

# Geochemical and isotopic data from streambed sediment, Animas River watershed, Colorado, 1995-1999

by

S.E. Church<sup>1</sup>, D.L. Fey<sup>1</sup>, D.M. Unruh<sup>1</sup>,

R.B. Vaughn<sup>2</sup> and J.E. Taggart, Jr.<sup>1</sup>

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<sup>&</sup>lt;sup>1</sup>Denver, Colorado

<sup>&</sup>lt;sup>2</sup>Retired.

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## INTRODUCTION

The USDA-DOI Abandoned Mine Lands (AML) Initiative (USGS, 1999) evaluates the effect of past mining practices on water quality and riparian and aquatic habitats of impacted stream reaches downstream from historical mining districts located primarily on federal lands. This problem is manifest in the eleven western states (i.e., west of 102°) where the majority of hardrock mines having past production are located on federal lands (Ferderer, 1996). In areas of temperate climate and moderate to heavy precipitation, the effect of rapid chemical and physical weathering of sulfides exposed on mine waste dumps and drainage from mines has resulted in elevated metal concentrations in streams and streambed sediments. The result of these processes is an unquantified impact on the quality of the water and the aquatic and riparian habitats that may limit their recreational resource value. One of the confounding factors in these studies is the determination of the component of metals derived from the hydrothermally altered but unmined portions of these drainage basins (Runnells and others, 1992). Several watersheds have been or are being actively studied to evaluate the effects of acid mine drainage (AMD) and acid rock drainage (ARD) on the near surface environment (<a href="http://amli.usgs.gov/amli/">http://amli.usgs.gov/amli/</a>). The Animas River watershed in southwestern Colorado contains a large number of past-producing metal mines that have affected the watershed. Beginning in October 1996, the USGS began a collaborative study of these impacts under the AML Initiative (Buxton and others, 1997).

The initial environmental characterization of the main tributary drainages in the Animas River watershed upstream from Silverton began in 1991 under the auspices of the Colorado Dept. of Public Health and Environment (Owen, 1997). These initial studies showed both seasonal and regional variability in surface water chemistry, and noted that upstream from Silverton many streams are generally acidic although pH is quite variable and depends on the geologic setting, precipitation, and amount of material that mining has exposed. An important geochemical process, which occurs as acidic waters mix with water downstream, is the dilution and neutralization of the acid and subsequent formation of iron and aluminum colloids (Runnells and Rampe, 1989. Kimball and others, 1995). The colloids precipitate in the water where they form larger aggregates and settle from the water to the bed sediment, coating the rocks in the stream. Ochre-colored stream beds are characteristic of many mine-affected streams as well as mineralized areas that have not been disturbed by mining (Runnells and others, 1992). These colloids are solids with effective diameters from less than one nanometer (10<sup>-9</sup> meters) when they first precipitate to greater than a few microns (10<sup>-6</sup> meters) after they aggregate (Ranville and others, 1989; van Olphen, 1977). Hydrous iron-oxide and aluminum-oxysulfate colloids have extensive surface areas that sorb toxic metals (Jenne, 1977; Stumm and Morgan, 1996). These particles may be carried downstream as suspended colloidal particles. They also may precipitate on or bind to the surfaces of rocks and sand grains in the stream bed where they form a chemical sediment component of the streambed sediment. Rocks in many tributary streams in the Animas River watershed are coated with aluminum-oxysulfates and iron-hydroxides indicating the movement of metals under acidic conditions.

The initial Animas River watershed study was funded in October 1995 under a cooperative program between the U.S. Geological Survey, the Bureau of Reclamation, the City of Durango, the Southern Ute Indian Tribe, and the Southwest Water Conservation District. The analytical work was continued in subsequent years (1997-1999) under the Animas River Abandoned Mine Lands project, a joint multidisciplinary study undertaken by the U.S. Geological Survey in cooperation with the U.S. Bureau of Land Management and the U.S. Forest Service (http://amli.usgs.gov/amli/). A group of local concerned citizens in the basin from Silverton and Durango known as the Animas River Stakeholders Group (ARSG), the Colorado Dept. of Public Health and Environment, and the U.S. Environmental Protection Agency (EPA) have cooperated in providing data, consultation, and advice on local conditions within the watershed. Sunnyside Gold allowed access to their property to collect samples as did several property owners downstream from the Animas Canyon. The Southern Ute Indian Tribe provided guided access to our sampling sites on the Southern Ute Indian Reservation. This work was greatly enhanced by consultations with USGS colleagues on the project and individual members of the ARSG.

