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Geochemical Data for Environmental Studies of Mercury Mines in Nevada

by

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Introduction

The primary objective of this study was to determine if weathering of abandoned mercury mines in Nevada has resulted in any significant effect to surrounding ecosystems. This study is part of a larger U.S. Geological Survey (USGS) project to evaluate the geology, mineral resource potential, and environmental concerns of the Humboldt River Basin, Nevada. Mercury is clearly the primary concern of the mercury mines, but other toxic elements were also evaluated in this study. In this report, we describe the samples collected in 1999 for this study, the methods used for the analysis of the samples, and the geochemical data for these samples.

Mercury is a heavy metal of environmental concern because highly elevated concentrations are toxic to living organisms, and thus, the presence of these abandoned mercury mines is a potential hazard to residents and wildlife when drainage from the mines enters streams and rivers that are part of local ecosystems. Mercury mines in Nevada are part of a broad mercury belt that consists of numerous deposits scattered throughout several tens of thousands of square kilometers, primarily in western and central Nevada (fig. 1). The dominant environmental concern of these mercury mines is inorganic mercury in cinnabar ore and elemental mercury remaining at the mine sites that may potentially erode into streams and rivers. Under certain conditions, inorganic mercury may be converted to organic forms of mercury that are water soluble and can be absorbed by biota in aquatic systems. When organisms are exposed to mercury contamination, mercury generally increases in concentration with increasing trophic position in the food chain (biomagnification).

At the abandoned mercury mines in Nevada, the presence of cinnabar remaining in ore and calcine piles (roasted ore), and any elemental mercury around the mill and retort areas are environmental concerns. For example, in all the districts studied, there is cinnabar visible in the area of the open pit cuts and trenches, ore piles and tailings, as well as in the calcine piles. However, elemental mercury was not observed during the 1999 fieldwork at any mine site in Nevada. Calcines from some deposits contain as much as 2,000 $\mu\text{g/g}$ Hg, suggesting that processing in the rotary furnaces was not always totally efficient. Detrital cinnabar and cobbles containing cinnabar visible in streams drainages below the mines indicate that mercury present at these sites is eroding down gradient from the mines.

We visited mercury mines in eight districts (fig. 1); these mines were selected for study because they represented variability in mine size (mercury production) and host rock geology (table 1). We studied districts that are within the Humboldt River Basin including the Imlay, Dutch Flat, Poverty Peaks, Goldbanks, and Ivanhoe districts, but also mines in the Antelope Springs, Bottle Creek, and Opalite districts (figs. 2-9) to evaluate any potential differences of mines in these districts. To evaluate environmental concerns of these mercury mines, we measured the concentration of mercury in cinnabar-bearing ore, calcines, stream-sediment (bed sediments), and stream-water samples collected proximal to several of the mines. However, due to the lack of surface water in the study area, stream water was collected from only Eldorado Canyon downstream from the Eldorado mine in the Imlay district (fig. 2). In addition, we collected sediment and water samples from several sites along the Humboldt River and the Rye Patch Reservoir to establish regional geochemical baselines (fig. 1). We also analyzed these samples for

other trace-elements (including As, Bi, Cd, Cu, Mo, Pb, Sb, and Zn) to evaluate any additional heavy-metal contamination related to the mines.

General Geology and Mineralogy

Mercury deposits in Nevada are found in a wide variety of rock types including sandstone, limestone, chert, granitic rocks, diabase dikes, rhyolitic tuffs and flows, andesites, and metamorphic rocks such as schists and phyllite (Bailey and Phoenix, 1944; Willden, 1964; Johnson, 1977). Ore and gangue minerals are typically found in highly silicified rocks, veins, and vein breccias. One of the most common types of mercury deposit in Nevada is “opalite,” which is composed of amorphous and cryptocrystalline quartz including opal. Opalite bodies are typically silicified volcanic tuffs. Siliceous sinter deposits formed by the surface deposition of hot-springs water are also common host rocks. Mineralized vein and vein breccias are common deposit forms in Nevada, especially in sedimentary rocks. Varieties of quartz are the most common gangue, but alunite, gypsum, barite, clay, and carbonate alteration minerals are locally found. The ore mineralogy of these mercury deposits is dominantly cinnabar, with subordinate amounts of metacinnabar, native mercury, calomel, and mercury oxychlorides found in some deposits (Bailey and Phoenix, 1944). Minor amounts of pyrite, marcasite, sphalerite, and stibnite are found with cinnabar ore in a few localities. The mercury deposits in Nevada are generally of Miocene age and are probably related to extensional magmatism (Noble and others, 1988).

Mercury deposits in Nevada were mined between about 1907 and 1991, when the McDermitt mine closed. Mercury mines in Nevada and throughout the United States are not presently operating because of low prices and low demand for mercury, although some minor byproduct mercury is recovered from a few precious metal mines. Historic production from mercury mines in Nevada exceeds 10,000 t (300,000 flasks; 1 flask=76 lbs), about 90 percent of which has come from the McDermitt mine (Willden, 1964; Johnson, 1977; Noble and others, 1988). At most mines in Nevada, mercury ore was processed on site in small retorts or in large rotary furnaces (Bailey and Phoenix, 1944). Geologic characteristics and mercury production of the districts studied are shown in [table 1](#).

Sample Collection and Preparation

Ore, stream-sediment, calcines, and stream-water samples were collected in and around the studied mine sites to evaluate the distribution of mercury and other elements around the sites. Sediment and surface-water samples were also collected from the Humboldt River and the Rye Patch Reservoir to evaluate mercury contents distant from the mines. Stream-sediment samples consisted of channel-bed alluvium. Lake sediment samples were collected along the shoreline of the Rye Patch Reservoir. Sediment samples were composited by collecting material from several localities in the channel, or from several locations just below the waterline for the lake sediments. About 2 kg of stream or lake sediment was screened to minus-10 mesh (2 mm) and collected in a stainless steel gold pan and saved as the sediment sample. Calcine samples collected were grab samples that were not sieved in the field. Prior to analysis, the calcine and stream- and lake-sediment samples were air dried, sieved to minus-80-mesh (0.18 mm), and pulverized to less than 100 mesh (0.15 mm).

Both filtered and unfiltered surface-water samples were collected at each site. All filtered samples were passed through a 0.45- μm sterile membrane. To minimize contamination during water sample collection, bottles for acidified samples were pre-cleaned for 24 hours in 10 percent hydrochloric acid and all sample bottles were rinsed with site water, and collection was made wearing new, unpowdered vinyl gloves, and using disposable filters and syringes at each site. Water samples collected for analysis included: (1) filtered and unfiltered water for mercury analysis collected in glass bottles and preserved with ultra-pure nitric acid saturated with sodium dichromate, (2) filtered and unfiltered water samples for major and trace cation analysis collected in polypropylene bottles and preserved with ultra-pure nitric acid, (3) an unacidified filtered water sample collected for anion analysis, and (4) an unacidified filtered water sample for measurement of alkalinity. Unacidified water samples were kept in an ice cooler in the field and then refrigerated until analysis.

