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Geochemistry of Background Sediment Samples at Technical Area 39, Los Alamos National Laboratory

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GEOCHEMISTRY OF BACKGROUND SEDIMENT SAMPLES AT TECHNICAL AREA 39, LOS ALAMOS NATIONAL LABORATORY

by

Steven L. Reneau, Katherine Campbell,
Patrick A. Longmire, and Eric V. McDonald

ABSTRACT

This report presents results of chemical analyses of 24 analytes in 16 background sediment samples collected from Ancho Canyon and Indio Canyon at Technical Area (TA) 39, Los Alamos National Laboratory. Preliminary upper tolerance limits (UTLs) for sediments are calculated from this data set but, because of the small sample size, these UTLs exceed the maximum values in the data set by up to 50% and will require revision as more background sediment data are obtained.

Systematic variations in the background chemistry of sediments at TA-39 occur between different geomorphic settings and different particle sizes. These differences indicate that the best comparison of potentially contaminated sediments to background should use the most comparable subset of the background data set. The lowest concentrations of most analytes occur within coarse, well-sorted sands in active stream channels (which are dominated by quartz and sanidine crystals), and the concentrations of most analytes generally increase with decreasing sediment particle size. The concentration of uranium within one sample of black sand (dominated by high-density magnetite grains) was within the range of other background samples. This relationship is important because the presence of higher concentrations of uranium in black sand deposits may thus indicate anthropogenic uranium that was concentrated by density as in a placer deposit.

Analyte concentrations in sediments are generally lower than those associated with B horizons in soils but are comparable to elemental concentrations within the A and C horizons. However, the A and C soil horizons possess greater ranges, and thus the use of UTLs developed for Laboratory soils may not be appropriate for evaluating potential contamination within sediments. Concentrations of elements in the sediments are strongly influenced by the total surface area available for adsorption, and concentrations of trace elements are minimal within the medium- and coarse-grained sediments with low surface areas relative to silt and clay. Different minerals concentrated in the sediments, such as magnetite, however, are higher in trace elements resulting in part from ionic substitution within the mineral lattice during primary crystallization. For example, a sample of magnetite-rich black sand is higher in As, Be, Cr, Mn, Ni, Pb, Th, U, V, and Zn relative to silicate-rich sediments.

Positive correlations exist between concentrations of different metals in the sediment samples (i.e., Fe and As, Fe and Be) that are similar to those present in soils at the Laboratory, although the concentrations of metals in the sediments are generally less than in the soils. Relationships between iron and other metals of concern can be used to evaluate whether anomalously high values in a data set are within background ranges or instead may reflect contamination.

Concentrations of many analytes from sampled prehistoric channel and floodplain sediments are higher than their concentrations in more recent deposits, possibly because of postdepositional additions of solutes associated with shallow groundwater flow within the alluvium. The processes that apparently increased concentrations of some trace elements within the prehistoric deposits may be similar to the processes affecting old sediments beneath the valley floor penetrated in core holes, suggesting that higher concentrations of many trace elements might be encountered in the subsurface than in surface sediment samples.

Principal components analysis (PCA) indicates that 89% of the variability in the background sediment data set can be accounted for by a single component, which is due to the strong correlations that occur between many major and trace elements. The remaining 11% is almost entirely accounted for by a second component that separates the two sample areas in Ancho and Indio Canyons. These results are similar to those obtained by PCA of the background soil data set of Longmire et al. (1995), for which overall variability is dominated by a strongly correlated variation of several major and trace elements, reflecting differences between soil horizons, and variation between sample sites is the second most important source of variability.

INTRODUCTION

Sixteen sediment samples were collected from Ancho and Indio Canyons in Technical Area (TA) 39, Los Alamos National Laboratory (Fig. 1), in August 1994, to provide background chemical concentrations from deposits comparable to those collected as part of Environmental Restoration Project site characterization activities in Ancho Canyon. TA-39 has been used as a high-explosives firing site since 1953, and contaminants of potential concern that may have dispersed during experiments include Ba, Be, Cr, Pb, Tl, and U (LANL, 1993).

