

Geophysical, Geochemical, Mineralogical, and Environmental Data for Rock Samples Collected in a Mineralized Volcanic Environment, Upper Animas River Watershed, Colorado



Data Series 595

Cover. A view of Velocity Basin in the Animas River watershed (photograph by David Fey).

Geophysical, Geochemical, Mineralogical, and Environmental Data for Rock Samples Collected in a Mineralized Volcanic Environment, Upper Animas River Watershed, Colorado

By A.E. McCafferty, R.J. Horton, M.R. Stanton, R.R. McDougal, and D.L. Fey

Data Series 595

**U.S. Department of the Interior
U.S. Geological Survey**

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2011

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit <http://www.usgs.gov> or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit <http://www.usgs.gov/pubprod>

To order this and other USGS information products, visit <http://store.usgs.gov>

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:
McCafferty, A.E., Horton, R.J., Stanton, M.R., McDougal, R.R., and Fey, D.L., 2011, Geophysical, geochemical, mineralogical, and environmental data for rock samples collected in a mineralized volcanic environment, upper Animas River watershed, Colorado: U.S. Geological Survey Data Series 595, 13 p.

Contents

Abstract	1
Introduction.....	1
Lithologic Units.....	3
Data Summary	4
Physical Property Data	4
Sample Preparation.....	4
Magnetic Susceptibility.....	4
Electrical Resistivity	5
Density	5
Porosity.....	6
Pore Fluid Conductivity and pH	6
Geochemical Data	6
Sample Preparation.....	6
Mineralogic Analysis by X-Ray Diffraction (XRD).....	6
Wavelength Dispersive X-Ray Fluorescence (WDXRF)	6
Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) and –Mass Spectrometry (ICP-MS).....	7
Total Carbon, Carbonate Carbon, and Sulfur Measurements	7
Mineralogical Data	8
X-Ray Diffraction.....	8
Rock Environmental Property Data.....	9
Net Acid Production.....	9
Acid Neutralizing Capacity.....	9
Geodatabase Description.....	10
References Cited.....	12

Figures

1. Index map of study area	2
2. Geologic units and number of samples collected per unit.....	3
3. Range of volume magnetic susceptibility for all rock types.....	4
4. Range of 1,000-hertz electrical resistivity (measured in a moist state) for all rock types.....	5
5. Range of calcium oxide measured by wavelength dispersion X-ray fluorescence for all rock types sampled	7
6. Range of zinc measured by inductively coupled plasma–atomic emission spectroscopy or –mass spectrometry	7
7. Range of sulfur	8
8. Range of calcite measured by X-ray diffractometry	8
9. Range of net acid production	9
10. Range of acid neutralizing capacity for rock types with less than 10 kg/ton CaCO ₃ net acid production	10

Tables

1. Geologic unit, age, and lithologic description of rocks sampled for this study	3
2. Attribute descriptions for data in the Microsoft Excel spreadsheet and ArcGIS geodatabase	11

Supplemental Files

Animas_samples_WGS84 (Arc/Info geodatabase)	link
Animas_samples_WGS84 (Microsoft Excel spreadsheet)	link
Animas_samples_metadata (XML file)	link

Geophysical, Geochemical, Mineralogical, and Environmental Data for Rock Samples Collected in a Mineralized Volcanic Environment, Upper Animas River Watershed, Colorado

By A.E. McCafferty, R.J. Horton, M.R. Stanton, R.R. McDougal, and D.L. Fey

Abstract

This report provides analyses of 90 rock samples collected in the upper Animas River watershed near Silverton, Colo., from 2001 to 2007. The samples are analyzed for geophysical, geochemical, mineralogical, and environmental rock properties of acid neutralizing capacity and net acid production. The database is derived from both published ($n=68$) and unpublished ($n=32$) data. New for all samples are geophysical measurements of electrical resistivity, density, and porosity. Rock samples were acquired from 12 geologic units that include key Tertiary volcanic and plutonic lithologies, all with varying degrees of alteration.

The purpose of this study is to

- provide a comprehensive and complete record of U.S. Geological Survey rock samples collected and similarly analyzed in the upper Animas River watershed for various physical, chemical, and geoenvironmental properties;
- provide measurements of geophysical rock properties of lithologic units to establish ground truth with respect to watershed-scale airborne magnetic and electrical survey data;
- use the data to interpret the airborne geophysical anomalies to characterize rocks in terms of acid neutralizing capacity or net acid production; and
- provide measurements to study the geochemical, mineralogical, and geophysical characteristics of rocks having weak to extreme degrees of alteration and to develop an understanding of how these characteristics change with alteration type.

Data are provided in two digital formats: an Arc/Info geodatabase and a Microsoft Excel spreadsheet.

Introduction

The study area covers the upper Animas River watershed, located north of Silverton in the rugged San Juan Mountains of southwest Colorado (fig. 1). Geologically, the study area consists of a Precambrian crystalline basement overlain by Paleozoic to Tertiary sedimentary and volcanic rocks. Two Tertiary-age caldera structures are present, the San Juan caldera and the younger Silverton caldera (Steven and Lipman, 1976), which are intruded by granitic rocks on the southern caldera margins. Formation of the calderas created ring structures that acted as conduits for intense hydrothermal alteration and mineralization. All the rocks in the area are hydrothermally altered or mineralized by hydrothermal alteration. Detailed information on the geologic setting and alteration assemblages is provided in Bove and others (2007).

The area has a rich mining history that began when significant gold deposits were first discovered near Silverton in the 1870s. Subsequent decades saw other mines producing silver, lead, zinc, and copper (Church and others, 2007). The extension of the Rio Grande railroad line from Durango to Silverton in 1882 resulted in the staking of thousands of mining claims. Ore production at various levels continued until 1991 when the Sunnyside Mine was closed (Jones, 2007). Many of the claims and mines are now abandoned and located on public land managed by the U.S. Bureau of Land Management, the U.S. Forest Service, and governmental agencies within the State of Colorado. These agencies are now charged with remediating abandoned mine sites, located on public lands, that require onsite remediation or disposal of mine waste rock and tailings.

The upper Animas River watershed has been the site of numerous U.S. Geological Survey (USGS) studies over the last decade (Church and others, 2007). The studies focused on a wide range of applications with the purpose of understanding the natural and anthropogenic effects of metals and minerals on water quality and ecosystem health. Much of what drives