Stream-water characteristics such as conductivity, pH, temperature, turbidity, and Fe^{2+} were also measured in the field at each sample site. Conductivity was measured with an Orion model 130 conductivity meter and was recorded in microsiemens per centimeter ($\mu\text{S}/\text{cm}$). Temperature ($^{\circ}\text{C}$) and pH were determined using an Orion model 230A pH meter. Turbidity was measured with a DTR-15CE Scientific, Inc. meter in standard nephelometric turbidity units (NTU). Determination of Fe^{2+} was made using CHEMetrics colorimetric field test kits and was measured in mg/L .

Analytical Methods

Samples in this study were analyzed by several single-element and multi-element chemical methods. The sediment and calcine samples were analyzed by XRAL Laboratories of Ontario, Canada, which was contracted by the USGS. The water samples were analyzed by the USGS in Denver, Colorado. Tables 2 and 3 list the elements determined and their limits of determination. A brief description of the methods used is given below. Quality control was addressed with the use of internal (hidden) reference standards, field blanks, and sample site duplicates. Based on analysis of the hidden standards, data precision for the methods used was within 20 percent.

Solid Sample Analysis

Inductively coupled plasma-atomic emission spectrometry

Two separate multi-element inductively coupled plasma-atomic emission spectrometry (ICP-AES) methods were used to measure major, minor, and trace element concentrations in the calcine and sediment samples collected in this study. In the first ICP-AES method, concentrations for 40 elements were determined following decomposition of 0.2 g of sample using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at about 100°C . This procedure is considered to be a total digestion method. The digested sample was aspirated into the ICP-AES discharge where the elemental emission signal was measured simultaneously for the 40 elements. Calibration was performed by standardizing with rock reference materials and a series of multi-element solution standards. This method is similar to that described by Briggs (1996).

The calcine and sediment samples were also analyzed by a 10 element ICP-AES method using a widely used extraction technique similar to the procedure described by Motooka (1988). A 1.0 g sample aliquot was digested with a hydrochloric acid-hydrogen

peroxide mixture, which dissolves metals not tightly bound in the silicate lattice of rocks, soils, and stream sediments. The metals were then extracted by a 10 percent aliquot 336-diisobutylketone solution as organic halides. The separated organic phase was pneumatically aspirated into a multichannel ICP instrument where the concentrations of the extracted metals (Ag, As, Au, Bi, Cd, Cu, Mo, Pb, Sb, and Zn) are determined simultaneously. This procedure is a partial digestion, and depending on the type of sample, there may be a significant discrepancy between the proposed value of the reference material and the laboratory value. This is primarily due to the availability of the metal in the sample. Since this is a partial digestion, those metals tightly bound in highly resistant minerals will not be extracted. Elements determined by ICP-AES and their limits of determination are listed in [table 2](#).

Atomic Absorption Spectrophotometry

Mercury and gold were measured in the calcine and sediment samples collected in this study by atomic absorption spectrophotometry (AAS). Mercury was determined by cold-vapor atomic absorption spectrophotometry (CVAAS) using a procedure modified from O'Leary and others (1996). A 0.1 g aliquot of sample was digested with a mixture of sulfuric acid, nitric acid, five percent potassium permanganate, and five percent potassium peroxydisulfate in a water bath for one hour. Excess potassium permanganate was reduced with hydroxylamine sulfate solution and then Hg (II) was reduced to Hg⁰ with stannous chloride. The mercury vapor was separated and measured using a LEEMAN PS200 automated mercury analyzer.

Gold was determined in the sediment and calcine samples by AAS after collection by fire assay. An assay fusion consists of heating a mixture of 15 g of finely pulverized sample with about three parts of a flux until the product was molten. One of the ingredients of the flux was a lead compound, which was reduced by other constituents of the flux or sample to metallic lead. The latter collects all the gold, together with silver, platinum metals, and small quantities of certain base metals present in the sample and settles to the bottom of the crucible to form a lead button. The gangue of the ore was converted by the flux into a slag sufficiently fluid so that all particles of lead may settle readily through the molten mass. The choice of a suitable flux depends on the character of the ore. The lead button was cupelled to oxidize the lead leaving behind a dore bead containing the precious metals. The dore bead was then transferred to a test tube, dissolved with aqua regia, diluted to a specific volume and analyzed by AAS. Elements determined by AAS and their limits of determination are listed in [table 2](#).

Water Sample Analysis

Inductively Coupled Plasma-Mass Spectrometry

Water samples collected in this study were analyzed by a multi-element inductively coupled plasma-mass spectrometry (ICP-MS) technique following the method of Lamothe and others (1999). The ICP-MS was calibrated using commercially available multi-element standard solutions in conjunction with one USGS standard reference sample. Samples must be acid-preserved prior to analyses, but no digestion was required for the determination of dissolved elements in aqueous samples. Internal standards were added to compensate for matrix effects and instrumental drift. Element isotopes measured were selected to minimize isobaric overlap from other elements and

molecular species that might be present. Elements determined by ICP-MS and their limits of determination are listed in [table 3](#).

Atomic Fluorescence

Water samples were analyzed for mercury by atomic fluorescence (AF) using a method modified from Kennedy and Crock (1987). Preserved water samples were analyzed directly. Mercury (II) was reduced to mercury gas with hydroxylamine hydrochloride/sodium chloride and stannous chloride in a flow injection system, releasing the gas into an atomic fluorescence detector where concentration was determined. Elements determined by AF and their limits of determination are listed in [table 3](#).

Ion Chromatography

The anions SO_4^{2-} , NO_3^- , F^- , and Cl^- were determined sequentially by ion chromatography (IC) on filtered water samples using a method modified from d'Angelo and Ficklin (1996). The samples were injected into a DX-120 Dionex Ion Chromatograph where the anions of interest separate through an anion-ion exchange separator column at different rates, depending on the affinity of each species for the ion-exchange resin. The sample then passes into a flow-through conductivity cell where the anions were detected and peak areas were determined. The peak areas of unknown samples were compared with that of five calibration standards for each anion in question to determine sample concentrations. Elements determined by IC and their limits of determination are listed in [table 3](#).

Alkalinity by Titration

Water samples collected in this study were analyzed for alkalinity in the laboratory using an Orion 960 Autochemistry System for preset endpoint alkalinity titration. Titrant (0.01 M H_2SO_4) was added to 50 mL of sample until a pH of 4.5 was reached. Alkalinity was then calculated and reported as mg/L CaCO_3 .

Description of the Data Tables

Geochemical data are given for the sediment and rock samples in [table 4](#), calcine samples in [table 5](#), and water samples in [table 6](#). Sample numbers in the tables correspond to those in figures 1-9. Field duplicates are numbered with a "D9" prefix in the data tables. Locations taken in the field by GPS are given in latitude and longitude in degrees, minutes, and seconds, as well as in decimal degrees. In the column header, there is an abbreviation for each element determined and the analytical method used as follows: ICP40 (40 element inductively coupled plasma-atomic emission spectrometry), ICP10 (10 element inductively coupled plasma-atomic emission spectrometry), CVAAS (cold-vapor atomic absorption spectrophotometry), AAS (atomic absorption spectrophotometry), ICP-MS (inductively coupled plasma-mass spectrometry), AF (atomic fluorescence), and IC (ion chromatography).

