A Method to Separate Phases of Sulphur in Mine-Waste piles and Natural Alteration Zones, and to Use Sulphur Isotopic Compositions to Investigate Release of Metals and Acidity to the Environment

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ABSTRACT

Assessment of metal mobility, acid rock drainage production, and toxic effects from weathering of mineralized materials (i.e. mine-waste piles and outcropping alteration/ore zones) is key in evaluating and mitigating metal mining sites. Many metal- and acid-generating materials at these sites are sulphur minerals (sulphides to sulphates) with differing reactivities, weathering characteristics and metal contents. Our working hypothesis predicts that data on the types and quantities of sulphur minerals, coupled with comparison of their sulphur isotopic compositions to that of aqueous sulphate in the surrounding environment, can be used to evaluate primary pathways of weathering reactions at mining sites.

We developed a sequential extraction scheme to separate the phases of sulphur in mineralized materials. Operationally defined phases, including monosulphides, disulphides, elemental sulphur, water-soluble sulpho-salts, acid-soluble sulphates, and resistant sulphate phases such as barite, are quantified gravimetrically and/or instrumentally. Several sets of experiments were designed to test the effectiveness of this extraction scheme. First, a variety of ore sulphides diluted in an inert matrix was analyzed with the scheme. Results showed that molybdenite and arsenic-bearing sulphides do not behave as predicted from just their sulphur oxidation states, indicating that samples containing these minerals need special treatment for complete phase recovery. Second, a natural mine-waste composite standard was analyzed by the scheme. The sum of the phases was equal to the total sulphur concentration analyzed independently. Each phase had a similar, but distinct sulphur isotopic composition. The results were verified with a laboratory prepared "proxy" having the same mineralogical composition as the standard, but with each phase having a very different sulphur isotopic composition. The sulphur isotopic compositions of the recovered phases from the "proxy" showed that the scheme effectively separated the sulphur with only minor cross contamination of phases.

The speciation and isotopic analyses were applied to both mineral waste piles and naturally occurring alteration zones at nine mine sites. A case study from one site comparing the sulphur isotopic composition of minerals in an alteration zone and dissolved sulphate in proximal streams is presented. This case study shows the application of our data to differentiating sources of sulphate in the surrounding environment.

INTRODUCTION

Mine-waste piles and outcropping alteration/ore zones are present at many metal-mining sites around the world. Assessment of metal mobility, acid rock drainage

production, and toxic effects from weathering of these waste piles and proximal mineralized rock is key to evaluating mine sites and developing mitigation strategies (among others see papers in Jambor and Blowes, 1994; King, 1995; Filipek and Plumlee, 1999; Society for Mining, Metallurgy, and Exploration, Inc., 2000). Although oxidation of sulphide minerals and metal-sulphate salt dissolution are important processes in generating acid and metals, few assessment methods developed to date analyze sulphur species directly.

This paper presents a sequential extraction scheme to separate the forms of sulphur in mine-waste piles and in naturally mineralized terrain. The information on sulphur species was critical in determining the amounts of primary and secondary sulphide minerals that have different weathering characteristics. In addition, secondary and tertiary sulphates, elemental sulphur, and refractory sulphates were quantified to further assess mobility of weathering products. The sulphur isotopic composition of phases in samples prepared with well-characterized sulphides was used to test the effectiveness of the scheme. Compositions in natural samples were used to assess primary pathways of weathering reactions.

METHODS

Sampling Methods

A variety of standards and natural samples were analyzed. Pure sulphide minerals diluted to 1.0 weight percent with powdered, clean quartz were used to classify less common sulphide minerals according to the operationally defined phases within the scheme. Because these sulphides were from natural specimens, some impurities may be present; therefore, recoveries are based on total sulphur analyses. Pure standards of water- and acid-soluble sulphates, common sulphide minerals, and elemental sulphur were used to evaluate the efficiency of the scheme. The sulphur isotopic composition of recovered phases from mixtures of these standards indicated whether cross contamination occurred during speciation.