The data published in this report supercede the data tables for streambed-sediment samples in Church and others (1997; available online at: http://greenwood.cr.usgs.gov/pub/open-file-reports/ofr-97-0151/). All the data tables in this report are presented as Excel (v. 7) spreadsheet files to facilitate digital transfer and analysis of the data. These data tables are available on our AML website (http://amli.usgs.gov/amli/).

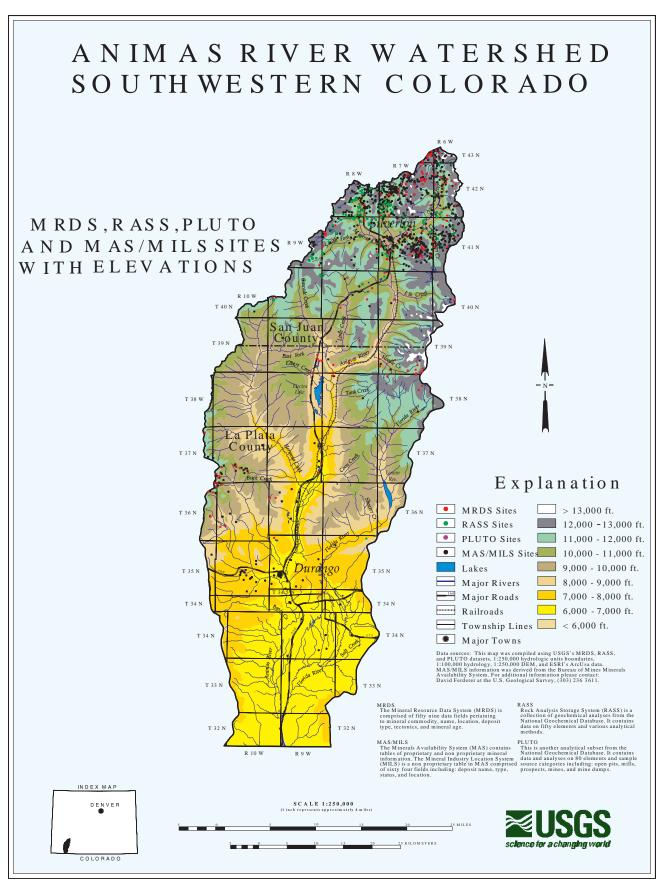
## THE ANIMAS RIVER WATERSHED

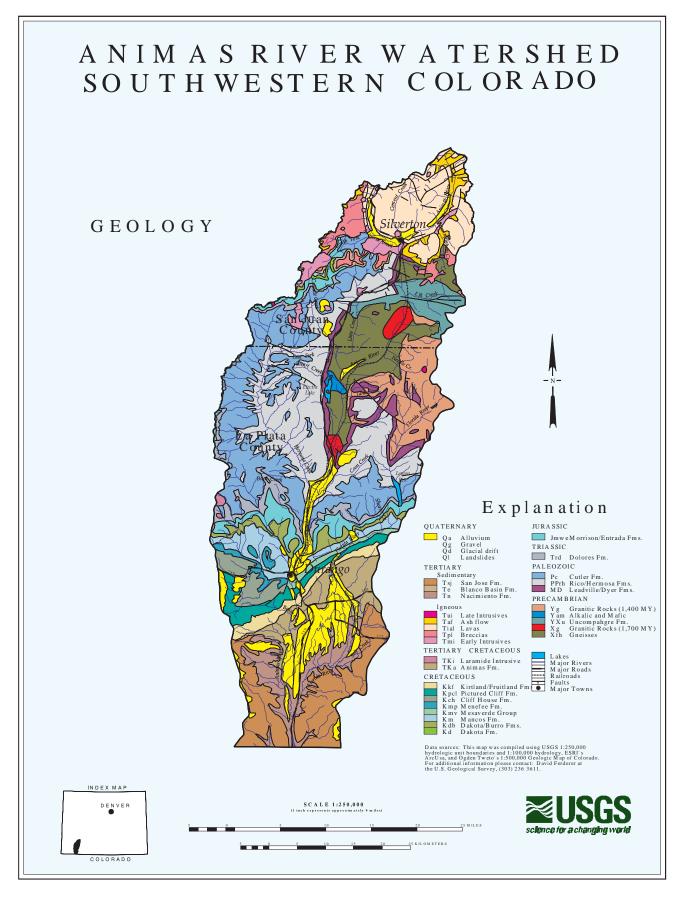
The Animas River watershed (fig. 1) has its headwaters in the mountainous terrain above Silverton, Colo. and drains south into the San Juan River in northern New Mexico. Elevations range from more than 13,000 ft. at the headwaters to less than 6,000 ft. at the confluence with the San Juan River near Aztec, New Mexico. The major population center in the basin is the city of Durango, Colo. The geology exposed at the surface and underlying the basin is varied. Precambrian rocks crop out in the eastern part of the drainage basin south of Silverton (fig. 2) forming the high rugged mountainous area of the Animas Canyon. Paleozoic, Mesozoic, and Cenozoic sedimentary rocks crop out in the southern part of the drainage basin. The headwaters of the Animas River watershed are underlain by the Tertiary igneous intrusive and volcanic rocks that formed as a result of a late Tertiary age episode of andesitic to dacitic volcanism followed by a later episode of ash-flows, lava flows and intrusions of dacitic to rhyolitic composition (Lipman and others, 1976). During this later episode of volcanism, the Silverton caldera formed. Pervasive and intense hydrothermal alteration and mineralization events postdate the formation of the Silverton caldera by several million years (Casadevall and Ohmoto, 1977). This area of the Animas River watershed above Silverton has been extensively fractured, hydrothermally altered, and mineralized by Miocene hydrothermal activity.

