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Acid–base account effectiveness for determination of mine waste potential acidity

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Abstract

The oxidation of sulfide minerals in mine waste is a widespread source of resource degradation, often resulting in the generation of acidic water and mobilization of heavy metals. The quantity of acid forming minerals present in mine waste, dominantly as pyrite (FeS_2) is routinely determined by acid–base account (ABA) analytical methods. The acid–base account method specifies the use of extraction techniques to determine the total quantity of acid forming sulfur compounds in a sample relative to the neutralizing potential. However, when common sulfide and sulfate minerals were subjected to ABA extraction methods, the ABA method failed to distinguish accurately the acid forming from nonacid forming minerals, resulting in errors in the determination of potential acidity. These analytical errors are subsequently reflected in inaccurate liming of acid producing waste materials resulting in either excessive cost when potential acidity is overestimated, or potential reclamation failure when potential acidity is underestimated.

1. Introduction

Acid–base account analytical methods are routinely applied to the analysis of mine waste materials to assess the ability of the material to generate acid upon weathering. Acid–base account (ABA) analytical methods by Sobek [1] and subsequent modifications by Schafer [2] serve to identify the sulfur forms in a sample by extraction methods. Acid–base account (ABA) is assessed by determining the neutralization potential (NP) and potential acidity (PA) of a sample:

$$ABA = NP - PA. \quad (1)$$

The units of ABA are tons $CaCO_3$ per 1000 tons waste material, indicating the quantity of liming materials required for neutralization of potential acidity. The

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results from PA analysis are broken into HCl soluble forms, HNO_3 soluble forms and residual sulfur forms. More recently, investigators [2] have attempted to distinguish acid producing from nonacid producing sulfates through the use of an additional hot water extraction step. The hot water extractable sulfur (e.g. $CaSO_4$) forms are considered to be nonacid forming while the HCl and HNO_3 are considered acid forming. Residual sulfur is commonly considered to be organically bound [3,4] and not acid generating by the Sobek method though the Schafer method includes the residual sulfur component as acid producing for calculation of ABA. For each 1% HNO_3 extractable sulfur, which is not offset by neutralization potential indigenous to a sample, 31.25 t $CaCO_3$ per 1000 t waste material is added during site reclamation to offset the potential acidity of the material. The lime rate to address potential acidity for a project area is subsequently calculated by comparing the neutralization potential to the potential acidity and adding lime to account for any deficit in neutralization potential. The ratio of 31.25 t $CaCO_3$/1000 t waste/1% HNO_3 extractable sulfur is derived from the stoichiometric neutralization of acidity generated by the oxidation of FeS_2, where 1 mol FeS_2 generates 4 mol H^+ which is neutralized by 2 mol $CaCO_3$ [5].

Attempts have been made by various authors to characterize the solubility of minerals in various solutions for purposes of mineral identification [6,7] and potential acidity determination [8–10] though none of these methods are in common use for potential acidity determination. Acid–base account is the accepted method used for determination of potential acidity, though other experimental results using standard reference material have confirmed that extraction methodologies frequently result in inaccurate determination of total concentrations [11].

The purpose of this experiment was to identify the effectiveness by which minerals, which are expected to yield acid upon weathering, are extracted by laboratory methods designed to identify their presence. Additionally, the extraction of nonacid forming, common, sulfur containing minerals, by the same extraction methods, are recorded to understand the dissolution of these minerals by ABA extractions.

2. Methods

Pure mineral samples containing sulfur were obtained from Ward's Scientific Establishment and from operational coal and metal mines. Samples obtained from operational mines were waste materials containing several percent sulfur. This material was subsequently high-graded by water separation methods (shaker table) followed by heavy liquid separation by 1,1,2,2-tetrabromoethane (density = 2.96 g cm^{-3}) [12]. Heavy liquid separation allows for the flotation of silicates (density = 2.65 g cm^{-3}) and their subsequent removal, while the heavier sulfides (pyrite density = 5.01 g cm^{-3}) pass through the liquid. Some impurities will not be removed by this method when light and dense particles are intergrown and not disaggregated.

All samples were crushed to −100 mesh (< 149 μm) by mortar and pestle and passed through a US Standard Sieve Number 100.

One gram (1.000 ± 0.001 g) samples of each mineral sample were submitted to a sequential extraction by hot water, 2:3 hydrochloric acid (4.91 *M*) and 1:7 nitric acid (1.99 *M*). A total of 17 mineral samples were used, with three replications of each sample. The treatments were barite, anhydrite, gypsum, anglesite, jarosite, arsenopyrite, Ward's pyrite, chalcocite, Ward's pyrrhotite, chalcopyrite, galena, marcasite, sphalerite, coal barite, hardrock pyrite, hardrock pyrrhotite, and coal pyrite. This experimental method, though not identical to methods established by Sobek or Schafer, is a close approximation of the extraction methods previously published.

Each 1.000 g sample was initially placed in a weighed filter paper (Whatman 40, 11 cm) located in a filtration funnel. Deionized water was heated to boiling, 95 °C (boiling temperature at laboratory altitude), and poured incrementally through the filter until 150 ml hot water had been added. The hot water was allowed to drain through the sample by gravity. At the termination of drainage, a leachate sample was collected for sulfur analysis by inductively coupled plasma emission spectroscopy (ICP), while the filter paper and residual sample were dried in a forced air oven at 40 °C for 2 h and reweighed.

