

# ACID NEUTRALIZING CAPACITY AND LEACHATE RESULTS FOR IGNEOUS ROCKS, WITH ASSOCIATED CARBON CONTENTS OF DERIVED SOILS, ANIMAS RIVER AML SITE, SILVERTON, COLORADO<sup>1</sup>

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**Abstract.** Mine planning efforts have historically overlooked the possible acid neutralizing capacity (ANC) that local igneous rocks can provide to help neutralize acid-mine drainage. As a result, limestone has been traditionally hauled to mine sites for use in neutralizing acid drainage. Local igneous rocks, when used as part of mine life-cycle planning and acid mitigation strategy, may reduce the need to transport limestone to mine sites because these rocks can contain acid neutralizing minerals. Igneous hydrothermal events often introduce moderately altered mineral assemblages peripheral to more intensely altered rocks that host metal-bearing veins and ore bodies. These less altered rocks can contain ANC minerals (calcite-chlorite-epidote) and are referred to as a propylitic assemblage. In addition, the carbon contents of soils in areas of new mining or those areas undergoing restoration have been historically unknown. Soil organic carbon is an important constituent to characterize as a soil recovery benchmark that can be referred to during mine cycle planning and restoration.

This study addresses the mineralogy, ANC, and leachate chemistry of propylitic volcanic rocks that host polymetallic mineralization in the Animas River watershed near the historical Silverton, Colorado, mining area. Acid titration tests on volcanic rocks containing calcite (2 – 20 wt %) and chlorite (6 – 25 wt %), have ANC ranging from 4 – 146 kg/ton CaCO<sub>3</sub> equivalence. Results from a 6-month duration, kinetic reaction vessel test containing layered pyritic mine waste and underlying ANC volcanic rock (saturated with deionized water) indicate that acid generating mine waste (pH 2.4) has not overwhelmed the ANC of propylitic volcanic rocks (pH 5.8). Sequential leachate laboratory experiments evaluated the concentration of metals liberated during leaching. Leachate concentrations of Cu-Zn-As-Pb for ANC volcanic rock are one-to-three orders of magnitude lower when compared to leached solution from mine waste used in the kinetic reaction vessel test. This finding suggests that mine waste and not ANC rock may generate the majority of leachable metals in a field scenario.

The organic carbon content of naturally reclaimed soils derived from weathering of propylitically-altered andesite was determined in catchments where ANC studies were initiated. Soils were found to have total carbon concentrations (TOC) that exceed global average soil TOC abundances by as much as 1.5 – 5 times. These data support an environmental management system involving use of ANC rocks as part of life-cycle mine planning to reduce post-mine closure acid mitigation measures. Carbon contents of undisturbed soils in mined catchments can possibly be used to validate post-reclamation success and help quantify carbon sequestration for CO<sub>2</sub> emission offset trading as carbon markets mature.

**Additional Key Words:** Acid neutralizing capacity, leachate, carbon sequestration, propylitic rocks, volcanic soils

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## **Introduction**

Land management agencies in partnership with mine owners, and local, State, and Federal stakeholders in several western United States watersheds are involved in the cleanup of abandoned hard-rock metal mines and mine-related features. These cleanup efforts are needed because many abandoned mine sites have acid-generating minerals, predominantly pyrite, that in the presence of oxygen and water produce sulfuric acid that is toxic to aquatic life. In addition, acidic water leaches major and trace elements from rocks in concentrations that can also exceed aquatic life survival criteria (Besser et al., 2007).

Mine-site remediation project managers must consider multiple variables in order to achieve the goal of reducing the impact that acid-mine drainage has on surface and ground water (Hutchison and Ellison, 1992). Mine-site configuration in relation to topography, hydrology, possible attenuation of metals and acidity by surficial deposits and bedrock, geologic structures that may be hydrologic flow paths, landslide or debris flow hazards, and transportation logistics are but a few examples of issues that need consideration when designing and implementing a mine-site remediation project.

Important information for any mine reclamation management strategy designed to reduce acid mine drainage should include data about net acid production (NAP) and acid neutralizing capacity (ANC) of local bedrocks. The emphasis of this report is on the ANC of igneous rocks that host base-metal and precious-metal mineralization in the Silverton, Colo., study area. The study area has a legacy of hard-rock mining and contains multiple sites that require cleanup (Church et al., 2007). Land management agencies in partnership with local stakeholders are actively involved in mine-waste remediation efforts near Silverton. ANC data can be used to understand the acid neutralizing capacity of waste rock that is commingled in mine-waste piles and can aid in the identification of catchments that attenuate acidity and metals. If the ANC of local bedrocks were known prior to new mining, these rocks could be mixed with acid generating mine waste in a “pay-as-you-mine” acid rock drainage prevention approach, or used during post-mine closure operations. Use of local ANC rocks to mitigate acid mine drainage may reduce remediation costs associated with amending mine waste with limestone (often hauled from long distances to remote sites).

When local ANC rocks are utilized in remediation projects, it is also important for land managers to understand the leachable constituents that may be liberated from ANC rocks during

weathering. This study investigates the major- and trace-elements leached from ANC rocks and from an acid generating mine waste collected at a site in the study area. These studies involve sequential extractions of leachate derived as the ANC rocks and mine waste are reacted with solutions of varying pH. Geochemical analyses of leachate are used to test, in controlled lab experiments, potential contaminants that may go into solution when water reacts with ANC rocks and mine waste in a field scenario.

In addition to NAP and ANC, this study also addresses the organic carbon contents in soils derived from areas underlain by propylitically altered, volcanic bedrock. Research on volcanic soils is consistent with these types of environments being important C-sinks (Rasmussen et al., 2006). Geochemical baseline data for soil carbon contents could prove valuable to land managers, especially as U.S. carbon offset markets mature and carbon sources need to be quantified as part of comprehensive land-use carbon management strategies (Yager et al., 2008a). If such programs are included in carbon market trading, C-reclaimed may have monetary value that could help to offset some of the costs associated with mine lands reclamation.

When land is disturbed, either through mining or by natural weathering processes that remove soil, the soil releases part of the C pool in the form of CO<sub>2</sub> to the atmosphere. Current research has suggested that atmospheric CO<sub>2</sub> should be stabilized at 350 ppm (Hansen, 2008) due to the climate forcing variables that are already affecting global climate and that are poised to possibly accelerate atmospheric and ocean warming. Therefore, land management to maximize C storage is consistent with CO<sub>2</sub> stabilization since soils could represent as much as 2 gigatons of annual terrestrial carbon storage (Houghton and Goodale, 2004). Further, sustainable land use management practices of soils could account for as much as 2 of the 7 Gt carbon sequestration sectors suggested to prevent atmospheric doubling of CO<sub>2</sub> (Pacala and Sokolow, 2004).

### **Study Area**

The historic mining town of Silverton, Colo., is remote, nestled between two mountain passes, and located 50 miles north of Durango, Colo. Elevations in the area range from 9,300 ft (2,835 m) to over 13,800 ft (4206 m). Mean annual precipitation for the study area is about 60 cm. The upper Animas River watershed above Silverton, Colo., (Fig. 1) is an excellent area to study the ANC of local rocks. Igneous bedrock exposures are exceptional and permit

sampling of the entire volcanic stratigraphy. A more than 100-year history of mining, primarily for silver, gold, and base metals (copper-lead-zinc), has left behind hundreds of abandoned mine-waste piles and associated mining-related features and deposits. The Animas River Stakeholders Group based in Silverton, Colo., along with federal and state partners, are involved in several mine-cleanup efforts that could benefit from detailed information on the ANC of local rocks.

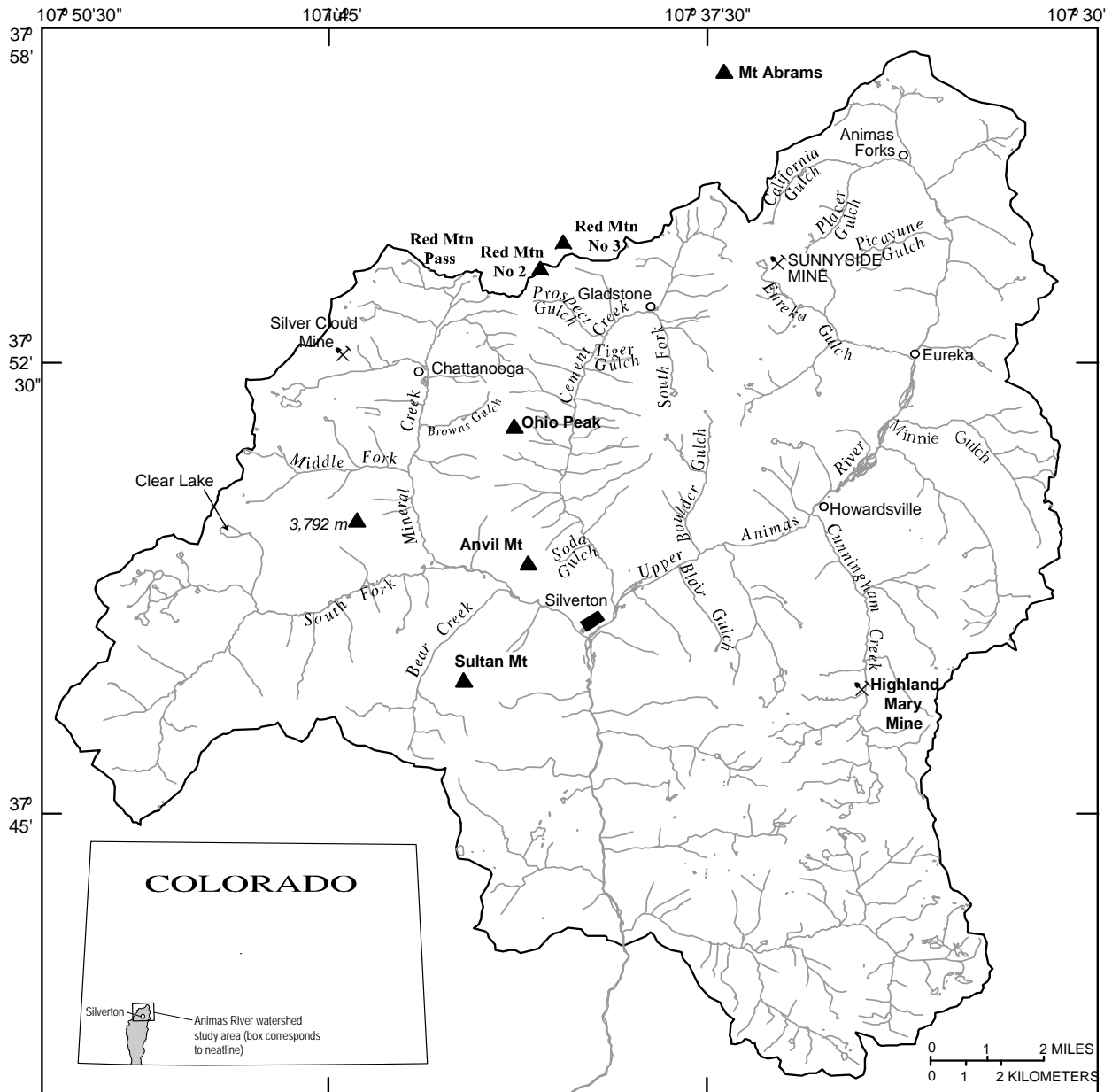


Figure 1. Location map and geographic features referred to in this and previous ANC studies (Yager et al., 2005; 2008B).

## **Geologic Setting**

The stratigraphy of the Animas River watershed study area consists of Precambrian crystalline basement overlain by Paleozoic-, Mesozoic-, and Eocene-age sedimentary rocks, and a 1- to 2-km-thick Oligocene- to Miocene-age volcanic cover (Yager and Bove, 2002; Yager and Bove, 2007).