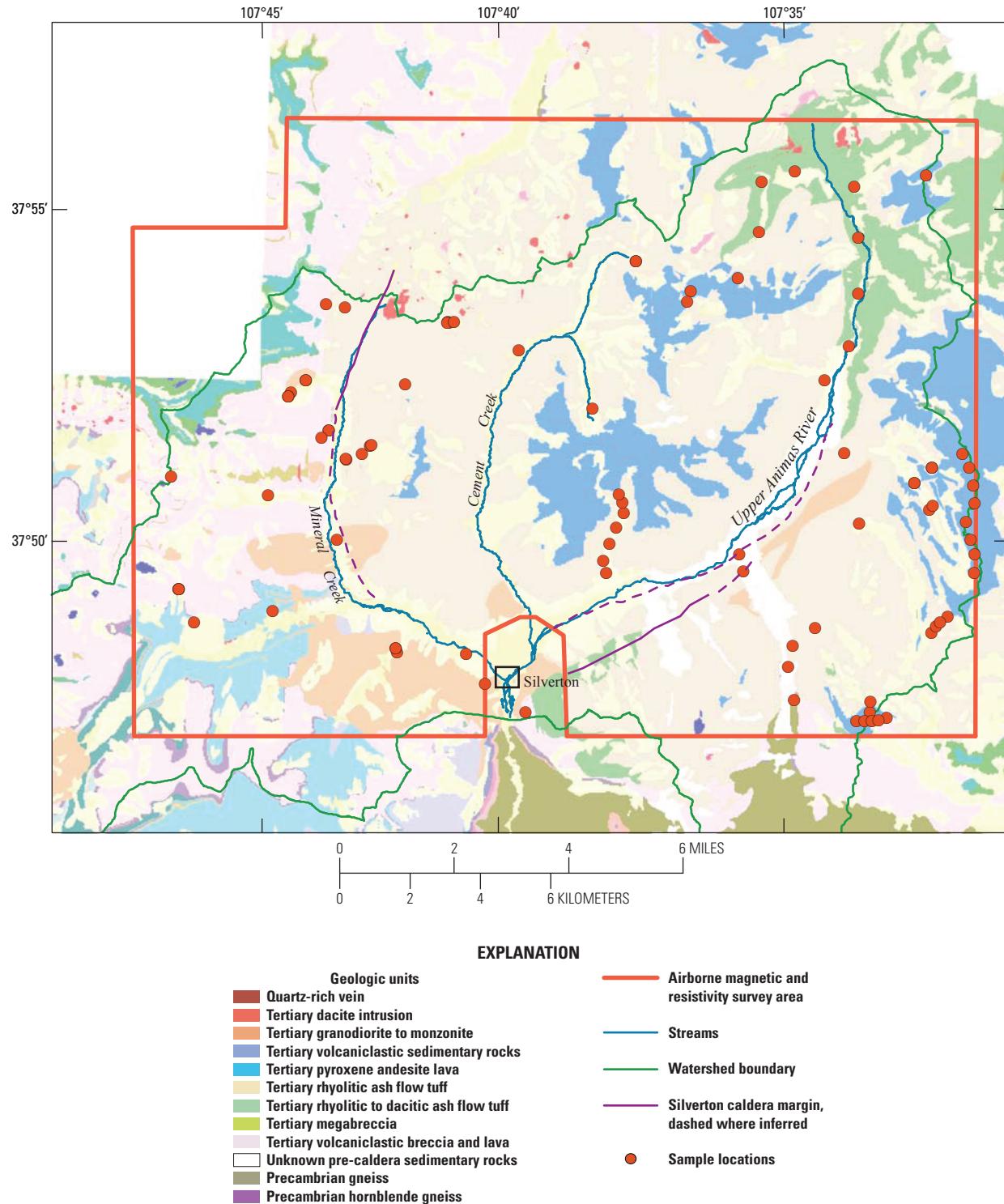


Figure 1. Index map of study area. Geology after Yager and Bove (2002). Descriptions of the geologic units sampled are given in table 1.

the quality of surface water and groundwater in the study area is the weathering of mineral assemblages formed from extensive hydrothermal alteration processes. The alteration has affected the original mineralogy of all the volcanic and plutonic rocks in the study area. The presentation of data in this report is to further the previous studies by improving the understanding of how the alteration of mineral assemblages might be shown through airborne geophysical anomalies and, ultimately, how we can use the airborne geophysical data to map a rock's ability to buffer or produce acidic waters on a watershed scale.

Studies that used data collected from 2001 to 2004 (McCafferty and others, 2006) determined that altered parts of specific lithologies provided significant acid neutralizing capacity and, in addition, have characteristic magnetic anomaly signatures. In contrast to previous studies that included analyses of samples collected from 2001 to 2005 (Yager and others, 2005; Yager and others, 2008), this report includes new electrical resistivity measurements for the majority of samples. Consequently, the data in this report provide an additional geophysical parameter, electrical resistivity, so that airborne resistivity data, collected in conjunction with the airborne magnetic data, can also be evaluated in the context of the geoenvironmental characteristics.

Lithologic Units

Rock samples were collected from bedrock in geologic units that contain most of the rocks exposed in the upper Animas River watershed. Sample locations were restricted to the area covered by an airborne magnetic and resistivity survey (fig. 1) flown over the study area (Smith and others, 2004). Individual geologic units that were targeted for sampling had undergone various types of hydrothermal alteration from propylitic to sericitic. Lithologic units were each sampled for a range of alteration types based on information provided from

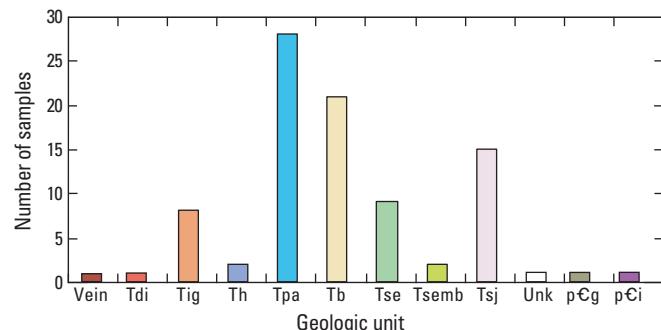


Figure 2. Geologic units and number of samples collected per unit. Descriptions of the geologic units are given in table 1. (Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; pCg, Precambrian gneiss; pCi, Precambrian hornblende gneiss)

field and remote sensing mapping (Bove and others, 2007). Samples were also collected along traverses where airborne geophysical signatures changed over an individual rock unit, and samples were collected from the same lithologies from both within and outside the Silverton Caldera margins.

Twelve geologic units were sampled in the upper Animas River watershed and include volcanic and plutonic rocks of Precambrian to Tertiary age that are exposed throughout the study area (table 1). The greatest number of samples was collected in the Tertiary Burns lavas and in the pyroxene andesite rocks of the Silverton Volcanic rocks (fig. 2). Early studies (Yager and others, 2005) indicated these two geologic units provided significant acid neutralizing capacity. Subsequent sampling focused on collecting more samples to better represent these two geologic units, which form the largest volume of exposed rock in the study area.

Table 1. Geologic unit, age, and lithologic description of rocks sampled for this study. Geologic descriptions after Yager and Bove (2002).