The filter paper and sample surviving the hot water extraction were replaced in the filter funnel apparatus. Hydrochloric acid solution (4.91 *M*) was prepared for use in extraction in the ratio of two parts reagent grade, concentrated HCl, to three parts deionized water. A total of 150 ml 2:3 HCl (4.91 *M*) was added to the filtration apparatus and allowed to drain by gravity. Ten milliliters of deionized water was added to the filter paper as a rinsing agent. The resulting leachate was collected and a sample was submitted for sulfur analysis by ICP, while the residual sample and filter paper were dried in a forced air oven at 40 °C for 2 h and reweighed.

The sample surviving the first two extraction steps was then removed from the filter paper and placed in a weighed 250 ml Erlenmeyer flask. The mass change of the filter paper used for the first two extractions was measured. The HNO_3 extraction solution (1.99 *M*) was prepared in the ratio of one part reagent grade, concentrated HNO_3 to seven parts deionized water. A total of 150 ml 1:7 HNO_3 was added to the flask containing the sample, which was then heated to 75 °C and allowed to remain in contact with the sample for 6 h. At the termination of 6 h, the sample and solution were poured through a weighed 11 cm Whatman 40 filter paper. A rinse of 30 ml deionized water was added to the flask and then poured through the filter paper. The resulting leachate was collected and a sample submitted for sulfur analysis by ICP. The residual sample and filter were dried at 40 °C in a forced air oven for 2 h and reweighed. Leachate chemistry results were statistically analyzed using one-way analysis of variance [13].

The residual sample material was retained for chemical analysis by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX). Polished aluminum stub mounts were prepared for submission to the SEM by applying a film of colloidal graphite paint to the aluminum stub and sprinkling the sample material onto the paint while wet. A conductive coating of Neutrastat spray was then applied to the surface. Both before extraction and after extraction EDAX records were collected for each sample from an area EDAX scan at 90X magnification.

3. Results and discussion

The dissolution response of each mineral sample to treatment with H_2O, HCl and HNO_3 is dependent on the inherent physical properties of each mineral. Mineral dissolution in response to treatment was recorded based on mass loss and leachate sulfur content (Table 1). When minerals are effectively removed by a treatment, the accrued sulfur component is catalogued as acid forming or nonacid forming, depending on methods identified by Sobek or Schafer.

A variety of errors in the application of ABA to calculate potential acidity is presented in these results. When acid forming minerals are reported present as a sulfur component considered to be nonacid generating, a false negative error occurs. A false negative error results in the underestimation of the potential acidity. A false positive error results when sulfur from a nonacid forming mineral is reported present as a sulfur component considered to be acid forming. Both false negative and false positive errors in ABA calculation are documented in the following results. The specific response of each mineral to the dissolution treatment, or treatments, which induced a prominent effect is discussed below.

3.1. Barite ($BaSO_4$)

Barite is a relatively insoluble sulfate mineral, which is minimally attacked by boiling H_2O and 2:3 HCl extractions (Table 1). Most of the barite was present as residual material after sequential extraction by boiling H_2O, 2:3 HCl (4.91 *M*) and 1:7 HNO_3 (1.99 *M*). The nitric acid extraction removed a mean 19.8% of the original 1.000 g mass surviving the first two extractions, while 78.8% of the mass survived all three extractions. The Sobek method predicts that sulfates will be removed by the HCl extraction, which does not occur in the case of barite. The Schafer method counts the residual fraction as acid generating, which is inaccurate in the case of barite, since barite is not an acid forming mineral. Since the HNO_3 acid extractable sulfur fraction is considered acid generating by both Sobek and Schafer, the 19.8% mass removed by HNO_3 and considered acid generating is in error for both methods. Barite can be a common accessory mineral in both coal and hardrock mine environments, so ABA analysis lacking knowledge of the mineralogy may lead to errors in potential acidity determination when barite is present.

3.2. Anhydrite ($CaSO_4$)

Anhydrite is strongly removed by both boiling H_2O and 2:3 HCl (4.91 *M*) extractions, which is in agreement with the predicted sulfate removal of both Sobek and Schafer methods (Table 1). The solubility of natural anhydrite is 0.1619 g per 100 ml in hot water [14]. In the H_2O extraction performed during this experiment, results suggest that the solubility limit of the solution was approached during the boiling H_2O extraction.