### **Tertiary volcanism**

Mid-Tertiary volcanism in the San Juan Mountains began with the eruption and deposition of voluminous intermediate-composition (52–63 percent SiO<sub>2</sub>) lava flows, flow breccias, volcanoclastics, minor mafic tuffs, and abundant mudflows of the San Juan Formation (Lipman et al., 1973; Steven and Lipman, 1976). The San Juan Formation is primarily composed of intermediate composition volcanoclastic sedimentary rocks. Minor intercalated andesitic lavas are typically porphyritic and consist of plagioclase, clinopyroxene, hornblende, and opaque oxide primary phases.

Subsequent to San Juan Formation deposition, multiple calderas formed and related volcanic units were deposited throughout the San Juan volcanic field (Lanphere, 1988; Lipman, 2000; Bove et al., 2001). Two caldera-forming events occurred in the upper Animas River watershed: the San Juan-Uncompahgre caldera complex and the younger, nested, Silverton caldera (Bove et al., 2001). San Juan caldera eruptives include the outflow units of the Sapinero Mesa Tuff and the intracaldera Eureka and Picayune Megabreccia Members.

The Eureka Member of the Sapinero Mesa Tuff is the intracaldera component of the Sapinero Mesa Tuff, is dacitic to rhyolitic in composition, and contains phenocrysts of plagioclase, with lesser amounts of sanidine, biotite, and trace augite. The Crystal Lake Tuff is volumetrically minor in comparison to the Sapinero Mesa Tuff and thus was not sampled.

Intermediate composition lavas infilled the San Juan caldera depression to a thickness exceeding 1 km. These rocks are named, from oldest to youngest in stratigraphic section: Burns, pyroxene andesite, and Henson Members of the Silverton Volcanics. The Burns Member is host to the majority of mineral deposits mined in the study area (Bejnar, 1957). Burns Member volcanics are characterized by propylitically altered lavas. The overlying pyroxene andesite Member is composed of intermediate composition lava flows with a trend toward more mafic compositions (Yager and Bove, 2007). The volcanoclastic sedimentary rocks of the Henson Member of the Silverton Volcanics interfinger with both the Burns and the pyroxene andesite

Members (Lipman, 1976). Lavas of the Silverton Volcanics are porphyritic and typically contain phenocrysts of plagioclase, amphibole, pyroxene, opaque oxides, and minor biotite in a fine-grained to aphanitic groundmass.

Beginning approximately 1 million years after Silverton caldera formation, numerous stocks, dikes, and other silicic intrusions formed along the Silverton caldera ring-fracture zone and are known as the Sultan Mountain stock. The oldest postcaldera granitic stocks (monzonite, monzodiorite, granodiorite, and monzogranite) are about 26.6 Ma and intrude along the southern part of the Silverton caldera ring fracture (Lipman, 1976; Ringrose, 1982; Bove et al., 2001).

### Propylitic Assemblage

An alteration type important for ANC rock properties is referred to as a propylitic assemblage. Regional propylitic alteration identified by Burbank (1960) and described further in Bove et al., (2007a, b) as a “pre-ore propylitization” event has affected most igneous rocks near the San Juan-Uncompahgre and Silverton caldera complex. The mineralogy of this assemblage, although variable, consists of a secondary assemblage of quartz, chlorite, epidote, calcite, potassium feldspar, albite, pyrite, and opaque Fe-oxides in the presence of unaltered to slightly altered primary feldspar crystals. ANC minerals calcite (the mineral that comprises limestone) and chlorite are common in the propylitic assemblage and occur in abundances as high as 20 wt % and 25 wt % respectively (Yager et al., 2008b, table 3).

Propylitization is thought to have formed as the nearly 1-km-thick sequence of lavas of Silverton Volcanics cooled, crystallized, and degassed volatile constituents. Carbon dioxide (CO<sub>2</sub>) was perhaps the primary volatile component that altered the original minerals and matrix of the country rock (Burbank, 1960). Propylitic rocks commonly have a greenish hue in outcrop due to the presence of chlorite and epidote. Propylitic alteration assemblages are commonly associated with metallic mineralization in many deposit types worldwide and are not unique to the study area (Evans, 1993). Thus, rocks that have ANC properties because of minerals introduced during propylitic alteration could be locally available in many areas for use in reducing acid mine drainage during mining or in post-mining remediation cleanup projects.

### Acid-Generating and Acid-Neutralizing Minerals

Complex weathering reactions of geochemical constituents of minerals in rocks determine whether a unit will produce or consume acid. Reactions at the water-mineral interface involving

oxidation, adsorption, desorption, ion exchange, dissolution, and surface area control the processes that ultimately result in the elements that are released into solution or are chemically bound or sequestered (Davis and Kent, 1990). The kinetic rates at which these reactions occur in place are variable and are thus difficult to reproduce or simulate in a laboratory setting. It is, therefore, important to emphasize that our laboratory data provide an estimate of readily available neutralizing or acid-generating capacity.

Important oxidation-weathering reactions for minerals that contribute to acid generation in some samples studied include pyrite and chalcopyrite, the principal acid-generating phases (Salmon and Malmström, 2004). Sphalerite (Salmon and Malmström, 2004), and galena (Blowes et al., 2003) are of secondary, acid generating importance. Weathering reactions are given below.

#### Acid-Generating Mineral Reactions

- Pyrite oxidation (FeS<sub>2</sub>) (ferric iron reaction path)  

$$\text{FeS}_2(\text{s}) + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$
- Chalcopyrite oxidation (CuFeS<sub>2</sub>) (ferric iron reaction path; trace abundances in some samples)  

$$\text{CuFeS}_2(\text{s}) + 16\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 17\text{Fe}^{2+} + \text{Cu}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$
- Sphalerite oxidation (ZnFeS) (ferric iron reaction path; trace abundances in some samples)  

$$\text{ZnS}(\text{s}) + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} + 8\text{Fe}^{2+} + 8\text{H}^+$$
- Galena (PbS) (ferric iron reaction path; trace abundances in some samples)  

$$\text{PbS}(\text{s}) + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} + 8\text{Fe}^{2+} + 8\text{H}^+$$

Weathering reactions for the high ANC minerals are given below for calcite (Jambor, 2003) with a fast dissolution rate, and for chlorite (Salmon and Malmström, 2004), having a slow dissolution rate.

#### Acid-Neutralizing Minerals

- Calcite (CaCO<sub>3</sub>)  

$$2\text{CaCO}_3(\text{s}) + 4\text{H}^+ \rightarrow 2\text{Ca}^{2+} + 2\text{H}_2\text{CO}_3$$
- Chlorite (MgFeAl)AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>  

$$(\text{Mg}_{4.5}\text{Fe}^{2+}_{0.2}\text{Fe}^{3+}_{0.2}\text{Al})\text{AlSi}_3\text{O}_{10}(\text{OH})_8(\text{s}) + 16\text{H}^+ \rightarrow$$

$$4.5\text{Mg}^{2+} + 0.2\text{Fe}^{2+} + 0.2\text{Fe}^{3+} + 2\text{Al}^{3+} + 3\text{SiO}_2(\text{s}) + 12\text{H}_2\text{O}$$

Additional phases locally present in Animas River watershed rocks that were shown in other studies to have some ANC are epidote ( $\text{Ca}_2(\text{Fe}^{3+},\text{Al})_3(\text{SiO}_4)_3(\text{OH})$ ) and hornblende ( $\text{Ca}_2(\text{Mg},\text{Fe})_4\text{Al}(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH},\text{F})_2$ ) (Jambor et al., 2002). Other silicate phases that are thought to have low reactivity and minimal ANC include the sodic feldspars, potassium feldspar, and sericite (Jambor, 2003; Jambor et al., 2002).

## **Methods**

### **Sample Preparation and Analyses**

Fifty-nine composite rock samples were collected between 2003 and 2006 for NAP, ANC, and geochemical, mineralogical, and rock physical property studies. Splits of all samples were jaw-crushed to pebble-size using steel plates and pulverized to approximately <200 mesh (70  $\mu\text{m}$ ) in an agate shatterbox for wavelength dispersive X-Ray fluorescence (WDXRF) analyses, x-ray diffractometry (XRD) semi-quantitative mineralogy using the Rietveld method (Young, 1993; Raudsepp et al., 1999; Raudsepp and Pani, 2003), total carbon-carbonate analyses, and inductively coupled plasma–mass spectrometric analyses (ICP–MS).

Results of these analyses are available in Yager et al., (2005; 2008b) and downloadable from:

<http://pubs.usgs.gov/of/2005/1433/> and <http://pubs.usgs.gov/sir/2008/5063/>.

Additional splits were crushed and sieved to less than 2 mm for ANC acid titration experiments. Samples were not subjected to grinding during preparation. Grinding can lead to preferential exposure of layered chlorite surfaces that may artificially enhance water–mineral reactions not commonly found in natural weathering processes. Such surfaces may not be exposed during normal weathering involving freeze–thaw cycles, rainfall precipitation events, and grain-to-grain abrasion that occurs during fluvial transport.

### **Net Acid Production Test**

The net acid production (NAP) test was developed as a screening tool to determine the acid-generating potential of mine-waste materials (Lapakko and Lawrence, 1993). This method is a static laboratory bench test that utilizes  $\text{H}_2\text{O}_2$  to oxidize sulfide minerals in a sample, creating  $\text{H}_2\text{SO}_4$  that subsequently reacts with other phases present. Because enhanced sulfide oxidation is achieved, this test provides an upper practical limit for acid-generating potential. A modified version of the Lapakko and Lawrence (1993) NAP method was used for this study. The steps used for this procedure are listed in Table 1.



Net acid production is calculated in calcium carbonate equivalent units (kg/t) that would be necessary to neutralize a sample to a final pH of 7.0. This calculation is based on the following formula:

$$\text{Net acid production in kg/t CaCO}_3 = 50 \times \text{ml}_b \times N_b / \text{sample weight},$$

where  $\text{ml}_b$  = total volume of NaOH used during titration to pH 7.0 from step nine (table 1), and  $N_b$  = normality of NaOH used.

Thus, progressively higher NAP values would require more calcite to neutralize a solution to pH 7.0.

Table 1. Procedure used to determine NAP. Steps listed in sequential order.

Step	Procedure
1	Powder rock in shatterbox to less than 200 mesh
2	Place 1 g representative split of rock powder from step 1 in 250 ml beaker
3	Incrementally add 100 mL 30 percent H <sub>2</sub> O <sub>2</sub> . Watch for energetic reaction with sulfides and record relative fizz response (low-moderate-high)
4	After reactions have subsided and all 100 ml of H <sub>2</sub> O <sub>2</sub> is added, place beaker on hot plate and heat to 94°C (near boiling) for 1 hour. Remove from hot plate and cool for 5 minutes. Initial pH is recorded prior to titration to pH 7. Note that some samples have no NAP and will have a pH of 7 or greater at the completion of this step
5	Add another 50 ml of H <sub>2</sub> O <sub>2</sub> and heat to 94°C for 30 minutes. Remove from hot plate and cool for 15 minutes. This step is used to help ensure (but not guarantee) complete oxidation. If oxidation is incomplete, the NAP calculated will be less than its maximum value
6	Add 1 ml of 0.016 M Cu nitrate solution and boil at 110°C for 10 minutes
7	Cool solution and remove solids by filtration with filter paper and thistle funnel
8	Rinse solids in filter paper with 1M CaCl <sub>2</sub>
9	Titrate solution by burette to pH 7 with reagent-grade 0.1N NaOH. A magnetic stirrer and Teflon stir bar are used to continuously mix the solution between pH measurements

#### Acid Neutralizing Capacity Test (Acid Titration)

The ANC method used in this study is similar to that described in Shaw et al., (2002) and initially described by Robertson Geoconsultants (written communication, 2000) and provides an estimate of the instantaneous and readily available ANC of rock and mineral particles. The procedure used to determine ANC is listed in Table 2.