Digital Data

The data in this report are also available as digital data on a CD-ROM in Gray and others (1999). The CD-ROM contains the geochemical data for the samples collected in this study as Excel (.xls) files and the text and figures are in a portable document format (.pdf) file. The geochemical data in this report are also part of the USGS National Geochemical Database in Denver that contains both descriptive geological information and analytical data. This report may also be obtained on the USGS web site at: greenwood.cr.usgs.gov/pub/open-file-reports/ofr-99-0576/.

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Table 1. Description and production of mercury mines studied.

District	Mines Studied	Host Rocks	Approximate Mercury Production Per District
Imlay	Eldorado (Blackjack)	Veins in Triassic limestone and shale	800 flasks
Dutch Flat	Dutch Flat	Veins in Paleozoic schist and phyllite cut by Tertiary granodiorite	90 flasks
Poverty Peaks	Cahill	Veins in Paleozoic and Triassic limestone and sandstone, and opalite altd volcanic rx	600 flasks
Ivanhoe	Silver Cloud	Opalite altered Tertiary volcanic tuff	>2,000 flasks
Goldbanks	Goldbanks	Opalite altered Tertiary volcanic tuff and breccia	2,700 flasks
Bottle Creek	White Peaks	Veins in Paleozoic and Triassic tuffs and sandstone and Tertiary diabase dikes	4,500 flasks
Antelope Springs	Pershing and Juniper	Veins in Triassic limestone, dolomite conglomerate, and shale	12,500 flasks
Opalite	McDermitt	Opalite altered Tertiary volcanic tuffs	270,000 flasks

Table 2. Limits of determination for sediments, rocks, and calcines by analyzed inductively coupled plasma-atomic emission spectrometry (ICP-AES) and atomic absorption spectrophotometry (AAS).

Reporting limits for the 40 element ICP-AES method

Element	Lower Limit	Upper limit
Aluminum, Al	0.005 %	50 %
Calcium, Ca	0.005 %	50 %
Iron, Fe	0.02 %	25 %
Potassium, K	0.01 %	50 %
Magnesium, Mg	0.005 %	5 %
Sodium, Na	0.005 %	50 %
Phosphorous, P	0.005 %	50 %
Titanium, Ti	0.005 %	25 %
Silver, Ag	2 µg/g	10,000 µg/g
Arsenic, As	10 µg/g	50,000 µg/g
Gold, Au	8 µg/g	50,000 µg/g
Barium, Ba	1 µg/g	35,000 µg/g
Beryllium, Be	1 µg/g	5,000 µg/g
Bismuth, Bi	50 µg/g	50,000 µg/g
Cadmium, Cd	2 µg/g	25,000 µg/g
Cerium, Ce	5 µg/g	50,000 µg/g
Cobalt, Co	2 µg/g	25,000 µg/g
Chromium, Cr	2 µg/g	25,000 µg/g
Copper, Cu	2 µg/g	15,000 µg/g
Europium, Eu	2 µg/g	5,000 µg/g
Gallium, Ga	4 µg/g	50,000 µg/g
Holmium, Ho	4 µg/g	5,000 µg/g
Lanthanum, La	2 µg/g	50,000 µg/g
Lithium, Li	2 µg/g	50,000 µg/g
Manganese, Mn	4 µg/g	50,000 µg/g
Molybdenum, Mo	2 µg/g	50,000 µg/g
Niobium, Nb	4 µg/g	50,000 µg/g
Neodymium, Nd	9 µg/g	50,000 µg/g
Nickel, Ni	3 µg/g	50,000 µg/g
Lead, Pb	4 µg/g	100,000 µg/g
Scandium, Sc	2 µg/g	50,000 µg/g
Tin, Sn	50 µg/g	50,000 µg/g
Strontium, Sr	2 µg/g	15,000 µg/g
Tantalum, Ta	40 µg/g	50,000 µg/g
Thorium, Th	6 µg/g	50,000 µg/g
Uranium, U	100 µg/g	100,000 µg/g
Vanadium, V	2 µg/g	30,000 µg/g
Yttrium, Y	2 µg/g	25,000 µg/g
Ytterbium, Yb	1 µg/g	5,000 µg/g
Zinc, Zn	2 µg/g	75,000 µg/g

Reporting limits for the 10 element ICP-AES method:

Element	Lower limit (µg/g)	Upper limit (µg/g)
Silver, Ag	0.08	400
Arsenic, As	1.0	6,000
Gold, Au	0.10	1,500
Bismuth, Bi	1.0	6,000
Cadmium, Cd	0.05	500
Copper, Cu	0.05	500
Molybdenum, Mo	0.10	900
Lead, Pb	1.0	6,000
Antimony, Sb	1.0	6,000
Zinc, Zn	0.05	500

Reporting limits for the AAS methods:

Element	Lower limit	Upper limit
Gold, Au	0.005 µg/g	10 µg/g
Mercury, Hg	0.020 µg/g	10 %

Table 3. Lower limits of determination for water samples analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence (AF), and ion chromatography (IC).

Reporting limits for the ICP-MS method:

Element	Lower limit
Silver, Ag	0.01 µg/L
Aluminum, Al	0.2 µg/L
Arsenic, As	3 µg/L
Barium, Ba	0.1 µg/L
Beryllium, Be	0.05 µg/L
Calcium, Ca	0.05 mg/L
Cadmium, Cd	0.02 µg/L
Cobalt, Co	0.02 µg/L
Chromium, Cr	1 µg/L
Copper, Cu	0.5 µg/L
Iron, Fe	30 µg/L
Potassium, K	0.03 mg/L
Magnesium, Mg	0.01 mg/L
Manganese, Mn	0.01 µg/L
Sodium, Na	0.01 mg/L
Nickel, Ni	0.1 µg/L
Lead, Pb	0.05 µg/L
Antimony, Sb	0.1 µg/L
Thallium, Tl	0.05 µg/L
Vanadium, V	0.1 µg/L
Zinc, Zn	0.5 µg/L

Reporting limits for the AF method:

Element	Lower limit
Mercury, Hg	0.005 µg/L

Reporting limits for the IC method:

Element	Lower limit (mg/L)
Chloride, Cl ⁻	0.1
Fluoride, F ⁻	0.1
Nitrate, NO ₃ ⁻	0.1
Sulfate, SO ₄ ²⁻	2.0