The Sobek method advocates a 2:3 HCl (4.91 *M*) extraction to remove sulfates, which successfully solubilizes anhydrite (Table 1). The 2:3 HCl (4.91 *M*) extraction

Table 1

Summary of mineral response to sequential acid–base account extraction

Sample chemical composition	Mineral sample name	H_2O extraction		HCl extraction		HNO_3 extraction		
		Mean[a] percent mass removed by H_2O extraction	Mean[a] leachate sulfur ($mg\,l^{-1}$)	Mean[a] percent mass removed by HCl extraction	Mean[c] leachate sulfur ($mg\,l^{-1}$)	Mean[a] percent mass removed by HNO_3 extraction	Mean[a] leachate sulfur ($mg\,l^{-1}$)	Mean[a] residual mass (%)
$BaSO_4$	Barite	0.5 D[b]	1.3 A	0.8 GH	10 AB	19.8 EFG	20 A	78.8 HI
$CaSO_4$	Anhydrite	18.3 B	255 C	76.1 B	1175 C	5.8 HI	41 A	– 0.2 A
$CaSO_4 \cdot 2H_2O$	Gypsum	40.6 A	488 D	56.5 C	612 C	3.3 I	12 A	– 0.4 A
$PbSO_4$	Anglesite	1.4 D	8.0 A	44.4 E	427 C	37.5 D	37 A	16.7 DC
$KFe_3(SO_4)_2(OH)_6$	Jarosite	0.6 D	2.0 A	2.5 G	19 AB	24.6 EF	71 A	72.2 GH
FeAsS	Arsenopyrite	0.5 D	1.7 A	1.1 GH	2 A	69.2 C	414 B	29.3 EF
FeS_2	Ward's pyrite	0.5 D	3.3 A	– 0.5[d] GH	1 A	83.9 AB	2711 CD	16.1 DC
Cu_2S	Chalcocite	0.3 D	0.7 A	– 3.3 H	1 A	79.9 B	23 A	23.1 DE
$Fe_{(1-x)}S$	Ward's pyrrhotite	0.7 D	5.7 A	80.2 A	114 BC	12.7 HG	96 A	6.4 AB
$CuFeS_2$	Chalcopyrite	0.6 D	1.3 A	– 0.7 GH	3 AB	27.1 E	163 AB	73.0 GH
PbS	Galena	0.4 D	0.3 A	32.3 F	424 C	35.9 D	0.7 A	31.4 F
FeS_2	Marcasite	0.8 D	7.0 A	– 0.4 GH	5 AB	90.4 A	2752 D	9.2 BC
(Zn, Fe)S	Sphalerite	0.7 D	0.7 A	2.7 G	11 AB	12.2 HG	0.7 A	84.4 I
$BaSO_4$ + impurities	Coal barite	1.4 D	1.3 A	3.0 G	25 AB	26.2 E	62 A	69.3 G
FeS_2 + impurities	Hardrock pyrite	0.4 D	0.3 A	2.7 G	2 A	68.0 C	2454 C	28.8 EF
$Fe_{(1-x)}S$ + impurities	Hardrock pyrrhotite	0.7 D	1.3 A	52.1 D	76 BC	16.3 FG	366 AB	30.9 EF
FeS_2 + impurities	Coal pyrite	3.0 C	32 B	0.5 GH	5 AB	77.0 B	2434 C	19.6 D

[a] Arithmetic mean of three replications

[b] Mean values in the same column followed by the same letter are not significantly different ($p \leqslant 0.05$). ANOVA mean separation tests performed by Newman–Keuls tests of significance.

[c] Geometric mean of three replications.

[d] Minus sign (–) indicates mass gain during extraction.

removed a mean 76.1% of the anhydrite sample mass surviving the boiling H_2O extraction, resulting in 1175 mg S^{-1}. Anhydrite is nonacid forming so no error to ABA is initiated by either Sobek (HCl extraction) or Schafer (H_2O extraction) methods. A small amount of sample was carried into the 1:7 HNO_3 (1.99 *M*) extraction where a mean 5.8% of the original mass was taken into solution, but in a natural sample where only a percentage of the entire sample was anhydrite it is anticipated that no sulfur would be contributed to the nitric acid extractable fraction due to prior removal by either H_2O or HCl.

3.3. Gypsum ($CaSO_4 \cdot 2H_2O$)

Gypsum was strongly removed by boiling H_2O and 2:3 HCl (4.91 *M*) as predicted by the Sobek and Schafer methods, resulting in no error to ABA calculation (Table 1). The dissolution of gypsum was similar to anhydrite, where little sample survived the H_2O and HCl extractions. The solubility of natural gypsum is 0.222 g per 100 ml in hot water [14] and very soluble in HCl. Gypsum is not an acid forming mineral, so no error to ABA calculation is initiated by either the Schafer or Sobek method.

3.4. Anglesite ($PbSO_4$)

Anglesite is not an acid forming mineral and represents potential error to both Sobek and Schafer methods of ABA calculation. Anglesite extraction by both 2:3 HCl (4.91 *M*) and 1:7 HNO_3 (1.99 *M*) resulted in mass loss, though a mean 16.7% of the original mass survived all three extractions (Table 1). The 2:3 HCl (4.91 *M*) extraction removed a mean 44.4% of the mass surviving the H_2O extraction, resulting in a mean 427 mg $S\,l^{-1}$ in the leachate. The error to the Schafer method results from counting the HCl extractable sulfur attributed to anglesite as acid generating, which it is not. Since a mean 37.5% of the anglesite mass was removed during 1:7 HNO_3 (1.99 *M*) extraction, the calculation of ABA by both Sobek and Schafer methods can result in error, due to treatment of the HNO_3 extractable sulfur as acid forming when anglesite contributed to the sulfur component. The mean leachate sulfur content after HNO_3 extraction was 37 mg $S\,l^{-1}$, a small sulfur content compared to the 427 mg $S\,l^{-1}$ resulting from 2:3 HCl (4.91 *M*) extraction. The anomalously low HNO_3 extracted leachate sulfur is unexplained.

