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A METHODOLOGY TO DETERMINE THE ACID-NEUTRALIZATION CAPACITY OF ROCK SAMPLES

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Abstract

Chemical calculations based on the molar quantity of neutralizing cations (Na, K, Mg, Ca, Mn) released to solution associated with the acidic dissolution of minerals provide a method to chemically quantify the acid-neutralization capacity (ANC) of carbonates, silicates, simple assemblages of mixed minerals, and waste-rock samples obtained from international mining operations. The acidity neutralized by each cation is equivalent to its valence within the mineral structure. Fe and Al are hydrolyzed during the ANC back-titration and thus are effectively non-acid- neutralizing cations. Sulfur derived from pyrite oxidation is equivalent to the release of two moles of H^+, although non-acid-forming S (*e.g.*, gypsum) should be addressed. Calculations based on these principles for the samples tested correlate well with the ANC determined by titration-type tests.

Keywords: acid-rock drainage, acid-neutralization capacity, Modified Sobek ANC test.

Sommaire

Des calculs fondés sur la quantité molaire des cations neutralisateurs (Na, K, Mg, Ca, Mn) relâchés dans une solution associée à la dissolution de minéraux en milieu acide fournissent une méthode de quantifier chimiquement la capacité à neutraliser les acides de carbonates, silicates, de simples assemblages de minéraux mixtes, et des échantillons de roches constituant des déchets d'opérations minières internationales. L'acidité neutralisée par chaque cation serait équivalente à sa valence dans le minéral hôte. Le Fe et l'Al sont hydrolysés lors de titration inversée de l'évaluation, et donc ne joueraient aucun rôle dans la neutralisation. Le soufre dérivé de l'oxydation de la pyrite serait l'équivalent à la production de deux moles de H^+, quoique le soufre non apte à former un acide, par exemple le soufre du gypse, devrait aussi être évalué. Pour les échantillons étudiés, les calculs fondés sur ces principes montrent une bonne corrélation avec la valeur du pourvoir neutralisateur déterminée dans des tests de titration.

(Traduit par la Rédaction)

Mots-clés: drainage acide de roches, pouvoir neutralisateur, test ANC modifié de Sobek.

Introduction

Prediction, management, and mitigation of acid rock-drainage resulting from the oxidation of sulfide minerals and associated releases of metal are crucial for environmental and economic viability of any mining operation. Historically, there was a lack of regard for, and understanding of, the problems associated with acid drainage of mine wastes. As a result, there are now, for example, approximately 200,000 acid rock-drainage sites within the United States of America (Hochella *et al*. 1999). Many of these could have been prevented if the waste rock had been accurately assessed for its acid rock-drainage capacity and then subsequently managed properly.

A variety of laboratory-based acid–base accounting tests are available to determine the geochemical behavior of waste rock-materials following exposure to oxygen and water. Several tests are commonly employed to validate the classification of the material as non-acid-forming or potentially acid-forming. The foundation for such a classification involves assessment of the net acid-production potential (NAPP):

$$\mathrm{NAPP} = \mathrm{MPA} - \mathrm{ANC} \qquad (1)$$

where MPA is the maximum potential acidity formed by the sample, ANC is the acid-neutralization capacity of the sample, and NAPP, MPA, and ANC are expressed in kg H_2SO_4/t (or $CaCO_3$/t) equivalent. MPA is typically

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determined from the total S content of the sample (in wt%) multiplied by the stoichiometric factor 30.6 (to convert to kg H_2SO_4/t) where all S is present as pyrite. There can be problems with the determination of MPA, although they are not addressed here (*e.g.*, Jennings & Dollhopf 1995, Paktunc 1999a, IWRI & EGi 2002). Typically, the ANC is determined by titration-type tests after an acid-digestion process (*e.g.*, Sobek *et al.* 1978, Lawrence 1990, Lapakko 1994, Skousen *et al.* 1997, IWRI & EGi 2002, Weber *et al.* 2004a), although uncertainties are also present with these tests (Paktunc *et al.* 2001). A negative NAPP result indicates that the sample is classified as non-acid-forming, and a positive NAPP indicates that the sample is classified as potentially acid-forming. Our objectives in this paper are 1) to improve the understanding of the acid-neutralizing reactions in the Modified Sobek ANC test (IWRI & EGi 2002) by analysis of the digestion liquor and subsequent calculations to determine the ANC based on neutralizing ions and acid-generating ions released, and 2) to determine the extent to which the dissolution of silicate minerals in the Modified Sobek ANC test contributes to the ANC measured.

MECHANISMS OF CARBONATE AND SILICATE NEUTRALIZATION

The inherent acid-neutralization capacity of a sample, as determined by acid–base accounting, is typically assumed to be dominated by the dissolution of carbonate minerals present. This is typified by the neutralization of 2 H^+ by 1 mole of calcite:

$$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + CO_2 + H_2O\ (pH < 6.4) \qquad (2)$$

However, the presence of siderite ($FeCO_3$) or the Fe fraction of carbonates such as ankerite $Ca(Fe,Mg)CO_3$ are exceptions (Paktunc 1999a, b, Jambor *et al.* 2003, Weber *et al.* 2004a). The dissolution of Fe-bearing minerals (carbonates and silicates) can have a significant impact on the validity of ANC results. For example, the dissolution of siderite followed by oxidation of Fe^{2+} to Fe^{3+} and its subsequent hydrolysis result in no overall consumption of acid, and hence no contribution to the ANC (Skousen *et al.* 1997, Jambor *et al.* 2003, Weber *et al.* 2004a):

$$FeCO_3 + 2\ H^+ \rightarrow Fe^{2+} + H_2O + CO_2 \qquad (3)$$

$$Fe^{2+} + {}^1/_4\ O_2 + H^+ \rightarrow Fe^{3+} + {}^1/_2\ H_2O \qquad (4)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_{3(s)} + 3\ H^+ \qquad (5)$$