Gold deposits were discovered in 1871 on Arrastra Creek above Silverton by prospectors who followed the occurrence of placer gold upstream. Following the signing of a treaty with the Ute Indians in 1873, between 1,000 and 1,500 mining claims were staked in the Animas River watershed upstream from Silverton. Mining activity spread rapidly throughout the area. The chimney deposits, which are mineralized breccia pipes in the headwaters of Mineral Creek (fig. 3), were discovered in 1881(see fig 4, Church and others, 1997). The railroad was brought up from Durango in 1882 providing cheap transportation to the smelters in Durango (Sloan and Skowronski, 1975). Mining continued in the Animas River watershed at various levels of activity until 1991 when the Sunnyside Mine was closed. The extent of mining activity within various portions of the Animas River watershed can be estimated from the distribution of mining claims and Minerals Availability System (MAS) records (Babitzke and others, 1982; McFaul and others, 2000) within the basin (fig. 1). Mineral deposits in several major mining districts have recorded production. Deposits in the Red Mountain district in the northwestern part of the Silverton caldera, the Eureka district in the Eureka graben within the Silverton caldera, and the South Silverton district along the southern margin of the Silverton caldera east of the town of Silverton (Burbank and Luedke, 1968; Leedy, 1971; Casadevall and Ohmoto, 1977) comprised the majority of the mineral production. There are also several porphyry molybdenum deposits discovered by drilling in the Mineral Creek area (oral commun., Tom Casadevall, 1996). Some of the porphyry molybdenum deposits are surrounded by large iron bogs at the surface. Iron bogs are found elsewhere within the basin associated with springs flowing from mineralized and altered areas within the basin (Mast and others, 2000).

Figure 1. Map of the Animas River watershed (from Church and others, 1997) showing elevation and mine localities from the USGS MRDS, RASS, and PLUTO databases (Ryder, 1994) and the USGS MAS database (Babitzke and others, 1982; McFaul and others, 2000). The digital elevation model data are from USGS (1990), towns, railroads, and roads are from ESRI (1992), and the hydrology data are from USGS (1989).