3.5. Jarosite ($KFe_3(SO_4)_2(OH)_6$)

Jarosite was not effectively extracted by boiling H_2O, 2:3 HCl (4.91 *M*) or 1:7 HNO_3 (1.99 *M*) resulting in potential error to ABA calculation since a mean 72.2% of the original mineral mass survived all three extractions (Table 1). Jarosite is a common secondary mineral in many mine environments, resulting from incomplete oxidation of pyrite, and the Schafer method considers it to be acid forming upon elevation of the mine waste pH. The Schafer method predicts that jarosite will be removed by the 2:3 HCl (4.91 *M*) extraction, though only a mean 2.5% of the mass surviving the H_2O extraction was removed during 2:3 HCl (4.91 *M*) extraction.

Many errors to ABA calculation are possible given the ineffectiveness of jarosite dissolution and extraction. The Sobek and Schafer methods count the HNO_3 extractable sulfur fraction as acid forming in calculation of ABA. Assuming that jarosite is not an acid forming mineral, the mean 24.6% of the sample mass removed by HNO_3 and counted as acid generating is in error. In addition, if it is assumed that jarosite will not be thermodynamically stable upon elevation of pH, and will yield acid, the liming rate required to neutralize the potential acidity attributed to jarosite would be in error. That is, the lime rate used for calculation of ABA for HNO_3 extractable sulfur is 31.25 t $CaCO_3$ per 1000 t waste material (Sobek and Schafer methods), while the lime rate for neutralization of the potential acidity due to jarosite is 23.44 t $CaCO_3$ per 1000 t waste material (Schafer method).

Since most of the jarosite was retained in the residual sulfur fraction and not extracted by ABA methods, the greatest potential error to ABA calculation could result from inaccurate treatment of the residual sulfur fraction. The Schafer method considers the residual sulfur fraction as acid forming while Sobek does not.

3.6. *Arsenopyrite (FeAsS)*

Arsenopyrite is an acid forming mineral which is dominantly removed by the 1:7 HNO_3 (1.99 *M*) extraction. A mean 69.2% of the original sample mass was removed by the 1:7 HNO_3 (1.99 *M*) extraction, while 29.3% of the original mass survived all three extractions (Table 1). Since both Sobek and Schafer methods count the 1:7 HNO_3 (1.99 *M*) extractable fraction as acid producing, no specific error to ABA is initiated, though the stoichiometry of arsenopyrite dissolution and resulting acid generation is unknown. The mean 29.3% of the sample retained in the residual sulfur fraction represents a potential error to the Sobek ABA calculation method because arsenopyrite is an acid forming mineral, yet the Sobek method counts the residual sulfur fraction as not acid forming.

3.7. *Ward's pyrite (FeS_2)*

Pyrite is an acid forming mineral, which was dominantly removed by 1:7 HNO_3, as it was anticipated to be removed by the Sobek and Schafer methods. A mean 83.9% of the pyrite sample mass was extracted by 1:7 HNO_3 (1.99 *M*) (Table 1). Though the HNO_3 extraction is effective at removal of pyrite, a mean 16.1% of the pyrite survived all three extractions and was residual even though HNO_3 was present in excess of the amount of pyrite present, so complete mineral dissolution was theoretically possible. The presence of pyrite in the residual sulfur fraction is not anticipated by ABA analysis and represents a potential error to the Sobek method of ABA calculation which counts the residual sulfur fraction as nonacid forming.

3.8. *Chalcocite (Cu_2S)*

Chalcocite was strongly removed by the 1:7 HNO_3 (1.99 *M*) extraction, though chalcocite is not an acid generating mineral. A mean 79.9% of the chalcocite sample

mass was removed during the 1:7 HNO_3 (1.99 *M*) extraction though only 23 mg $S\,l^{-1}$ was measured in the leachate (Table 1). The leachate resulting from 1:7 HNO_3 (1.99 *M*) extraction was notably blue after extraction so the mass loss data may reflect selective removal of copper while the sulfur is carried forward to the residual fraction. Characterization of the elemental composition of the residual sample material by scanning electron microscopy (SEM) indicated that the residual sample material was nearly pure sulfur, containing no copper.

The error to ABA resulting from chalcocite dissolution is that sulfur extracted during the 1:7 HNO_3 (1.99 *M*) extraction is considered acid forming by both Sobek and Schafer methods, though chalcocite is not an acid generating mineral. Further error is introduced by the Schafer method, since the residual sulfur fraction is considered acid forming, and most of the sulfur resulting from mineral dissolution in the HNO_3 extraction was carried forward to the residual sulfur fraction as pure sulfur, not as the mineral chalcocite.