The hydrolysis of Fe^{3+} is complete at pH values above 4. The same hydrolysis process can be applied to minerals containing Al and Mn:

$$Al^{3+} + 3\ H_2O \rightarrow Al(OH)_3 + 3\ H^+ \qquad (6)$$

$$Mn^{2+} + {}^1/_2\ O_2 + H_2O \rightarrow MnO_2 + 2\ H^+ \qquad (7).$$

Aluminum hydrolyzes in the pH range 4.0 – 5.0 (Ott 1986, 1988). In the case of Mn, hydrolysis is not considered important under Modified Sobek ANC test conditions (maximum pH 7.0), as hydrolysis reactions typically commence at a pH above 8.0 and an Eh of 0.5 (Brookins 1988). The influence of Mn^{2+} present in rhodochrosite was found to contribute to neutralization during the Sobek ANC test (Sobek *et al.* 1978) and the SobPer ANC test (Skousen *et al.* 1997), and H_2O_2 addition during back-titration does not readily oxidize Mn^{2+} (Jambor *et al.* 2003). The results of Jambor *et al.* show that two samples of rhodochrosite, $(Mn_{0.94}Mg_{0.05}Fe_{0.01})CO_3$ and $(Mn_{0.93}Mg_{0.05}Ca_{0.02})CO_3$ have, respectively, a calculated ANC of 879 and 885 kg $CaCO_3$/t (calculated ANC is based on the fact that 104.95 g $MnCO_3$ produces the same amount of ANC as 100.09 g $CaCO_3$), Sobek ANC values of 797 and 868 kg $CaCO_3$/t, and SobPer ANC values obtained with H_2O_2 of 776 and 853 kg $CaCO_3$/t.

Silicate minerals typically have a greater overall ANC compared to calcite per mole of mineral. This fact has been determined by maximum neutralization-capacity calculations of carbonates and silicates (Paktunc 1999a). However, rates of silicate dissolution are much slower, and thus the acid-neutralization capacity of silicates is realized in the longer term. If the dissolution of secondary minerals is not considered, then calculations of the maximum neutralization-capacity (Paktunc 1999a) show that 1 mole of calcite is required to neutralize 1 mole of sulfuric acid, whereas only 0.11 mole of hornblende, 0.2 mole of muscovite, 0.5 mole of K-feldspar, and 0.5 mole of forsterite (Fo_{100}) is required to neutralize 1 mole of sulfuric acid. The acid-neutralization capacity of silicates is particularly significant in that most rocks types are dominated by silicate minerals, and they are thus the significant overall source of acid neutralization in the longer term. Strömberg & Banwart (1994) reported that within the Aitik waste-rock dump in northern Sweden, the pH encountered, in the range 3.5–4.0, is controlled by the relative level of dissolution of sulfide and primary silicate minerals after depletion of the accessible calcite. Similarly, at the Waite–Amulet tailings impoundment, in northern Ontario, Nesbitt & Jambor (1998) found that chlorite and biotite were neutralizing the remnant acidity (after partial neutralization by the limestone cover) generated by the oxidation of pyrite and pyrrhotite in the vadose zone of the impoundment (pH in the range ~2.4–4.5) to circum-neutral pH values in the underlying saturated zone.

The precipitation of secondary phases, such as Fe oxyhydroxides and Al hydroxides, can reduce the overall acid-neutralizing capacity owing to the release of acidity (*e.g.*, Equations 5 and 6). This fact is demonstrated by the influence of forsterite and fayalite. The complete dissolution of fayalite and the subsequent oxidation of Fe^{2+} consumes six protons, but the hydrolysis of Fe^{3+} results in the release of six protons. Therefore the dissolution of fayalite does not consume any acid, in theory. In contrast, the dissolution of forsterite does not release hydrolyzable ions, and the overall process consumes four protons. Jambor *et al.* (2003) showed that fayalite, $(Fe_{1.79}Mg_{0.20}Mn_{0.03})Si_{0.99}O_4$, dissolved completely in the Sobek ANC test (80 mL 0.5 M HCl), indicating an acid-neutralization capacity of 553 kg $CaCO_3$/t. However, the addition of H_2O_2 significantly reduced the acid- neutralization capacity value (to 172 kg $CaCO_3$/t by the H_2O_2 method), indicating that Fe released to solution by silicate dissolution did not fully hydrolyze in the Sobek ANC test. These findings are similar, although not as significant, as the effects of siderite in the ANC test. Silicate minerals containing Fe^{2+} (*e.g.*, Equation 8) and Fe^{3+} (Equation 11) can dissolve by releasing both cations from the mineral structure in exchange for H^+ ions, where the number of H^+ ions exchanged is equal to the valence state of the Fe. Overall, neither contributes to acid neutralization:

$$\text{Silicate}{=}Fe^{2+} + 2\,H^+ \rightarrow \text{Silicate}{=}2H^+ + Fe^{2+} \text{ (= double bond)} \qquad (8)$$

$$Fe^{2+} + {}^1/_4\,O_2 + H^+ \rightarrow Fe^{3+} + {}^1/_2\,H_2O \qquad (9)$$

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_{3(s)} + 3\,H^+ \qquad (10)$$

$$\text{Silicate} \equiv Fe^{3+} + 3\,H^+ \rightarrow \text{Silicate} \equiv 3H^+ + Fe^{3+} \text{ (≡ triple bond)} \qquad (11)$$

$$Fe^{3+} + 3\,H_2O \rightarrow Fe(OH)_{3(s)} + 3\,H^+ \qquad (12)$$

The release of single cations from the structure of a silicate mineral initially proceeds *via* cation–proton exchange reactions, and the number of protons involved in these reactions equals the valence of the cation (Casey & Ludwig 1996, Oelkers 2001). By analogy, it seems likely that in multioxide silicate minerals, these cations also are liberated by cation–proton exchange reactions (Oelkers 2001). However, the final step in dissolution involving the liberation of the partially attached Si atoms involves H_2O adsorption rather than a Si-for-H^+ exchange reaction (Dove & Crerar 1990, Lasaga 1995, Oelkers 2001):

$$(\equiv Si - O - Si \equiv) + H_2O \rightarrow (Si - O - Si{\bullet}OH_2^+) \rightarrow 2(\equiv Si - O - H) \qquad (13)$$