Acid neutralization capacity is calculated in calcium carbonate equivalent mass units (kg/t) with the following formula, where total acid added in this example is 50 ml, N is the normality of acid used, grams (g) of sample = 50, mol = moles, formula weight for calcite (CaCO<sub>3</sub>) is 100 g:

$$\text{H}_2\text{SO}_4 (0.05 \text{ liters}) \times 0.1 \text{ N H}_2\text{SO}_4 = 0.005 \text{ equivalents CaCO}_3 (0.005 \text{ mol CaCO}_3)$$

$$0.005 \text{ mol CaCO}_3 \times \frac{100 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = 0.50 \text{ g CaCO}_3$$

$$\frac{0.50 \text{ g CaCO}_3}{30 \text{ g sample}} \times \frac{1,000 \text{ g}}{1 \text{ kg}} \times \frac{1,000 \text{ kg}}{1 \text{ t}} \text{ CaCO}_3 \times \frac{1 \text{ kg CaCO}_3}{1,000 \text{ g CaCO}_3}$$

$$\approx 17 \text{ kg/t CaCO}_3$$

Table 2. Procedure used to determine ANC. Steps listed in sequential order.

Step	Procedure
1	Rock sample is crushed using jaw crusher to approximately 2 mm. Samples are not ground to avoid heating and preferential orientation of chlorite <u>001</u> crystal lattice planes
2	Material from step 1 is sieved using a stainless steel sieve; all material less than 2 mm is saved for acid titration
3	A representative 30-g split from step 2 is weighed and the starting mass recorded
4	The 30-g sample is added to a 100-ml beaker with 30mL deionized water and stirred; the initial pH and titration start time is recorded
5	Sample is stirred continuously for the duration of the experiment using a mechanical mixer with a stainless steel shaft and Teflon propeller, and the starting pH is recorded. Nitrogen gas is bubbled through titrant to reduce effects of atmospheric CO <sub>2</sub> on pH during titration
6	Reagent-grade 0.1N H <sub>2</sub> SO <sub>4</sub> titrant is added incrementally to samples using a pH stat controller that allows pH set points to be pre-set from the starting titration pH to the ending pH 2. In this study, whole pH set-point intervals were used; for example, pH 7, 6, 5, 4, 3, and 2. The pH stat controller measures and records milliliter increments of titrant added to achieve titration set-point stability. Stability is reached when the pH stat controller detects that a pH set point is achieved and stops adding acid. Total acid added is summed for each pH set point and the cumulative total for all set points; the cumulative total is used to determine ANC for a sample. Note that titrant addition by burette is used on some samples with high ANC and the quantity added by burette is added to the total added by the pH stat controller. Completed titration duration times range from a few minutes (low ANC) to several hours (high ANC)

### ANC Reaction Vessel Test

A 19-cm diameter by 75-cm tall plexiglass reaction vessel was designed to react acid-generating mine waste and ANC rock (Fig. 2). A central perforated polyvinyl chloride, 5-cm diameter tube permitted sampling of leachate, and measuring pH, specific conductance, and temperature. Two valves allowed withdrawal of leachate from the ANC rock and mine-waste zones. An electrode array placed in the mine waste and in the ANC rock zones was used to monitor self-potential and resistivity; however, these results are not reported here. The reaction vessel built for this study is smaller in scale but similar to that described by Vaughn et al., (1999); however, their study only evaluated mine waste reactions.

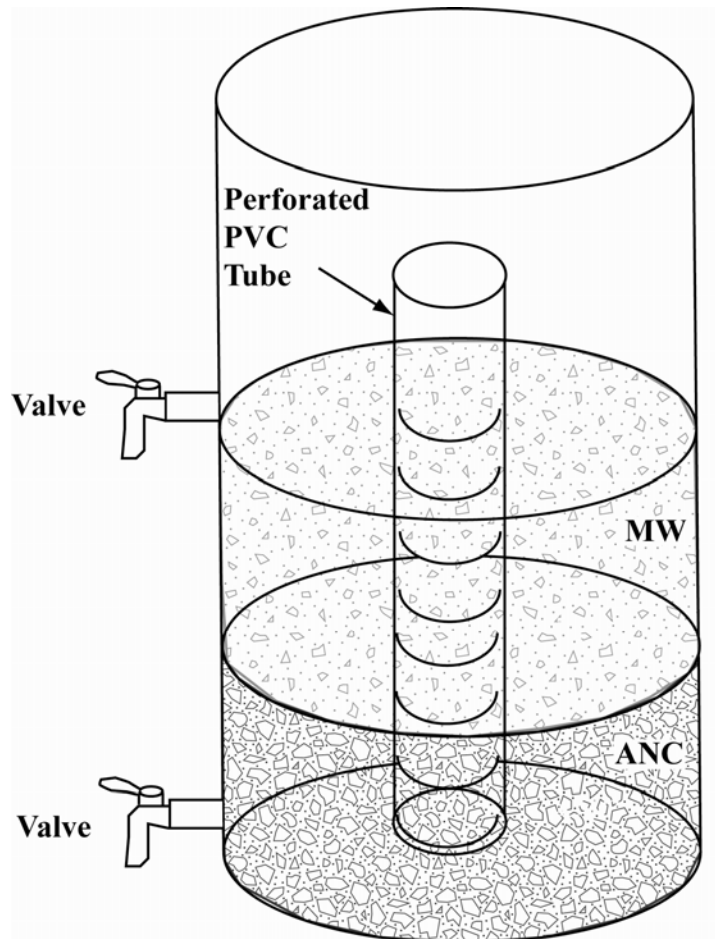


Figure 2. ANC reaction vessel test. MW, Grand Mogul mine waste; ANC, primarily pyroxene andesite Member of Silverton Volcanics, ANC rock sampled from Minnie Gulch.

The initial configuration used for the reaction vessel was 4 kg waste from the Grand Mogul mine (located in upper Ross Basin in the Cement Creek catchment), layered on top of 6 kg of

ANC rock. A representative mine waste sample was collected using a 30-cell grid of the Grand Mogul mine waste surface. Surface samples were collected from each 3m by 3m cell, in 5-gal plastic buckets using a shovel. Cell material was composited and mixed on site, and re-composited and mixed again in the lab. The size distribution of material used in the initial vessel test was determined and detailed in Table 3. Deionized water (pH 6.2 initial) was used to saturate the vessel contents and leachate was extracted every day initially using a plastic syringe and pre-rinsed glass tubing. Most samples were collected near the mine waste and ANC rock interface during the first month of saturation. The vessel test was static during saturation, i.e., communication of water between the layers was controlled by gravity with no continuous flow of leachate through the vessel.

Table 3. Size fraction distribution determined for ANC rock and mine waste material used in ANC reaction vessel test.

<b>Size fraction</b>	<b>Mass percent</b>
<b>ANC Rock</b>	
>19mm	50.6
<19 to > 2mm	42.4
<2mm to > 600 $\mu\text{m}$	3.8
< 600 $\mu\text{m}$	3.2
<b>Mine Waste</b>	
>19mm	22.1
<19 to > 2mm	49.5
<2mm to > 600 $\mu\text{m}$	21.8
< 600 $\mu\text{m}$	6.3

The vessel was drained completely once after 52 days, and resaturated with deionized water. After resaturation, water samples were collected once daily initially and intermittently for 6 months, from both the ANC and mine waste layers. Several liter aliquots of water were also collected from a lower drain for analysis.

### Sequential Extraction Procedure

Volcanic rocks were prepared for sequential extractions using the same method as described above in the sample preparation section. A < 2-mm, 1 gram split from each rock and from the composite Grand Mogul mine waste was obtained using a Jones splitter.

A seven-step sequential leachate extraction procedure (Yager et al., 2008b, Table 9) was used to determine the metals released from specific phases and total elements liberated. A separate nine-step sequential leachate extraction procedure (Yager et al., 2008b, Table 10) having two pH extractions for chlorite was added to determine possible metals released from chlorite species. Chlorite species were specifically targeted in sequential extraction studies because in a previous study (Yager et al., 2005), clinocllore and chamosite in propylitically altered volcanic rocks were found to have high ANC. After each extraction step, the samples were centrifuged at 15,000 rpm for 15 min., then decanted. Five hundred micro liters ( $\mu\text{L}$ ) of concentrated ultra pure nitric acid was added to the decantate for the following fractions: (1) water soluble, (2) exchangeable, (3) carbonate, (4) pH 4, (5) pH 2, (6) amorphous Fe- and Al-hydroxides, and (7) amorphous and crystalline Mn-oxides. With the exception of the water soluble fraction, all other fractions were diluted with ultra-pure 18 mega-ohm water to a final volume of 50 mL. All extractions were analyzed by ICP–MS. A total digest was also performed on the nine samples and three duplicates using a four-acid digest procedure.

### Soil Carbon and radiometric ages

Soils in catchments where rock samples were collected for NAP and ANC studies were also sampled for total organic carbon (TOC). Sample sites were selected to represent maximal reclamation recovery potential in naturally reclaimed or undisturbed forested areas that are in close proximity to non-reclaimed mine sites. Most sample sites were selected in subalpine to alpine terrain with northerly aspects and in non-boggy environments. Mine waste was also sampled for comparison with reclaimed or undisturbed adjacent soils. The number of soil sample sites in a basin was limited due to analytical costs but are thought to be representative of each catchment sampled.

A 4-inch diameter steel, bucket-type soil auger was used to sample continuous core (at 5-cm intervals) from the surface to 55 cm or until the soil auger could not penetrate rocks or tree roots. Soils were sieved in the lab using stainless steel sieves and a representative < 2mm split of each sampled interval was analyzed for TOC, N-species, metals, and soil enzyme activities.

Preliminary data for organic carbon contents only are presented here as an estimate for reclamation recovery potential for reclamation projects in the study area. Total organic carbon was analyzed by total combustion and described in Brown and Curry (2002).

Black carbon (charcoal) was observed in several cores. Splits of soils intervals that contain charcoal were submitted for radiocarbon dating. The charcoal collected represents burn horizons that have occurred periodically during soil accumulation and provide a minimum age for the dated horizon. Selected soil horizons were dated using  $^{14}\text{C}$ , accelerator mass spectrometry methods on charred material.

## **Results**

### **Net Acid Production**

Prior to ANC acid titration, NAP was determined using the method described in Lapakko and Lawrence (1993). This test was an effective method for identifying high NAP samples that could be excluded from further ANC testing. Samples with less than 10 kg/t  $\text{CaCO}_3$  NAP were subsequently tested for ANC. The NAP value is reported in kg/t  $\text{CaCO}_3$  equivalent, and can be interpreted as the amount of  $\text{CaCO}_3$  required to neutralize a sample to pH 7. Low or non-detectable NAP values are suggestive that a sample may have ANC. NAP values for 59 samples tested in our previous studies range from not detectable (27 samples) to 182 kg/t  $\text{CaCO}_3$  equivalent (Yager et al., 2005; 2008b).

### **Summary of NAP results**

The highest NAP determinations were observed for rocks from Tertiary dacite, Sultan Mountain stock, Eureka Member of the Sapinero Mesa Tuff, and the San Juan Formation (Fig. 3). Burns and pyroxene andesite Members of the Silverton Volcanics have relatively low NAP. Burns Member lavas have lower NAP where exposed near the caldera structural and topographic margins compared to equivalent rocks exposed within the central core of the San Juan and Silverton caldera complex. This could be a function of a greater depth of burial and higher intensity of propylitic alteration affecting the intracaldera fill rocks. Caldera margin lavas are thinner, were not buried as deeply as intracaldera equivalents, and perhaps experienced cooler propylitic alteration temperatures. The Picayune Megabreccia Member of the Sapinero Mesa Tuff also occurs near the Silverton caldera margin and has relatively low NAP. The low NAP of the Picayune Megabreccia Member is likely a result of being composed of a

combination of propylitized low NAP, San Juan Formation-equivalent clasts, and intercalated, propylitized Sapinero Mesa Tuff clasts with high calcite and chlorite.