Figure 2. Geologic map (from Church and others, 1997) of the Animas River watershed area (after Tweto, 1979). The digital geology is from Green (1992); hydrology data are from USGS (1989); and the towns, railroads, and roads are from ESRI (1992).





## PREVIOUS STREAMBED SEDIMENT GEOCHEMICAL WORK

Previous reconnaissance exploration streambed-sediment geochemical sampling of the watershed had been done in the mid-1970's under the National Uranium Resource Evaluation (NURE) program (Shannon, 1980; Warren and others, 1981). These data were used to evaluate the sources of metals in small tributary drainage basins (areas of 2-10 km² or more). These data were of adequate sample density and analytical quality to characterize the geochemical landscape of the Animas River watershed. Geochemical data from small tributary streams from the USGS National Geochemical Data Base (Smith, 1999) were used to prepare regional geochemical maps of the Animas River watershed following the procedure outlined by Smith (1994) and are in Church and others (1997).

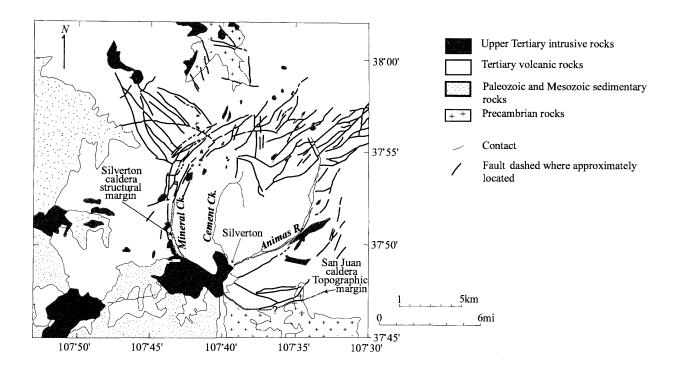


Figure 3. Generalized regional geologic map of the upper Animas River watershed. The Animas River and Mineral Creek follow the structural margin of the Silverton caldera. In addition to the ring-fractures that were created when the Silverton and the earlier San Juan calderas formed, radial and graben faults, which host much of the subsequent vein mineralization, are shown schematically (modified from Casadevall and Ohmoto, 1977).

## FIELD SAMPLING METHODS

Streambed-sediment samples were collected from the larger tributaries of Cement and Mineral Creeks and the Animas River to evaluate stream reaches where major sources of metal loading might be expected. This suite of samples was also used to supplement and validate the previous streambed geochemical data set. The initial streambed-sediment survey was conducted during the week of Oct. 16-20, 1995 during low-flow conditions. Supplementary sampling of the streambed sediments was done annually during the weeks of Aug. 25 and Oct. 24, 1996; during Aug. 14-16, 1997, and during Aug 20-23, 1998 to evaluate the stability of the geochemical maps and their response to annual variations in precipitation and runoff.

Streambed-sediment samples were collected from sites within selected stream reaches to characterize the reach as well as to supplement previous sampling. At individual sites, the sample was composited along 50-100 feet of the stream from several localities on both sides of the stream below the active water level. This composite

sample was sieved through a minus-10-mesh stainless steel sieve (2 mm) into a plastic gold pan and 1-2 kg sample of fine-grained streambed sediment was transported to the laboratory. The sample was dried at room temperature (about 20°C) and then sieved again to collect the minus-100-mesh (minus-149-μm) grain-size fraction so that the samples would be comparable with the NURE data collected for the regional geochemical mapping (Shannon, 1980; Church and others, 1997; Smith, 1999). This minus-100-mesh streambed sample was used for all geochemical, and lead and strontium isotopic work. Sample localities from Mineral Creek, Cement Creek, and the Animas River are plotted on figure 4 and are described in table 1.

Additional samples of overbank sediments, composed of fine-grained sand and silt deposited at high water, were collected in the same manner from the sides of the stream channel to evaluate the effect of wetting and drying of these sediments on the availability of water-soluble metals. These samples were dry-sieved in the field. Some water-soluble efflorescent salts and mill tailings were also collected from along the stream reaches. These special samples are identified and briefly described in the data tables.

