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Chemical data and lead isotopic compositions in stream-sediment samples from the Boulder River watershed, Jefferson County, Montana

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INTRODUCTION

Metal-mining related wastes in the Boulder River basin study area in northern Jefferson County, Montana, have been evaluated for their environmental effects as a part of the U.S. Geological Survey Abandoned Mine Lands Project (Buxton and others, 1997). Many mine and prospect waste dumps, and mill wastes are located in the drainage basins of Basin Creek, Cataract Creek, and High Ore Creek, the three major tributaries to the Boulder River in the study area. Throughout the study area, mine-waste material has been transported into and down streams, where it mixes with and becomes incorporated into the bed sediments. In some locations, waste material was placed by mine operators directly in stream channels, and has been transported downstream forming fluvial tailings deposits along the stream banks. Water quality and aquatic habitat have been affected by acid generation and toxic-metal mobility during snowmelt and storm water runoff events. Colloids formed by the raising of pH downstream from these mine sites sorb metals contributing to the high concentrations observed in both bed and suspended sediments within the watershed. This report presents geochemical data for bed sediments from 67 sites and lead isotope data for 59 sites. Also included are geochemical data for seven suspended-sediment samples, and one smelter slag sample.

METHODS OF STUDY

Sample collection

Bed sediments

In October 1996, we collected 47 active bed-sediment samples from the Boulder River, Basin Creek, Cataract Creek, High Ore Creek, and the Little Boulder River. In July 1997, we collected 36 active bed-sediment samples, and in July 1998, we collected 18 active bed-sediment samples. In July 1999, we collected one additional active bed sediment. These sites were chosen to supplement the geochemical data collected during the National Uranium Resource Evaluation (NURE) program in the mid-1970's (Aamodt, 1978; Broxton, 1980) and in the US Geological Survey study of the area (Campbell and others, 1982).The new samples provide additional information on the detailed dispersion pattern of metals in the bed sediments within the Boulder River study area. Some sampling sites were visited and sampled from for two or three years to assess the annual variation in the geochemical and isotopic signatures. Along the Boulder River, we collected bed-sediment samples above and below the confluences with the three major tributaries (Basin Creek, Cataract Creek and High Ore Creek) to assess the contributions of these major tributaries to contamination by ore-related elements in the bed sediments of the Boulder River. In addition, at those sites, we collected bed sediment from approximately 30 m (100 ft) above and below the confluence on both the north side and the south sides of the Boulder River. This was done to evaluate the mixing of sediments from the tributaries as they enter the river from the north. The locations of the bed-sediment samples are shown in figure 1 and table 1. Analyses of bed-sediment samples represent the chemistry of material eroded upstream of the sample site and of the colloidal material coating the detrital grains. An integrated bed-sediment sample was collected at each site by compositing 10 to 20 individual subsites within 15 m (50 ft)