Natural composites from individual mine-waste piles and mineralized terrains were collected, homogenized, and ground to -100 mesh. Mineralogy of these samples was determined by X-ray diffraction (XRD), providing some information about the sulphur-bearing minerals in the sample. In several areas, waters in proximal streams were collected, filtered (0.45 µm) in the field, and refrigerated until analyzed.

Analytical Methods

The summation of sulphur concentrations in solid phases determined through the speciation scheme was compared to a total sulphur concentration measured with a LECO[1] sulphur analyzer. This comparison allowed us to monitor the effectiveness of the scheme to recover all sulphur within the sample.

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[1] Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

The solid phases of sulphur in the standards and samples were separated using an analytical scheme modified from Tuttle, Goldhaber and Williams (1986) (fig. 1; Appendix). Phases recovered are operationally defined as sulphur minerals that are:

1. soluble in acetone at ambient temperatures (elemental sulphur)
2. readily soluble in water at ambient temperatures (water-soluble sulphates)
3. soluble in hot 6 N HCl (acid-soluble sulphates)
4. volatile as H_2S in hot 6 N HCl (acid-volatile sulfides, which are many of the monosulphides[2])
5. volatile as H_2S in hot HCl/Cr^{2+} (disulphides[3])
6. residual after all other phases removed (refractory sulphates such as barite).
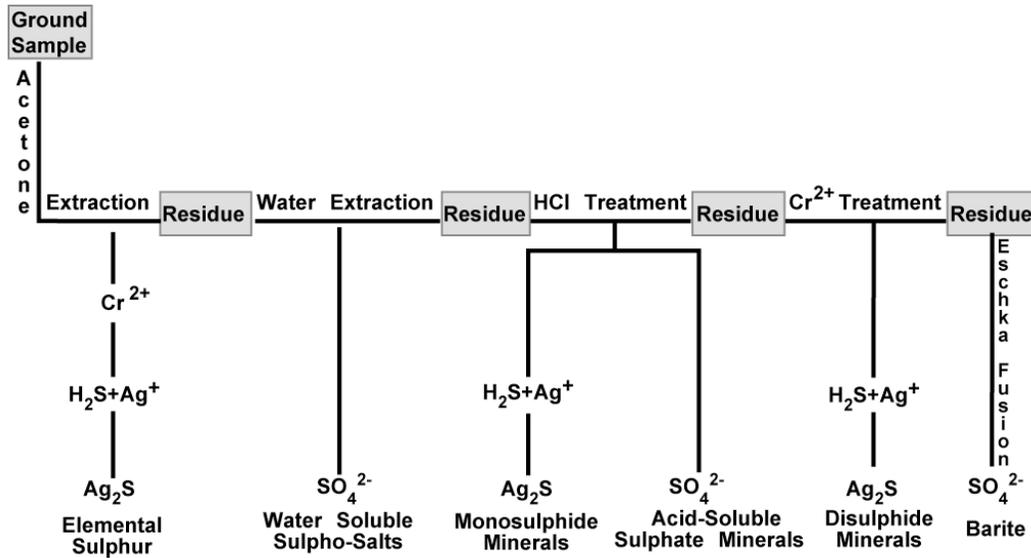

Figure 1. Schematic showing the analytical scheme used to speciate sulphur phases in mine-waste piles and mineralized terrains.

Sulphur in each phase was gravimetrically determined and collected as Ag_2S or $BaSO_4$ for sulphur isotopic analysis. Tin chloride ($SnCl_2$) was added to the sample during the acid-volatile sulphide treatment because ferric iron in the mine waste affected recovery of the H_2S (Tuttle, Goldhaber and Williams, 1986; Rice, Tuttle and Reynolds, 1993). This treatment reduced small amounts of microcrystalline pyrite in some sediment, thus slightly overestimating the acid-volatile sulphide phase and underestimating pyrite. Sulphate and metals in the solutions from the water and acid extractions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES); however, the metal data are not presented in this paper.

The sulphur isotopic composition of the phases were determined by analyzing the Ag_2S and $BaSO_4$ produced during sulphur speciation. Solids were combusted and

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[2] Monsulphides are minerals with sulphur in the negative two oxidation state, includes galena, sphalerite, and pyrrhotite.
[3] Disulphides are minerals with sulphur in the net negative one oxidation state, includes pyrite and marcasite.

analyzed on-line by an elemental analyzer coupled to a mass spectrometer (Kester *et al*, 2001).