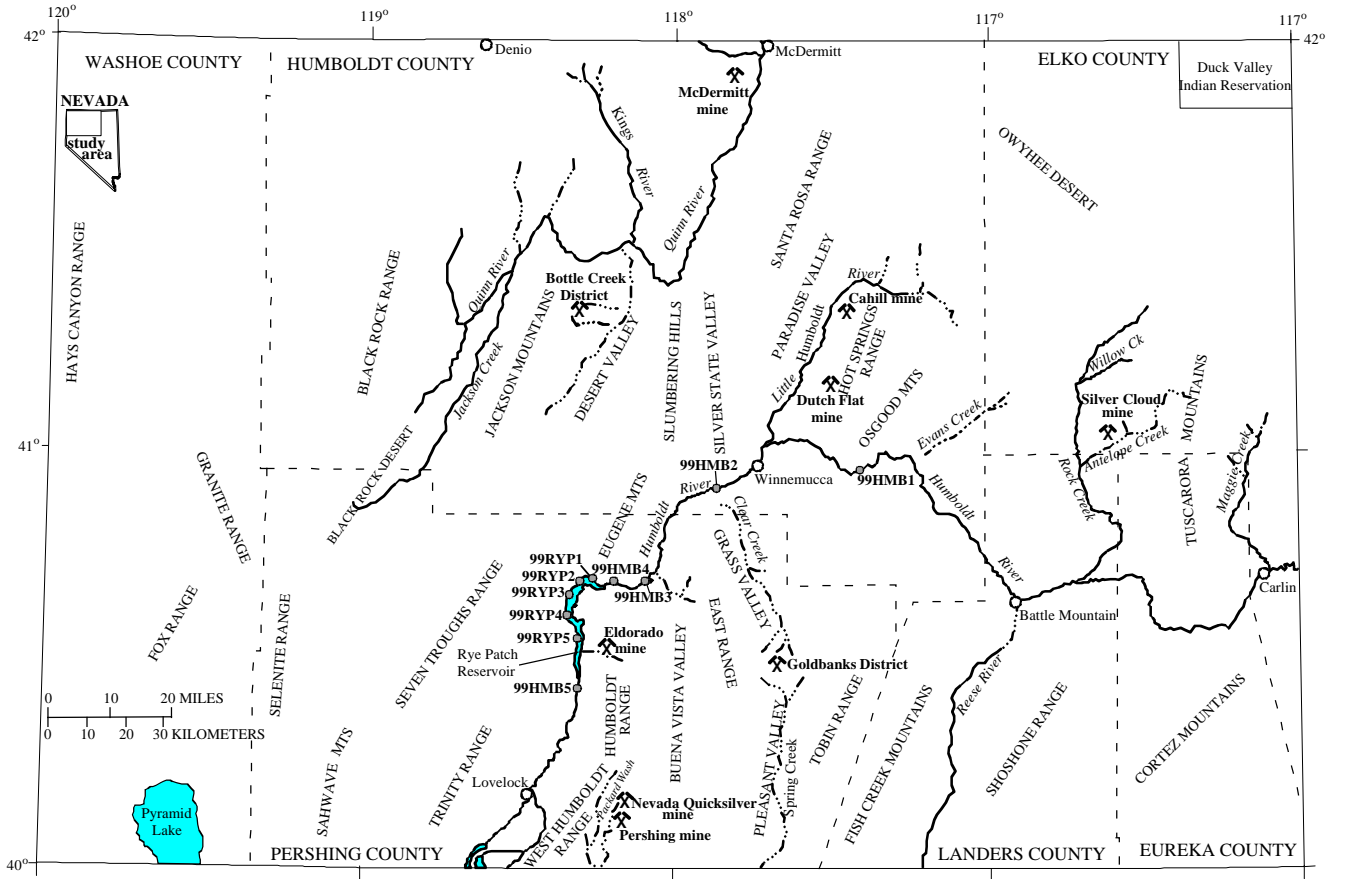


Figure 1. Location of the mercury districts studied and samples collected from the Humboldt River and Rye Patch Reservoir.

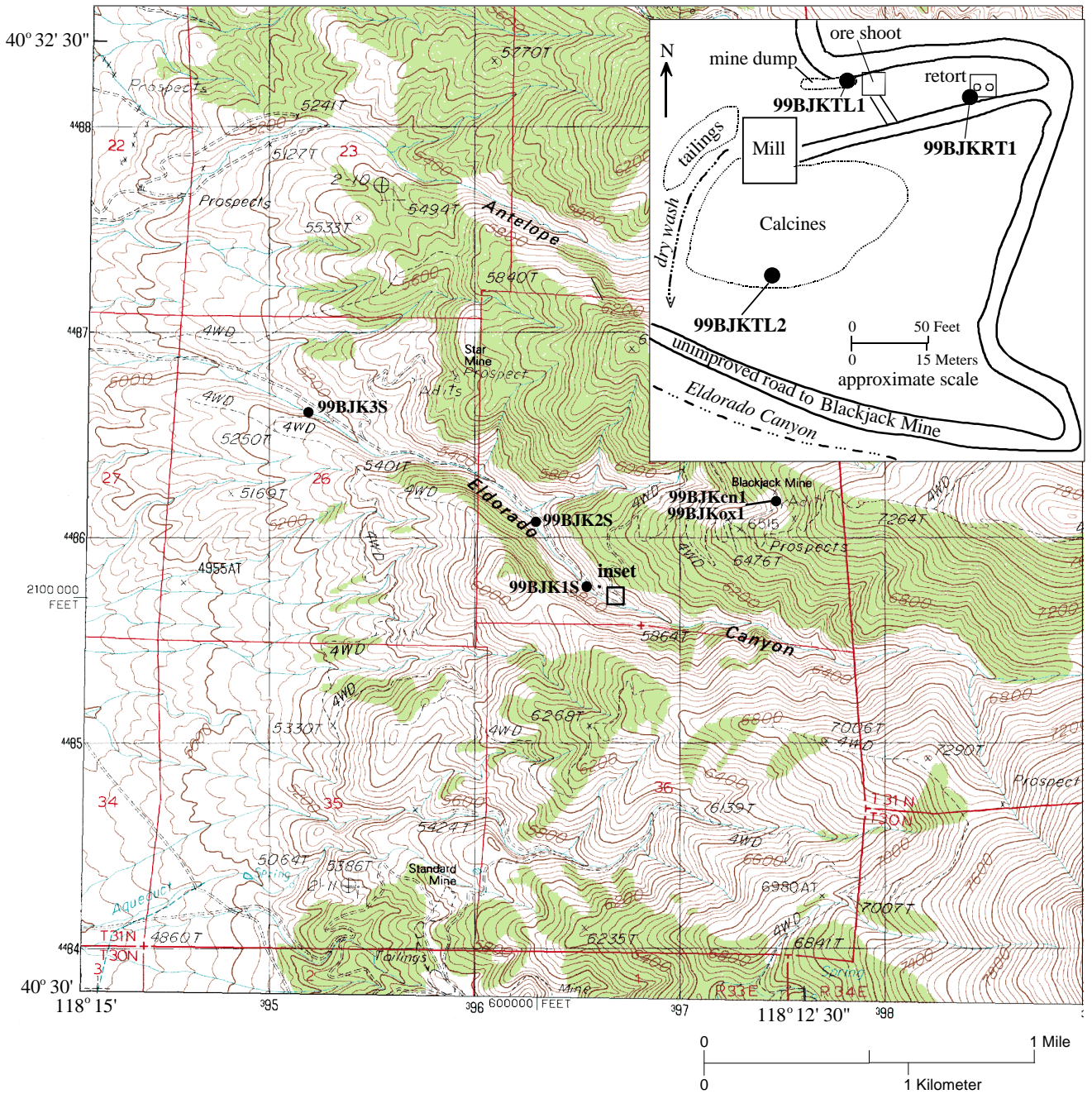


Figure 2. Location of samples collected from the Eldorado mine (also known as the Blackjack mine) in the Imlay District. Inset figure is a sketch map showing the location of samples collected around the mill and retort areas