Two primary sample areas were chosen to increase the chance that the range of variability in natural sediment deposits would be included and that any unanticipated contamination would be detected. The main sample areas are Indio Canyon, the largest drainage basin in the Laboratory entirely within Bandelier Tuff that has had no Laboratory facilities, and a small tributary to Ancho Canyon near State Road 4 that also has no upstream Laboratory activities (Fig. 2). An additional sample site is a stream bank along Ancho Canyon that exposes prehistoric (1000–3000 yr old) sediments, which was chosen to evaluate whether such old deposits could also be used to provide valid background values (site discussed in Reneau and McDonald, 1996, pp. 68–72). Sampled deposits were chosen to maximize the natural variability that exists within these sediments and to evaluate systematic variations in chemistry that may exist between different geomorphic settings (i.e., channel versus floodplain; Fig. 3) and between different size fractions. Descriptions of the samples analyzed in this study are presented in Table 1. Although we cannot be certain that all of the sampled sediments (particularly the active channel samples) have not been affected by airborne dispersion of contaminants from firing sites, procedures that we use to exclude outliers from the data set are expected to remove any potentially elevated analytes.

One limitation of this sampling program is the small size of the sample set from any specific geomorphic setting or type of deposit (i.e., coarse sands in an active channel), at most two per sample set. These data, therefore, may not encompass the full range of variability that exists in sediments at TA-39. However, there is generally an internal consistency in this data set, and systematic variations exist between settings and size fractions, suggesting that this limited data set may be