Geologic unit	Lithology	Number of samples
vein	Quartz-rich vein	1
Tdi	Tertiary dacite intrusion	1
Tig	Tertiary granodiorite to monzonite	8
Th	Tertiary volcaniclastic sedimentary rocks of the Silverton Volcanic rocks	2
Tpa	Tertiary pyroxene andesite lava; Member of the Silverton Volcanic rocks	28
Tb	Tertiary rhyolitic ash flow tuff, Burns Formation of the Silverton Volcanic rocks	21
Tse	Tertiary rhyolitic to dacitic ash flow tuff; Eureka Member of Silverton Volcanic rocks	9
Tsemb	Tertiary megabreccia consisting of andesitic to dacitic blocks encased in ash flow tuff; Eureka Megabreccia Member of the Silverton Volcanic rocks	2
Tsj	Tertiary volcaniclastic breccia and lava; San Juan Volcanic rocks	15
Unk	Unknown pre-caldera sedimentary rocks	1
pCg	Precambrian gneiss	1
pCi	Precambrian hornblende gneiss; Irving Formation tailings	1

Data Summary

Geophysical rock properties measured include magnetic susceptibility, electrical properties, density, porosity, and pore fluid conductivity. Geochemical data include individual elemental analyses for 32 elements measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) or inductively coupled plasma–mass spectrometry (ICP-MS), major-element oxide analyses by wavelength dispersion X-ray fluorescence (WDXRF) instrumentation, total carbon and total sulfur analyses by combustion, and carbonate carbon analysis by coulometric titration. Semi-quantitative analyses of key mineral assemblages were determined by X-ray diffractometry (XRD). The environmental property, net acid production (NAP), was determined by digesting powdered material with hot hydrogen peroxide and titrating the resulting slurry with dilute sodium hydroxide. Another environmental property, acid neutralizing capacity (ANC), was determined using alkaline titration methods. Details specific to methods used are provided in the following sections.

Physical Property Data

Sample Preparation

Samples were prepared for measurements of magnetic susceptibility (MS), electrical resistivity, density, and porosity from cores or slabs of field samples. Cylindrical cores 1 inch (in) (2.54 centimeters [cm]) in diameter and approximately 1 inch in length were drilled from field samples using a 1-in-diameter diamond drill core bit. Core ends and slabs were trimmed with a trim saw and then dressed on a flat lapping wheel to remove cut marks. Slabs were cut on a trim saw and trimmed surfaces were dressed on a flat lapping wheel to remove cut marks. Clean water was used as the cutting and drilling fluid to minimize sample contamination and alteration of the sample's physical properties.

All physical rock property data are presented in terms of volume. For the cores, volume was calculated by multiplying the core's length in centimeters by πr^2 . Because of the irregular edges of a rock slab, a simple length \times width \times height volume calculation for the slabs was not sufficient. Instead, the volume of the slabs was determined by calculating the areas of the flat sides of the slab through digital scanning, then taking the geometric mean of the two areas and multiplying by the thickness of the slab.

Magnetic Susceptibility

Magnetic susceptibility is a quantitative measure that determines the presence of ferrimagnetic minerals in rocks and soils. In the samples we collected in the Animas River watershed, the magnetic susceptibility is almost entirely related to the abundance of the mineral magnetite. Other magnetic minerals such as pyrrhotite, maghemite, and ilmenite also produce measurable magnetic susceptibility but are scarce or not present in rocks exposed in the study area.

Magnetic susceptibility (MS) was measured for all samples using a Sapphire susceptometer. Samples were measured in a 0.1-nanotesla (nT) induction at a low frequency of 600 hertz (Hz) (MSlf, MS at low frequency) and high frequency of 6,000 Hz (MShf, MS at high frequency). For each sample, the MS value was determined as the arithmetic mean of four measurements. Mean MS values from the 600 Hz measurement in electromagnetic units (emu) are provided in this report. Each sample MS was divided by its core's volume (in cubic centimeters [cm^3]) and reported here as volume susceptibility, in the centimeter-gram-second (CGS) system of units in emu/cm^3 (fig. 3).

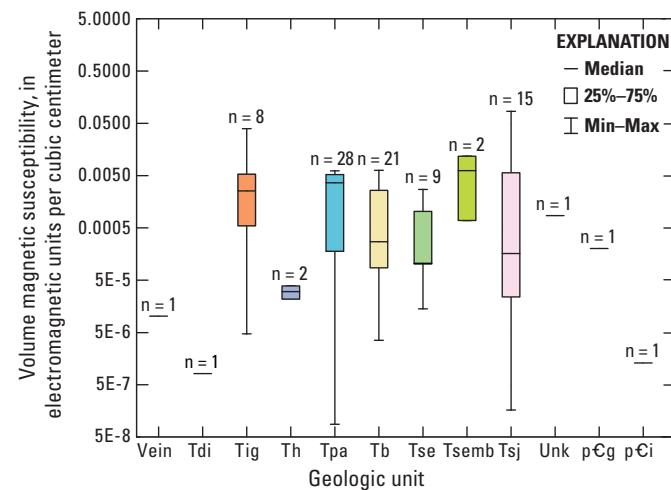


Figure 3. Range of volume magnetic susceptibility (in emu/cm^3) for all rock types. Descriptions of the geologic units are given in table 1. (emu, electromagnetic unit; cm^3 , cubic centimeters; min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; p€g, Precambrian gneiss; p€i, Precambrian hornblende gneiss)

Electrical Resistivity

Electrical resistivity is defined as a measure of how strongly a material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electrical charge. The International System of Units (SI) of electrical resistivity is the ohm meter ($\Omega \cdot \text{m}$), a measure of a rock's ability to conduct an electrical current.

Electrical properties of samples were measured using an inductance-capacitance-resistance (LCR) meter over a frequency range of 100 Hz to 100 kilohertz (kHz). This frequency range spans the operating frequency of many sensors used in airborne, surface, and borehole geophysical applications. The samples were measured in three different hydration states: dry, moist, and saturated. Sample resistance was measured using a Hewlett Packard HP4274A LCR meter, which has a frequency range of 100 Hz to 100 kHz. The HP4274A was programmed to measure resistance in a parallel circuit mode. Each recorded resistance value is an average of 10 repeat measurements. The test signal voltage was 800 millivolts rms (root mean square). At the beginning of each measurement session, the residual capacitance, inductance, and resistance of the test leads and sample holder were measured and then compensated for using the HP4274A zero offset function (Hewlett Packard, 1979).

The LCR meter was computer controlled through a Hewlett-Packard Interface Bus using an unpublished LabView program (contact USGS Crustal Geophysics and Geochemistry Science Center for more information). The program collects LCR measurements at user specified frequencies and stores the data for later processing. The electrical property data were collected over a period of several years. During this time, several different instrument configurations were used. Resistance was always measured, and phase measurements were also collected in some cases.

A two-electrode measurement was used for electrical resistivity measurements in this study (fig. 4). The samples were bar-clamped between a pair of metal foil electrodes. The electrodes consist of metal foil backed by a thin rubber pad on a thick plastic or ceramic tile. The metal foil, typically aluminum, makes electrical contact with the sample and provides a means to connect instrument leads to the sample. The rubber pad allows the metal foil to conform to the trimmed face of the sample. The plastic or ceramic tile insulates the electrodes from the bar clamp and provides a flat, rigid surface that evenly distributes clamping pressure over the electrode-sample interface. The bar clamp generates approximately 200 pounds of clamping pressure distributed over the electrode-sample contact area. Typically one clamp is used for relatively small samples of a 1- to 2-in-diameter core. Multiple clamps may be used for larger samples.