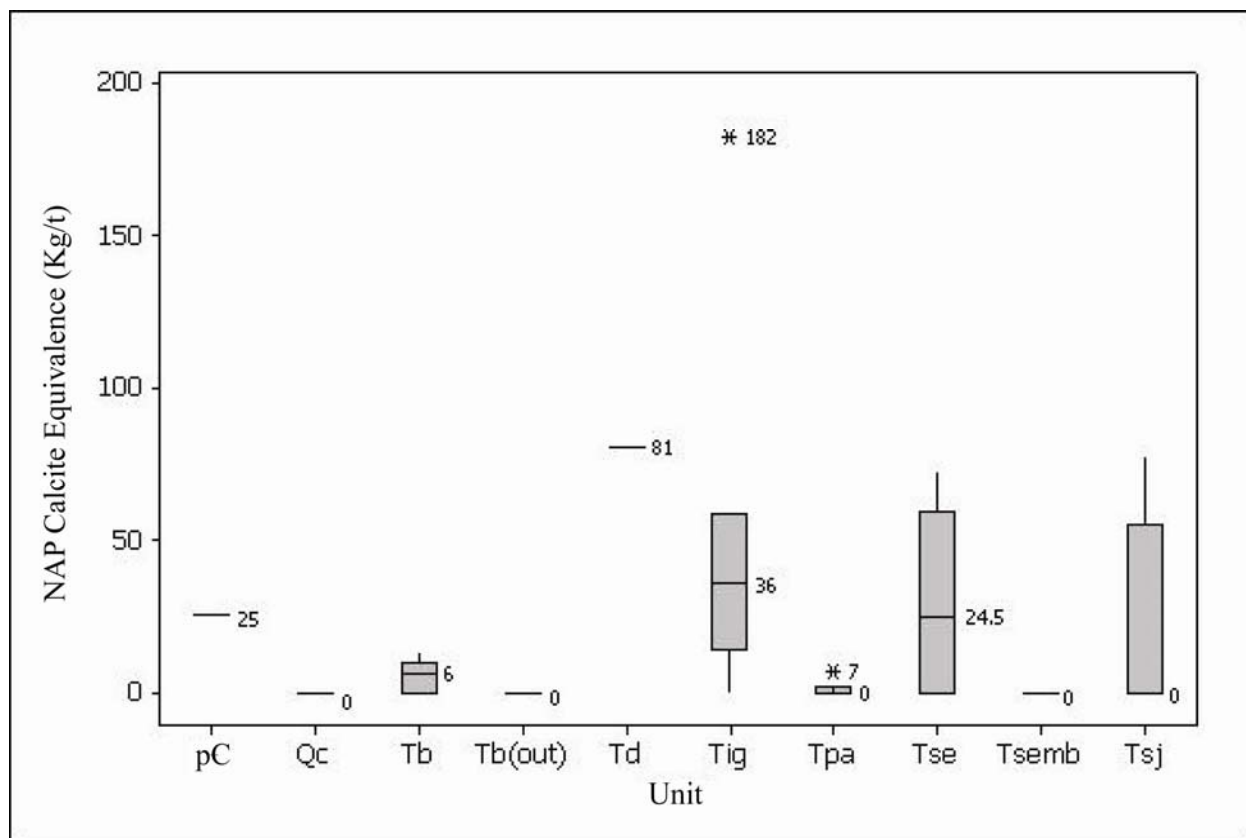


Figure. 3. Box plot of NAP titration results for Silverton, Colo., geologic units. Median values adjacent to box; outlier values indicated by asterisk. Unit abbreviations pC, Precambrian Irving Formation; Qc, Quaternary colluvium; Tb, Burns Member of the Silverton Volcanics sampled inside the Silverton caldera margin; Tb(out), Burns Member of the Silverton Volcanics sampled outside the Silverton caldera margin; Td, Tertiary dacite; Tig, Sultan Mountain stock, Tpa, pyroxene andesite Member of the Silverton Volcanics; Tse, Eureka Member of the Sapinero Mesa Tuff; Tsemb, Picayune Megabreccia Member of the Sapinera Mesa Tuff; Tsj, San Juan Formation. pC, n = 1; Qc, n = 1; Tb, n = 9; Tb(out) n = 4; Td, n = 1; Tig, n = 7; Tpa, n = 6; Tse, n = 6; Tsemb, n = 2; Tsj, n = 11.

### Acid Neutralization Capacity

The ANC acid titration method used in this study (Robertson Geoconsultants, written comm., 2000; Shaw et al., 2002; Yager et al., 2005; Yager et al., 2008b) provides an estimate of the instantaneous ANC of rock and mineral particles. ANC was calculated in terms of kg/t CaCO<sub>3</sub>

equivalent and assumes that all of the ANC is attributable to calcite. However, many samples contain mixtures of the ANC minerals calcite, chlorite species (clinochlore and chamosite), and epidote. The ANC for samples, while variable, ranges from 0.4 to 146 kg/t CaCO<sub>3</sub> equivalent (Yager et al., 2005; 2008b; Yager, 2008) (Fig. 4).

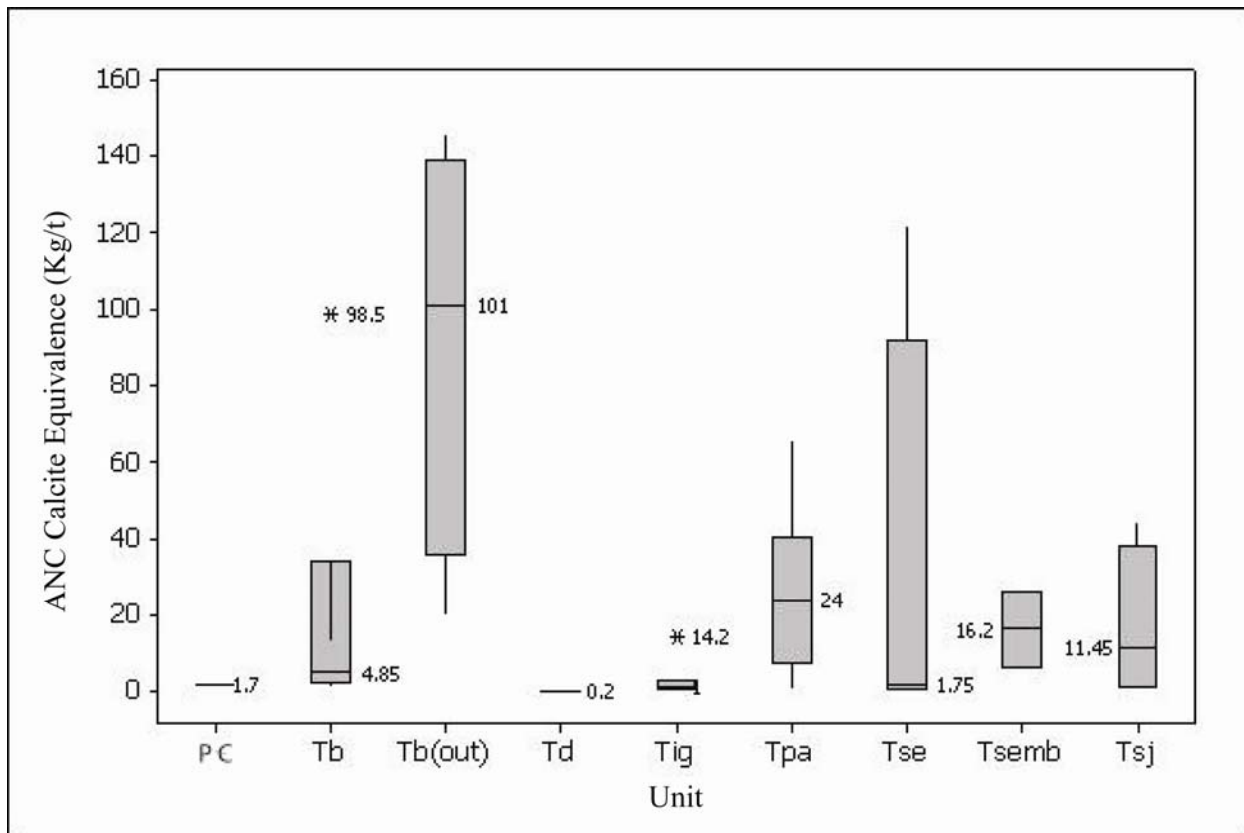


Figure 4. Box plot of ANC acid titration results for Silverton, Colo., geologic units. Median values adjacent to box; outlier values indicated by asterisk. Unit abbreviations pC, Precambrian Irving Formation; Qc, Quaternary colluvium; Tb, Burns Member of the Silverton Volcanics sampled inside the Silverton caldera margin; Tb(out), Burns Member of the Silverton Volcanics sampled outside the Silverton caldera margin; Td, Tertiary dacite; Tig, Sultan Mountain stock, Tpa, pyroxene andesite Member of the Silverton Volcanics; Tse, Eureka Member of the Sapinero Mesa Tuff; Tesmb, Picayune Megabreccia Member of the Sapinera Mesa Tuff; Tsj, San Juan Formation. pC, n = 1; Tb, n = 6; Tb(out) n = 4; Td, n = 1; Tig, n = 7; Tpa, n = 6; Tse, n = 3; Tsemb, n = 5; Tsj, n = 4.

Calcite reacts quickly and has a neutralizing effect at acidic pH. Clinochlore, however, dissolves more slowly than calcite (Jambor and Blowes, 1998), but was shown to have some ANC effect in acidic solutions of pH of about 4.0. Previous studies also indicate that clinochlore



and chamosite have ANC properties (Kwong and Furgeson, 1997, Jambor et al., 2002). Chlorite species also tend to be more important in terms of ANC when compared to other silicate phases including sodic plagioclase, alkali feldspar, and muscovite (Jambor et al., 2002). Some rocks in our studies that lack calcite have high ANC (98 kg/ton  $\text{CaCO}_3$ ), low carbon from carbonate concentration (0.05 wt %  $\text{CO}_2$ ), and contain 18 wt % chlorite (Yager et al., 2005; Table 4; Fig. 14).

### Summary of ANC results

Arguably the most important unit for our ANC study is the Silverton Volcanics lavas. The Silverton Volcanics lavas are composed of the Burns Member that occurs lower in stratigraphic section, whereas the pyroxene andesite Member occurs higher in stratigraphic section. These rocks are important because they host the majority of base- and precious-metal deposits, are adjacent to vein mineralization and are thus invariably commingled with mine waste and mill tailings. These volcanics are also the most voluminous rock types in the study area comprising a nearly 1-km-thick by 15 km wide volcanic fill within the area affected by collapse of the San Juan and Silverton calderas (Yager and Bove, 2002). Consequently, it is important to understand the ANC of these rocks and the importance that they might have in attenuating metals and acidity derived from weathering processes of the mountain bedrocks and mine waste piles.