No H^+ ions are consumed in the final stages of silicate-mineral dissolution that involves the removal of Si from the structure (Equation 13). This dissolution step is also applicable to quartz, in that it too does not neutralize any acidity during dissolution (Dove & Crerar 1990, Stumm & Morgan 1996, Dove 1999, Plumlee 1999). H_4SiO_4 is the dominant species in solution up to pH 8.5 (at pH 9 the weakly acidic H_4SiO_4 dissociates appreciably) (Stumm & Morgan 1996); thus monosilicic acid is not assessed in an ANC back-titration to pH 7.0. Hence, if the Si component of a silicate mineral is ignored, together with Fe and Al due to their capacity to hydrolyze, a calculation based on the molar quantity of neutralizing ions (*e.g.*, Na, K, Mg, Ca, and Mn) released to solution during the ANC test can provide an approximation of the number of moles of acid consumed during the test.

METHODS AND MATERIALS

Samples

Silicate minerals (Table 1) obtained from the Museum of South Australia include tremolite (sample AM–5e, from Ontario), tremolite (de Kalb, New York), hornblende (Arkaroola Bore, South Australia), muscovite obtained from Australian Industrial Minerals, and a locally derived altered chlorite – mixed layer clay, (hence called altered chlorite). Five samples of waste rock from Australian and southeastern Asian mining operations were characterized as part of the Australian Minerals Industry Research Association (AMIRA) P387A project: Prediction and Kinetic Control of Acid Mine Drainage and provide a precharacterized suite of samples. Several samples have been described previously (Weber *et al.* 2004b). The mineralogical makeup of the samples is presented in Table 2.

Analytical techniques

The nature of the silicate minerals was confirmed by X-ray diffraction (XRD) using a Philips PW1050 X-ray diffractometer (Weber 2003). Bulk elemental composition was determined by X-ray fluiorescence (XRF) using a Philips 1480 wavelength-dispersive spectrometer (Table 1). Electron-probe micro-analysis (EPMA) of the two tremolite samples and the hornblende was made using a CAMECA SX51 instrument, employing the PAP correction procedure (Pouchou & Pichoir 1984) and a beam current of 20 nA, an accelerating voltage of 15 kV, and calibration against standard samples. Results for the silicates are based on 23 atoms of oxygen. The "fizz" test (see below under Modified Sobek ANC test) using HCl was used to test for the presence of carbonates, which was validated by LECO analysis techniques to determine the inorganic C content (Lewis & McConchie 1994). Where possible, the composition of these carbonates was determined by EPMA and calibrated against standards. Carbon was determined by difference.

TABLE 1. COMPOSITION OF THE SILICATE MINERAL SAMPLES

Sample	Inorg. C	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO
Ontario tremolite (XRF)	0.26	55.6	0.42	2.59	20.25	15.70	0.17	0.05	0.03	0.08
Ontario tremolite (EPMA)		56.60	0.45	1.04	22.62	12.91	0.17	0.09	n.a.	0.08
*Anthophyllite (EPMA)		60.54	0.67	0.25	30.67	0.08	0.05	0.01	n.a.	0.09
de Kalb tremolite (XRF)	1.02	53.2	0.68	1.45	22.02	16.29	0.55	0.24	0.03	0.11
de Kalb tremolite (EPMA)		57.38	0.66	0.61	23.78	12.66	0.69	0.23	0.04	0.08
Hornblende (XRF)	0.2	53.5	2.6	6.68	20.65	11.88	1.12	0.74	0.11	0.06
Hornblende (EPMA)		55.74	2.12	2.52	21.94	11.61	1.45	0.25	0.09	0.04
Muscovite (XRF)	0	48.0	33.8	1.07	0.33	0.0	0.97	8.67	1.07	0.01
Altered chlorite (XRF)	0	39.5	9.5	7.79	29.1	0.0	1.1	0.0	0.0	0.02

Composition (wt%) determined by XRF or EPMA. Inorganic C determined by LECO analysis. * The anthophyllite fraction of the Ontario tremolite was also assessed by EPMA. n.a.: not analyzed.