The measured resistance is dependent on the size and shape of the sample. In order to compare samples of different sizes, resistance measurements are converted to resistivity. Resistivity is an intrinsic material property, independent of sample size or shape. Resistance measurements are converted

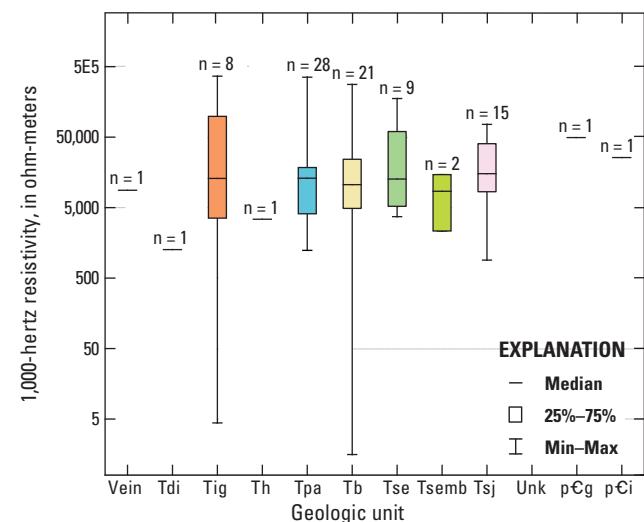


Figure 4. Range of 1,000-hertz electrical resistivity (measured in a moist state) for all rock types. “Unknown” rock type samples not measured. Descriptions of the geologic units are given in table 1. (min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; pEg, Precambrian gneiss; pCi, Precambrian hornblende gneiss)

to resistivity by applying a geometric correction which includes the area of electrode contact and distance between electrodes:

$$\rho = \frac{Ra}{d} \quad (1)$$

where

ρ is the resistivity in ohm meters,
 R is the measured resistance in ohms,
 a is the electrode area in square meters, and
 d is the electrode separation in meters.

Density

Density is a physical property defined as mass per unit volume. The more mass an object contains in a given space, the denser it is. The density of the core samples in this study was determined from weight (mass) and volume measurements. The sample weight was determined using an analytical balance, whereas the sample volume was determined using the buoyancy method (Hunt and others, 1979). For each sample, three density measurements were made at different hydration states; dry, moist, and saturated samples were prepared and their weights measured.

6 Geophysical, Geochemical, Mineralogical, and Environmental Data for Rocks in a Mineralized Volcanic Environment

For the dry density measurement, samples were placed in a vacuum oven at 50°C and 15 pounds per square inch (psi) vacuum pressure. The samples were removed and weighed every 24 hours to determine whether the weights were changing. Once a sample weight became constant, the sample was assumed to be dry and the dry weight was recorded. Typically, a sample would dry in 48 hours.

For the moist density measurement, the dry samples were placed in a desiccator along with a beaker of deionized water. The atmosphere inside the desiccator hydrated the samples at approximately 100 percent relative humidity at room temperature and pressure. The samples were allowed to absorb the moisture for 48 hours and then were weighed to determine their moist weight.

For the saturated density measurement, the samples were placed in individual glass beakers filled with deionized water. To maximize the rock-to-water ratio, only enough deionized water was added to completely cover the sample. The beakers were placed in a vacuum chamber at 15 psi vacuum pressure. As the vacuum was applied, the samples vented air trapped in pore spaces as bubbles. The vacuum was cycled from 0 to 15 psi several times until the bubbling stopped. The samples were kept under vacuum for 36–48 hours, then removed from the beakers and weighed to determine their saturated weight.

Immediately after being weighed, the volume of each saturated sample was measured using the buoyancy method. The samples are suspended by a thin wire and immersed into a beaker of water, the volume being determined by the weight of water displaced. For the volume determination, the saturated samples were used because a saturated sample cannot adsorb water into pore spaces when immersed, which would result in an error in the volume measurement.

Porosity

The amount of water present in a sample's pore space was determined by subtracting the dry sample weight from the saturated weight. If one assumes that water has a density of 1 gram per cubic centimeter (g/cm^3), then the pore space water weight is equivalent to the pore space volume. Thus, the weight difference divided by the volume is the pore space fraction.

Pore Fluid Conductivity and pH

The water remaining in the beakers after saturating the samples contains ions dissolved from the samples. This water has a composition similar to the sample's pore space fluid; however, it may not have the same concentration as the pore fluid. The physical properties of pore fluids are important factors in controlling the observed electrical properties of the rock samples. Therefore the conductivity, pH, and volume of the water remaining in each beaker were measured to gain

basic information regarding the sample's pore fluid. The conductivity and pH were measured using Horiba B-173 and B-213 meters, respectively. Water volume was measured using a graduated cylinder.

A sample's rock-to-water ratio can be used to normalize the conductivity and pH measurements for samples prepared in different volumes of water. For the conductivity and pH data presented here, two values are given, the measured value and the normalized value. The normalized value is the measured value divided by the sample's weight to water volume (grams per milliliter, g/mL).

Geochemical Data

Sample Preparation

Rock samples were crushed using a mechanical jaw crusher into fragments about 1 cm in size. They were then ground in a vertical pulverizer to -140 mesh (<105 micrometers [μm]) for most of the geochemical analyses. A subsample was further reduced in particle size to -200 mesh (<74 μm) in an agate shatterbox for net acid production determination.

Mineralogic Analysis by X-Ray Diffraction (XRD)

For X-ray diffraction analysis, a 20-percent (by weight) addition of an internal standard was added to each sample. Internal standard materials include corundum, zincite, or rutile and are selected according to which material yields the least interference with the sample mineralogy. Three grams of the sample/internal standard powder were placed in a McCrone Micronizing mill with 15 mL of 2-propanol and processed for 4 minutes (min), which reduced the particle size to approximately 1 micron. The slurry was poured onto a glass watch dish to dry overnight, and then the powder was collected for X-ray analysis (William Benzel, USGS, written commun., 2011).

Wavelength Dispersive X-Ray Fluorescence (WDXRF)

Rock samples were analyzed for ten major element oxides by the method described by Taggart and Siems (2002). A 0.80-gram portion of the powdered material is ignited at 925°C. After cooling, a charge of lithium metaborate (LiBO_2) is added, and then the mixture is fused at 1,125°C. The resulting fusion disc is analyzed by wavelength dispersive X-ray fluorescence for the k-alpha lines of the elements of interest. Figure 5 shows the range of CaO for all samples.