3.9. *Ward's pyrrhotite ($Fe_{1-x}S$)*

Pyrrhotite is an acid producing mineral which was dominantly removed by the 2:3 HCl (4.91 *M*) extraction, resulting in liberation of H_2S gas. A mean 80.2% of the sample mass was removed during sample extraction by 2:3 HCl (4.91 *M*), though only 114 mg $S\,l^{-1}$ was measured in leachate (Table 1). The smell of H_2S gas was very evident upon treatment of pyrrhotite with HCl.

The error to ABA calculations are unique for pyrrhotite. The Sobek method considers sulfur forms extracted by 2:3 HCl (4.91 *M*) as nonacid forming, which is in error when pyrrhotite is present. The error to ABA when pyrrhotite is present may also be repeated when iron monosulfide minerals other than pyrrhotite are present which may be acid forming and HCl soluble [15, 16]. Iron monosulfide minerals such as greigite (Fe_3S_4) and mackinawite ($Fe_{1+x}S$) have been observed in reduced depositional sedimentary environments [17]. The Schafer method error to ABA results from counting sulfur extracted during the HCl extraction as jarosite upon calculation of potential acidity, when the neutralization of acid generated by pyrrhotite oxidation is likely 31.25 t $CaCO_3$ per 1000 t waste material, and not 23.44 t $CaCO_3$ per 1000 t waste material as required for jarosite neutralization.

3.10. *Chalcopyrite ($CuFeS_2$)*

Chalcopyrite was not effectively removed by any of the three ABA extractions, subsequently most of the sample was retained in the residual sulfur fraction. A mean 73.0% of the original sample mass survived all extractions and was counted as residual sulfur (Table 1). Since chalcopyrite is an acid forming mineral [18], an error in ABA calculation is induced by the Sobek method of ABA calculation since the residual sulfur fraction is considered as nonacid generating. The Schafer method of ABA calculation is not in error when counting the residual sulfur fraction as acid generating in the presence of the mineral chalcopyrite. The mean 27.1% sample mass

removed during the 1:7 HNO_3 (1.99 *M*) extraction step is considered acid generating by both Sobek and Schafer Methods, resulting in no ABA error.

The difficulty in managing sulfur forms in ABA calculation for any mineral is illustrated by chalcopyrite. When the entirety of a mineral sample is not removed during a single extraction, skepticism will exist whether field remediation lime rates based on ABA are accurate or reasonable. Chalcopyrite was only partially extracted by 1:7 HNO_3 (1.99 *M*) during treatment, resulting in sulfur from a single mineral being erroneously considered present in two different sulfur fractions. In the case of chalcopyrite, when the Sobek method was used to calculate the ABA, significant error would be induced when 27.1% of the sulfur was counted as acid generating and 73.0% of the sulfur was counted as nonacid forming while 100% of the sulfur would be acid forming.

3.11. Galena (PbS)

Galena is not an acid generating mineral and represents a complication to ABA calculation since a significant portion of the mineral was extracted by HCl and HNO_3, and a significant portion of the sample was residual (Table 1). A mean 32.3% of the galena sample was removed by the 2:3 HCl (4.91 *M*) extraction resulting in 424 mg $S\,l^{-1}$ in the leachate. No error to ABA calculation is induced by the Sobek method since the HCl extractable sulfur is counted as nonacid forming. The Schafer method of ABA calculation results in error when sulfur due to galena is extracted by 2:3 HCl (4.91 *M*) since the Schafer Method counts the HCl extractable sulfur fraction as acid generating and galena is not an acid generating mineral.

Error to ABA calculation result for both Sobek and Schafer methods when sulfur due to galena is extracted by 1:7 HNO_3 (1.99 *M*) since both methods treat the nitric acid extractable sulfur fraction as acid forming. A mean 35.9% of the sample mass was removed during treatment with 1:7 HNO_3 (1.99 *M*), though only a mean leachate 0.7 mg $S\,l^{-1}$ resulted. Some sulfur may have been lost to a gaseous phase when treated with HNO_3 since the leachate sulfur content was low, or sulfur may have been carried partially into the residual fraction while lead was selectively removed by the 1:7 HNO_3 (1.99 *M*) treatment.

The residual sulfur fraction contained a mean 31.4% of the original 1.000 g sample which survived all three extractions. The Sobek method of ABA calculation would not be in error in the case of galena since galena is nonacid generating and treated as such by the calculation. The Schafer method of ABA calculation can result in potential error when galena is present since the residual sulfur fraction is treated as acid generating.

3.12. Marcasite (FeS_2)

The removal of marcasite proceeded as expected by both the Sobek and Schafer methods of ABA calculation. A mean 90.4% of the marcasite sample was removed by the 1:7 HNO_3 (1.99 *M*) extraction resulting in a mean leachate 2752 mg $S\,l^{-1}$.

Marcasite is an acid forming mineral [19] and was extracted by the HNO_3 extraction as expected, resulting in no error to ABA calculation.

3.13. Sphalerite ((Zn, Fe)S)

The removal of sphalerite by ABA extractions was ineffective, resulting in a mean 84.4% of the original sample surviving all three extractions. Sphalerite is an acid generating mineral so treatment of the residual fraction as nonacid forming (Sobek method) is in error when sphalerite is present in a sample.