Highest median ANC values were determined for the Burns and pyroxene andesite Members of the Silverton Volcanics, Picayune Megabreccia Member of the Sapinero Mesa Tuff, and some San Juan Formation samples (Fig. 4). The highest ANC, 146 kg/t  $\text{CaCO}_3$  equivalent, was observed for the Burns Member lavas exposed near the Silverton and San Juan caldera topographic margins and is correlative with lower NAP values for equivalent intracaldera rocks. The higher ANC for Silverton Volcanics lavas near the caldera margins may be attributed to a shallower depth of burial during cooling when compared with intracaldera equivalent rocks that were subjected to deeper burial, slower cooling due to insulation by overlying lavas, and possibly higher propylitic alteration temperatures (Bove et al., 2007b). Picayune Megabreccia Member samples also collected along the San Juan caldera margin exhibit some ANC. One sample, HDY0314 in the Yager et al., (2005) study that was originally assigned to unit Tse, has a high ANC (123 kg/t  $\text{CaCO}_3$  equivalent). It is likely part of the megabreccia unit Tsemb and is composed almost completely of propylitized Sapinero Mesa ash flow tuff. Pyroxene andesite Member lavas, in all but one locality, had some ANC and a corresponding low NAP. San Juan

Formation volcaniclastic rocks and lavas have variable ANC that can be as high as 110 kg/t CaCO<sub>3</sub> equivalent. San Juan Formation outcrops with high ANC are exposed outside the northwest margin of the Silverton caldera. More intense alteration along the structural margin of the Silverton caldera has eliminated much of the ANC of the San Juan Formation in these areas. Units that lack significant ANC include the Precambrian Irving Formation, Tertiary dacite intrusive rocks, Sultan Mountain stock, and intracaldera Eureka Tuff.

#### ANC Reaction Vessel Test

Acid titration ANC tests in previous studies (Yager et al., 2005; Yager et al., 2008b), were usually completed during an 8 hour period. The ANC reaction vessel described above (Fig. 2) was designed to test the longer-duration ANC of igneous bedrocks. The pH and specific conductance results for the initial vessel test are shown in figure 5.

The vessel was first filled and saturated with deionized water on 3/3/2008 for the phase I test. An initial 0.5 unit pH increase was observed for both the ANC and mine waste zones upon saturation with 4.5 liters of deionized water (Fig. 5A). After 2 days, pH in the mine waste zone decreased and pH in the ANC rock zone continued to increase. The pH increase in the ANC rock zone occurred during 1 month, until the vessel was drained on 4/1/2008. Note that the pH increase in the mine waste zone between 3/10/2008 and 3/17/2008 was likely caused by mixing of water near the interface of mine waste water with ANC water, as the volume of water in the mine waste zone was depleted due to sampling and draw down until 3/17/2008, when the water level reached the ANC rock zone. After the vessel was re-saturated with deionized water on 4/2/2008 for the phase II test, and allowed to react until past 6/01/2008, water in the ANC rock zone eventually attained pH 5.8. Water in the mine waste zone remained very acidic in the phase II test (pH 2.4) (Fig. 5B).

Specific conductance measurements were completed on water extracted from the ANC rock zone prior to draining during phase I. An overall decrease in specific conductance was observed between 3/3/2008 and 4/1/2008 (Fig. 6). ANC reactions during phase I were effective in neutralizing acid generated and also reducing specific conductance by precipitating metals during the first month of the experiment. Initial variability of specific conductance may be due to leaching of sulfide phases and efflorescent salts in the mine waste.

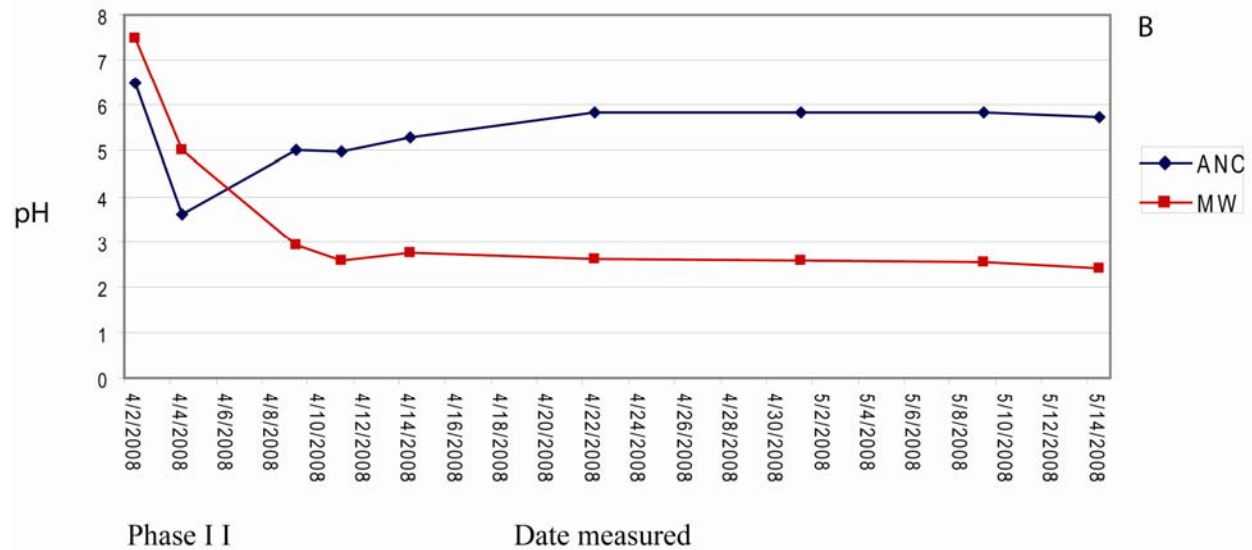
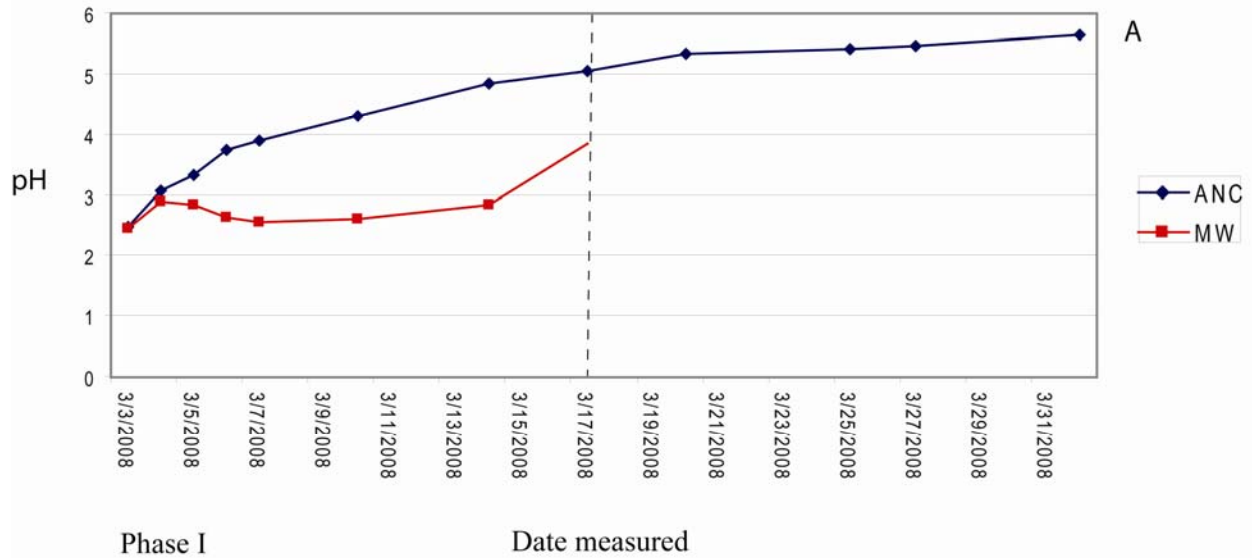


Figure. 5. ANC reaction vessel test pH measurements for: (A) 3/1/2008 to 3/31/2008 (phase I) and (B) 4/2/2008 to 5/1/2008 (phase II). Dashed vertical line (A) denotes when water level reached top of ANC rock. Vessel was drained and re-saturated with deionized water between 3/31/2008 and 4/2/2008 for phase II.

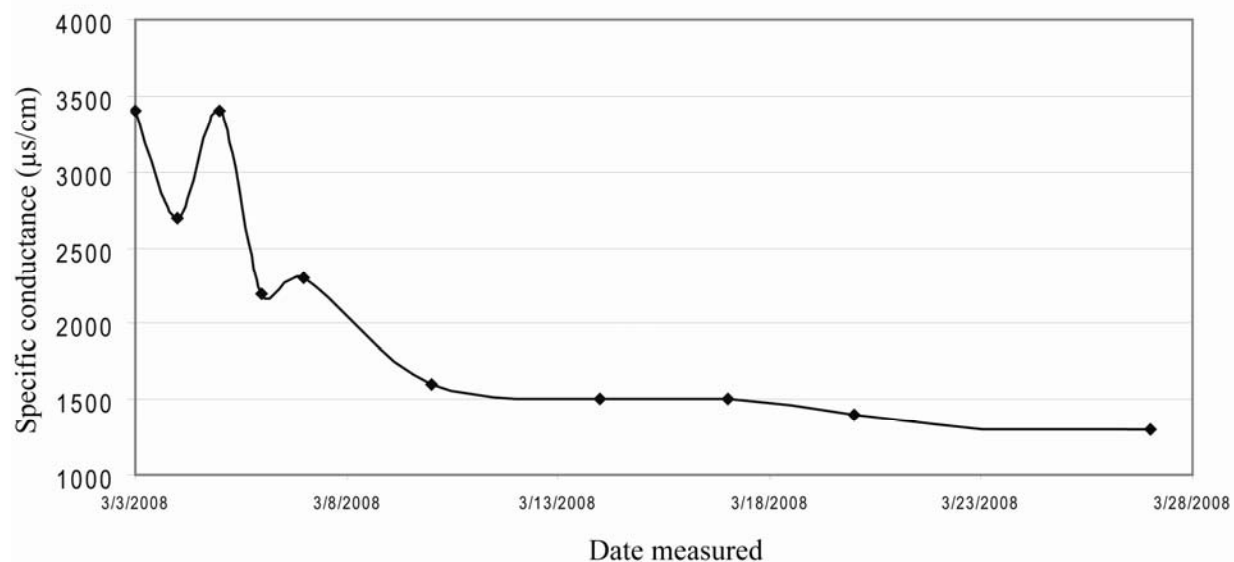


Figure 6. ANC reaction vessel test specific conductance measurements between 3/3/2008 and 3/28/2008. Measurements were done on water sampled from base of vessel in ANC rock layer.

Reactivity of the mine waste relative to the ANC rock may have been enhanced because of the overall smaller (higher surface area), and perhaps more reactive mine waste size fractions. The mine waste initially had one-half (>19 mm), 5.7 times greater (< 2mm to > 600µm), and nearly 2 times greater (< 600µm) mass size fractions compared to ANC rock.

### **Sequential Leachate Analyses**

A suite of seven major elements (Mg, Al, P, K, Ca, Ti, and Fe) and ten trace elements (Mn, Ni, Cu, Zn, As, Sr, Mo, Cd, Ba, and Pb) were investigated as part of the sequential leaching study (Yager et al., 2008b, Appendixes, A thru P). Only results for elements Fe-Cu-Zn-As-Pb associated with base metal mineralization in the study area are discussed here. These elements are of interest because of possible contamination that could be released by ANC rocks when the materials are used in mine-waste remediation projects. The suite of samples chosen for sequential leachate studies represents a range of ANC between 9 and 123 kg/t CaCO<sub>3</sub> equivalent and varying whole-rock metal abundances (Yager et al., 2008b, table 8).

The elements released during leaching can be used to evaluate the minerals that might participate in weathering reactions. Each sequential step is designed to react with specific mineral or amorphous phases. In the following section, sequential steps are referred to as

“phases.” The term “phase” in this context refers to the sequential step that has been developed to target a specific mineral species or group, such as carbonates or silicates. Note that all samples were also digested using the four-acid step described in Briggs (2001) to determine totals for each element. Disparities between totals measured from the four-acid step and totals from the seven- and nine-step methods are likely caused by sample inhomogeneity, as only 2-g splits were analyzed by each method. Leachate results for elements in ANC rocks and mine waste are discussed below in order of increasing atomic number. Leachate concentrations referred to in text are in Yager et al., (2008b, Appendixes).

