Sr/Ca and $^{87}Sr/^{86}Sr$: A tracer for geochemical processes in mine wastes.

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Abstract

Understanding geochemical processes in mining environments are essential to waste management decisions including remediation. In an attempt to understand geochemical processes, chemical data have mostly been used but these have often led to inaccurate conclusions. Therefore, in this work $^{87}Sr/^{86}Sr$, Sr/Ca and other elemental ratios (Ca/K and Rb/Sr) in leachates were employed to constrain the geochemical processes in an abandoned tungsten (W) tailings in Yxsjöberg, South-Central Sweden. The results of this study indicate that coupling chemical ratios with $^{87}Sr/^{86}Sr$ ratios offer better insights in discriminating between different geochemical processes in mine wastes.

Keywords: Acid Mine Drainage, Yxsjöberg, Skarn tailings, Sr isotopes, Silicate weathering.

Introduction

Negative effects of acid mine drainage (AMD) generated from sulphide oxidation and other acid generating sources have resulted in environmental considerations gaining prominence in the assessment of the economic feasibility of mine projects (Azcue 2012). The roles of buffering minerals in neutralizing acidity are therefore critical in mine environments. In typical mine settings, carbonates, silicates and (oxy)-hydroxides play major roles in acid neutralization (e.g. Jurjovec et al. 2002).

Strontium (Sr) and calcium (Ca) are geochemically similar in terms of ionic radius and ionic charge (Marcus and Kertes 1968) and can substitute for each other in mineral lattices such as in carbonates and some silicates. This allows the use of Sr as a proxy for Ca in many studies (e.g. Pett-Ridge et al. 2009; Tipper et al. 2006). Rubidium (Rb) on the other hand, is geochemically similar to potassium (K) and substitutes for K in K-bearing mineral lattices. ^{87}Rb undergoes radioactive β- decay to produce stable ^{87}Sr. As a consequence, K-bearing minerals (e.g. biotite, K-feldspar, muscovite) are high in $^{87}Sr/^{86}Sr$ ratios (Faure 1986; Clow et al. 1997). In addition, $^{87}Sr/^{86}Sr$ ratios have the advantage of not being fractionated by low temperature geochemical processes such as mineral precipitation (Capo et al. 1998).

Considering that the acid neutralizing minerals are either enriched in Rb and K or Sr and Ca, then their dissolution should release variable $^{87}Sr/^{86}Sr$ ratios into leachates, since they have distinct $^{87}Sr/^{86}Sr$ ratios. In this study, $^{87}Sr/^{86}Sr$ and Sr/Ca as well as other chemical ratios (Ca/K and Rb/Sr) and concentrations in leachates, tailings and minerals have been used to trace geochemical processes including acid-neutralization that have occurred within mineralogically-complex historical tungsten (W)- skarn deposit in Yxsjöberg, South Central Sweden.

Methods

Tailings were collected by percussion drilling from the Yxsjöberg W-skarn deposit. The drill core extends to a depth of 6m and is subdivided into 18 subsamples. Minerals including K-feldspar, garnet, plagioclase, amphibole, pyroxene, calcite, scheelite, fluorite and helvine were separated from diamond drill cores belonging to the orebodies from which the tailings originated. *Batch leaching tests* were performed on tailings with a 1:10 solid (tailings) to liquid (MilliQ water) ratio following the procedure outlined in the Swedish standard institute's compliance test for granular wastes and sludges (SS-EN 12457-2:2003).

Sr isotope compositions of whole-rock tailings, individual minerals and leachates were analyzed using multicollector inductively-coupled plasma mass spectrometry (MC-ICP-MS). *Chemical compositions* of seventy (70) elements in leachates were carried out by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS). All analyses (chemical compositions and isotopes) were carried out at ALS Scandinavia AB, Luleå, Sweden. *Mineralogical studies* of the tailings profiles were carried out using optical microscopy, X-ray diffraction (XRD) (PANanalytical Empyrean) and Raman spectroscopy (Bruker).