3.14. Coal barite ($BaSO_4$ + impurities)

The coal barite sample was not effectively removed by any ABA extraction, consequently, most of the sample was residual. A mean 69.3% of the sample was retained as residual material (Table 1). The coal barite is significantly different ($p \leqslant 0.05$) from the Barite sample which had a measured mean residual mass of 0.788 g, or 78.8% of the original sample mass. The difference between the pure barite sample (barite) and natural environment barite sample (coal barite) is the purity of the sample. The coal barite contained some pyrite which was extracted by the 1:7 HNO_3 (1.99 M) extraction, though the sample was dominantly barite. Error to ABA calculation could be introduced by the Schafer method of ABA calculation, since the residual fraction is dominantly barite, which is not acid generating, though the residual sulfur fraction is treated as acid forming.

3.15. Hardrock pyrite (FeS_2 + impurities)

The hardrock pyrite sample is acid forming and most of the sulfur was extracted by the 1:7 HNO_3 (1.99 M) extraction in accordance with ABA calculation. A mean 68.0% of the original sample was extracted by the HNO_3 extraction, which is significantly different ($p \leqslant 0.05$) than the other two pyrite samples, Ward's pyrite and coal pyrite, which were more aggressively removed by HNO_3 extraction.

Since a mean 28.8% of the hardrock pyrite sample survived all ABA extractions, potential error to ABA calculation is possible depending on the treatment of the residual sulfur fraction. The Sobek method treats the residual fraction as nonacid sulfur forms, which is in error when the residual sulfur fraction contains pyrite as it does in the case of Hardrock pyrite. Since pyrite is the most common sulfide mineral, the ineffectiveness of pyrite extraction by 1:7 HNO_3 (1.99 M) may be commonly observed in laboratory analysis of ABA, resulting in a residual sulfur component when none is expected. If the residual sulfur component is characterized as nonacid forming organic sulfur compounds when ABA is applied to samples derived from hardrock mine environments, skepticism pertaining to the validity of the analysis will occur since organic sulfur compounds are relatively uncommon in hardrock mines. The characterization of the residual sulfur fraction as acid generating (Schafer Method) is not in error in the case of the hardrock pyrite sample.

3.16. Hardrock pyrrhotite ($Fe_{1-x}S$ + impurities)

The hardrock pyrrhotite sample is acid generating and was primarily removed by the 2:3 HCl (4.91 M) extraction. A mean 52.1% of the sample was extracted by the HCl extraction (Table 1) resulting in liberation of H_2S gas. The sample mass loss of the hardrock pyrrhotite is significantly different ($p \leqslant 0.05$) from the Ward's pyrrhotite sample, though the presence of silicate impurities in the hardrock pyrrhotite contributed to the difference.

3.17. Coal pyrite (FeS_2 + impurities)

The coal pyrite sample was dominantly extracted by the 1:7 HNO_3 (1.99 M) treatment, resulting in removal of a mean 77.0% of the original mass (Table 1). The mass removed from the coal pyrite sample is not significantly different ($p \leqslant 0.05$) from the Ward's pyrite sample. The mean leachate sulfur content attributed to the coal pyrite (2434 mg Sl^{-1}) is not significantly different ($p \leqslant 0.05$) from the mean leachate sulfur of the Ward's pyrite (2711 mg Sl^{-1}). The calculation of ABA is not notably in error for sulfur extracted by HNO_3, though not all of the sample was extracted by HNO_3.

The coal pyrite sample which survived all three sample extractions (19.6%) is potentially in error to ABA calculation. Calculation of ABA by the Sobek method, which considers the residual sulfur fraction as nonacid forming, would result in error.

The coal pyrite sample also presents potential error to ABA calculation in treatment of the H_2O extractable sulfur fraction (Schafer method). The sulfur extracted by boiling water is considered nonacid generating, though a mean 3.0% of the coal pyrite sample was removed by the H_2O extraction. Surface iron sulfate salts present on this pyrite sample are responsible for the mass loss noted during the H_2O extraction. Numerous iron sulfates are known in mine environments including melanterite ($FeSO_4 \cdot 7H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$), and szomolnokite ($FeSO_4 \cdot H_2O$) [20], which may demonstrate solubility in water though samples of these materials were not obtained for use in this experiment. The rapid dissolution of hydrated iron sulfate minerals may result in mine environment acidity undetected by ABA analytical methods.

4. SEM/EDAX analysis of initial and residual sample material

The impact of ABA extraction on mineral chemistry was examined by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) to assess changes in solid phase chemistry during extraction. Samples were prepared to compare mineral elemental concentration before and after ABA extraction. Result of sample analysis by SEM/EDAX are presented in Figs. 1 and 2 and indicate that some minerals were unchanged during ABA extraction while others were chemically altered.