TABLE 2. MINERAL QUANTITIES (wt%) AND RESULTS OF ACID–BASE ACCOUNTING TEST (kg H_2SO_4/t) FOR AMIRA P387A WASTE-ROCK SAMPLES

Sample	PF	MS	PAF-H	PAF-L	T
Quartz	19.2	18.9	49.3	16	44
Kaolinite	21.5	9.0			
Illite	3.9	16.4			
Smectite	3.4	45.8			
Muscovite	12.7		31.7	11	
Chlorite $(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$			2.2	0.1	1.6
Orthoclase			7.6	54	6.8
Albite				9	41
Calcite			0.1	0.1	0.2
Ferroan magnesite $(Mg_{0.53}Fe_{0.44}Ca_{0.03}CO_3)$	0.04	3.6			
Siderite	0.08	1.4			
Pyrite (Euhedral)	1.7	1.1	9.1	3	2.3
Pyrite (Framboidal)	7.5	1.8			
Pyrite (Oxidized)		0.1			
Chalcopyrite			0.03	0.8	0.4
Magnetite			0.1		
Fe Oxides (Fe_2O_3)				6	3.7
Organic matter	30	2.2			
LECO inorganic C (wt%)	0.01	0.4	0.01	0.01	0.02
ANC_{carb}	0.4	13-20	1	1	2
ANC_{Actual}	7.1	17.4	11	21	6
MPA	143	40	141	52	46
NAPP	136	22.6	130	31	40

MPA, ANC, and NAPP values in kg H_2SO_4/t; all other units in wt%. ANC values for PF, MS, PAF-H, PAF-L, and T utilize ANC_{Actual}, as does NAPP for these samples. The composition of the ferroan magnesite was established by EPMA (Weber *et al.* 2004b).

Characterization of the AMIRA P387a samples involved XRF and XRD analysis (as described above), LECO total S, and LECO organic and inorganic C. Thin sections and polished mounts were prepared from rock fragments mounted in epoxy for transmitted and reflected light microscopy, respectively. Assessment of the sulfide component using reflected light provided good estimates of the pyrite component and morphology. This step was particularly important for samples PF and MS, that contain both framboidal and euhedral pyrite; the results have been previously published (Weber *et al.* 2004b). Mineral quantities were determined by XRD–XRF data (*e.g.*, Weber *et al.* 2004b); mineralogical reconciliation was determined on the samples as they were affected by acid generation (derived from acidic sulfate salts and reactive sulfides) during the ANC test, which provided an unbiased ANC not affected by acid formation (further details are provided below); NAPP is base d on the difference between MPA and ANC_{Actual}.

The modified Sobek ANC test

The Modified Sobek ANC test is based on the methodology of Sobek *et al.* (1978) as initially adapted by Environmental Geochemistry international (IWRI & EGi 2002). This adaptation included the addition of two drops of H_2O_2 at pH 4.5 during the back-titration (to a final pH of 7.0) and the exclusion of the Sobek boiling step. Results (Weber 2003, Weber et al. 2004a) indicate that this method can hydrolyze up to 5.2 mmole of Fe released from the dissolution of 2 g of siderite. The silicate minerals tested used a variety of "fizz" ratings dependent on their carbonate content. Fizz rating, and thus acid quantity and molarity of acid to be used in the ANC test, were determined by adding one or two drops of 10% HCl to a pulverized sample placed on a ceramic plate. A "fizz" rating (see IWRI & EGI 2002, Weber *et al.* 2004a) is given based on the degree of effervescence observed.

The Modified Sobek ANC test involved adding the prescribed quantity and molarity of acid to 2 g dry pulverized sample (<75 μm) in a 250 mL flask. Twenty mL of deionized water is used to flush any sample adhering to the flask walls to the bottom. The flask (covered by a watch-glass) is heated to 80–90°C on a hot plate for 2 h, and then cooled at room temperature for 1 h. This step is considered the digestion process. A back-titration using the prescribed quantity and molarity of NaOH (see IWRI & EGi 2002, Weber *et al.* 2004a) is then conducted. This is stopped at pH 4.5 to add two drops of 30% H_2O_2 to oxidize remaining Fe^{2+} in solution and promote hydrolysis reactions (Equations 4 and 5). The titration is continued to pH 7.0, and the volume of NaOH recorded. The pH of the solution was measured by a Meterlab PHM201 pH – T meter calibrated with standard buffers at pH 4.0 and 7.0. Blanks were also conducted to quality-check results and improve the ANC calculation process, where:

$$\mathrm{ANC}\ (\mathrm{kg\ H_2SO_4/t}) = [\text{Volume of HCl added} \times Ma] - [\text{Volume of NaOH titrated} \times Mb] \times B \times 49\ \mathrm{wt} \qquad (14)$$

where *Ma* is the molarity of the acid, *Mb* is the molarity base, *B* is the standard difference associated with the blank procedure (should be within the range 0.95 to 1.05), and is equal to (*Ma* × Volume of HCl in blank) / (*Mb* × Volume of NaOH titrated in blank); wt is the weight of the sample in g. Complete details of the Modified Sobek ANC test are provided in the ARD Test Handbook (IWRI & EGi 2002).

A variation to the Modified Sobek ANC test is the Filtered ANC test. This is the same as the Modified Sobek ANC test except that the residue is filtered from the digestion liquor prior to back-titration, which prevents any further oxidation of reactive sulfides during back-titration after H_2O_2 addition at pH 4.5.

Tremolite (Ontario) was tested four times (fizz rating 1) by the Modified Sobek ANC test, muscovite and the altered chlorite were tested twice (fizz rating 0), waste-rock samples PF and MS were tested by a variety of ANC methods (Weber *et al* 2004b), although only the filtered ANC tests are shown here, waste-rock sample T, PAF–H, and PAF–L were assessed three, two, and three times, respectively, by the Modified Sobek ANC test, and the tremolite (de Kalb) and hornblende samples were assessed only once. Both tremolite samples and the hornblende were also assessed by autotitration by Environmental Geochemistry International as a check.