Results and Discussions

Mineralogical and isotopic characterization of tailings

Minerals identified in the tailings include amphibole, pyroxene, biotite, plagioclase, K-feldspar, garnet, calcite, fluorite, hematite, helvine, muscovite, Fe-(oxy)hydroxides, magnetite, scheelite and gypsum.

The distribution of Sr isotope ($^{87}Sr/^{86}Sr$) ratios in the tailings profile is shown in figure 1. The tailings have been categorized into four zones namely; upper oxidized zone (UOZ), lower oxidized zone (LOZ), upper unoxidized zone (UUZ) and lower unoxidized zone (LUZ) based on pH, chemical data and colour. The oxidized zones (upper and lower) are characterized by low pH, ranging from 3.6 to 4.5 whereas the unoxidized zones (upper and lower) have pH values between 5.3 and 7.9. The oxidized zones recorded radiogenic signatures (0.8479 -1.2664) compared to the less radiogenic ratios (0.8329- 1.0679) in the underlying unoxidized zones.

$^{87}Sr/^{86}Sr$ ratios in minerals

The average $^{87}Sr/^{86}Sr$ ratio of the minerals is shown in table 1. All minerals analyzed for $^{87}Sr/^{86}Sr$ are present in the tailings. Scheelite recorded the lowest $^{87}Sr/^{86}Sr$ values of 0.7085 whilst K-feldspar recorded the highest ratio of 2.3984.

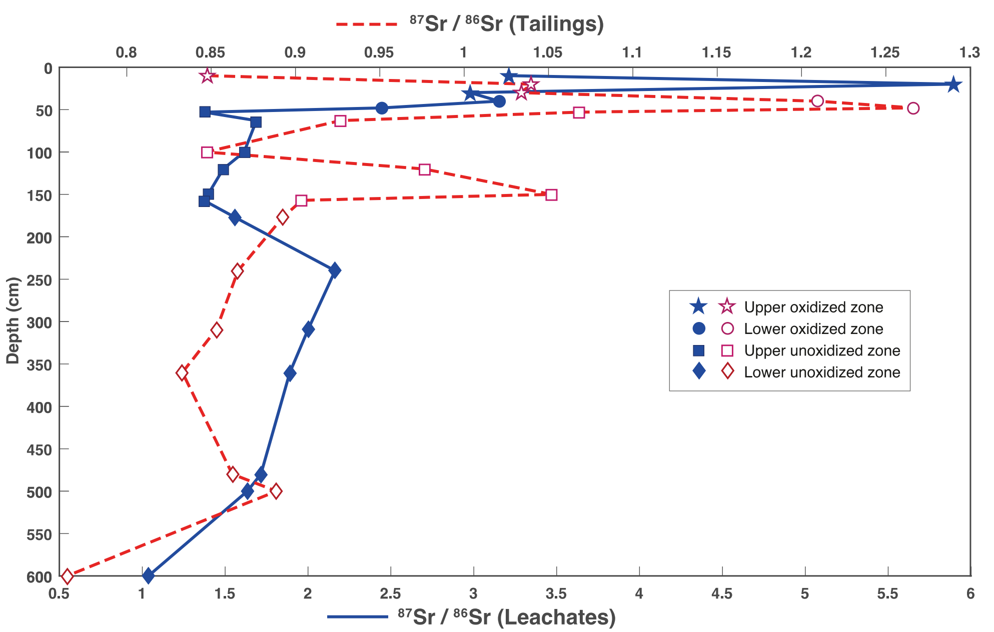

Figure 1: *Sr isotopes ratios ($^{87}Sr/^{86}Sr$) in leachates (____) and tailings (_ _) from Yxsjöberg mine site, Sweden. The $^{87}Sr/^{86}Sr$ signatures at 600 cm depths represents a mixture of tailings and till and have been neglected in this study.*