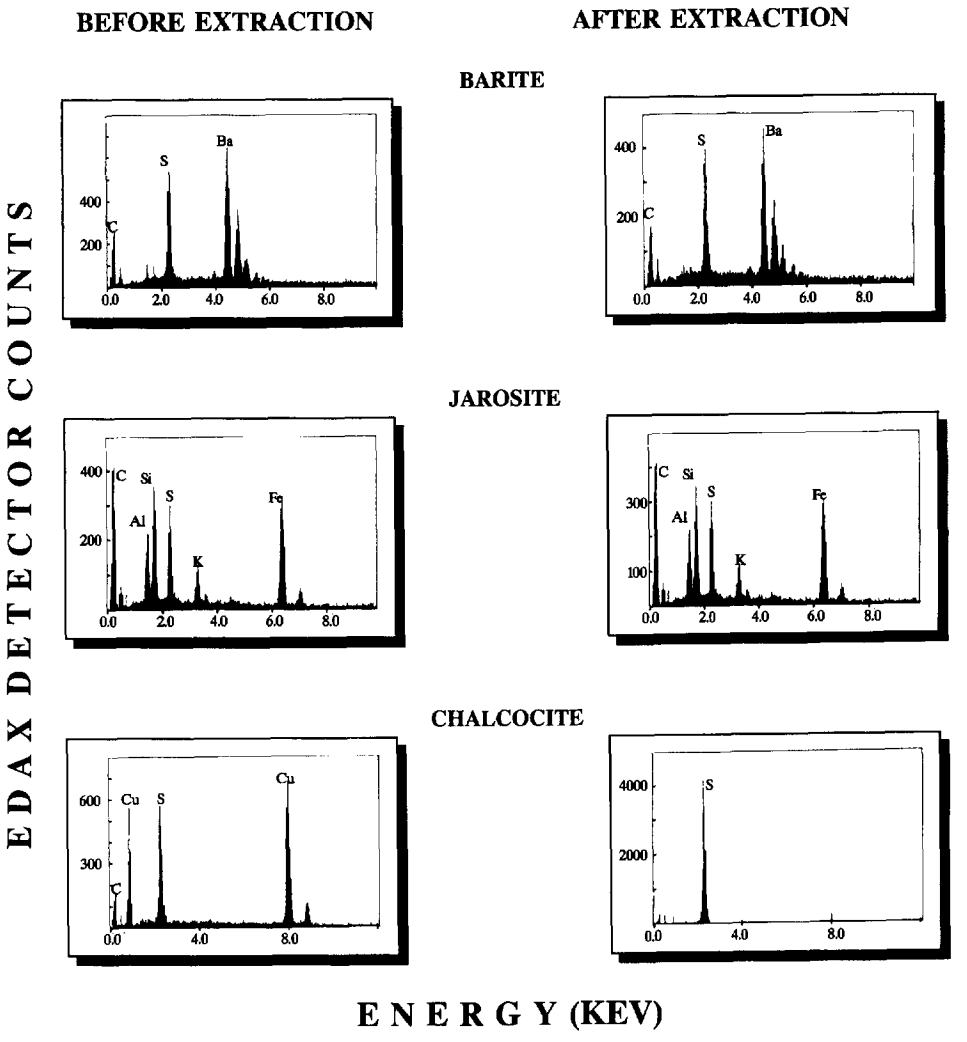

Fig. 1. Elemental composition of nonacid forming mineral samples before (left column) and after (right column) ABA extractions as determined by energy dispersive analysis of X-rays (EDAX) for the barite, jarosite and chalcocite samples.

The samples which were unchanged during ABA extraction displayed EDAX spectra after extraction which were nearly identical to the EDAX spectra prior to treatment. The samples barite, jarosite, Ward's pyrite, chalcopyrite, galena, coal barite, and hardrock pyrite were unchanged during ABA extraction. The relative intensity of the EDAX elemental peaks remained in approximately the same ratio.

The samples anglesite, arsenopyrite, chalcocite, Ward's pyrrhotite, marcasite, sphalerite, hardrock pyrrhotite and coal pyrite, changed notably between the before and after extraction EDAX analysis composition. The changes in chemistry are