Actual ANC (*ANC_{Actual}*)

It was shown previously that reactive sulfides and acidic sulfate salts can generate acidity in the ANC test (Weber *et al*. 2004b). This fact needs to be addressed to determine an actual ANC (ANC_{Actual}) that is not biased by acid formation masking the ANC. This sulfide or sulfate acidity (SA_{max}) was determined by assessing the Modified Sobek ANC digestion liquor for dissolved S, which can be used to determine the ANC_{Actual} of the sample, where:

$$\mathrm{ANC_{Actual}} = [\text{ANC determined by the Filtered ANC test}] + {}_{\mathrm{Samax}} \qquad (15)$$

$$\mathrm{SA_{max}} = [(\text{S in ANC digestion solution} - \text{non-acid-generating S}) \times 2] \times 49/\mathrm{wt} \qquad (16)$$

where ANC_{Actual} and SA_{max} are in kg H_2SO_4/t and wt is the weight of the sample in g. In this instance, all *S* measured in the digestion solution is equivalent to two moles of acid (H^+) released per mole of S. Any non-acid-generating sulfate can be deducted from the total S in solution to give a better indication of SA_{max}. The multiplication factor 49 converts mmole S released to solution to an ANC expressed in kg H_2SO_4/t. Further details of this methodology, as applied to samples PF and MS, have been reported (Weber *et al.* 2004b). However, in brief, the non-acid-generating S is determined by the acidity difference between back titration of an argon-purged deionized water leach-solution and the S content of that solution, where all S is assumed to generate two moles of acid (H^+).

Calculated ANC

After the Modified Sobek ANC digestion process, the ANC test digestion-liquor is filtered (0.45 μm) and analyzed for dissolved species prior to back-titration. A calculated ANC (ANC_{chem}) can be determined on the basis of the dissolved constituents present within the digestion liquor. After determination (ICP–AES) of the quantity (mmole) of each cation released to solution, the ANC_{chem} is determined on the basis of the Na, K, Mg, and Ca (Mn was not addressed, as this ion is not present in sufficient quantities within the samples investigated). We assumed that each of these cations neutralized either one or two H^+ ions depending on their ionic charge, and that they were derived from both carbonates and silicates. Aluminum, Fe, and Si were not included in the ANC_{chem} calculation for reasons discussed previously. Thus ANC_{chem} was determined from:

$$\mathrm{ANC_{chem}} = [(\mathrm{Na} + \mathrm{K}) + \mathrm{Mg} + \mathrm{Ca}) \times 2] \times 49/\mathrm{wt} \qquad (17)$$

where Na, K, Mg, and Ca are in mmoles; the conversion factor 49 converts mmole H^+ ions to kg H_2SO_4/t equivalent; wt is the weight of the sample in g. The ANC of samples affected by acid formation (pyrite oxidation or dissolution of acidic sulfate salt) can be calculated by including SA_{max} into Equation 17 to determine the ANC expected by titration (*e.g.*, $ANC_{chemtitrat}$):

$$\mathrm{ANC_{chemtitrat}} = |[(\mathrm{Na} + \mathrm{K}) + (\mathrm{Mg} + \mathrm{Ca}) \times 2] \times 49/\mathrm{wt}] - \mathrm{SA_{max}} \qquad (18)$$

where Na, K, Mg, and Ca are in mmoles, SA_{max} is determined by Equation 16, and wt is the weight of the sample in g; $ANC_{chemtitrat}$ and SA_{max} are in kg H_2SO_4/t. However, the $ANC_{chemtitrat}$ will also be influenced by non-neutralizing cations derived from the dissolution of salts (*e.g.*, sample MS contains the equivalent of 12.4 kg H_2SO_4/t of non-neutralizing cations: Weber *et al.* 2004b). These non-neutralizing cations should be subtracted from the $ANC_{chemtitrat}$ and the ANC_{chem} calculations.

The theoretical carbonate ANC (ANC_{carb}) was also determined for the samples examined and is based on LECO inorganic C determination in conjunction with EPMA to determine a mineralogical carbonate ANC (Paktunc 1999b). These methods have been reported previously for carbonates and waste-rock samples (Weber *et al.* 2004a, b).

RESULTS

Mineralogy

EPMA results indicate that the chemical composition of the Ontario tremolite is $(Ca_{1.94}Na_{0.05}K_{0.02})(Mg_{4.74}Fe_{0.27}Mn_{0.03})(Si_{7.94}Al_{0.07}O_{23})$, and was identified by XRD as tremolite. A small quantity of anthophyllite $(Ca_{0.01}Na_{0.01})(Mg_{6.24}Fe_{0.06}Al_{0.11}Mn_{0.01})(Si_{8.25}O_{23})$ was identified by EPMA within this sample. Bulk XRF data (Table 1) are comparable to EPMA data for this tremolite sample, confirming that tremolite is the dominant species. The addition of 10% HCl to a pulverized sample of the Ontario tremolite resulted in a slight fizz ("fizz" rating 1 as per the Modified Sobek ANC test procedure), indicating the presence of carbonates. LECO analysis indicated 0.26 wt% inorganic C, and the composition of this carbonate was determined to be calcite by EPMA ($Ca_{0.994}Mg_{0.004}Fe_{0.002}CaCO_3$). Optical observations indicated the presence of trace amounts of magnetite and Fe oxides. Magnetite was confirmed by magnetic separation. The modal proportion of minerals, calculated using MODAN (Paktunc 2001), indicates that the sample contains 91.4 wt% tremolite, <5 wt% anthophyllite, 2.2 wt% calcite, and minor quantities of magnetite and Fe oxides. The de Kalb tremolite sample was identified as tremolite by XRD. Mineral composition was determined by EPMA as $(Ca_{1.87}Na_{0.21}K_{0.04})(Mg_{4.88}Fe_{0.16}Mn_{0.01})(Si_{7.90}Al_{0.11}O_{23})$. Results of a LECO analysis indicated 1.02 wt% inorganic C. Several inclusions were removed by hand selection ((10 magnification) and crushed for separate XRD analysis. Results indicated these inclusions are predominantly calcite with minor quartz, which was evident from the high "fizz" rating of 5 for this concentrate. EPMA results confirmed the presence of calcite ($Ca_{0.993}Mg_{0.004}Fe_{0.001}Mn_{0.002}CO_3$). The composition of hornblende was determined to be $(Na_{0.44}K_{0.04})(Ca_{1.71}Fe_{0.64}Mg_{4.51})(Si_{7.68}Al_{0.35}Ti_{0.01}O_{23})$ by EPMA, and the sample was identified as ferroan magnesiohornblende by XRD. Minor biotite also was determined by XRD in this sample. A "fizz" rating of 2 was determined for the hornblende, and a LECO analysis indicated 0.2 wt% inorganic C; no carbonate was found by EPMA, however. Thus for theoretical calculations, we assumed that the composition is $CaCO_3$. Muscovite was determined to be $(K_{0.79}Na_{0.15})(Al_{2.3}Fe_{0.13}Mg_{0.03}Ti_{0.06})(Si_{3.45}Al_{0.56})O_{10}(OH)_2$, on the basis of 12 atoms of oxygen. A LECO analysis indicated that inorganic C is not present. The "fizz" rating was 0, as no effervescence was observed. The composition of the altered chlorite (based on 18 atoms of oxygen) was determined to be $(Mg_{4.88}Fe_{1.47}Na_{0.27})(Al_{1.25}Si_{4.4})O_{10}(OH)_8$. An XRD analysis indicated a ferroan clinochlore, although the presence of subsidiary peaks suggested the presence of an indeterminable mixed-layer clay, possibly a vermiculite (Weber 2003). The "fizz" rating was 0, and results of a LECO analysis indicated that inorganic C is not present.