### Iron

Iron has a similar trend as that observed for magnesium (Yager et al., 2008b, Fig. 12) with the most abundant iron present in the crystalline Fe- and Al-oxide phase, followed by the silicate and sulfide leachate phases. A smaller proportion of leachable iron was derived from the sulfide phase (Fig. 7).

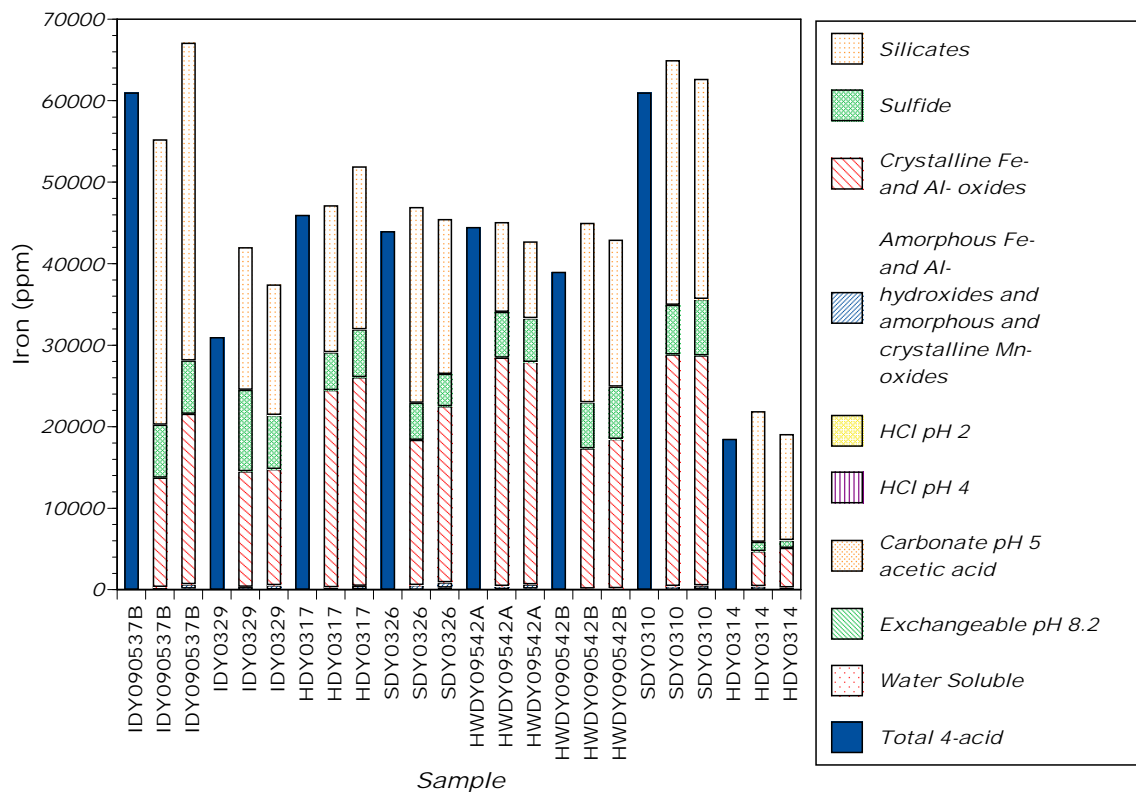


Figure 7. Histogram of whole-rock leachate results for Fe. Total digestion shown by solid blue bar; next histogram bars for each sample are for seven- and nine-step methods respectively.

Small quantities of Fe (< 0.05 wt %) are present in the amorphous Fe- and Al-hydroxide and amorphous and crystalline Mn-oxide phases. The highest concentrations of leachable iron are derived from the most mafic lavas (samples IDY090537B and SDY0310), which have the highest iron abundances (6.4 wt %). The primary sources for leachable Fe are (a) groundmass, (b) the Mg-Fe-Al silicate chlorite (clinochlore) formed after pyroxene, hornblende, plagioclase, and groundmass during propylitic alteration, and (c) magnetite and or titanomagnetite.

### Copper

Copper is derived from several leachate phases indicating that this element is mobile at multiple acidic pH intervals. The sample with the highest Cu concentration (54 ppm) is SDY0310, which was found to contain trace chalcopyrite in Yager et al., (2005). Unit Tpa sample SDY0326 has slightly higher Cu concentrations compared to the other unit Tpa sample HDY0317. The leachate phases that produce the most Cu, while highly sample dependent, include silicate, sulfide, and crystalline Fe- and Al-hydroxide and crystalline Mn-oxide phases (Fig. 8). In general, copper abundances are low and near or below crustal abundances of 68 ppm (Fortescue, 1992).

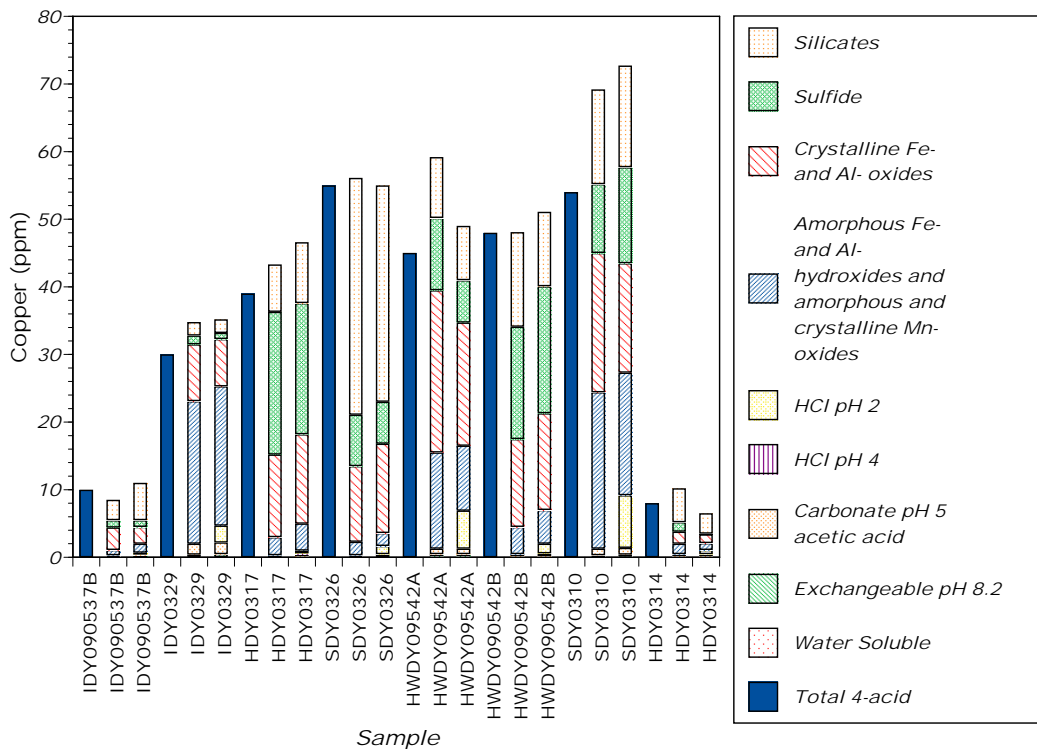


Figure 8. Histogram of whole-rock leachate results for Cu. Total digestion shown by solid blue bar; next histogram bars for each sample are for seven- and nine-step methods respectively. Crustal abundance = 68 ppm.

## Zinc

The crystalline Fe- and Al-oxide, and the amorphous Fe- and Al-hydroxide, and amorphous and crystalline Mn-oxide phases, are host to the majority of zinc (Fig. 9). The silicate and sulfide phases are of secondary importance in most samples. Unit Tsj sample IDY0329 has the highest leachable Zn concentrations (between 0.14 and 0.15 wt %) and a correspondingly high whole-rock Zn concentration (0.1 wt %).

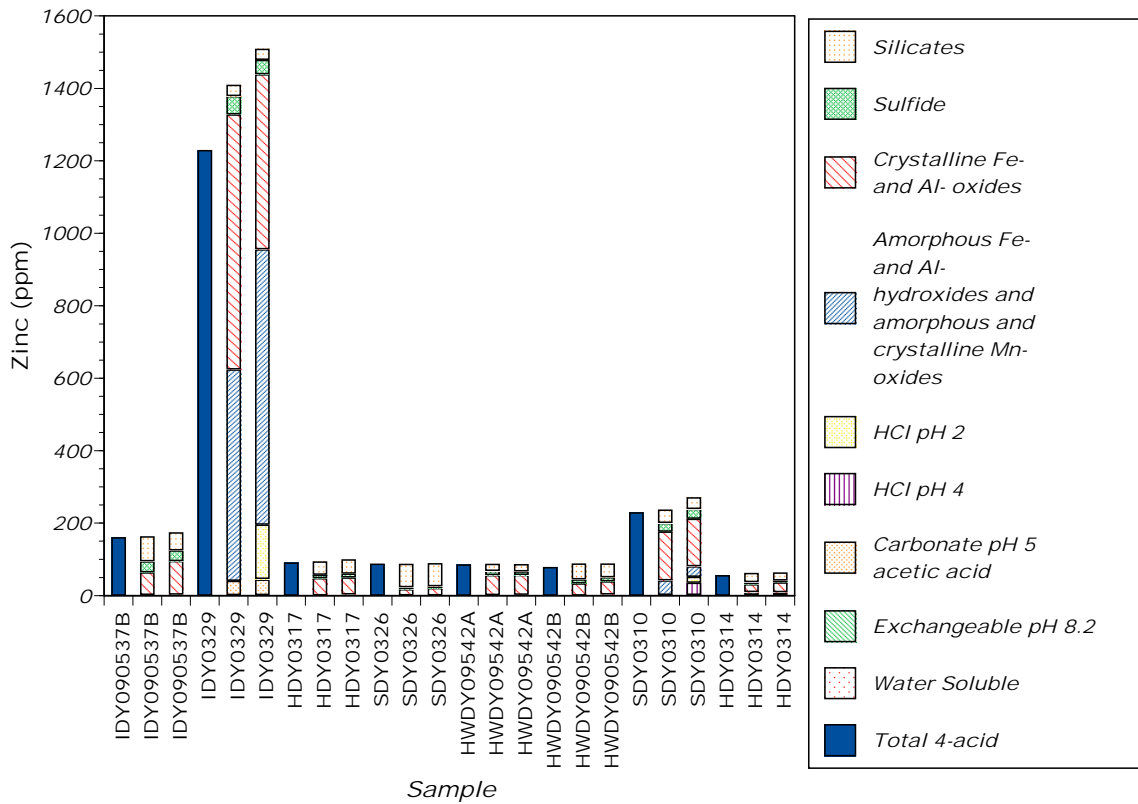


Figure 9. Histogram of whole-rock leachate results for Zn. Total digestion shown by solid blue bar; next histogram bars for each sample are for seven- and nine-step methods respectively. Crustal abundance = 76 ppm.

## Arsenic

Arsenic tends to be concentrated in the silicate and sulfide phases (Fig. 10). The crystalline Fe- and Al-oxide and the amorphous Fe- and Al-hydroxide and amorphous and crystalline Mn-oxide phases are of secondary arsenic abundance. The sample with the highest leachable arsenic (IDY0326) is exposed near the relatively high-As acid-sulfate mineralized system centered near Red Mountain Pass and on Anvil Mountain (Bove et al., 2007a, b).