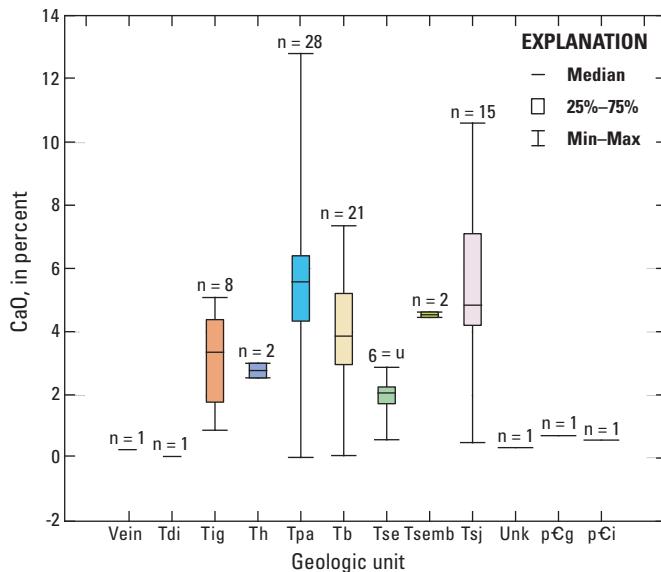


Figure 5. Range of calcium oxide (CaO, in percent) measured by wavelength dispersion X-ray fluorescence for all rock types sampled. Descriptions of the geologic units are given in table 1. (Min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; p€g, Precambrian gneiss; p€i, Precambrian hornblende gneiss)

Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) and –Mass Spectrometry (ICP-MS)

The powdered rock samples were digested by weighing out 0.2 g of powder and applying a mixed-acid procedure consisting of hydrochloric, nitric, perchloric, and hydrofluoric (HCl, HNO₃, HClO₄, and HF) acids, with a final dilution factor of 1:100. The resulting solutions were then analyzed by either ICP-AES or ICP-MS (Briggs, 2002; Briggs and Meier, 2002). This four-acid dissolution technique is effective in completely dissolving most minerals, including silicates, oxides, and sulfides, but it only partially dissolves resistant minerals such as zircon, spinels, and tin oxides. Previous investigations support the completeness of this digestion (Church and others, 1987; Wilson and others, 1994), and it is well suited to the samples of this study. The results are shown in figure 6.

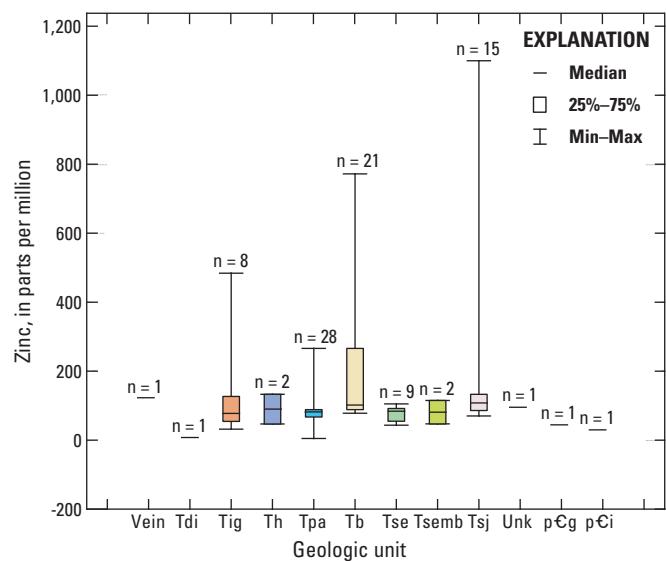


Figure 6. Range of zinc (in parts per million) measured by inductively coupled plasma–atomic emission spectrometry or –mass spectrometry. Descriptions of the geologic units are given in table 1. (min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; p€g, Precambrian gneiss; p€i, Precambrian hornblende gneiss)

Total Carbon, Carbonate Carbon, and Sulfur Measurements

Rock samples were also analyzed for total carbon, carbonate carbon, and total sulfur. The total carbon was determined by combustion (Brown and Curry, 2002a), where a 0.2-g sample of the -140 mesh powder is heated to 1,350°C in a furnace to oxidize all forms of carbon to carbon dioxide, which is then measured using a solid state infrared detector. Carbonate carbon is determined by a coulometric titration (Brown and others, 2002). The sample is treated with hot 2N perchloric acid, and the evolved carbon dioxide is passed through a solution of monoethanolamine, where it is quantitatively absorbed. The solution is then coulometrically titrated.

Total-sulfur analyses were determined (fig. 7) by combustion (Brown and Curry, 2002b), where a 0.25-g sample of the -140 mesh powder is mixed with 1 g of vanadium pentoxide flux. The sample is combusted in an oxygen atmosphere at 1,350°C where the sulfur is oxidized to sulfur dioxide gas, which is then measured by a solid state infrared detector.

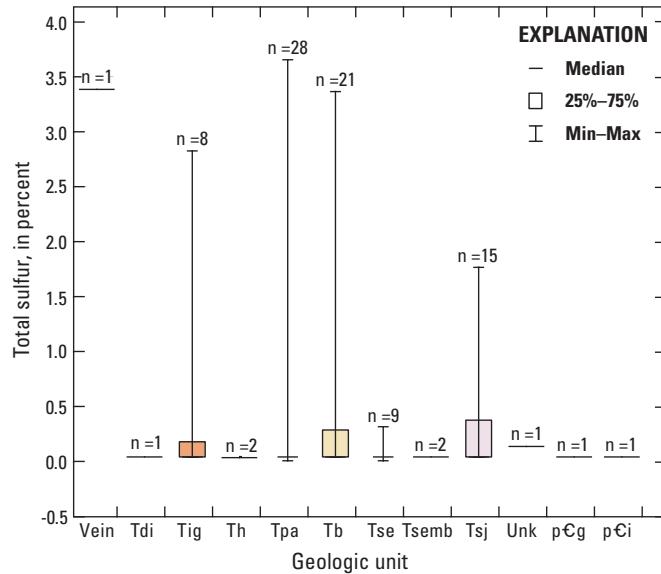


Figure 7. Range of sulfur (in percent). Descriptions of the geologic units are given in table 1. (min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; p€g, Precambrian gneiss; p€i, Precambrian hornblende gneiss)

Mineralogical Data

X-Ray Diffraction

Mineral phases identified for samples collected from 2001 to 2005 are described in Yager and others (2005) and Yager and others (2008). Identification of mineral phases was done for samples collected during the 2006 and 2007 field seasons with Material Data Inc. (MDI) Jade (version 9.1) search-match software using the International Centre for Diffraction Data's "2009 PDF-4" and National Institute Standards and Technology and Fachinformationszentrum Karlsruhe cooperatively developed Inorganic Crystal Structure Database. Semi-quantitative mineral estimates were calculated using MDI Whole Pattern Fit software, which simultaneously calculates a whole pattern fit and a Rietveld refinement of the minerals. Reference minerals are selected from the database, some of which are "structure"

references that represent perfect crystals of the mineral and other entries are more typical mineral specimens. Each card contains a full crystallographic description of the mineral. A calculated model of the observed pattern is produced by non-linear, least-squares optimization. The calculations, performed by the software, involve the application of various parameters to improve the fit of the model to the observed data. Modeling parameters include background reduction, profile fitting, and lattice constants. The software iterates and minimizes a residual error between the calculated X-ray diffraction pattern from the selected references in comparison to the measured scan of the sample. All data were normalized to 100 percent based on the identified minerals. A full description of the Whole Pattern Fit algorithm is available from MDI (William Benzel, USGS, written commun., 2011). The results of calcite concentration in samples are shown in figure 8.