Silicate mineral ANC

Bulk inorganic C (LECO), micro-analysis of the carbonate inclusions, and ANC_{carb} values for the silicate minerals are shown in Table 3. The ANC_{carb} was not determined for muscovite or the altered chlorite, as no carbonate is present in these samples. The difference between ANC_{carb} and the ANC determined by the Modified Sobek ANC test must be a reasonable indication of the silicate acid-neutralization capacity as determined by this testing procedure.

The ANC values presented here for the calcic amphiboles are much greater than the ANC values determined for other samples of calcic amphibole tested by Jambor *et al.* (2000, 2002) using Sobek (<250 μm) and Lawrence ANC test (<75 μm) methods, even after the carbonate ANC has been accounted for. This discrepancy can be explained by the much finer size of particles used during this study (~50% fines <40 μm) (Weber 2003). As previously discussed (*e.g.,* White *et al.* 1999, Jambor *et al.* 2002), variations in grain size can significantly affect ANC results, with greater ANC values being recorded from smaller grain-size fractions. Repeat assessments of the Ontario tremolite by the Modified Sobek ANC test on sized (38–75 μm; measured BET surface area of 1.04 $m^2 g^{-1}$) indicated an ANC of 46.8 kg H_2SO_4/t and, therefore, after deduction of ANC_{carb}, a silicate acid-neutralization capacity of 24.8 kg H_2SO_4/t. Variation in the measured ANC values for the Ontario tremolite (Table 3) reflects significantly variable carbonate content. This variability was also demonstrated by flow-through experiments to assess dissolution kinetics under acid conditions (pH in the range 1.5–7.0) on washed homogenized 38–75 μm sample (Weber 2003). Deduction of Ca derived from carbonates in the samples and stoichiometric assessment of the ions released to solution (Table 4) indicate that Mg is preferentially released from the de Kalb tremolite and hornblende; owing to variable carbonate content of

TABLE 3. SILICATE CARBONATE DETERMINATION AND ANC RESULTS

Sample	Wt% carbonate	ANC_{carb}	ANC (difference)	SiANC	Jambor *et al.* (2000) L(HCl)	L(H_2SO_4)	ANC test Sobek
Tremolite (O)	2.17	22	59.6, 59.9, 62.9, 68.4 (IW) 47 (EGi)	40.07	3.7	5.1	5.1
Tremolite (de)	8.49	83	99 (IW) 101 (EGi)	16			
Hornblende	1.66	16	82 (IW) 77 (EGi)	66	17.2	18.3	4.3
Muscovite	0	0	2.5, 3.2 (IW)	2.9	1.7	1.9	0.3
Altered chlorite	0	0	40.4, 40.2 (IW)	40.3	14.0	16.7	10.1

ANC values in kg H_2SO_4/t. ANC_{carb} calculated from mineral quantities and composition (*e.g.*, Paktunc 1999a, b). (IW) represents ANC determined by hand titration. (EGi) indicates replicate tests conducted by Environmental Geochemistry International by autotitration. SiANC (silicate acid-neutralization capacity) based on average hand-titration results for the Modified Sobek ANC test. O: Ontario tremolite; de: de Kalb tremolite. Minerals tested by Jambor *et al.* (2000) include tremolite $(Ca_{1.86}Na_{0.33}K_{0.06})(Mg_{4.71}Fe_{0.51}Mn_{0.02})(Si_{7.65}Al_{0.26}Ti_{0.01})O_{23}$; hornblende (pargasite) $(Na_{0.94}K_{0.10})(Ca_{1.55}Fe_{0.42}Na_{0.03})(Mg_{3.17}Fe_{0.98}Al_{0.76}Ti_{0.09})(Si_{6.06}Al_{1.94})O_{23}$; muscovite $(K_{0.70}Na_{0.09})(Al_{1.85}Fe_{0.18}Mg_{0.03}Ti_{0.03})(Si_{3.10}Al_{0.90})O_{10}(OH)_2$, and chlorite (clinochlore) $(Mg_{4.41}Fe_{0.57})Al_{1.08}(Si_{2.77}Al_{1.23})O_{10}(OH)_8$ by the Lawrence test (using HCl, H_2SO_4) (Lawrence 1990), which has a specified grain-size of <75 μm, and the Sobek test (Sobek *et al.* 1978), which has a specified grain-size of <250 μm.