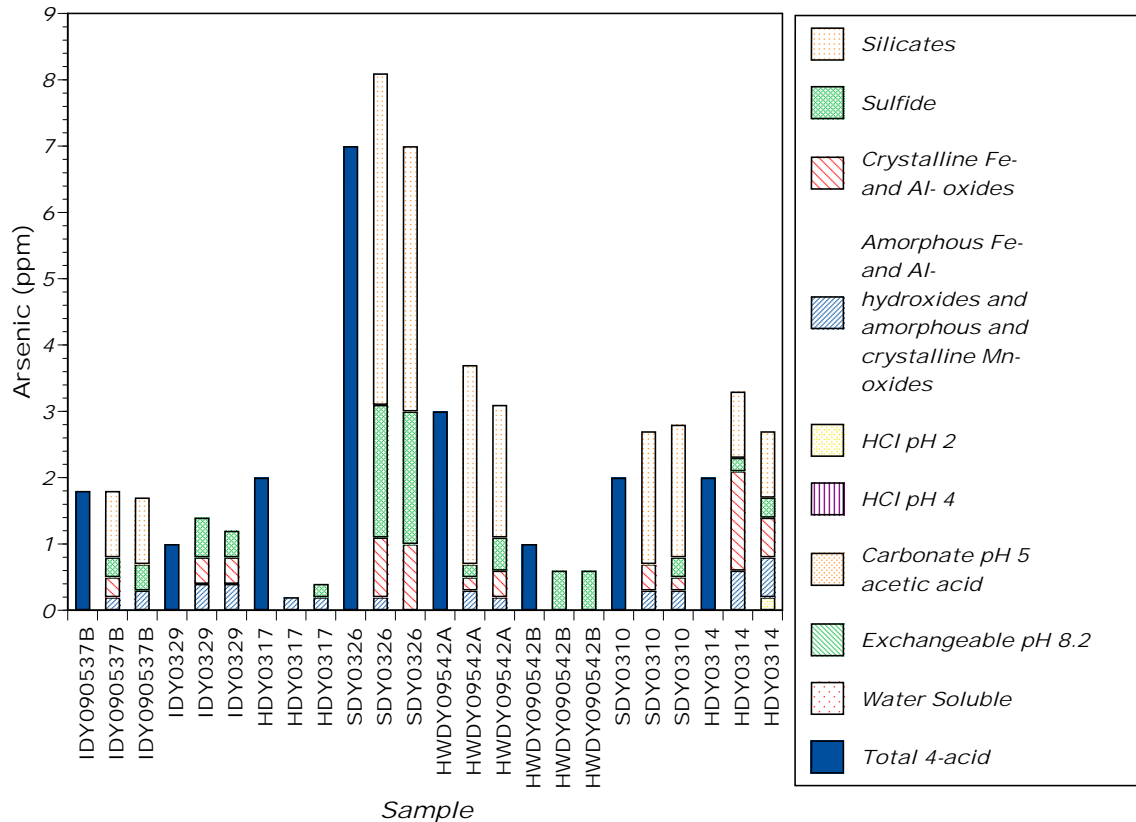


Figure 10. Histogram of whole-rock leachate results for As. Total digestion shown by solid blue bar; next histogram bars for each sample are for seven- and nine-step methods respectively. Crustal abundance = 2 ppm.

### Lead

The phases producing leachable lead are highly variable, with no clear trend being consistently observed between samples (Fig. 11). Sample IDY0329 produced the highest total lead (between 70 and 80 ppm) and has a high pyrite abundance (3 wt %) (Yager et al., 2005, Table 3). No other sulfide minerals were observed in SEM analyses that could be used to identify the source of the Pb. However, sample IDY0329 does have a high (27 wt %) illite concentration based on prior x-ray diffraction analysis (Yager et al., 2005, Table 3), and it is possible that there has been lead substitution for potassium in the illite lattice. Whole-rock concentrations are high (51 ppm) in sample IDY0329 compared with other samples, and leachable lead is approximately proportional with whole-rock lead abundances (Yager et al., 2008b, Table 8).



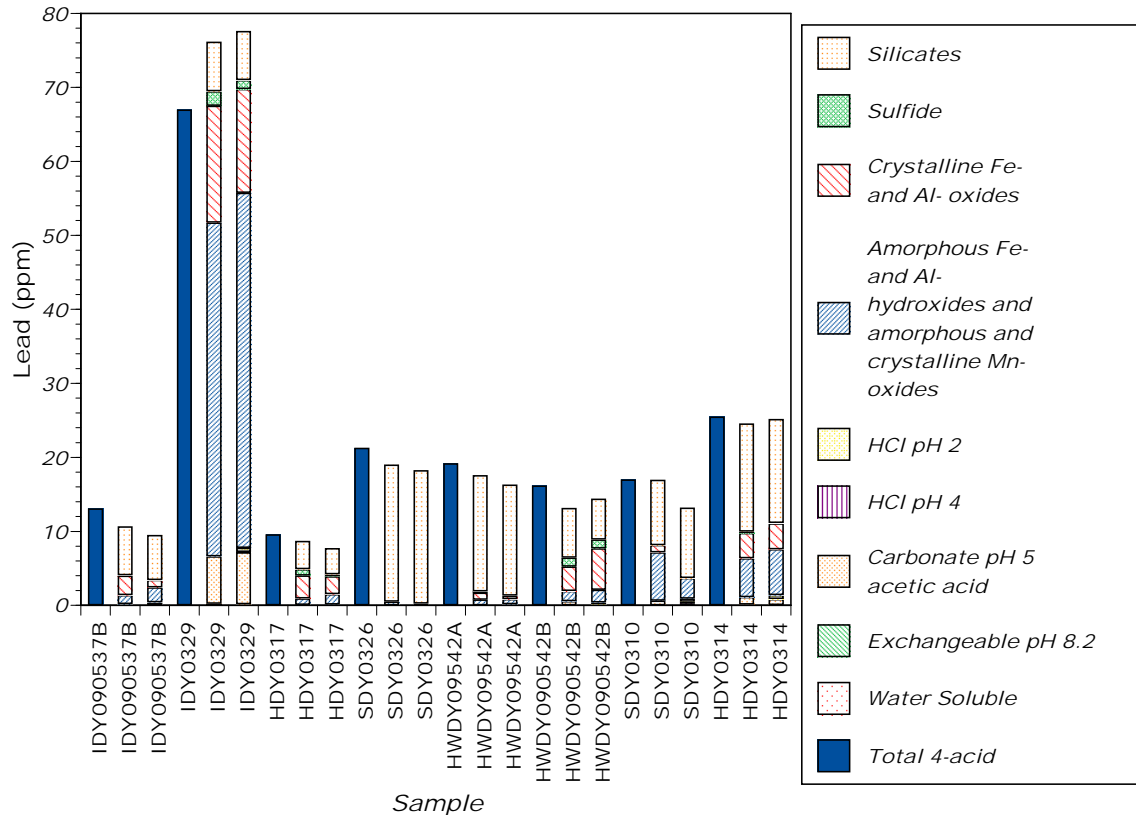


Figure 11. Histogram of whole-rock leachate results for Pb. Total digestion shown by solid blue bar; next histogram bars for each sample are for seven- and nine-step methods respectively. Crustal abundance = 13 ppm.

### Sequential Leachate Results (Grand Mogul Mine Waste)

Sequential leachate analyses were performed on a composite, representative split of Grand Mogul mine waste (Yager et al., 2008b, Appendixes, A thru P). These data are useful for comparing the relative proportions of leachable metals between ANC rocks and mine waste. As with ANC rock samples, only the elements Fe-Cu-Zn-As-Pb associated with base metal mineralization in the study area are discussed here.

### Iron

Iron is concentrated primarily in the silicate, sulfide, crystalline Fe- and Al-oxide, and amorphous Fe- and Al-hydroxide and amorphous and crystalline Mn-oxide phases (Fig. 12A). The mine waste has three times the quantity of leachable Fe in the amorphous Fe- and crystalline Mn-oxide phase (0.15 wt %) compared with ANC rocks (about 0.05 wt %), even though the host ANC rocks have as much as 6 to 7 wt % total Fe. This suggests that the mine waste and derived leachate may be the primary source of Fe in Fe flocculent.

## Copper

Leachable Cu concentrations are elevated in mine waste (500 ppm) compared with ANC rocks (< 80 to about 10 ppm) (Figs. 8, 12C). Most Cu is concentrated in the sulfide and crystalline Fe- and Al-oxide phases with small abundances being concentrated in the silicate phase. Chalcopyrite is the likely source of leachable copper in the mine waste. Copper concentrations are nearly equal or lower between the sulfide and crystalline Fe- and Al-oxide phases for the 7- and 9-step methods. Since primary sulfide minerals are the likely principal source of Cu, this suggests these leachate techniques may underestimate Cu concentrations derived from the sulfide phase.

## Zinc

Zinc concentrations are highly elevated in the mine waste (> 1.5 wt %) (Fig. 12A). Zinc is primarily concentrated in the sulfide phase with the mineral sphalerite (ZnS) being the source of Zn. The other two-leachate phases where Zn was concentrated are the silicate and crystalline Fe- and Al-oxide phases.

## Arsenic

Arsenic abundances are higher by a factor of 6 to 25 in mine waste compared with ANC rocks. Leachable As concentration from mine-waste is about 50 ppm (Fig. 12B); leachable As abundances in ANC rocks range from about 1 ppm to 8 ppm (Fig. 10). The sulfide and crystalline Fe- and Al-oxide phases are host to most of the As. The source mineral for As is not known, although at the low concentrations observed in ANC rocks, arsenic may be dispersed in matrix or in As-bearing pyrite.

## Lead

Lead is concentrated by a factor of 100 to 1,000 in Grand Mogul mine waste compared to ANC rocks. Lead attains a concentration of 1 wt % in Grand Mogul mine waste and is concentrated primarily in the crystalline Fe- and Al-oxide and sulfide phases (Fig. 12A).

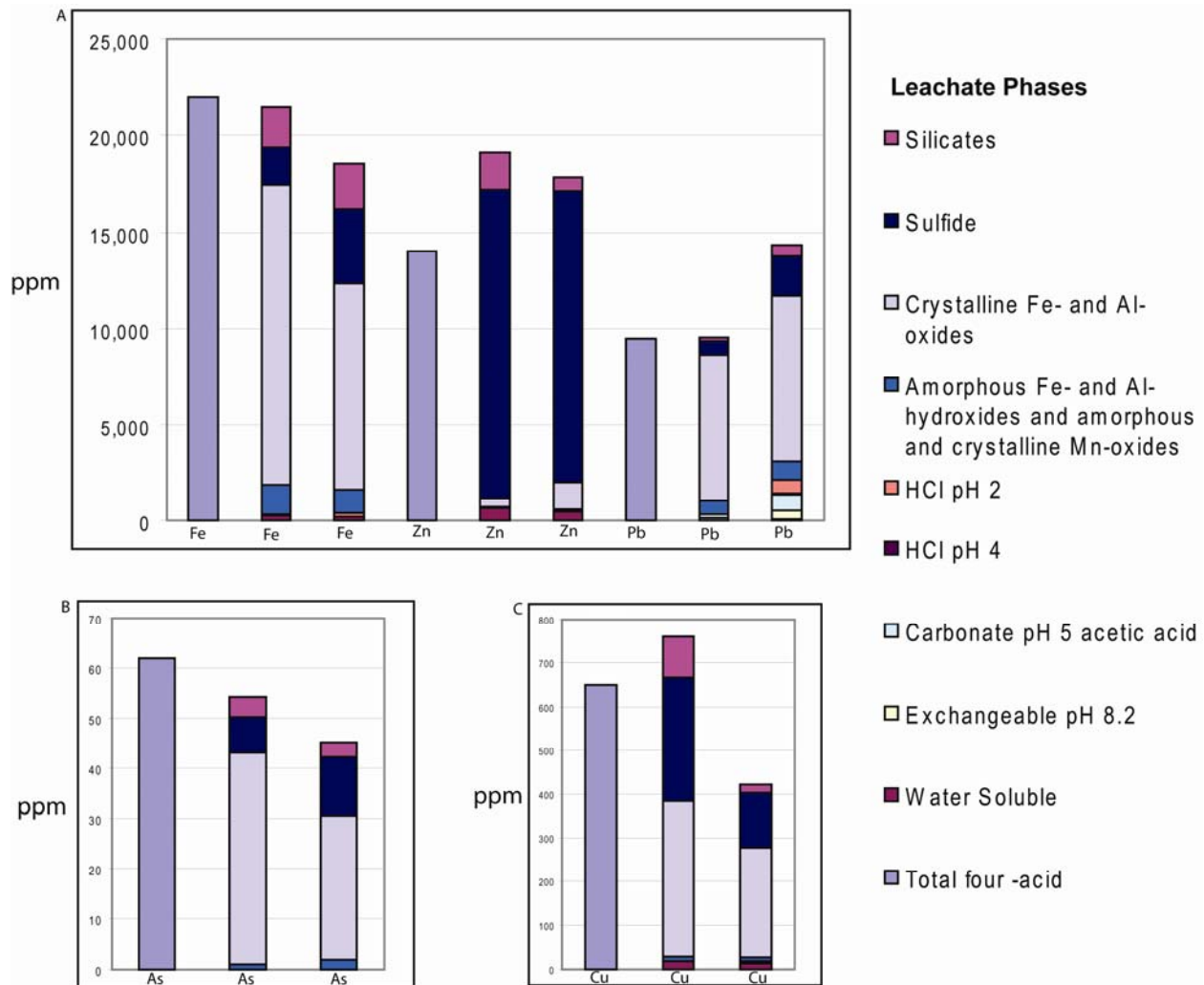


Figure 12. Histogram for Grand Mogul mine waste leachate results for (A) Fe, Zn, Pb; (B) As; and (C) Cu. Total four-acid digestion shown by solid blue bar; next histogram bars for each element are for seven- and nine-step methods respectively.