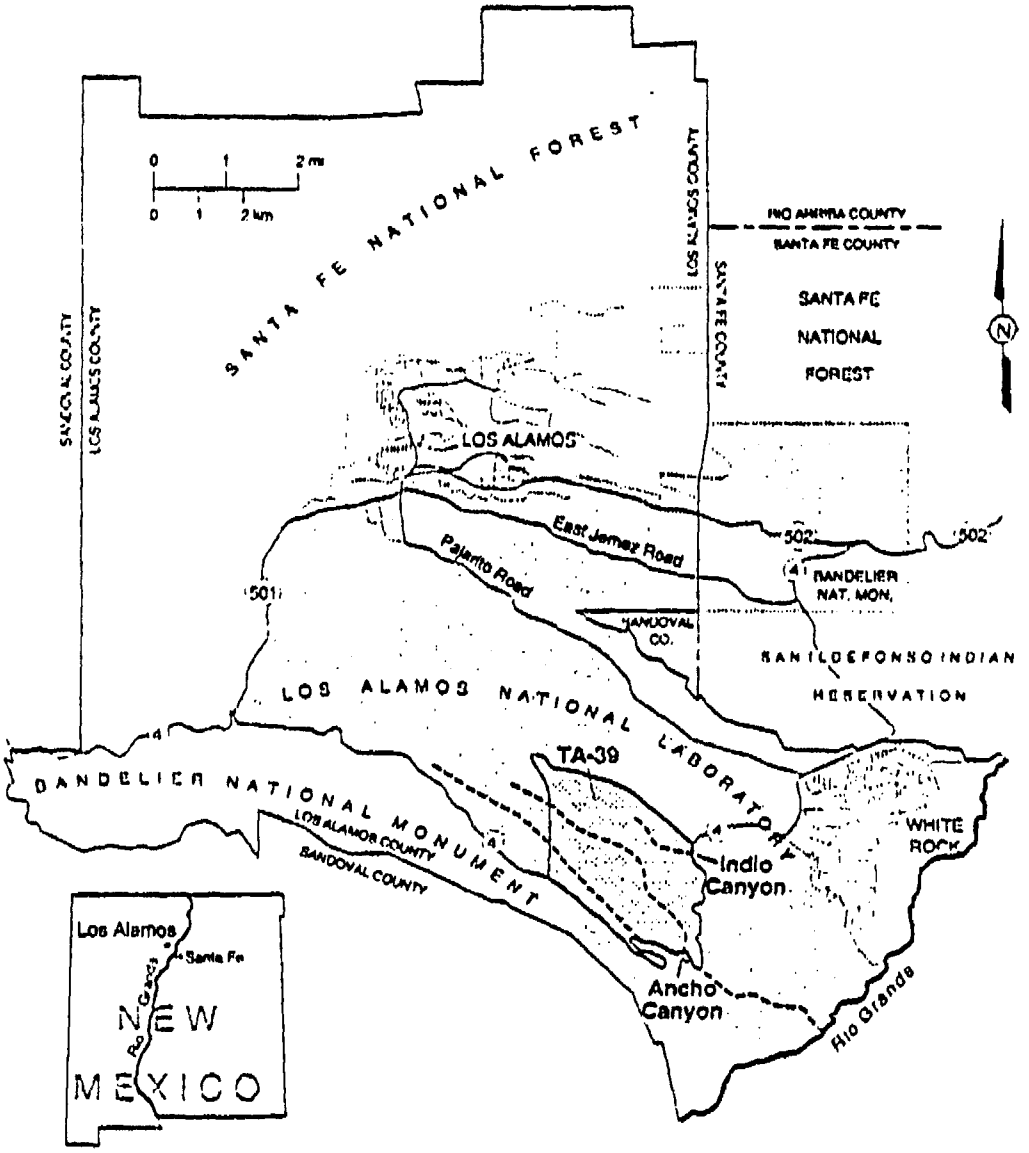

Fig. 1. Location map of TA-39.

generally representative of similar settings in drainage basins that are entirely within the Bandelier Tuff.

Since completion of this study, additional background sediment samples have been collected from Guaje, Los Alamos, and Pueblo Canyons. These more recent analyses have been combined with the Ancho Canyon and Indio Canyon analyses to develop an updated sediment background data set (McDonald et al., 1997; Ryti et al., 1998). As a result, the estimates of the upper level of background values in this report have been superseded, but they are retained here to allow examination of the sensitivity of background estimates to the size of the data set and the sample locations.

LABORATORY METHODS

Sediment samples were dried at a low temperature in a laboratory oven and sieved to remove gravel (>2 mm) and roots. Splits of two large floodplain samples were dry sieved to separate the samples into three different size fractions: 0.25 to 2 mm