RESULTS AND DISCUSSION

Effectiveness of Speciation Scheme

The recoveries of the diluted monomineralic sulphide samples are given in Table 1. The presence of sulphate in the HCl leach indicated that sulphur oxidation products contaminate some of the sulphides. In most cases, sulphate, when present, is <10 percent of the total sulphur. Although molybdenite is a monosulphide (sulphur in the 2-oxidation state), it was highly refractory during the acid-volatile treatment, as well as during the chromium treatment. Other studies have shown that molybdenite only dissolves under highly aggressive conditions (e.g., HNO_3 boiled to dryness; Chao and Sanzolone, 1977). Recoveries of sulphur in arsenic-bearing minerals were low and, unexpectedly, recoveries with $SnCl_2$ were lower than without $SnCl_2$. More experimental work is needed to modify the scheme to accommodate abundant molybdenite and arsenic sulphides. Bornite and chalcopyrite seem to have both mono- and disulphide properties, and only were recovered effectively after both the acid and chromium treatment. Stannous chloride, however, did increase recoveries of these two sulfides during the acid treatment. Fortunately, many of these "problem" sulphides, if present, are minor to trace phases in many waste piles and uneconomic alteration zones.

Our preliminary work on mine waste (Briggs and Tuttle, 2000) speciated sulphur phases in composites from waste piles at different mines from Colorado and New Mexico. Results showed that the sum of sulphur species recovered was usually the same as the concentration of total sulphur analyzed by the Leco instrument. The data, however, did not verify which minerals were extracted into each phase. One of the composites was chemically characterized and adopted as a geochemical reference standard (NIST Hard Rock Mine-waste Reference Material SRM 2780; Wilson, *et al*, 1999). This standard contains 1.2 weight percent sulphur. XRD identified the minerals jarosite, sphalerite, and pyrite. Elemental sulphur and a small amount of water-soluble sulphate were identified by the separation scheme (table 2). A NIST "proxy" was prepared with well-characterized sulphur minerals (standards) using the same concentrations of elemental sulphur, jarosite, sphalerite, and pyrite in a quartz/clay matrix. Speciation of the proxy effectively separated the mineral phases with only minor contamination (see sulphur isotopic compositions in table 2). The sulphur isotopic composition of the recovered acid-volatile phase was isotopically heavier (enriched in [34]S) than the composition of the sphalerite standard, likely reflecting a small amount of contamination from pyrite reacting with the $SnCl_2$. Isotopic mass balance calculations indicated that 8 percent of the acid-volatile sulphur phase collected was from pyrite and 92 percent from sphalerite.

Table 1. Percent of total sulphur recovered during acid-volatile sulphide and disulphide extractions. Results are given for runs with and without $SnCl_2$ (Sn).

Mineral	Ideal Formula	% of total S w/o Sn		% of total S w Sn		% of total S	% recovered
		S_{AV}[1]	S_{DI}[1]	S_{AV}	S_{DI}	S_{SO4}[1] in HCl	
arsenopyrite	FeAsS	0	9	0	7	7	14 - 16
bornite	Cu_5FeS_4	37	22	67	43	5	64 - 115
chalcocite	Cu_2S	71	5	88	0	0	76 - 88
chalcopyrite	$CuFeS_2$	24	47	65	24	9	80 - 98
enargite	Cu_3AsS_4	25	51	34	27	0	61 - 76
galena	PbS	83	11	100	0	9	103-109
molybdenite	MoS_2	0	4	1	3	0	4
orpiment	As_2S_3	41	11	35	13	0	48 - 52
pentlandite	$(Fe,Ni)_9S_8$	51	8	73	0	12	71 - 85
pyrite	FeS_2	0	89	2	77	7	86 - 96
pyrrhotite	FeS	63	8	88	0	9	80 - 97
realgar	AsS	53	31	37	37	0	74 - 84
sphalerite	ZnS	94	0	94	0	0	94

[1]S_{AV}, sulphur in monosulphides; S_{DI}, sulphur in disulphides; S_{SO4}, sulphur in soluble sulphate salts.