Table 1. *Average $^{87}Sr/^{86}Sr$ ratios in minerals.*

Mineral	Amp (n=4)	Px (n=2)	Grt (n=2)	Hel (n=2)	Plag (n=2)	Kfs (n=1)	Cal (n=1)	Fl (n=2)	Sch (n=2)
$^{87}Sr/^{86}Sr$	0.8124	0.7270	0.8107	1.2010	0.7114	2.3984	0.7163	0.7086	0.7085

n= number of minerals analyzed. Am= amphibole; Px= pyroxene; Grt= garnet; Hel=helvine; Pl=plagioclase; Kfs= K-feldspar; Cal=calcite; Fl= fluoride, Sch= scheelite

Table 2. *Chemical composition of leachates from the Yxsjöberg W-tailings deposit, Sweden.*

Description	Depth(cm)	pH	Ca (mg/L)	K (mg/L)	Rb (ug/L)	Sr (ug/L)	SO_4^{2-} (ug/L)
UOZ	10	4.5	6	5	33	1.6	16
UOZ	20	4.4	9	8	94	1.5	29
UOZ	30	3.9	16	9	179	2.3	60
LOZ	40	3.7	214	13	434	15	593
LOZ	48	3.6	441	25	645	39	1106
UUZ	49	5.3	127	5	121	18	257
UUZ	63	6.3	62	4	82	10	84
UUZ	100	7.3	211	7	135	23	469
UUZ	120	6.7	615	12	255	54	1369
UUZ	150	6.8	590	11	221	56	1322
UUZ	157	6.9	525	11	199	48	1205
LUZ	177	7.2	65	12	91	11	150
LUZ	240	7.4	56	7	100	7	130
LUZ	309	7.6	41	7	75	6	92
LUZ	360	7.9	27	6	54	5	60
LUZ	480	7.7	38	5	59	6	90
LUZ	500	7.6	86	8	102	16	201
LUZ[a]	600	7.3	251	10	147	64	576

[a] mixture of tailings and till. UOZ= upper oxidized zone, LOZ= lower oxidized zone, UUZ= upper unoxidized zone, LUZ= lower unoxidized zone.

Chemical and isotopic composition of the leachates

The chemical composition of the leachates is presented in table 2. Ca concentrations ranged from 6 - 441 mg/L in the oxidized zones and 27 - 615 mg/L in the unoxidized zones. For K, the concentrations ranged from 5 - 25 mg/L in the oxidized zones whilst the unoxidized zones had values between 4 and 12 mg/L. The highest concentrations of Rb were registered in the oxidized zones (33 - 645 μg/L) compared to the unoxidized zones (54 - 255 μg/L). In contrast to the trend of Rb, the unoxidized zones had the highest Sr and sulfate (SO_4^{2-}) concentrations.

The Sr isotopes ratios ($^{87}Sr/^{86}Sr$) in the oxidized zones were more radiogenic relative to the unoxidized zones. The $^{87}Sr/^{86}Sr$ ratios ranged from 2.4448- 5.8755 in the oxidized zones whilst the unoxidized zones had $^{87}Sr/^{86}Sr$ ratios ranging between 1.3712 and 2.1634 (Figure 1).

Geochemical processes

The leachates in the upper oxidized zone showed *very* radiogenic $^{87}Sr/^{86}Sr$ ratios ranging from 2.9776 to 5.8755. This feature points towards weathering of biotite, K-feldspar and muscovite which are the only known radiogenic minerals identified in this zone. The decomposition of Rb-rich minerals such as biotite, K-feldspar and muscovite could result in $^{87}Sr/^{86}Sr$ enrichment in pore water with a resultant depletion in the residual weathered material (Blum et al. 1993; Bullen et al. 1997; Blum and Erel 1997). This is consistent with the observations in figure 1 where the leachates showed high $^{87}Sr/^{86}Sr$ ratios whereas the tailings revealed low $^{87}Sr/^{86}Sr$ ratios. In addition, since biotite, K-feldspar and muscovite are Rb-K rich or Sr-Ca poor, a leachate primarily controlled by the dissolution of these minerals should result in high Rb/Sr and low Ca/K ratios. Furthermore, although these minerals (biotite, K-feldspar, muscovite) are considered