## **ANALYTICAL METHODS**

## **Sample Analyses**

#### **Total Digestion**

The bed-sediment samples were digested with a mixed-acid procedure consisting of hydrochloric, nitric, perchloric, and hydrofluoric acids (HCI, HNO<sub>3</sub>, HCIO<sub>4</sub>, and HF). This procedure is effective in dissolving most minerals, including silicates, oxides and sulfides; resistant or refractory minerals such as zircon, chromite, and some tin oxides are only partially dissolved. Previous investigations using a variety of materials support the completeness of the digestion (Church, 1981, Church and others, 1987; Wilson and others, 1994).

Results are reported for 34 elements analyzed by ICP-AES (inductively coupled plasma-atomic emission spectroscopy; Crock and others, 1983; Briggs, 1996). Limits of determination for the total digestion method as well as a statistical summary of mean values, standard deviations, and median values for four National Institute of Standards and Technology (NIST) standard reference materials (SRM-2704, SRM-2709, SRM-2710, and SRM-2711) are given by Fey and others (1999). Comparisons with certified values for these standards (NIST, 1993a; 1993b; 1993c; and 1993d) are also given by Fey and others (1999). Both analytical precision and accuracy are well within acceptable ranges.

#### Warm 2M HCl-1 Percent H<sub>2</sub>O<sub>2</sub> Partial Digestion

The use of a partial-digestion extraction enables one to determine concentrations of trace elements bound within different mineral phases, whereas a total digestion releases all trace elements in a sample (Chao, 1984). The leaching solution used in this study, a freshly prepared mixture of 2M HCL and hydrogen peroxide ( $H_2O_2$ ), dissolves hydrous amorphous iron- and manganese-oxide minerals, as well as some crystalline iron- and manganese-oxides. We used a 2-g sample in 15 mL of reagent. The samples were placed in 90 mL Teflon FEP jars, sealed, and placed in an agitating waterbath at  $50^{\circ}$  C for three hours to ensure complete removal of the iron- and manganese-oxide coatings from the sediment grains. The leachates were subsequently analyzed by ICP-AES for 32 elements (Appendix III in Church and others, 1993). This partial extraction releases trace elements associated with hydrous amorphous iron- and manganese-oxide mineral coatings and colloidal particles. Mineral coatings such as those observed in the study area contain a significant percentage of the trace elements in a sample (Church and others, 1993, 1997).

Residues from the 2M HCl-1 percent  $H_2O_2$  leach extraction were also digested using the total digestion procedure described above to document the percentages of ore-related trace-elements in the residues and to determine their mineralogical residence.

#### Selenium, Arsenic, and Mercury Determinations

Selenium was determined using hydride generation-atomic absorption spectrophotometry (Hg-AAS), as was arsenic for those samples whose ICP-AES values were less than 20 ppm. Samples were digested using a combination of nitric, hydrochloric, perchloric, sulfuric and hydrofluoric acids in open teflon vessels resulting in total dissolution. The solutions were split and arsenic in the solutions was reduced to the +3 state using a potassium iodide-ascorbic acid solution; selenium was reduced to the +4 state using HCI. The respective

hydrides were generated by the addition of and mixing with sodium borohydride. The gaseous hydrides were introduced into a heated quartz tube in the optical path of an atomic absorption spectro-photometer and analyzed (Hageman and Welsch 1996).

Mercury was determined using a cold vapor-atomic absorption spectrophotometric method (CV-AAS). Samples were digested using concentrated nitric acid, with the addition of sodium dichromate (O'Leary and others, 1996). The solutions were then introduced into a continuous flow manifold and mixed with air and a sodium chloride-hydroxylamine hydrochloride-sulfuric acid solution. The divalent mercury was then reduced to elemental mercury using stannous chloride, and the vapor introduced into the optical path of an atomic absorption spectrophotometer and analyzed.