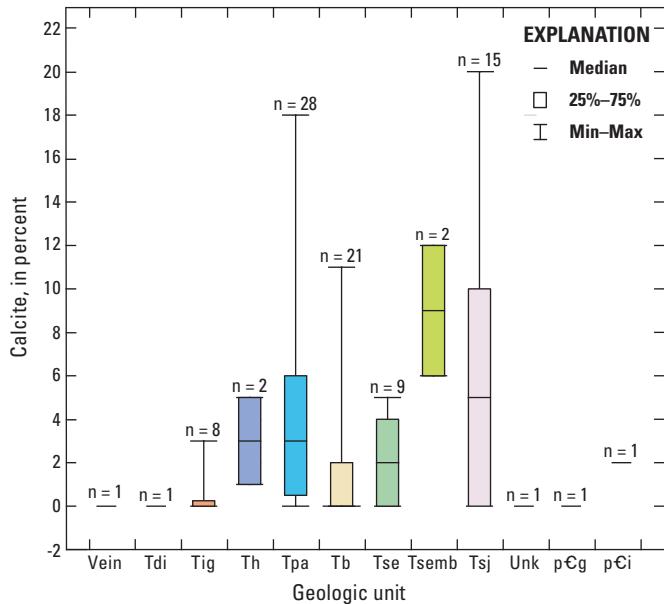


Figure 8. Range of calcite (in percent) measured by X-ray diffractometry. Descriptions of the geologic units are given in table 1. (min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; p€g, Precambrian gneiss; p€i, Precambrian hornblende gneiss)

Rock Environmental Property Data

Net Acid Production

The Net Acid Production test (NAP) was developed as a screening tool to determine acid-generating potential of mine-waste materials (Lapakko and Lawrence, 1993). The test utilizes 100 mL or more of a hot 30-percent hydrogen peroxide solution (H_2O_2) applied to 1.0 gram of -200 mesh ($<74 \mu m$) powdered sample to oxidize sulfide and possibly other minerals to create sulfuric acid. This acid subsequently reacts with other phases present that, depending on their abundance, partially neutralize the acid. Such phases include carbonate minerals and some silicate minerals such as chlorite or epidote. The resulting solution, if still acidic, is titrated with dilute (0.1 or 0.01 N) sodium hydroxide (NaOH) to a pH of 7.0 to determine the net acidity. The calculated result refers to the amount of calcium carbonate equivalent, in kilogram (kg)/ton, needed to neutralize a material to a pH of 7.0. Because a hot, strong oxidizer is used, this method provides an upper limit for the net acid-generating potential.

Net acid production was calculated for the samples (fig. 9) and was used as an initial screening tool prior to measuring acid neutralizing potential. In samples where NAP values exceeded 10 kg/ton $CaCO_3$, it was deemed that these samples would not have sufficient ANC to provide significant buffering to acidic waters. Hence, only those samples with less than 10 kg/ton $CaCO_3$ NAP were measured for ANC.

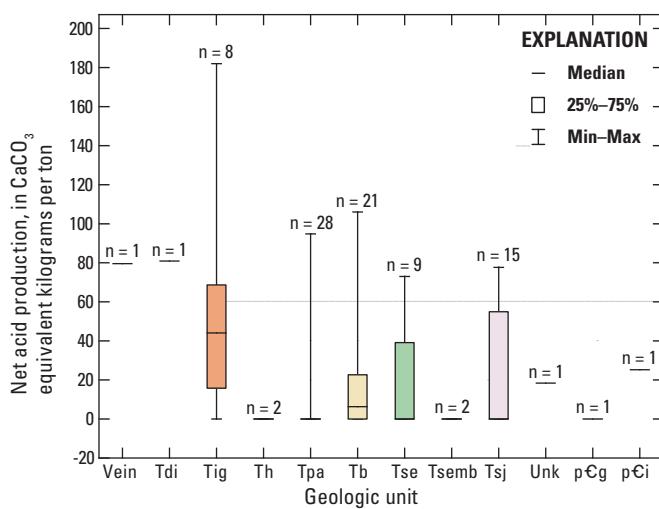


Figure 9. Range of net acid production. Descriptions of the geologic units are given in table 1. ($CaCO_3$, calcium carbonate; min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcaniclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcaniclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; pEg, Precambrian gneiss; pEi, Precambrian hornblende gneiss)

Acid Neutralizing Capacity

Acid-neutralizing capacity (ANC) is the total alkalinity contributed by mineral species undergoing dissolution during an acid titration. Thus, ANC and the resultant total alkalinity are measures of the potential of the rock (that is, its mineral components) to buffer aqueous acid species. Because the ANC is initially “confined” within the solid rock and not measurable until the minerals react with acid, the ANC parameter is often called the acid neutralizing potential (ANP). The purpose of the ANC determinations was to identify rock samples present in the study area that had the capacity (potential) to neutralize acid solutions generated from the weathering of sulfide minerals, primarily FeS_2 , that are also abundant in many rocks of the upper Animas River watershed.

The most important mineral contributing to ANC is calcite ($CaCO_3$). Calcite is present at up to 20 weight percent (wt. %) in propylitically-altered rocks that are found in most areas of the upper Animas River watershed. Another important mineral is chlorite (up to 25 wt. % in some rocks), which can provide ANC upon dissolution at lower pH (<5.0). Other silicate minerals may contribute to the total ANC-derived alkalinity, but as their abundance in different rock types is variable, their contribution to ANC will also vary. One assumption of the method is that ANC minerals that are readily available for reaction were measured by the titration, but less reactive or unavailable minerals (for example, those deeper within the rock grains) do not contribute alkalinity during the time frame of the titration.

All rock samples were crushed to pebble size (2 to 64 mm; 10 mesh) then sieved to recover at least 100 g of the <2 mm fraction. Sieve results from selected samples showed that the <2 mm fraction consisted of approximately 70–80 wt. % of either <10 mesh or >30 mesh particles (<2 mm to >600 μm) and 20–30 wt. % of <30 mesh (<600 μm) particles. The smaller particles are likely to be the most reactive because they have the greatest available surface area.

The titration acid was prepared from reagent-grade concentrated acid with deionized water (DI) that had been boiled for 0.5 hours to expel dissolved gases such as O_2 and CO_2 . The prepared acid was standardized against a 0.05 N reagent-grade Na_2CO_3 solution (2.5 g/1 L). To begin the titration, a 30-g split of the <2 mm fraction was placed into a 250-mL glass beaker and covered with 50 mL of DI water. After 10 minutes, the initial pH (pH_i) was measured and the acid addition was started (time = 0). Samples were titrated with either 0.1 N HCl or 0.1 N H_2SO_4 for 1–10 hours through whole-unit endpoints of pH (for example, from 8.0 to 7.0, etc.) down to pH 2.0. The duration of the titration depended on whether the rock had low or high abundances of ANC minerals. Technical grade $N_{2(g)}$ (99.5 percent N_2) was bubbled through the acid reagent during titration to inhibit re-solution of atmospheric gases. A pH stat (Radiometer Corp.) controlled the addition of acid to the sample in the beaker at a rate of ≤ 10.0 mL/min. Acid addition in most titrations was generally lower than the maximum rate,

although some rapid rates of addition ($>10.0 \text{ mL/min}$) were observed in samples that had high ANC. An overhead stirrer equipped with a Teflon impeller running at 1,200 revolutions per minute (rpm) was used to keep the mineral grains in suspension and thus in contact with the solution. Stirring also helped to reduce formation of coatings or precipitates on the pH electrode surface.