Table 2. Sulphur phases in NIST SRM 2780, their sulphur isotopic composition, sulphur isotopic composition of standards in NIST "proxy", and the sulphur isotopic composition of recovered "proxy" phase.

NIST SRM 2780				NIST "proxy"	
Treatment	Phases ID'd[1]	S_{phase} (wt%)	$\delta^{34}S_{phase}$ (‰)	$\delta^{34}S_{standard}$ (‰)	$\delta^{34}S_{phase}$ (‰)
acetone	elemental S	0.12	-2.2	12.9	11.2
H_2O	sulphate salts	.04	-1.6		13.8
HCl	jarosite	.42	-3.3	-25.1	-24.9
acid-volatile	sphalerite	.05	-1.2	1.9	3.2
Cr^{2+} reduction	pyrite	.47	-2.8	19.4	18.4
Total S % (Σ phases)		1.1			
Total S % (Leco)		1.2			

[1]Phases ID'd, phases detected by XRD or chemically.

Application of Sulphur Speciation Results: A Case Study

A large molybdenum porphyry deposit in the Red River Valley, New Mexico, USA is surrounded by valleys that have formed in expansive areas of hydrothermally altered rocks referred to as "alteration scars" (Meyer and Leonardson, 1990). The composition of the material in these scars is very similar to that in many mine-waste piles (amorphous silica- and iron-rich compounds, pyrite, minor ore sulphides, jarosite, gypsum, and highly soluble sulpho-salts such as copiapite and coquimbite). Weathering of these minerals produces significant natural loads of acid rock drainage and metals flowing into the streams. To determine which minerals have the greatest effect on loads, the sulphur

isotopic compositions of phases in rock composites and of dissolved sulphate in water from three "alteration scar" drainages were compared (table 3).

Table 3. Sulphur phases in rock composites and grab samples, their sulphur isotopic composition, and isotopic composition of sulphate in proximal streams.

Treatment	Probable Phases	Straight Creek (n=4)	Hottentot Creek (n=2)	June Bug Creek (n=2)
		$\delta^{34}S_{phase}$ (‰)	$\delta^{34}S_{phase}$ (‰)	$\delta^{34}S_{phase}$ (‰)
acetone	elemental S	--[1]	nd[1]	nd
H_2O	sulphate salts	-1.9	nd	nd
HCl	jarosite	-3.5	nd	nd
acid-volatile	?	-1.3	-7.3	-4.3
Cr^{2+} reduction	pyrite	-1.6	-4.1	-4.1
Dissolved sulfate		-4.2 to -6.8	-3.9 to -4.6	-3.4 to -4.1

[1]--, amount separated to small to analyze; nd, not determined.

The sulphur isotopic composition of dissolved sulphate in Straight Creek decreased with increasing elevation (-6.8 per mil at the top to -4.2 per mil at the bottom). The -6.8 per mil value is isotopically lighter (depleted in ^{34}S) than any of the sulphur phases analyzed (table 3). One explanation consistent with these data was that some unknown, isotopically light source contributes to the sulphate near the head of the stream. As the stream flows through the altered rock, this sulphate is titrated with isotopically heavier sulphate from the oxidation of sulphides (near -1.1 per mil) and dissolution of metal salts (near –1.9 per mil). In comparison, the sulphur isotopic composition of the sulphate dissolved in Hottentot and June Bug Creeks was very similar to that of the pyrite, and, in some cases, the acid-volatile sulphides as well. No addition sulphate source was needed to explain the isotope data in these two drainages.

Although the interpretation of the data from these three drainages is by no means conclusive, results did provide a basis for formulating and testing working hypotheses as to the processes controlling acid and metal loading to the environment.

Cautions

The method used to analyze samples in this study is presented in cookbook format in the Appendix. The blanket application of this method to all sample types, however, is not advised. Several recommendations we found useful when applying this scheme are listed below.
   1. Design sampling protocol to assure representative sample.
   2. Know as much about the mineralogy as possible (e.g., XRD, SEM, and petrography).
   3. Grind sample well and maximize sample size to decrease effects of mineralogical heterogeneity.