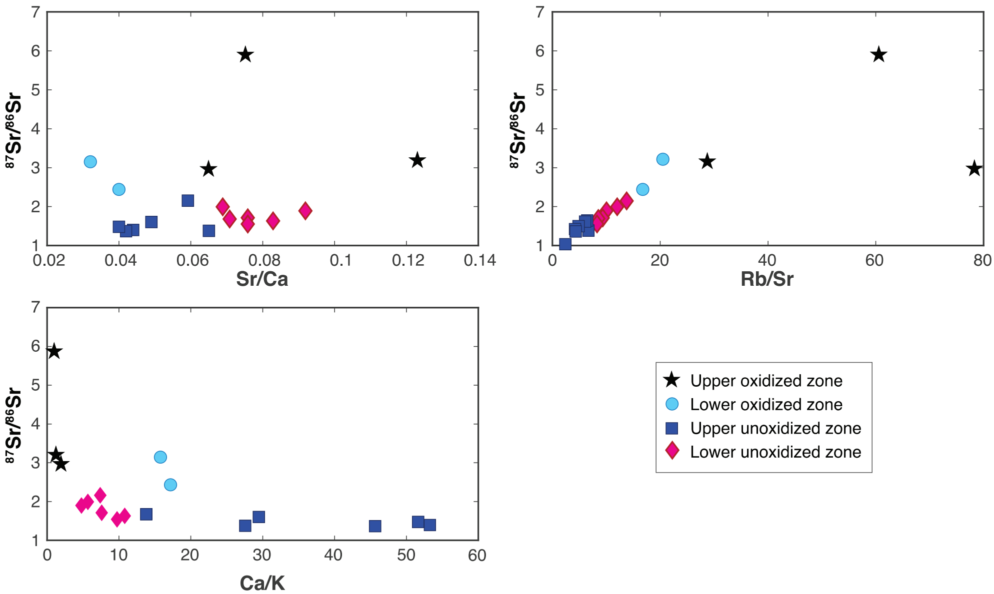

Figure 2: *Sr/Ca, Rb/Sr and Ca/K ratios in leachates from the Yxsjöberg W-tailings deposit, Sweden. Ratios are in molar units.*

Sr-Ca poor, their weathering will elevate Sr/Ca ratios in leachates since they have negligible Ca relative to Sr. Leachates in the upper oxidized zone shows relatively high Sr/Ca and Rb/Sr ratios but a low Ca/K ratio (figure 2). This indicates that the leachates are controlled by the dissolution of K-Rb bearing minerals.

Trends of Sr/Ca, Rb/Sr and Ca/K ratios in the leachates in the lower oxidized zone are in contrast to the upper oxidized zone although the $^{87}Sr/^{86}Sr$ ratios are still radiogenic (figures 1 & 2). Reduction in Sr/Ca and Rb/Sr ratios and corresponding increment in Ca/K ratio in this zone suggest additional dissolution of Ca-bearing minerals. Considering the prevailing pH conditions (pH= 3.6-3.7), the dissolution of amphibole, plagioclase and fluorite could be favoured (Schott et al. 1981; Brantley et al. 1998; Wong et al. 2003). In addition, a positive trend between Ca and SO_4^{2-} (figure 3) suggests that gypsum dissolution is also a possible mechanism controlling the decreased Sr/Ca and increased Ca/K ratios.

Less radiogenic $^{87}Sr/^{86}Sr$ ratios (1.3712-1.6884) were recorded in leachates of the upper unoxidized zone relative to the overlying oxidized zones (figure 1). These $^{87}Sr/^{86}Sr$ ratios do not directly reflect the signature of any of the minerals analyzed. In addition, the Sr/Ca and Ca/K ratios display similar trends to that of the lower oxidized zone (figure 2). This zone also shows positive anomalies of Ca and SO_4^{2-} (figure 3) as observed in the lower oxidized zone. Since $^{87}Sr/^{86}Sr$ ratios are not affected by dilution, this could indicate the dissolution of gypsum.