TABLE 4. CALCULATED ANC (kg H_2SO_4/t) AND SOLUTION COMPOSITIONS OBTAINED FROM THE DIGESTION LIQUOR (mg/L)

Sample	Fizz rating	Digestion vol. (mL)	Na	K	Mg	Ca	Fe	Al	Si	ANC_{chem}	Mod. Sobek ANC Test
Tremolite (O)	1	79	5	n.a.	61	580	10	2	35	66	59
	5	80	5	n.a.	77	551	12	4	60	66	63
Tremolite (de)	2	80	10	<5	129	841	10	6	92	104	99
Hornblende	2	80	18	183	436	170	156	152	134	89	82
Muscovite	0	61	16	54	4.5	n.a.	13	126	78	4	3
Altered chlorite	0	77	286	n.a.	226	n.a.	53	9	68	59	40

n.a.: not analyzed. O: Ontario tremolite; de: de Kalb tremolite. Acid quantity and molarities based on the predetermined fizz rating are: Fizz rating 0 (4 mL 0.5M HCl), 1 (8 mL 0.5M HCl), 2 (20 mL 0.5M HCl), 5 (60 mL 1.0M HCl).

the Ontario tremolite, however, a similar result could not be determined.

The muscovite has the lowest measured ANC, which is in agreement with the mineral-stability series (*e.g.*, Sverdrup 1990, Paktunc 1999a), which indicates that muscovite is very slow in weathering compared to calcite, and thus the release of neutralizing cations (and ANC) also is slow. This finding agrees with similar results for muscovite determined by Jambor *et al.* (2000). The altered chlorite is slightly anomalous in that the ANC is moderate, which does not match the mineral's rank in the stability series of slow weathering (Sverdrup 1990). This moderate ANC is most likely associated with cation-exchange reactions whereby H^+ ions are exchanged for interlayer cations. We identify the ANC associated with these clay minerals as ANC_{CEC}, which may therefore be temporary if equilibrium conditions change in the solution. Further work is required to understand this ANC derived from cation-exchange reactions.

Values of silicate ANC_{chem} were calculated on the basis of analytical data in the ANC digestion liquor (Table 4) using Equation 18. The results for all minerals tested are higher than the ANC_{carb}; they are in good agreement with the ANC as determined by the Modified Sobek ANC test, which again suggests that there is a measurable acid-neutralization capacity associated with the silicate.

Results from this work and the literature confirmed that there is a real ANC derived from silicates that could erroneously be considered carbonate-induced acid-neutralization capacity if silicate acid-neutralization capacity is not addressed. Results presented here for the silicates also confirm that ANC_{chem} provides a good indication of the ANC as determined by the Modified Sobek ANC test.

Waste-rock sample ANC

Five samples of waste rock were assessed to determine the $\mathrm{ANC_{chem}}$ (Table 5). The $\mathrm{ANC_{chemtitrat}}$ also was assessed, as these samples also generated acidity during the Modified Sobek ANC test owing to acidic salts or reactive sulfides (or both). Samples PF and MS have been discussed previously (Weber *et al.* 2004b); significant acid was generated in the Modified Sobek ANC test owing to the dissolution of acidic sulfate salts and reactive framboidal pyrite in these samples. The samples investigated here have a minor to significant sulfide or sulfate component (or both), which in some cases substantially affected the $\mathrm{ANC_{Actual}}$.

For sample PF, the ANC determined by the Modified Sobek ANC test is comparable to the $\mathrm{ANC_{chemtitrat}}$ calculation, and likewise the $\mathrm{ANC_{Actual}}$ is comparable to the $\mathrm{ANC_{chem}}$, which is expected if all S released to solution generates two moles of acidity, and all neutralizing ions released neutralise acidity in the process. The match between the Modified Sobek ANC test and the $\mathrm{ANC_{chemtitrat}}$ calculation, and the $\mathrm{ANC_{Actual}}$ and the $\mathrm{ANC_{chem}}$ for sample MS is less comparable owing to non-neutralizing cations and non-acid-forming S, released during the test (Weber *et al.* 2004b). For sample PAF–H, the $\mathrm{ANC_{chem}}$ is comparable to the $\mathrm{ANC_{Actual}}$, and similarly, the ANC determined by titration is comparable to the $\mathrm{ANC_{chemtitrat}}$ calculated. Although slightly less closely comparable, the results for sample PAF–L indicate that the Modified Sobek ANC test is comparable to the $\mathrm{ANC_{chemtitrat}}$ calculated, and the $\mathrm{ANC_{Actual}}$ is reasonably comparable to the $\mathrm{ANC_{chem}}$. Minor formation of acid occurred in the Modified Sobek ANC test for sample T, and results indicate that the $\mathrm{ANC_{Actual}}$ was low. Again, results for sample T indicate that the Modified Sobek ANC test is comparable to the $\mathrm{ANC_{chemtitrat}}$ calculated, and likewise the $\mathrm{ANC_{Actual}}$ is also comparable to the $\mathrm{ANC_{chem}}$.

DISCUSSION AND CONCLUSIONS

Generally, complete dissolution of the silicates is unlikely during the ANC tests. Knowing that Si does not neutralize acidity and that Fe and Al are hydrolyzed during back-titration (to pH 7.0) meant that the silicate-neutralization potential in the Modified Sobek ANC test can be determined by the concentration of the neutralizing ions (Na, K, Mg, Ca) in the ANC digestion liquor.