#### X-ray Fluorescence Analyses

Sample residues from the 2M HCl-1 percent  $H_2O_2$  digestion were analyzed for strontium isotopic analysis were also analyzed by x-ray fluorescence to determine accurately the major element compositions for use in multi-variant analysis of the streambed sediment chemistry to determine sediment loads to the Animas River watershed. Major element (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe) chemistry was determined on the samples using wavelength dispersive X-ray fluorescence spectrometry (WDXRF) using the method of Taggart and others (1981, 1987). The samples were first ignited at 970°C for 40 minutes and the loss on ignition (LOI) determined, after which they were fused with lithium tetraborate for 46 minutes at 1120°C (Taggart and Wahlberg, 1980b). The resultant molten material was then poured into a mold (Taggart and Wahlberg, 1980a) yielding a homogeneous, optically flat glass disk for presentation to the X-ray spectrometer. Details of the method and a summary of the analytical performance are in Mee and others (1995).

## **Isotopic Analyses**

#### **Lead Isotopic Analyses**

Because we have shown that the vast majority of the contaminant lead exists within the amorphous ironand manganese-oxide mineral coatings and colloidal particles (Church and others, 1993, 1994, 1995, 1997), only the leachates from the streambed sediment were analyzed for lead isotopic compositions. Lead from the 2M HCl-1 percent  $H_2O_2$  digestion solution was used to determine the impact of the contaminant sources on the streambed sediment in the study area. Lead-isotopic analysis of the leachate solutions greatly reduces dilution effects from lead bound within the major mineral phases such as potassium-feldspar and volcanic glassy rock matrix that would be encountered if we had used the total digestion solution from the samples.

The lead-isotopic data on the streambed-sediment samples were measured using two different mass spectrometer procedures. The initial work was done by R.B. Vaughn using a 68° sector, 12-inch radius, solidsource-single collector, thermal-ionization mass spectrometer (Church and others, 1997). Analytical precision, based upon replicate analyses of NIST SRM materials is better than 0.1 percent per mass unit for the reported lead-isotopic ratios. Later lead-isotopic work was carried out by D.M. Unruh using a VG Sector-54 multi-collector mass spectrometer. Lead was separated using the procedure described below with minor variations (see appendix IV of Church and others, 1993; Tatsumoto and Unruh, 1976; and Unruh and others, 1979). The ICP-AES concentration value for lead was used to calculate the volume of leachate needed to contain approximately 0.5 µg of lead; this aliquot was then evaporated to dryness in a teflon beaker. Then 0.5 to 1.0 mL of 1.0 N hydrobromic acid (HBr) was added to the sample and warmed gently for 5 to 10 minutes. The sample was cooled to room temperature, centrifuged, and the supernatant loaded onto a column containing Dowex AG1-x8 anion-exchange resin (0.8-1.0 mL resin volume). The column is washed with 1.2 N HBr and water, and the lead eluted with either 8N HCl or 0.5 N HNO<sub>3</sub>. The sample was again evaporated to dryness and then loaded onto a second anion-exchange column with a resin volume of 0.1-0.2 mL. The column was washed with 1.2 N HBr and water, and the lead was eluted with 0.5 N HNO<sub>3</sub>. Two or three drops of dilute (0.25-0.5 percent) phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) were added to the sample, and then it was evaporated again to dryness.

Approximately one-half of the sample was taken up in approximately 10  $\mu$ L of dilute colloidal silica gel, loaded onto a rhenium-ribbon filament, and evaporated to dryness. The filament was then loaded into a solid-source, thermal-ionization mass spectrometer and heated to 1150-1350°C for data acquisition. Most analyses were made using a VG Sector 54, 7-collector mass spectrometer run in "static" mode. A few samples were run on a VG Isomass 54R, single-collector mass spectrometer. No systematic biases have been observed between

the two mass spectrometers (Taylor and others, 1999). Analyses of NIST SRM-981 were used to monitor mass fractionation during mass spectrometry (Cantanzaro and others, 1968; Todt and others, 1993). Methods of calculation of the analytical uncertainty and replicate analyses of the SRM-981 lead isotopic standard are presented in Unruh and others (2000).