### Organic carbon contents in volcanic soils

In order to verify the organic carbon contents of soils derived from weathering of propylitically altered volcanic bedrocks studied for ANC, adjacent soils in naturally-reclaimed, undisturbed, and mined areas were also sampled. Information on the carbon contents of non-mining-affected or naturally reclaimed soils is useful to land managers because it provides a soil carbon recovery target goal that may be achieved through reclamation. Our initial geochemical baseline studies indicate that un-reclaimed mine waste can have as little as 0.1 wt % TOC and adjacent naturally reclaimed or non-mining-affected lands can exceed 20 wt % TOC (Yager et al., 2007; 2008a) (Table 6).

TOC abundances in Silverton, Colo., volcanic soils exceed those commonly found in most soils by 1.5 to 5 times (Fig. 13, Table 6). Global soil TOC abundances seldom exceed 5 wt % in the upper 3 cm (Buringh, 1984). Volcanic soils derived from weathering of andesite and basalt bedrocks in the Silverton study area, Colo., Rocky Mountain forests, and other forested areas such as the Sierra Nevada have high TOC values that exceed average global abundances (Rasmussen et al., 2006; Yager et al., 2007, 2008a).

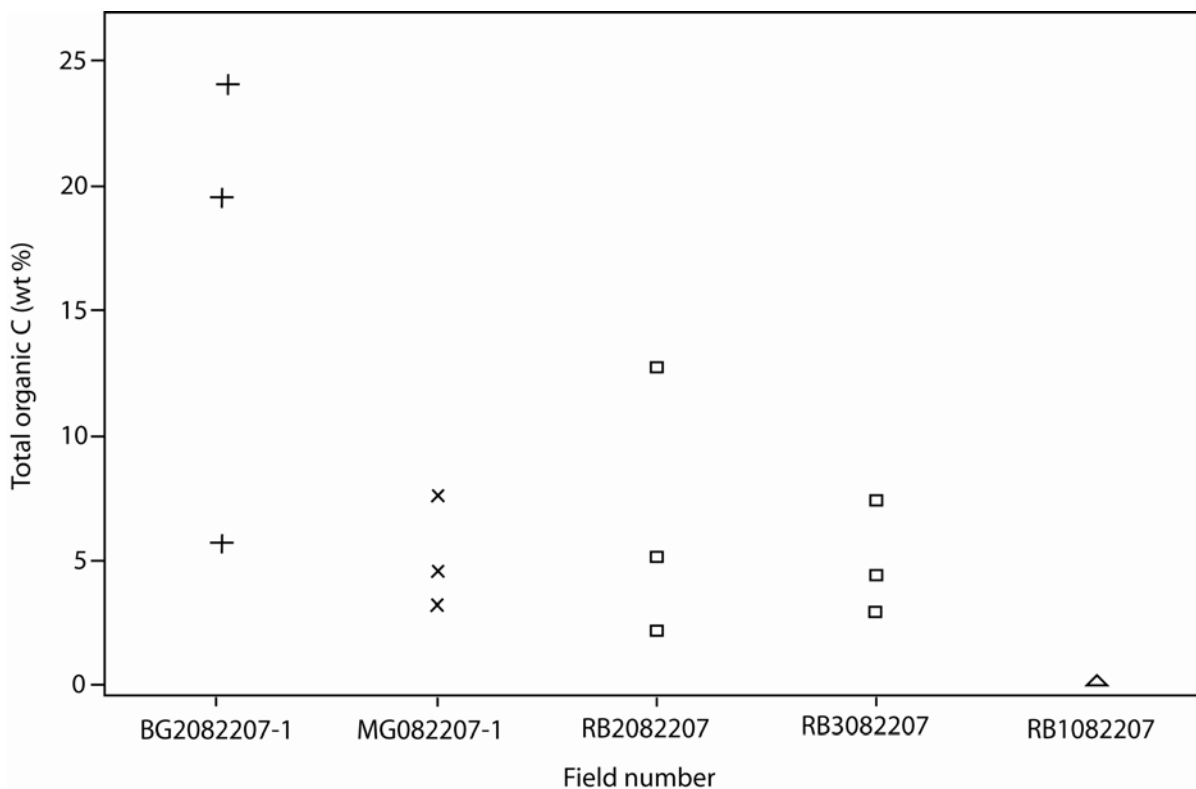


Figure 13. Total organic carbon contents for Silverton Colo., study area soils derived from weathering of propylitically altered bedrocks. Data points represent soil samples collected at 5 cm intervals from A horizon (highest TOC concentrations) to B horizon (lower TOC concentrations). Soils were collected in catchments where Silverton, Colo., ANC rocks were sampled. Global average of A horizon soils is about 4 to 5 wt % (Buringh, 1984). Mine waste, RB1082207 (far right) shown for reference.

Radiocarbon dates on black carbon (charcoal) collected from Silverton, Colo., soil cores range in age from 500 yrs. to 2,360 yrs. (Table 6), (Yager, unpublished data; Yager et al., 2007; 2008a). The historically old radiocarbon dates indicate that part of the soil organic carbon pool is stable, and if left undisturbed, could sequester C for millennia. This is significant because

black carbon may play an important role in the terrestrial C cycle by balancing atmospheric CO<sub>2</sub> released due to land-use disturbance (Seiler and Crutzen, 1980). When black carbon is formed under the optimal temperature conditions and protected in soil aggregates, it can remain non-mineralized and thus store C in a form that will not be easily released to the atmosphere (Liang et al., 2008; Nishimiya, et al., 1998).

Table 6. Total organic carbon analyses for Silverton, Colo., study area catchment soils. Radiocarbon dates determined on charred material from two sites.

Field ID	Site	Interval below surface (cm)	Total Carbon wt %	Radiocarbon Age (Charcoal) ±40 years B.P.
RB1082207-1	Grand Mogul Mine Waste	10 to 16 cm	0.10	n.a.
RB2082207-1	Ross Basin	0 to 5	13.5	n.a.
RB2082207-2		5 to 10	5.37	
RB2082207-3		10 to 15	2.86	
RB3082207-1	Ross Basin	0 to 5	7.25	n.a.
RB3082207-2		5 to 10	3.89	
RB3082207-3		10 to 33	3.13	
MG082207-1	Minnie Gulch	0 to 5	7.56	<b>870</b>
MG082207-2		5 to 10	4.45	
MG082207-3		10 to 25	3.01	
MG082207-4		25 to 40	1.88	
BG2082207-1	Browns Gulch	0 to 5	19.80	<b>2,360</b>
BG2082207-2		5 to 10	24.60	
BG2082207-3		10 to 15	6.16	
BG2082207-4		15 to 40	2.80	
BG2082207-5		40 to 50	1.63	

Total organic carbon by combustion and solid state infrared detection (U.S. Geological Survey); radiocarbon dates on charred material by accelerator mass spectrometry (Beta Analytic)

### Summary and Conclusions

Our studies have identified local igneous bedrocks that can supply both NAP and ANC, depending on rock type and degree of alteration. When propylitically altered rocks with an ANC assemblage of calcite-chlorite-epidote are present in mineralized areas, these bedrocks can supply significant ANC up to 146 kg/ton CaCO<sub>3</sub> equivalent. Instantaneous ANC, acid titration tests were useful in identifying those bedrocks that could supply ANC in the short term. A long-term (6-month duration) reaction vessel test evaluated ANC of propylitized andesite bedrocks.

The reaction vessel experiment has shown thus far that propylitic ANC bedrocks are effective in neutralizing acid generated by sulfide-bearing mine waste over several months duration.

Additional experiments that vary the vessel material configuration, size distribution, as well as wetting and drying intervals could be useful in further testing the long-term ANC effectiveness of propylitic bedrocks. If information on acid producing or neutralizing rock types were available prior to mining, this data could aid in predicting the environmental response of new mining and could be used to address possible acid mine drainage issues initially, rather than after mining ceases. Use of local ANC rock might not only aid in improving acid drainage at mine sites, but could lower a mine operator's carbon emissions footprint and monetary costs by possibly reducing the need to transport ANC material to mine sites.

Sequential leachate experiments were useful in identifying the mineral sources for major- and trace-elements when subjected to fluids of varying pH. The Grand Mogul mine waste was subjected to the four-acid total-digestion and the seven- and nine-step sequential-leaching methods for comparison with ANC material whole-rock sequential-leachate data.

Several trace elements are elevated in mine waste compared to the volcanic rocks: Cu (1 order of magnitude), Zn (1 order of magnitude), As (1 order of magnitude), Pb (2 to 3 orders of magnitude). Iron is also elevated in the mine-waste, amorphous Fe- and crystalline Mn-oxide phase compared to volcanic rocks. Elevated iron in the amorphous-leachate phase may shed light on the primary source of iron flocculent when water, mine waste, and ANC rocks interact. These data suggest that mine waste may be the principal source of amorphous Fe flocculent and leachable metals. In addition, leachable metals are variable in ANC rocks, suggesting that geochemical trace element analysis of ANC rocks targeted for use in remediation is warranted. While it is not surprising that ANC rocks have low contributions of leachable trace element constituents compared to mine waste, the trace element abundances in ANC rocks can exceed crustal abundances for several elements. Of the ANC rocks studied, however, most have low concentrations of leachable constituents, suggesting that 4-acid total digestions are sufficient to adequately characterize these rock types.

Soils derived from weathering of propylitically altered igneous bedrocks have high TOC abundances. Not only do the volcanic soils have high TOC that exceeds global abundances, part of the carbon pool is stable on a millennial time-scale and occurs in the form of black carbon that does not release C to the atmosphere unless disturbed. Additional research on synergistic

mechanisms of C-sequestration is needed to help quantify the natural terrestrial C-sequestration potential of volcanic forest soils. Such research includes C-N fixation in allophanic components of volcanic soils (Woigner et al., 2007), and mineral carbonation reactions, possibly involving dissolution of chlorite species that may permanently sequester carbon. Carbon accounting for mine reclamation projects could be useful to land managers who can use this information as part of a comprehensive land-use carbon management strategy and possibly for future carbon trading that may help to recover a part of reclamation costs. Geochemical baseline information on undisturbed or naturally reclaimed soils may also be used to gauge reclamation recovery potential and success as carbon is reestablished in soils in reclaimed areas, once mining operations cease.

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