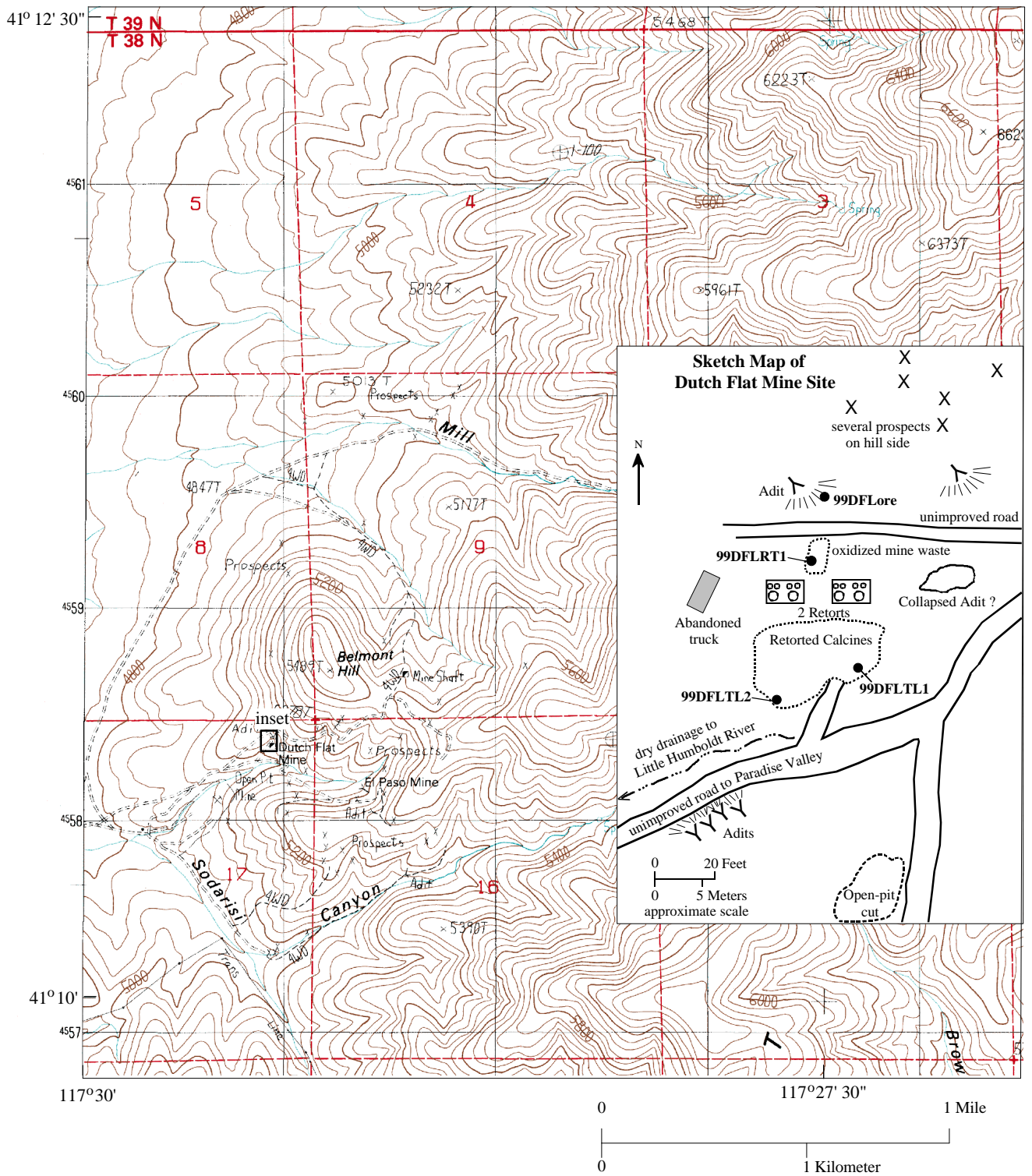


Figure 3. Location of samples collected from the Dutch Flat mine in the Dutch Flat District. Inset figure is a sketch map showing the location of samples collected around the retort site.