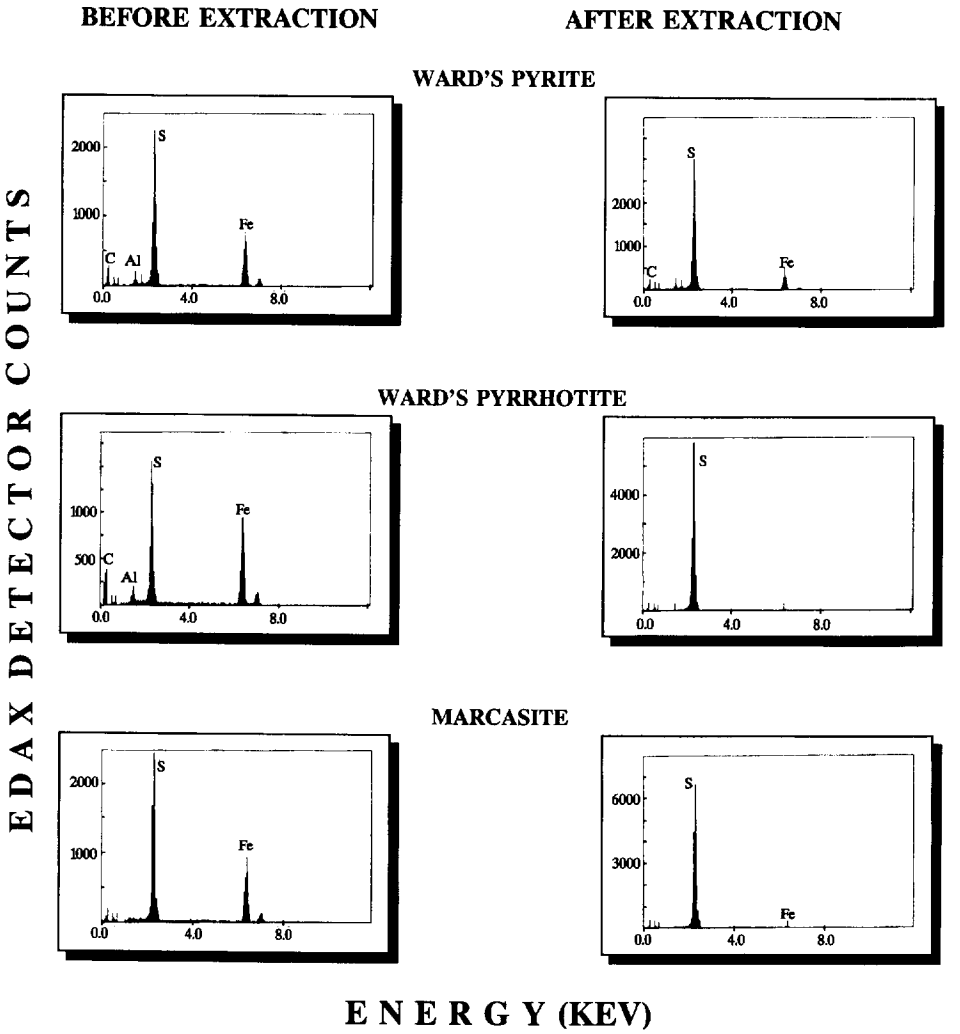

Fig. 2. Elemental composition of acid forming mineral samples before (left column) and after (right column) ABA extractions as determined by energy dispersive analysis of X-rays (EDAX) for the Ward's pyrite, Ward's pyrrhotite and marcasite samples.

attributed to chemical reactions initiated by the extraction agents, but are not known in specific.

For both the nonacid forming minerals (Fig. 1) and acid forming minerals (Fig. 2) changes in the elemental composition of the sample are observed for some of the minerals. Barite and jarosite are nonacid forming minerals which are unaltered during extraction while selective removal of copper from chalcocite is observed during extraction (Fig. 1). The acid forming mineral samples also responded dissimilarly to the extracting agents (Fig. 2). The Ward's pyrite sample was unaltered while the

Ward's pyrrhotite and marcasite samples demonstrated preferential removal of the metallic cation iron, resulting in solid-phase sulfur accumulation in the residual fraction.

Significant error to ABA calculation is possible when sulfur is carried into the residual sulfur fraction from minerals which are acid generating. In the case of marcasite, a mean 90.4% of the mineral mass was removed by the 1:7 HNO_3 and 9.2% of the mineral mass is carried into the residual fraction (Table 1). Since marcasite is an acid generating mineral, error to ABA is incurred by the Sobek method of ABA calculation when the residual sulfur fraction is treated as nonacid forming. The error to ABA is further accentuated by the atomic weight differential between iron and sulfur. Since iron is more dense than sulfur and is removed during HNO_3 extraction, the mean 9.2% residual mass of marcasite in the residual sulfur fraction is entirely attributed to sulfur and not to iron and sulfur. Therefore, the stoichiometric fraction of sulfur from marcasite represented by the 9.2% residual sulfur is greater than if the residual sulfur fraction had been comprised of both iron and sulfur.

5. Conclusion

The ability of acid-base account analytical methods to distinguish acid producing from nonacid producing sulfur forms is very deficient. Potential acidity is calculated differently between the Schafer and Sobek methods, but errors emanating from both methods were revealed.

The general intent of both the Schafer and Sobek methods is to extract in one step the nonacid producing minerals which contain sulfur, and to extract the acid producing sulfur forms in a subsequent step or steps. Management of the residual sulfur fraction is a consequence of incomplete extraction of sulfur forms in a sample. The residual sulfur component is considered nonacid forming by the Sobek method since it is commonly applied to the analysis of samples derived from coal deposits where organic sulfur compounds are present. The Schafer method was developed to assess potential acidity in materials contaminated by hardrock mining activities; consequently the residual sulfur fraction was considered acid forming. Neither method (Sobek or Schafer) was entirely accurate or entirely inaccurate, but results from ABA analysis without supporting characterization of the associated mineralogy invite error.

Potential errors exist in ABA calculation for each extraction depending on mineral assemblages present. The degree to which the errors impact site remediation planning is a consequence of the quantity and chemistry of the minerals present, and can result in either false positive or false negative determinations of potential acidity.

The successful application of ABA calculations to the remediation of lands containing sulfur compounds, and especially reduced sulfur compounds, will require knowledge of the specific mineralogy. To consider the nitric acid extractable fraction as the only potential acid producing sulfur forms would be an oversimplification of the potentially complex relationship of dissimilar mineral assemblages.

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