In the lower unoxidized zone, the $^{87}Sr/^{86}Sr$ ratios are more radiogenic (1.6341-2.1634) than the overlying upper unoxidized zone. These increased $^{87}Sr/^{86}Sr$ ratios correspond to a Sr/Ca ratio similar to the upper oxidized zone (figure 2). Furthermore, the Ca/K ratios are "sandwiched" between that of the upper and lower oxidized zones but skewed towards the upper oxidized zone. This suggests the influence of a radiogenic source particularly K-bearing minerals. Sr losses from biotite and K-feldspar have been reported to be rapid (Clow et al. 1997) and as such the radiogenic Sr could be attributed to these minerals.

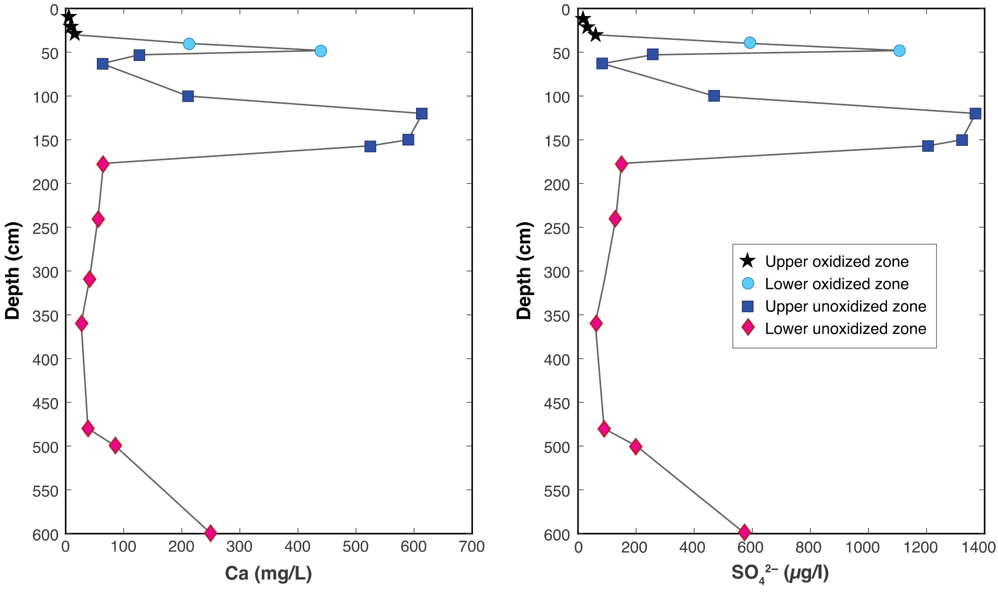

Figure 3: *Ca and SO_4^{2-} distribution in leachates from the Yxsjöberg W-tailings deposit, Sweden.*

Conclusions

The $^{87}Sr/^{86}Sr$ ratios and chemical ratios (Ca/K, Sr/Ca and Rb/Sr) in leachates shows variations in the four main zones of the tailings namely; upper oxidized, lower oxidized, upper unoxidized and lower unoxidized zones. These variations are reflections of the different geochemical processes occurring in the tailings. Radiogenic $^{87}Sr/^{86}Sr$ ratios recorded in the oxidized zones suggests the weathering of biotite, K-feldspar and muscovite. High Ca/K and low Sr/Ca ratios in the lower oxidized zone indicates dissolution of Ca-bearing minerals including gypsum. Similarity between Sr/Ca and Ca/K ratios as well as correlation between Ca and SO_4^{2-} in the upper unoxidized zone to that of the lower oxidized zone points to gypsum dissolution. In the lower unoxidized zone, Sr/Ca ratios and Ca/K depicts that of the upper oxidized zone with an increased $^{87}Sr/^{86}Sr$ ratio which is attributed to biotite and K-feldspar.

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