The total volume of acid consumed was employed in the following calculation that gives the solution alkalinity from the titration:

$$\text{Alkalinity, mg/L CaCO}_3 = (A)(N)(1.0 \times 10^5),$$

where

A = total volume (L) of acid used,

N = normality of acid, and

1.0×10^5 = conversion factor to obtain mg CaCO₃.

Acid neutralizing capacity for each rock sample was derived from the solution alkalinity results and is expressed as kg CaCO₃/ton. Duplicate titrations indicated that the method determines ANC (alkalinity) to within ± 15 percent, which suggests that the titration provides a fairly reliable estimate of the total ANC in each sample but that reproducibility is more dependent upon rock type, sample preparation, and sample inhomogeneity. Figure 10 shows the results of the ANC procedure.

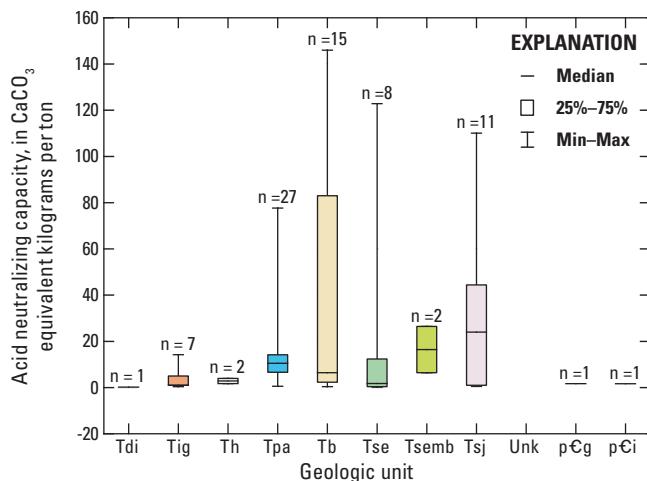


Figure 10. Range of acid neutralizing capacity for rock types with less than 10 kg/ton CaCO₃ net acid production (see fig. 9). “Unknown” rock type samples not measured. Descriptions of the geologic units are given in table 1. (kg, kilogram; CaCO₃, calcium carbonate; min, minimum; max, maximum; n, number of samples; Tdi, Tertiary dacite intrusion; Tig, Tertiary granodiorite to monzonite; Th, Tertiary volcanioclastic sedimentary rocks; Tpa, Tertiary pyroxene andesite lava; Tb, Tertiary rhyolitic ash flow tuff; Tse, Tertiary rhyolitic to dacitic ash flow tuff; Tsemb, Tertiary megabreccia; Tsj, Tertiary volcanioclastic breccia and lava; Unk, Unknown pre-caldera sedimentary rocks; pCg, Precambrian gneiss; pCi, Precambrian hornblende gneiss)

The procedure measures the ANC available during the titration but does not account for longer-term dissolution reactions (days to weeks) that might further contribute to the ANC value. It also does not account for possible subsequent reactions that might cause alkalinity to decrease, for example, dissolution of pyrite (if present). However, measurements taken up to one month after the titration showed that the solution remained within about ± 1.0 pH unit of the final titration pH, indicating that the solution plus minerals system had reached a near steady state.

Geodatabase Description

Because of the complexity and abundance of rock property data presented here (table 2), the most efficient method of accessing the various data tables was to construct a relational geodatabase. The geodatabase is designed to store, query, and manipulate geographic information, spatial data, and rock properties all within a geographic information system (GIS) environment. When samples are selected based on criteria such as geographic location, geology, or alteration type, the related rock properties are also selected. The selection of samples can be done manually from the attribute table or can be based on a number of query selections.

There are two main components to the geodatabase produced for this study. First is a feature classes file, which is a point layer containing the geographic locations of the sample sites, the sample field and laboratory identifiers, a description of the sample locality, geologic unit for the sample, and the alteration environment for the sample. Second are the database files including sample chemistry, X-ray diffraction (XRD) mineralogy, acid neutralizing capacity (ANC), net acid production (NAP), magnetic susceptibility, electrical resistivity, and rock density and porosity. The feature class is correlated with the database files using a series of “relates” within the geodatabase. The common field within the feature class and database attribute tables used to establish the relationships was the “Sample_ID.” The relate files are not selected when loading the geodatabase components into ArcGIS, only the *.shp and *.dbf files.

Once the geodatabase components are loaded, the user opens the attribute table for the feature class. In the attribute table, he or she selects “options” and then “related tables.” The list of related tables is shown, and any table of interest can be selected. When a table is selected, its attribute table will open and any sample selected in one attribute table will also be highlighted in the other. Joins and relates can then be used to symbolize the feature class based on selected analytical methods.

Table 2. Attribute descriptions for data in the Microsoft Excel spreadsheet and ArcGIS geodatabase.[ppm, parts per million; kg/ton CaCO₃, kilograms per ton calcium carbonate; cgs, centimeter-gram-second; cm³, cubic centimeter; ohm-m, ohm-meter; Hz, hertz]

Attribute/Worksheet heading	Description	Notes
Location and Geology	Latitude and longitude location of sample, geologic unit (table 1), and type of alteration	Latitude and longitudes presented in decimal degrees in WSG84 datum. Alteration types defined from Bove and others (2007). Geologic descriptions are available in Yager and Bove (2002).
Chemistry	Major-element oxides and Loss on Ignition by wavelength dispersive X-ray fluorescence (WDXRF)	In percent. Values reported as “less than detection limit” in original file are reported as 0.9 times respective detection limit plus “....1111” for incorporation into database as a number. For example: <5 ppm becomes 4.51111.
ICP-AES	Thirty major, minor, and trace elements by inductively coupled plasma–atomic emission spectroscopy (ICP-AES)	Major elements in percent; minor and trace elements in ppm. Values reported as “less than detection limit” in original file are reported as 0.9 times respective detection limit plus “....1111” for incorporation into database as a number. For example: <5 ppm becomes 4.51111.
ICP-MS	Thirty major, minor, and trace elements by inductively coupled plasma–mass spectrometry (ICP-MS)	Major elements in percent; minor and trace elements in ppm. Values reported as “less than detection limit” in original file are reported as 0.9 times respective detection limit plus “....1111” for incorporation into database as a number. For example: <5 ppm becomes 4.51111.
Total Carbon	Total carbon content by combustion	In percent. Values reported as “less than detection limit” in original file are reported as 0.9 times respective detection limit plus “....1111” for incorporation into database as a number.
Carbon Carbonate	Carbonate carbon by coulometric titration	In percent. Values reported as “less than detection limit” in original file are reported as 0.9 times respective detection limit plus “....1111” for incorporation into database as a number.
Total Sulfur	Total sulfur content by combustion	In percent. Values reported as “less than detection limit” in original file are reported as 0.9 times respective detection limit plus “....1111” for incorporation into database as a number.
XRD Mineralogy	Semi-quantitative measurements of mineral phases by X-ray diffraction (XRD)	In percent. Mineral phases identified as present but less than 1% are defined as 0.5 in data files.
Acid Neutralizing Capacity	A measure of the total alkalinity contributed by mineral species undergoing dissolution during an acid titration	In kg/ton CaCO ₃ equivalent (parts per thousand).
Net Acid Production	The acid producing potential of a material after digestion with hydrogen peroxide	In kg/ton CaCO ₃ equivalent (parts per thousand).
Magnetic Susceptibility	Quantitative measure of the magnetic strength of a rock	Presented as volume susceptibility in cgs units of electromagnetic units divided by cm ³ .
Electrical Resistivity	The measure of how strongly a rock material opposes the flow of an electrical current	Resistivity in ohm-m for samples measured under moist and saturated conditions with a range of frequencies including 100 Hz, 1,000 Hz, 30,000 Hz, and 100,000 Hz.
Density and Porosity	Density is defined as the mass per volume and is a function of individual grains, the porosity, and fluid filling pore space; porosity is the percent of void space in a rock	Density reported in cgs units of g/cm ³ . Porosity reported in percent of pore space.