4. Add only sufficient SnCl$_2$ to reduce HCl-soluble ferric iron in the sample, thereby minimizing reaction with pyrite.
5. Analyze total sulphur by an independent method to assess recovery of all sulphur phases.

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APPENDIX
Details of speciation scheme

Acetone Extraction

1. Weigh approximately 5 g of sample for total sulphur concentrations around 1.0 weight percent; if >1.0 weight percent, decrease weight accordingly.
2. Place sample in 250-mL polyethylene bottle with 125 mL reagent acetone and shake for 18-24 hours.
3. Filter acetone solution (0.45 µm, polycarbonate[4]), wash with reagent acetone, and save residue for water extraction.
4. Place acetone solution in reaction vessel (see apparatus in Tuttle, Goldhaber, and Williams, 1986) and continually flush with nitrogen.
5. Add 20 mL 12 M HCl and 50 mL 1 M $CrCl_2$ solution (reduce $CrCl_3$ in Jones Reductor; see Skoog and West, 1982).
6. Add heat to reaction vessel and collect evolved H_2S in a 0.1 M $AgNO_3$ solution after passing through a pH 4 buffer to collect any HCl vapors.
7. Collect Ag_2S on a filter (0.45µm), dry, weigh, and calculate elemental sulphur concentration.

Water Extraction

1. Place residue from acetone extraction in a 250-mL polyethylene bottle and add 100 mL distilled water.
2. Shake for 30 minutes.
3. Filter water solution and save residue for acid treatment.
4. Either precipitate the sulphate as $BaSO_4$ with 10 percent w/w $BaCl_2$ solution after acidifying sample, or analyze sulphate concentration with ICP-AES.
5. If precipitating the sulfate, filter $BaSO_4$ (0.45 µm), dry, weigh, and calculate water-soluble sulphur concentration.

Acid-volatile Treatment

1. Place residue from water extraction in reaction vessel as used in acetone extraction and continuously flush with nitrogen.
2. Add 80 mL 6 N HCl with 2 - 15 g $SnCl_2$.
3. Add heat to the reaction vessel and collect evolved H_2S in a 0.1 M $AgNO_3$ solution after passing through a pH 4 buffer to collect any HCl vapors.
4. Collect Ag_2S on a filter, dry, weigh, and calculate acid-volatile sulphur.
5. Filter HCl solution and save residue for disulphide extraction.

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[4] Polycarbonate filters do not dissolve with acetone or ethanol.

6. Either precipitate the sulphate as $BaSO_4$ with 10 percent w/w $BaCl_2$ solution, or analyze sulphate concentration with ICP-AES.
7. If precipitating $BaSO_4$, add bromine water and boil; then precipitate the sulphate as in step 5 of water extraction.

Disulphide Extraction

1. Place residue from acid treatment in reaction vessel as used above and continuously flush with nitrogen.
2. Add 10 mL ethanol, 20 mL 12 N HCl, and 50 mL 1 M $CrCl_2$ (Cr^{2+} is used to reduce disulfides to H_2S).
3. Add heat to reaction vessel and collect evolved H_2S in a 0.1 M $AgNO_3$ solution after passing through a pH 4 buffer to collect any HCl vapors.
4. Collect Ag_2S on a filter (0.45μm), dry, weigh, and calculate disulphide sulphur concentration.
5. Filter $HCl/CrCl_2$ solution (0.45μm, polycarbonate) and save residue for residual-sulphur extraction.

Residual Sulphur Extraction

1. Mix residue from disulphide extraction with three times its weight of Eschka mixture (three parts MgO and two parts Na_2CO_3).
2. Place in porcelain crucible and cover with Eschka mixture.
3. Fuse in muffle furnace at 800° C for two hours, then remove and cool.
4. Dissolve cake in distilled water, heat, and filter (0.45 μm), discarding solid.
5. Heat solution, adjusting pH to <4.0 with HCl.
6. Add 10 mL bromine water, and boil.
7. Precipitate $BaSO_4$ as in step 5 of water extaction.