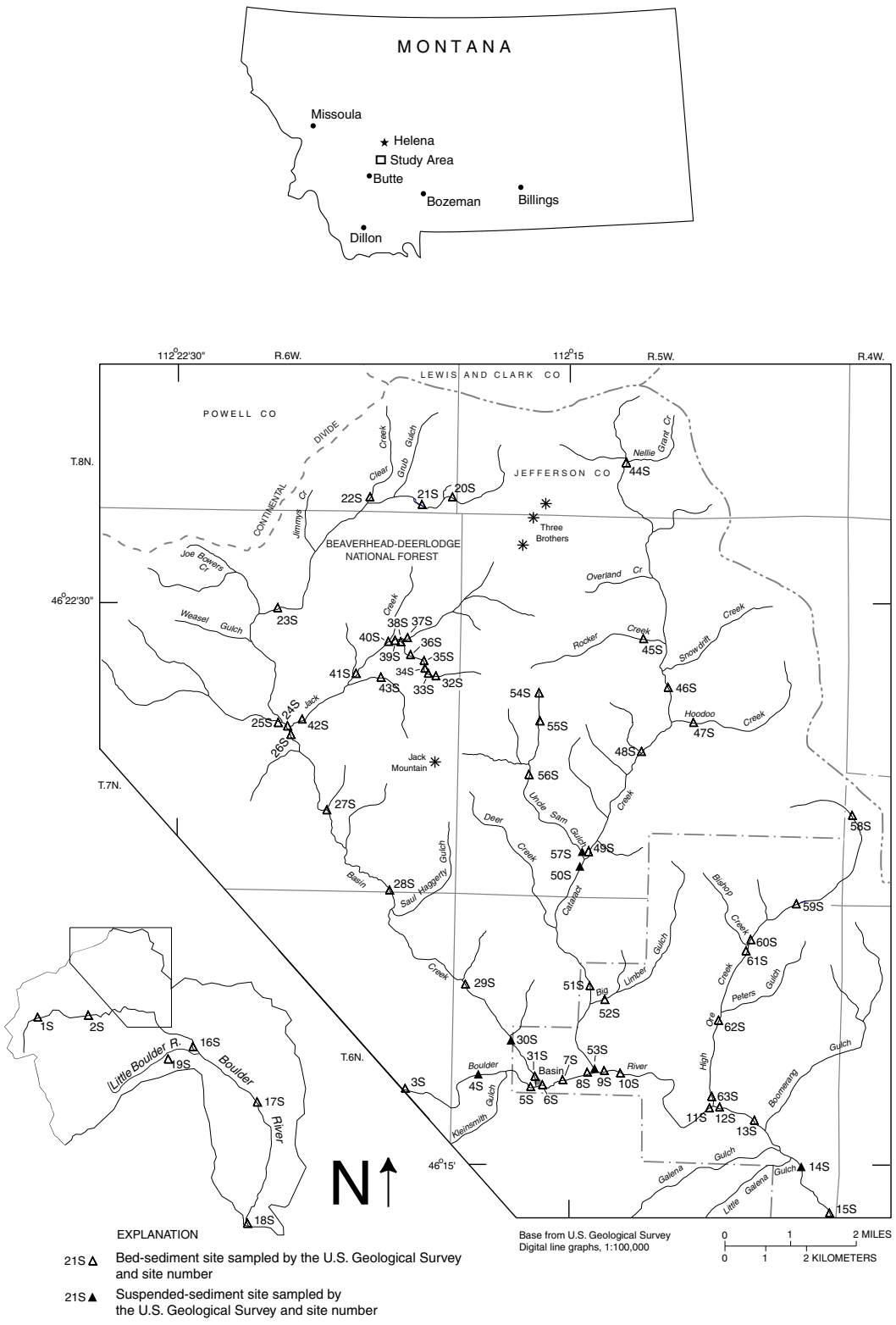

Figure 1. Index map of Montana showing Boulder River study area, and location map for bed- and suspended-sediment sampling sites in the Boulder River Watershed.

of the plotted site, collecting material from the active channel alluvium. In the field, each composited sample was sieved through a 2 mm (10 mesh) stainless-steel screen, and the minus-2 mm fraction retained; the larger size fractions were discarded.

Suspended sediments

In May 1997, D.A. Nimick collected seven suspended-sediment samples in the study area, during spring runoff. These samples were collected using a DH-74-TM sampler, and were depth- and width-integrated. Approximately 8 L of water was transferred into 2-gallon jugs for each sample. The locations of the suspended-sediment samples are also shown in figure 1 and table 1.

Sample Preparation

Bed-sediment samples were dried at ambient room temperature (25°C) and sieved to minus-80-mesh (<0.18mm) prior to laboratory analyses. The suspended-sediment samples were processed for analysis by pouring off the water and saving the solid material; the weight of solid material contained ranged from 0.03 g to 0.72 g. The solid material from each suspended-sediment sample was hand-ground in an agate mortar to minus-100-mesh (<0.14 mm) prior to analysis.

Sample Analysis

Total digestion

The bed-sediment samples, suspended-sediment samples, and leach residues from partial extractions (described below) were digested with a mixed-acid procedure consisting of HCl, HNO_3, $HClO_4$, and HF. Results are reported for 34 elements analyzed by ICP-AES (inductively coupled plasma-atomic emission spectroscopy) (Crock and others, 1983; Briggs, 1996). 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 and others, 1987; Wilson and others, 1994). The values for total-digestion analyses of the bed sediments are given in table 2, and the values for the total-digestion analyses of the bed-sediment leach residues are given in table 3. Values for the total-digestion analyses of the suspended sediments are presented in table 4. Limits of determination for the total digestion method are given in table 5. 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) is given in table 6. Comparisons with certified values for these standards (NIST, 1993a, 1993b, 1993c and 1993d) are also given in table 6.

The accuracy and precision of multiple analyses of reference materials are affected by variability both in the digestion and in the instrumental analyses. Long-term variation is generally greater than short-term variation; the reference materials reported here were analyzed over a three-year time span. Another important factor affecting the accuracy and precision of analyses involves the concentration of individual elements relative to the reporting limits for those elements. The U.S. Geological Survey Mineral

Resources Program defines an instrumental detection limit as the concentration of an element that is three times the standard deviation obtained from multiple (n>30) analyses of either a blank solution or a solution containing just enough analyte to produce a signal detectable above background noise (Arbogast, 1996). Briggs (1996) used a blank solution of 1 percent nitric acid to determine instrumental detection limits. The actual limits of determination, or reporting limits, are higher because the instrumental detection limits are determined under ideal conditions, with no interfering matrix effects from other elements. The reporting limits also vary according to sample weight. Those given in table 5 are for sample weights of 0.2 g. Smaller sample weights (for example the suspended-sediment samples) result in proportionately higher reporting limits.