As demonstrated by Fey and others (1999), data from analyses of the leachates are inherently less reproducible than those from total digestion analyses. As a test of the leaching procedure for lead isotopic analyses, leachates of four NIST standards SRM-2704, SRM-2709, SRM-2710, and SRM-2711 were analyzed for lead isotopic ratios. The lead isotopic analyses of replicate solutions of the four NIST standards are in good agreement with previous work (Church and others, 1993).

#### Strontium Isotopic Analyses

Residues from the 2M HCl-1 percent  $H_2O_2$  leach extraction of selected streambed sediments were analyzed for their strontium isotopic compositions to determine the detrital sediment loading from various sources to the Animas River. Analytical procedures for strontium isotopic analyses are similar to those reported by Birck and Allegre (1978) and Stille and others (1986). Approximately 100 mg of powdered residue was decomposed in a solution of HF and  $HNO_3$  in a screw cap PFA-Teflon jar at approximately  $70^{\circ}C$  for at least 48 hours. Isotopic data for two unleached whole-rock samples (98-ABS-238, 96-ABS-111) were also analyzed. Strontium was separated using a double cation exchange procedure in 2.5N HCl and 2N HCl media, respectively.

Strontium isotopic data for most samples were obtained on a VG Isomass 54R single-collector mass spectrometer. Isotopic data were normalized to  $^{86}$ Sr/ $^{88}$ Sr = 0.119400 in order to correct for mass-dependent fractionation that occurs during the analysis. The  $^{88}$ Sr ion intensity was regulated between 1 and 4 x 10 $^{-11}$ A.  $^{85}$ Rb was also monitored in order to correct for isobaric interference from  $^{87}$ Rb on  $^{87}$ Sr. Data are considered acceptable when this correction is less than 100 ppm (<0.01 percent).

Strontium isotopic analyses of NIST standard SRM-987 were also made in order to monitor the consistency of the mass spectrometric procedure and to provide a comparison for interlaboratory and instrumental biases. Thirteen analyses of the SRM-987 standard on the VG Isomass 54R mass spectrometer during the course of this study gave a mean  $^{87}$ Sr/ $^{86}$ Sr = 0.710254  $\pm$  0.000010 (2 sigma mean; Table 2).

Isotopic data for eleven samples (95-ABS-CC, EC; 95-ABS-137, 138, 140, 141, 142, 143, 148; 96ABS-111, 125) were measured on the VG Sector 54, 7-collector mass spectrometer run in "dynamic" mode. Analyses of two aliquots of the SRM-987 standard gave a mean value of 0.710317  $\pm$  0.000015 (2 sigma mean; VG Sector 54 I in Table 2). Consequently, a bias correction of -0.000063 has been applied to the <sup>87</sup>Sr/<sup>86</sup>Sr values of these samples in order to make them directly comparable to the data obtained from the VG Isomass 54R mass spectrometer.

During the summer of 1999 modifications to both the hardware and software of the VG Sector 54R mass spectrometer were made. Analyses of five aliquots of the SRM-987 run after modification standard yielded a mean value of  $0.710267 \pm 0.000011$  (2 sigma mean; VG Sector 54R II in Table 2). A small bias correction of -0.000013 has been applied to four samples (95-ABS-131A, 95-ABS-147; 97-ABS-225; 98-ABS-238) run after the hardware modifications were completed.

## RESULTS

## Streambed Sediment Data

The analytical results from the total digestions of the streambed sediment from the Animas River watershed are presented in Table 3. The data are arranged by stream segment in order by site no. (fig. 4 and fig 5 and Table 1) from the head of the stream segment down to the confluence. The Mineral Creek, Cement Creek, the upper Animas River, and the lower Animas River below the confluence with Mineral Creek are the four segments used in all data tables. Total digestion results and statistical summaries of data for samples collected from individual sites over several years are listed in Table 4. Analytical data from the 2M HCl-1 percent H<sub>2</sub>O<sub>2</sub> leach extraction are in Table 5. Data from and statistical summaries of the 2M HCl-1 percent H<sub>2</sub>O<sub>2</sub> partial digestion of samples collected for each of several years at the same site are in Table 6. Lead-isotopic analyses of the 2M HCl-1 percent H<sub>2</sub>O<sub>2</sub> leachates of samples from the sites analyzed by R.B. Vaughn are in Table 7 and by D.M. Unruh are in Table 8. Strontium isotopic analyses of residues from the 2M HCl-1 percent H<sub>2</sub>O<sub>2</sub> partial digestions of selected samples are in Table 9. Analytical data from the residues from the leach extraction are in Table 10