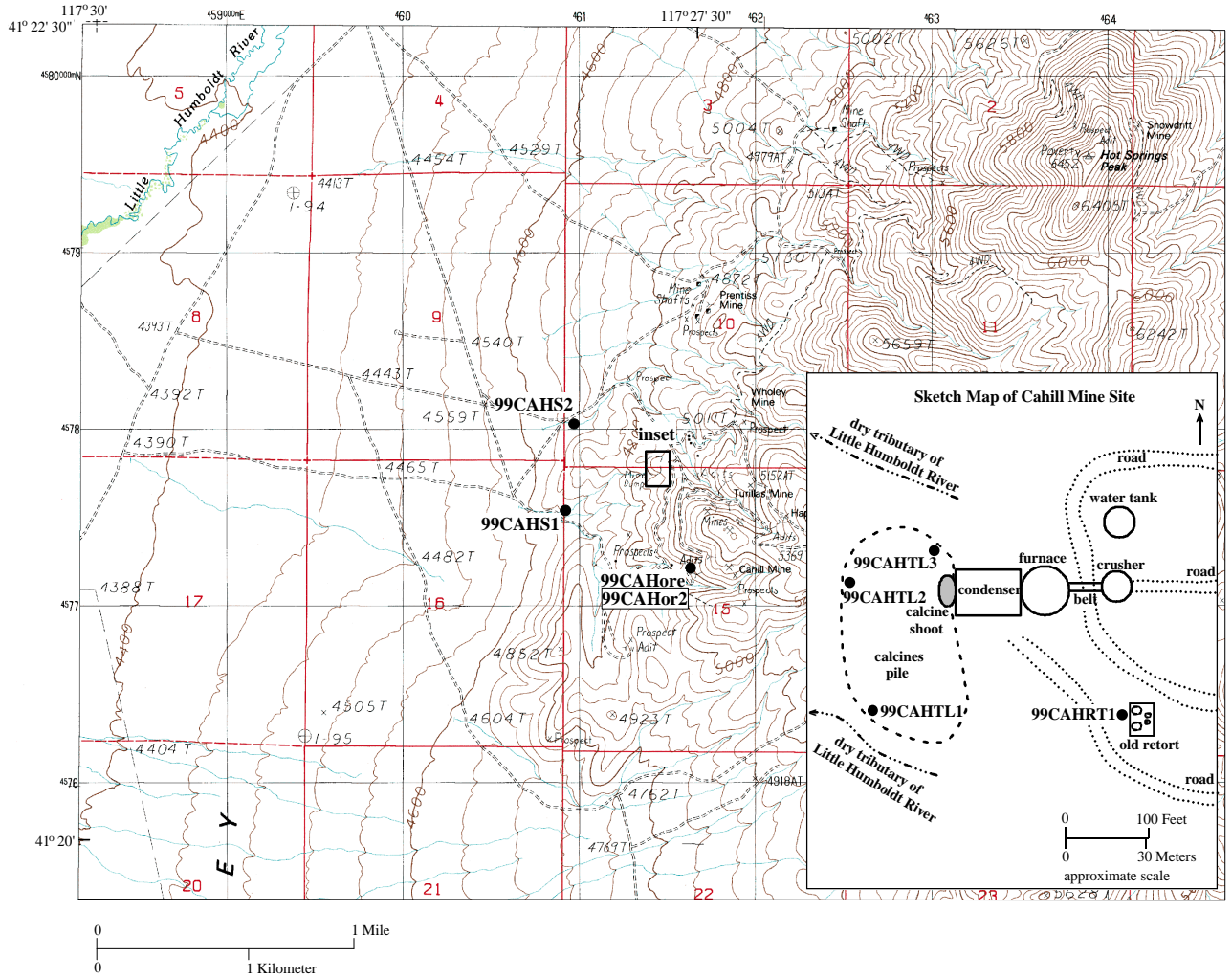


Figure 4. Location of samples collected from the Cahill mine in the Poverty Peaks District. Inset figure is a sketch map showing the location of samples collected around the retort site.

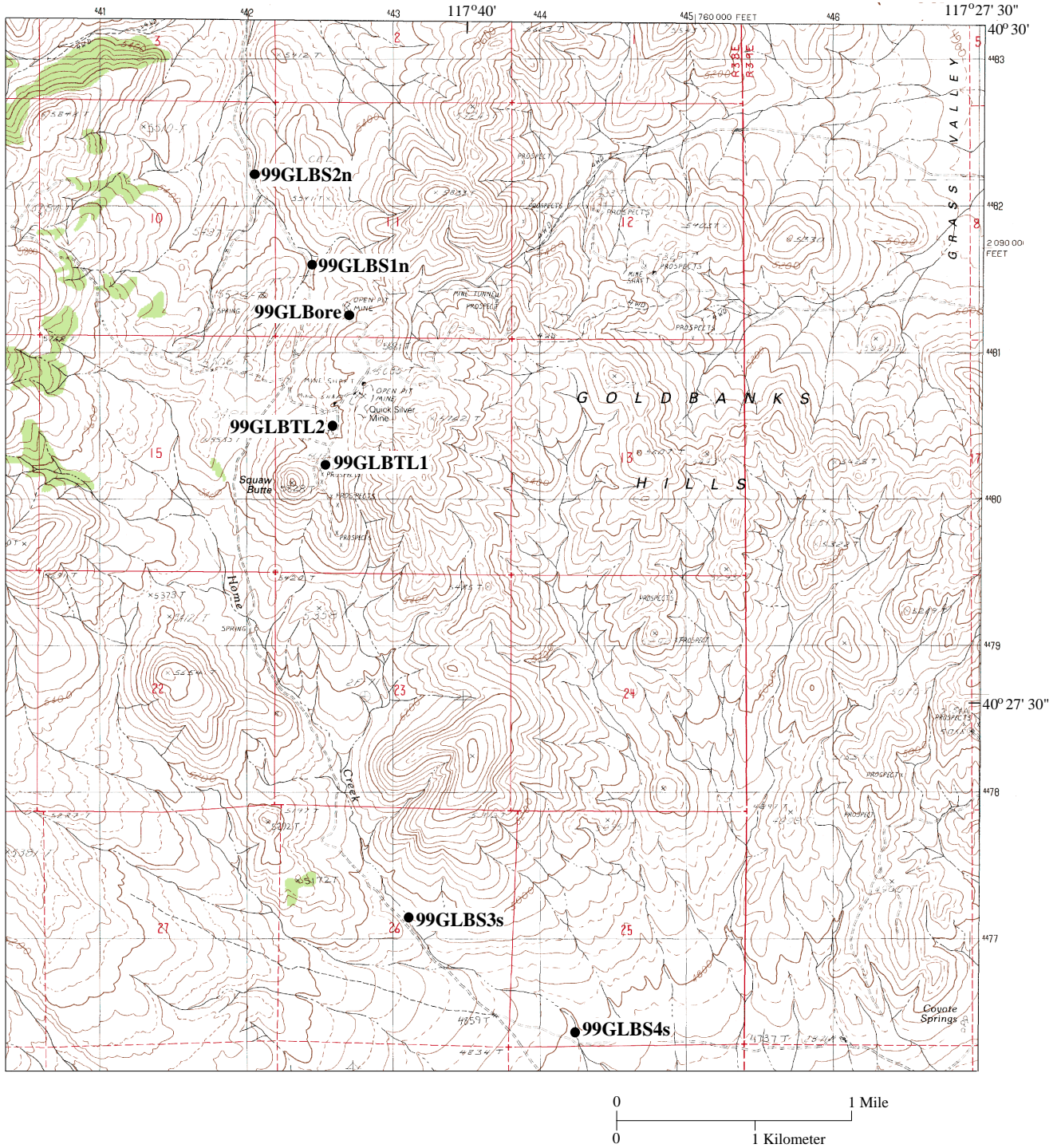


Figure 5. Location of samples collected from the Goldbanks mine in the Goldbanks District.