Empirical evidence indicates that the variation in an analytical signal is about 100 percent when approaching the limit of determination. Analyses of elements whose concentrations are greater than ten times the reporting limits will yield results with better precision and accuracy than analyses of elements whose concentrations are at the reporting limits. An evaluation of the entire data set for the total digestions of the Standard Reference Materials (table 6) shows that the relative standard deviation for elements with concentrations more than ten times the limit of determination (table 5) is generally in the range of 3 to 6 percent. There is no detectable difference between data analyzed in different years. The statistical summaries for arsenic analyses of SRM-2704 and SRM-2711 illustrate the effect of concentration on precision and accuracy (table 6). The certified value for arsenic in SRM-2704 is 23.4 ppm, about 2 times the reporting limit. The mean obtained from 48 analyses is 21.1 ppm (90 percent of the certified value), and the relative standard deviation is 26 percent. The certified value for arsenic in SRM-2711 is 105 ppm, about 10 times the reporting limit. The mean obtained from 54 analyses is 102 ppm (97 percent of the certified value), and the relative standard deviation is 6.5 percent.

Warm 2M HCl-1 percent H_2O_2 leach extraction

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 bed sediments were subjected to a partial-digestion extraction consisting of warm (50^0 C) 2M HCl-1 percent H_2O_2 for three hours with continuous agitation; the leachates were subsequently analyzed by ICP-AES for 32 elements. This partial extraction releases trace elements associated with hydrous amorphous iron- and manganese-oxide mineral coatings and colloidal particles (Appendix III of Church and others, 1993; Church and others, 1997). Mineral coatings such as those observed in the study area can contain a significant percentage of the trace elements in a sample (Church and others, 1997). The residues from this extraction were then dried, weighed, and subjected to the total digestion described above to determine trace element concentrations bound in the oxide, silicate, and more-resistant sulfide phases. The data obtained from the 2M HCl-1 percent H_2O_2 extraction are presented in table 7. Analytical limits of determination for the partial-digestion leach method are also given in table 5. A statistical summary of mean values, standard deviations, and median values obtained from the leach procedure for the same four National Institute of Standards and Technology standard reference materials (SRM-2704, SRM-2709, SRM-2710, and SRM-2711) is given in table 8. The variation is inherently greater for the leach analyses than for the total-digestion analyses. Examination of the relative standard deviations for elements present at more than ten times the limit of determination is generally in the 7 to 10 percent range (table 8). This is mostly a result of the

variability in strength of the hydrogen peroxide with age, despite refrigeration. However, the same general relation exists between elemental concentrations in the standard reference materials and precision of analyses as was discussed for the total-digestion analyses. There are no certified values for leach analyses of these reference materials; therefore accuracy can not be evaluated.

Ion exchange and mass spectrometry for lead isotope analyses

The lead separation procedure used on the 2M HCl-1 percent H_2O_2 extraction solutions to obtain the lead isotopic data in table 10 is similar to those reported by Tatsumoto and others (1976) and Unruh and others (1979). ICP-AES analyses of the above leachates provide an in-solution concentration for lead (Church and others, 1993). This concentration value is then used to calculate the volume of leachate needed to contain approximately 0.5 µg of lead; this aliquot is then evaporated to dryness in a teflon beaker. Then 0.5 to 1.0 ml of 1.0 N hydrobromic acid (HBr) is added to the sample and warmed gently for 5 to 10 minutes. The sample is allowed to cool, is centrifuged, and the supernatant loaded onto an anion-exchange column (0.8-1.0 ml resin volume) using Dowex AG1-X8 anion-exchange resin. The column is washed with 1.2 N HBr and water, and then the lead is eluted with either 8N hydrochloric acid (HCl) or 0.5-1.0 N nitric acid (HNO_3). The sample is 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 is washed with 1.2 N HBr and water, and the lead is eluted with 0.5 N nitric acid. Two or three drops of dilute (0.25-0.5 percent) phosphoric acid (H_3PO_4) are added to the sample, and it is then evaporated again to dryness.

The sample is taken up in approximately 10 µL of dilute colloidal silica gel, loaded onto a rhenium-ribbon filament, and evaporated to dryness. The filament is then loaded into a solid-source thermal ionization mass spectrometer and heated to 1150-1350°C for data acquisition. Data for four isotopes of lead are collected: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Analysis of NIST SRM 981 is used to monitor mass fractionation during mass spectrometry (Cantanzaro and others, 1968; Todt and others, 1993). The lead isotope data are presented in table 10 as five isotopic ratios: $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ $^{207}Pb/^{206}Pb$, and $^{208}Pb/^{206}Pb$.

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