The $\mathrm{ANC_{chem}}$ results reported here are comparable to the results determined by the Modified Sobek ANC test for the silicate minerals, and simple assemblages of mixed minerals. Typically, the $\mathrm{ANC_{chem}}$ overestimates the ANC determined by the Modified Sobek ANC test by 1–7 kg H_2SO_4/t, except for the altered chlorite, in which the overestimate was 17 kg H_2SO_4/t owing to the release of excess Na and Mg. This discrepancy for the altered chlorite requires further work to validate the $\mathrm{ANC_{chem}}$ results. For waste-rock samples affected by acid formation, the $\mathrm{ANC_{chemtitrat}}$ is comparable to the ANC recorded in the Modified Sobek ANC test, although the difference for sample PAF–L is greater and may be a function of non-acid neutralizing salts.

Figure 1 shows the correlation between $\mathrm{ANC_{chem}}$ or $\mathrm{ANC_{chemtitrat}}$ (for those affected by acid formation in the ANC test) and the ANC determined by titration for carbonates (Weber *et al.* 2004a), silicates, simple assemblages of mixed minerals, and waste-rock samples. There is a good match for samples that generate low values of ANC (*e.g.*, less than 300 kg H_2SO_4/t); however, greater variation occurs for high-ANC samples that included dolomite and calcite (as assessed by Weber *et al.* 2004a), which show that $\mathrm{ANC_{chem}}$ underestimates the ANC for these samples. This disagreement may be due to precipitation reactions

TABLE 5. ANC RESULTS (kg H_2SO_4/t)
FOR SAMPLES PF, MS, PAF-H, PAF-L, AND T

Sample	Fizz Rating	$\mathrm{SA_{max}}$	ANC (Mod. Sobek)	$\mathrm{ANC_{chemtitrat}}$	$\mathrm{ANC_{chem}}$	$\mathrm{ANC_{Actual}}$
PF	0	43.5	-36.4*	-37.1	6.2	7.7
MS	1	11.8	5.6*	10.2	21	17.4
PAF-H	0	4.8	6.3	8.9	13.7	11.1
PAF-L	1	4.1	17.2	22.9	27	21.3
T	1	0.5	5.1	5.5	6.0	5.6

* assessed by the filtered ANC test (Weber *et al.* 2004b). $\mathrm{ANC_{chem}}$ should be comparable to $\mathrm{ANC_{Actual}}$; ANC (Sobek) should be comparable to the $\mathrm{ANC_{chemtitrat}}$.

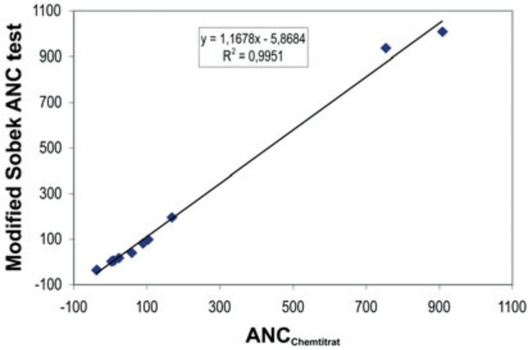

FIG 1. Modified Sobek ANC *versus* $\mathrm{ANC_{chemtitrat}}$. For minerals that are not affected by sulfide or sulfate acidity ($\mathrm{SA_{max}}$) (*e.g*, carbonates and silicates), the $\mathrm{ANC_{chemtitrat}}$ is the same as $\mathrm{ANC_{chem}}$, *i.e.*, $\mathrm{SA_{max}} = 0$. Results include carbonates (calcite, dolomite, siderite from Weber *et al.* 2004a), silicates (tremolite, hornblende, muscovite, altered chlorite) and rock samples PF, MS, PAF–H, PAF–L, T. The siderite value was determined by H_2O_2 ANC test, and those for samples PF and MS were determined by the Filtered ANC test (Weber *et al.* 2004b).

for those samples that released significant ions upon (total) dissolution.

The concentration of inorganic C indicates that for the waste-rock samples assessed, the carbonate ANC (ANC_{carb}) is low at < 2 kg H_2SO_4/t, except for sample MS, which has a moderate content of carbonate, 13–20 kg H_2SO_4/t (Table 6). The ANC values determined by either the Modified Sobek ANC test or the Filtered ANC test indicate an ANC that is higher than this carbonate ANC, which suggests that silicate-induced acid neutralization reactions are occurring, and to a greater extent than the carbonate neutralization. On the basis of the results presented here and the assessments of individual mineral by Jambor *et al*. (2000), the most likely sources of silicate-induced acid neutralization in the rock samples are the clay minerals and chlorite. The other silicate minerals do not contain neutralizing cations (quartz, kaolinite) or their dissolution rate is so low, with minor cation exchange capacity, that ANC is negligible (muscovite, albite, orthoclase).

Of the silicates, simple mixed minerals, and waste-rock samples assessed by the Modified Sobek ANC test, there is a significant contribution to the overall ANC by silicate minerals. This silicate acid-neutralization capacity is a function of sample preparation and the formation of a highly reactive surface-layer on silicate particles (*e.g*., Busenberg & Clemency 1976, Suarez & Wood 1996), formed during crushing and grinding, which is available to neutralize acidity in the short term. In the field, the neutralization of acidity by silicate minerals and the generation of circum-neutral pH values will only be possible for (1) low-sulfide samples, where the mass of silicate minerals having slow dissolution-kinetics and ANC can neutralize the subsequent minor amount of acid generated, and (2) after peak oxidation of sulfide, where the declining acidity load matches the low ANC derived from the remaining silicate minerals present.

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