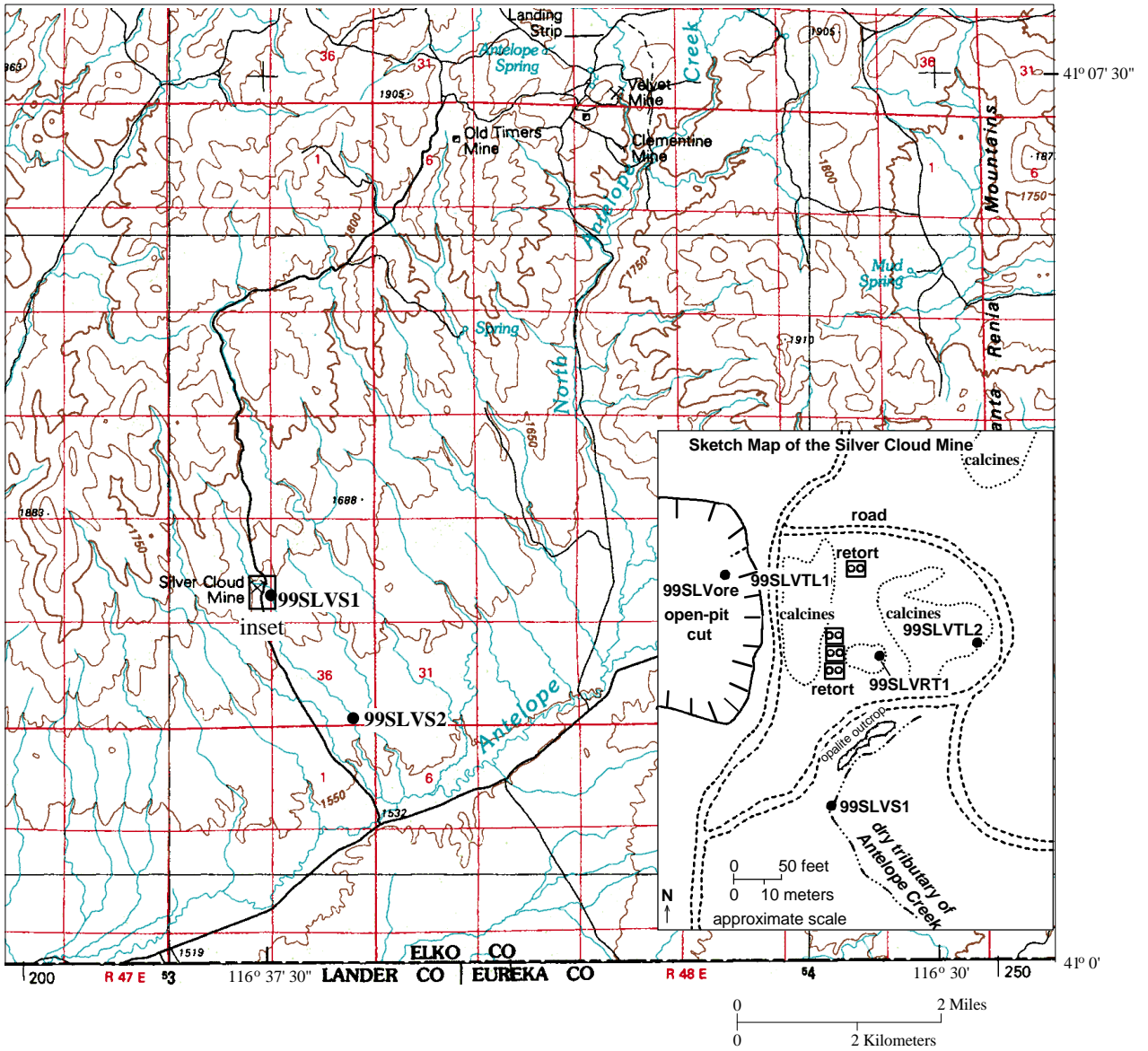


Figure 6. Location of samples collected from the Silver Cloud mine in the Ivanhoe District. Inset figure is a sketch map showing the location of samples collected around the mine site.

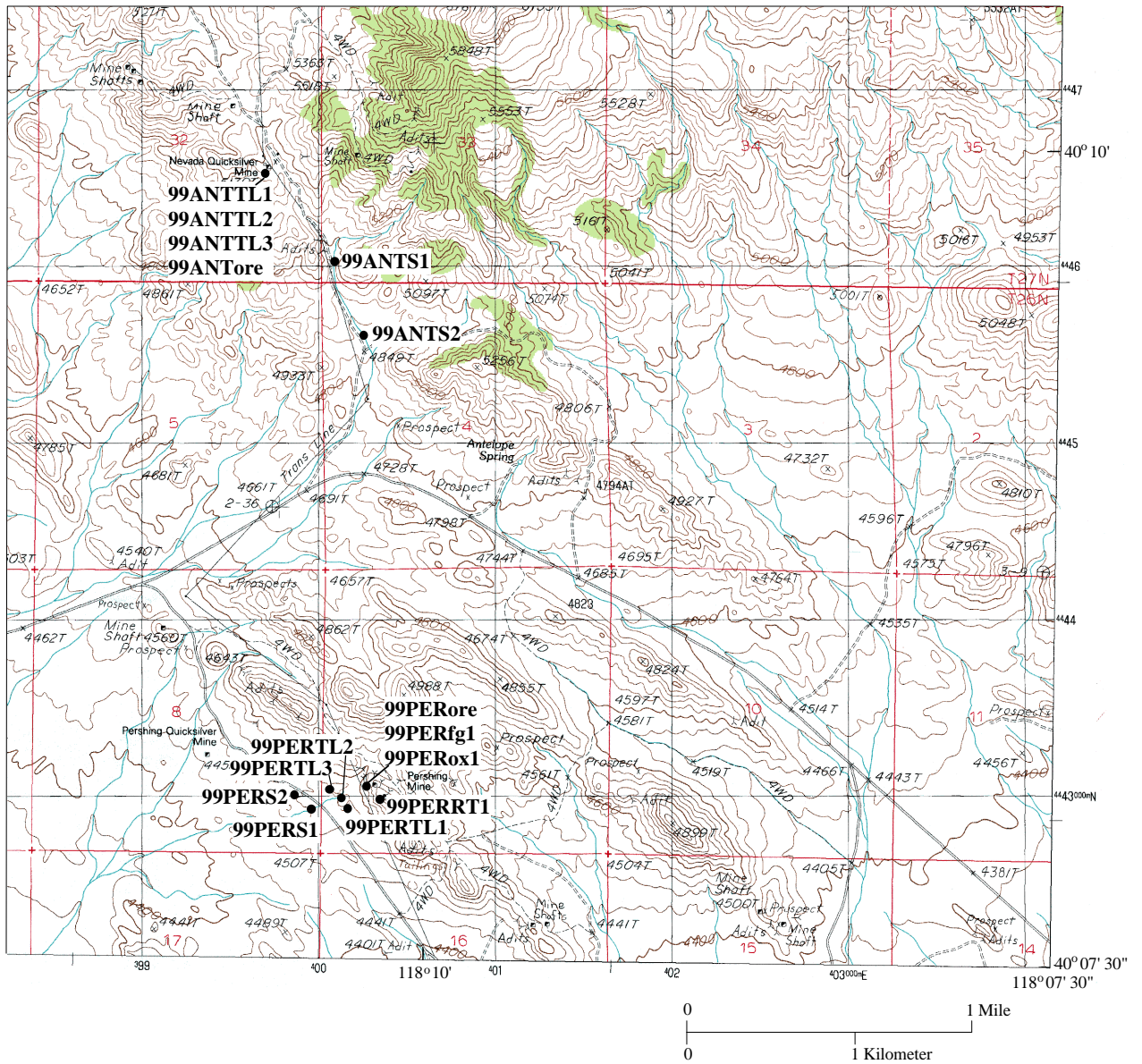


Figure 7. Location of samples collected from the Pershing mine and the Juniper (Nevada Quicksilver) mine in the Antelope Springs District.