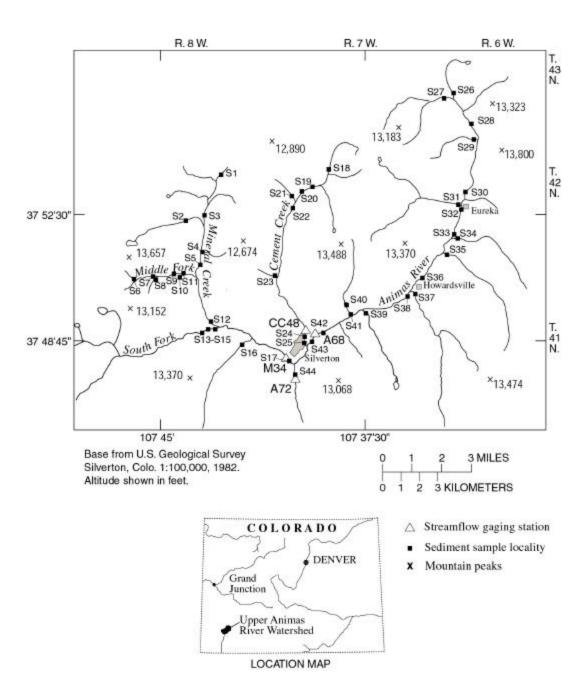


Figure 4. Map of the upper Animas River watershed showing localities for sediment samples collected from Mineral Creek, Cement Creek, and the Animas River, Colo.

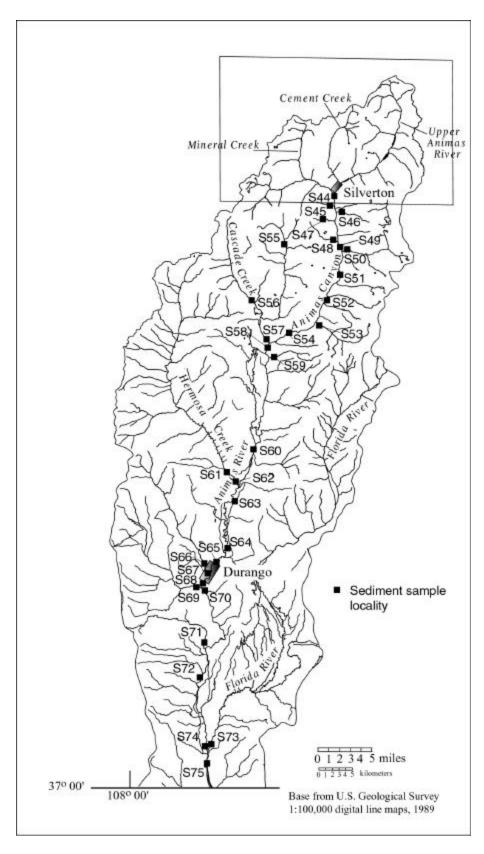


Figure 5. Map of the upper Animas River watershed showing the area of figure 4 and the sample localities for sediment samples collected from the Animas River below Silverton, Colo.

## Comparison of the 1995 and the 1996 Streambed-Sediment Data

Comparisons of the yields from samples collected at the same sites in both 1995 and 1996 indicates that the metals associated with the iron-hydroxide phases, that is copper, lead, and zinc in particular, are enriched in the 1996 data set from 10-50 percent over what these same sites were in 1995. This indicates that the hydrograph affects the amount of colloidal component that accumulates at any given site during the year. The snowpack in 1996 was low and the resulting low-volume spring runoff may not have completely flushed the streams of cumulated colloidal components. Whereas the general form of the metal profiles from year-to-year are the same, it would be difficult to use the sediment samples as a monitoring tool to evaluate the effects of remediation because of the variability caused by this annual flushing process.

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