2000 mg/L depending on calcium and iron concentrations), except for the tailings at Endako. The limited data for Kitsault are not clear, but sulphate can apparently reach more than 1000 mg/L in a few locations. This general lack of site-wide gypsum saturation is not often seen at minesites with sulphide minerals, like copper porphyries (Morin and Hutt, 1997). Therefore, the relatively low sulphate concentrations indicate the site-wide rates of sulphide oxidation and acid generation are relatively low, and this is likely a key to the observed violation of ABA predictive rules.

TABLE 1 Summary of ABA Parameters for the Molybdenum-Related Sites							
Parameter	Statistic ²	Boss Mountain	Brenda	Endako	Highland Valley	Kitsault	Trout Lake
Paste pH	95 p ²	8.8	9.03	8.89	9.23	8.7	9.05
	mean ²	8.07	8.65	8.51	8.63	6.57	8
	5 p ²	6.36	8.14	8.13	8.1	2.8	5.86
Titratable Neutralization Potential (kg/t)	95 p	25	64	53	60	60	47
	mean	18	34	33	30	26	19
	5 p	9.3	16	19	11	1.6	1.6
Net Neutralization Potential (kg/t) ¹	95 p	22	55	46	58	35	24
	mean	-5.8	28	22	25	-2.4	-4.4
	5 p	-74	14	0.9	-0.7	-31	-26
Net Potential Ratio ¹	95 p	77	11	15	130	3.1	2
	mean	11	7.5	5.3	38	1.5	0.84
	5 p	0.12	3.8	1	1.1	0.08	0.06
Count		46	35	581	63	60	32
¹ Values based on sulphide where available; otherwise based on total sulphur; NNP = Neutralization Potential (NP) - Acid Potential (AP); NPR = NP/AP.							
² The statistical values are: 95 th percentile, mean, and 5 th percentile.							

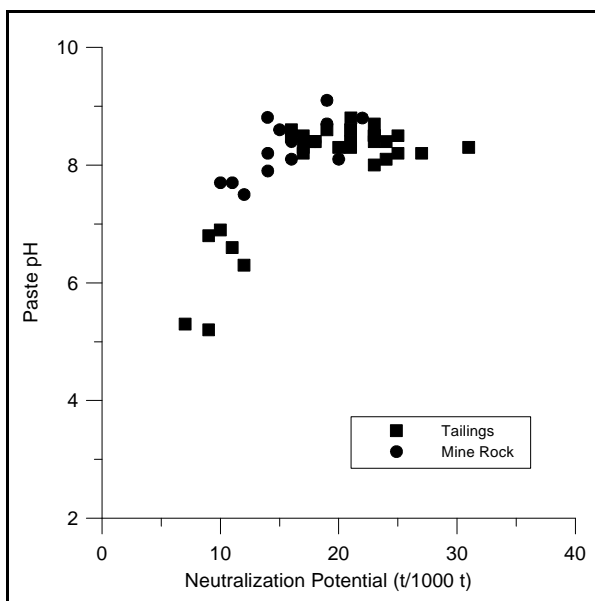


FIGURE 2. Paste pH vs Bulk Neutralization Potential at Boss Mountain.

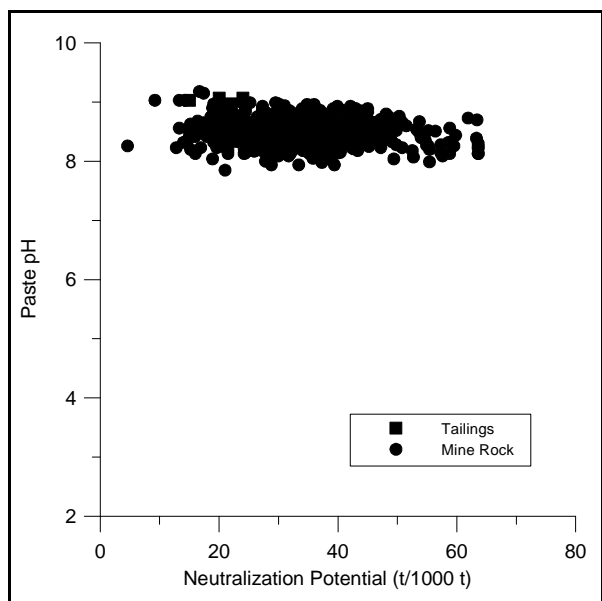


FIGURE 3. Paste pH vs Bulk Neutralization Potential at Endako.

In standard predictions of acid generation, silicate minerals are often relegated to partial neutralization without fully alleviating acidic conditions. However, where oxidation rates are low, reflected in non-gypsum-saturated waters, the rate of silicate dissolution has a greater opportunity to fully neutralize the less-acidic waters. Because of this, the silicate-derived NP is not detected in the short-term NP analyses, but forms an undetected reservoir that can neutralize large amounts of acidity across a minesite.

Based on information available on these six molybdenum deposits in British Columbia, silicate minerals containing calcium and sodium represent the undetected reservoir of additional NP that maintains near-neutral conditions on a large scale at these minesites, but not always on a small scale. Again, this undetected reservoir of NP is successful only because of relatively low site-wide oxidation rates, which are apparently slow enough to allow these silicates to fully neutralize on a large scale.

There is insufficient information to evaluate the detailed causes of the lower oxidation rates found at these molybdenum deposits. The causes could possibly include the presence of significant amounts of non-iron-based sulphides like molybdenite, galvanic interaction with the non-iron-based sulphides, a consistently slow oxidation rate and/or incorporation of molybdenum, tungsten, or other elements into sulphide minerals which could retard their oxidation rates.

It is apparent that such exceptions to standard rules are not necessarily limited to molybdenum-related deposits. This further justifies the use of site-specific assessments involving a large suite of geochemical tests, sometimes called the “Wheel” Approach (Price et al., 1997; Morin and Hutt, 1999b).

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