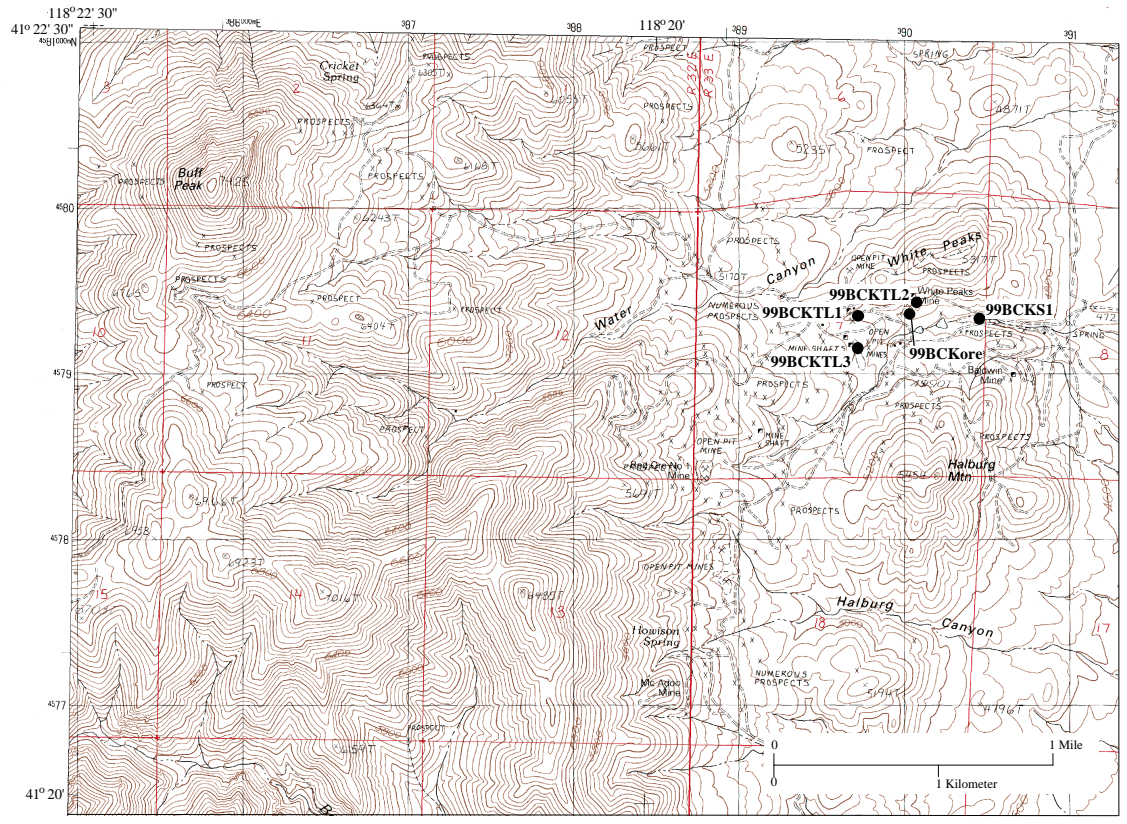


Figure 8. Location of samples collected from the White Peaks mine in the Bottle Creek District.

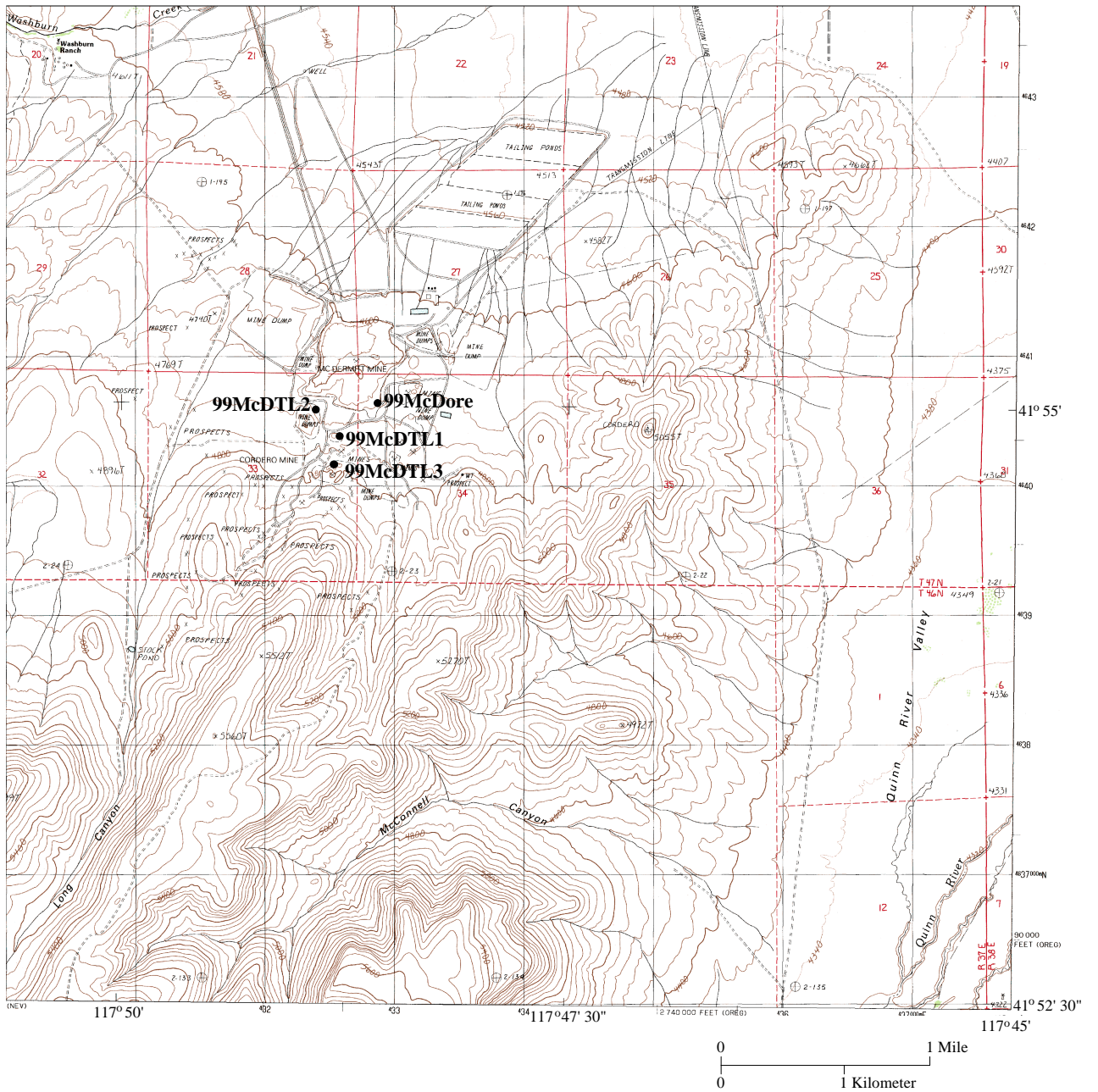


Figure 9. Location of samples collected from the McDermitt mine in the Opalite District.