References Cited

- Bove, D.J., Yager, D.B., Mast, M.A., and Dalton, J.B., 2007, Alteration map showing major faults and veins and associated water quality signatures of the Animas River watershed headwaters near Silverton, southwest Colorado: U.S. Geological Survey Scientific Investigations Map 2976, 18 p. pamphlet, 1 plate, scale 1:24,000. (Also available at <http://pubs.usgs.gov/sim/2976/>.)
- Briggs, P.H., 2002, The determination of forty elements in geological and botanical samples by inductively coupled plasma-atomic emission spectrometry, in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey Open-File Report 02-223, chapter G, 18 p.
- Briggs, P.H., and Meier, A.L., 2002, The determination of forty-two elements in geological materials by inductively coupled-mass spectrometry, in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey Open-File Report 02-223, chapter I, 14 p.
- Brown, Z.A., and Curry, K.J., 2002a, Total carbon by combustion, in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey Open-File Report 02-223, chapter R, 4 p.
- Brown, Z.A., and Curry, K.J., 2002b, Total sulfur by combustion, in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey Open-File Report 02-223, chapter Q, 4 p.
- Brown, Z.A., Papp, Clara, Brandt, Elaine, and Aruscavage, Phillip, 2002, Carbonate carbon by coulometric titration, in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey Open-File Report 02-223, chapter S, 6 p.
- Church, S.E., Mosier, E.L., and Motooka, J.M., 1987, Mineralogical basis for the interpretation of multielement (ICP-AES), oxalic, and aqua-regia partial digestions of stream sediments for reconnaissance exploration geochemistry: Journal of Geochemical Exploration, v. 29, p. 207–233.
- Church, S.E., von Guerard, Paul, and Finger, S.E., eds., 2007, Integrated investigations of environmental effects of historical mining in the Animas River watershed, San Juan County, Colorado: U.S. Geological Survey Professional paper 1651, 1096 p. (Also available at <http://pubs.usgs.gov/pp/1651/>.)
- Hewlett Packard, 1979, Operating manual, model 4274A, multi-frequency LCR meter: Tokyo, Japan, Hewlett Packard LTD., Part Number 04274-90004.
- Hunt, G.R., Johnson, G.R., Olhoeft, G.R., Watson, D.E., and Watson, K., 1979, Initial report of the petrophysics laboratory: Geological Survey Circular 789, 74 p.
- Jones, W.R., 2007, History of mining and milling practices and production in San Juan County, Colorado, 1871–1991, chapter C of Church, S.E., Von Guerard, Paul, and Finger, S.E., eds., Integrated investigations of environmental effects of historical mining in the Animas River watershed, San Juan County, Colorado: U.S. Geological Survey Professional Paper 1651, p. 39–86.
- Lapakko, Kim, and Lawrence, R.W., 1993, Modification of the net acid production (NAP) test, in Proceedings of the Seventeenth Annual British Columbia Mine Reclamation Symposium, Port Hardy, British Columbia, 1993: [Victoria, B.C.], Ministry of Energy, Mines, and Petroleum Resources, p. 145–159.
- McCafferty, A.E., Yager, D.B., Horton, R.J., and Diehl, S.F., 2006, Magnetic properties, acid neutralization capacity, and net acid production of rocks in the Animas River watershed, Silverton, Colorado, in Symposium on the Application of Geophysics to Engineering and Environmental Problems, 19, Seattle, Wash., April 2–6, 2006, Proceedings: Environmental and Engineering Geophysical Society, 10 p.
- Smith, B.D., McDougal, R.R., McCafferty, A.E., Deszcz-Pan, M., and Yager, D.B., 2004, Helicopter electromagnetic and magnetic survey of the upper Animas River watershed—Application to abandoned mine land studies, in Symposium on the Application of Geophysics to Engineering and Environmental Problems, 17, Colorado Springs, Colo., February 22–26, 2004, Proceedings: Environmental and Engineering Geophysical Society, 16 p. (Also available at <ftp://ftpext.usgs.gov/pub/cr/co/denver/musette/tmp/ANIMAS/>.)
- Steven, T.A., and Lipman, P.W., 1976, Calderas of the San Juan volcanic field, Southwestern Colorado: U.S. Geological Survey Professional Paper 958, 35 p.
- Taggart, J.E., and Siems, D.F., 2002, Major element analysis by wavelength dispersive X-ray fluorescence spectrometry in Taggart, J.E., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey Open-File Report 02-223, chapter T, 9 p.
- Wilson, S.A., Briggs, P.H., Mee, J.S., and Siems, D.F., 1994, Determination of thirty two major and trace elements in three NIST soil SRMs using ICP-AES and WDXRF: Geo-standards Newsletter, v. 18, p. 58–89.
- Yager, D.B., and Bove, D.J., 2002, Generalized geologic map of part of the upper Animas River watershed and vicinity, Silverton, Colorado: U.S. Geological Survey Miscellaneous Field Studies Map MF-2377, scale 1:48,000. (Also available at <http://pubs.usgs.gov/mf/2002/mf-2377/>.)

Yager, D.B., Choate, L., and Stanton, M.R., 2008, Net acid production, acid neutralizing capacity, and associated mineralogical and geochemical characteristics of Animas River watershed igneous rocks near Silverton, Colorado: U.S. Geological Survey Scientific Investigations Report 2008-5063, 73 p. (Also available at <http://pubs.usgs.gov/sir/2008/5063/>.)

Yager, D.B., McCafferty, A.E., Stanton, M.R., Diehl, S.F., Driscoll, R.L., Fey, D.L., and Sutley, S.J., 2005, Net acid production, acid neutralizing capacity, and associated geo-physical, mineralogical, and geochemical characteristics of Animas River Watershed rocks near Silverton, Colorado: U.S. Geological Survey Open-File Report 2005-1433, 79 p. (Also available at <http://pubs.usgs.gov/of/2005/1433/>.)

Publishing support provided by:
Denver Publishing Service Center

For more information concerning this publication, contact:
Center Director, USGS Crustal Geophysics and
Geochemistry Science Center
Box 25046, Mail Stop 964
Denver, CO 80225
(303) 236-1312

Or visit the Crustal Geophysics and Geochemistry
Science Center Web site at:
<http://crustal.usgs.gov/>