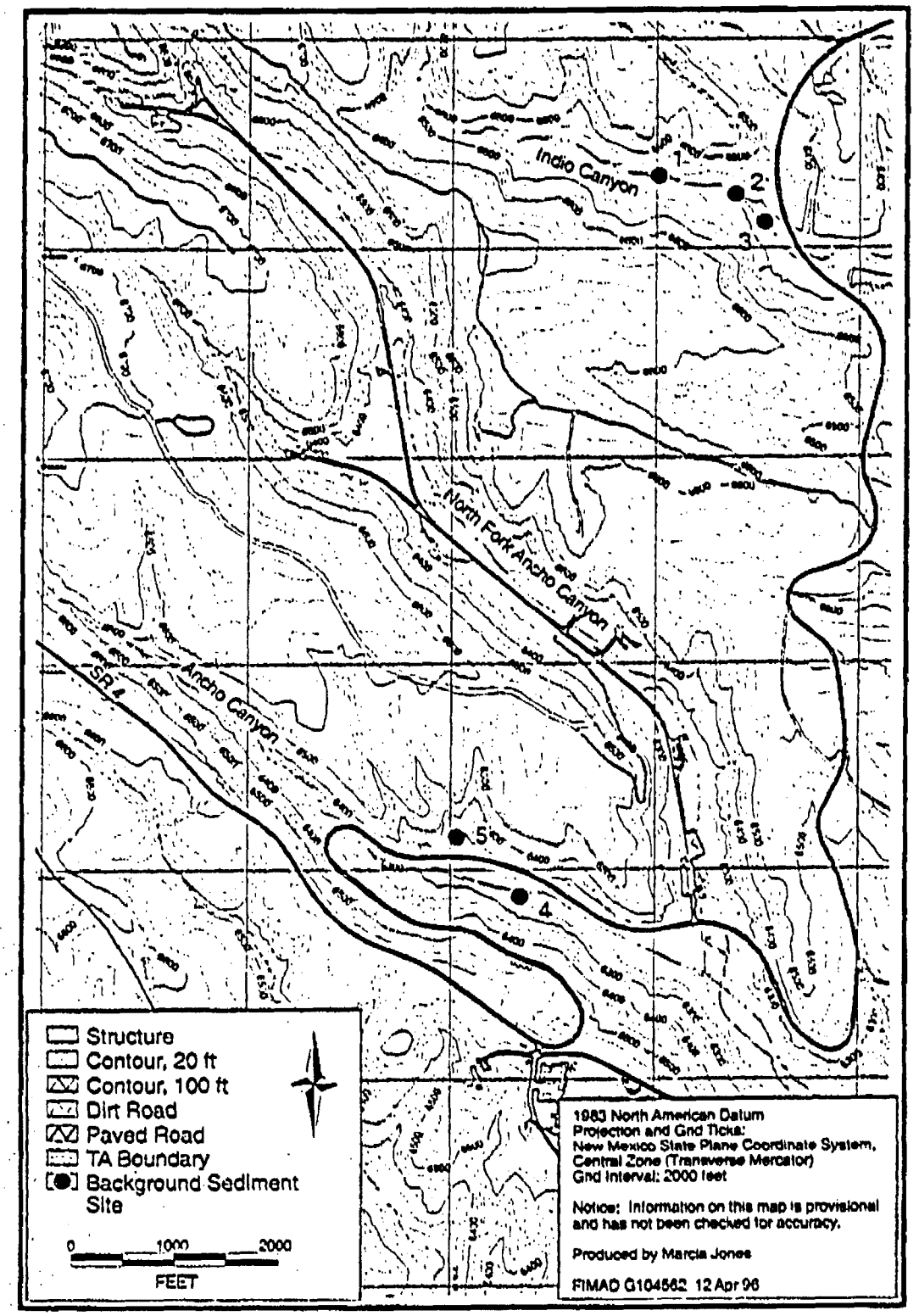

Fig. 2. Location map of background sediment sample sites in Ancho and Indio Canyons. Site numbers referenced to samples in Table 1.

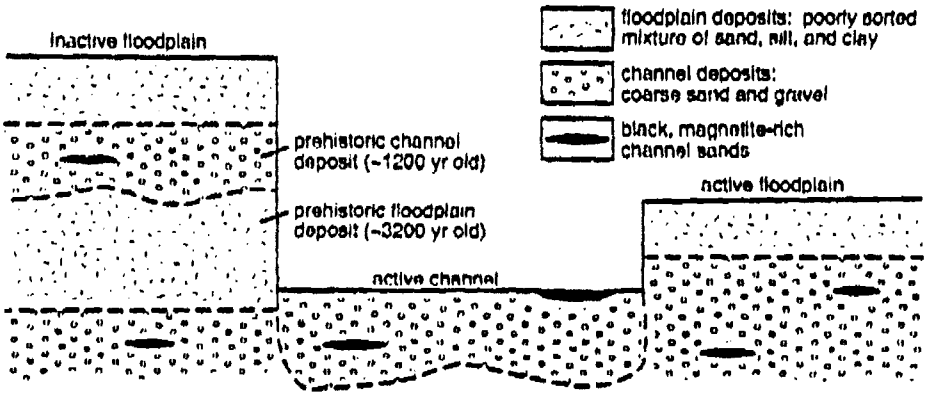

Fig. 3. Schematic sketch showing geomorphic setting of background sediment samples. Approximate ages of sediments are from radiocarbon analyses of charcoal collected from an Ancho Canyon sample site (Site 4 of Fig. 2).

(coarse and medium sand), 0.075 to 0.25 mm (fine sand), and <0.075 mm (very fine sand, silt, and clay). Clumps of sediment were manually crushed but no chemical dispersants were used, and the larger size fractions may therefore contain small portions of finer particle sizes.

Sample splits of all sediment samples were subject to three laboratory pretreatment procedures: partial digestion using nitric acid (HNO_3) at pH 1 (using standard extraction and analysis procedures specified in Environmental Protection Agency [EPA] Method 3050), which simulates the bioavailability of elements by humans through ingestion; leaching with deionized water, for the analysis of easily dissolved Cl and SO_4; and complete digestion using hydrofluoric acid (HF), to provide whole-sample elemental concentrations. Analysis of As was by electrothermal vapor atomic absorption (ETVAA); of Cl and SO_4 by ion chromatography (IC); of Ta, Th, Tl, and U by inductively coupled plasma mass spectroscopy (ICPMS); and the remainder by inductively coupled plasma emission spectroscopy (ICPES). Results of the chemical analyses are presented in Tables 2, 3, and 4.

QUALITY ASSURANCE CHECKS

Sample splits of two bulk floodplain samples were submitted for analysis to provide an independent quality assurance (QA) check of the reproducibility of the analyses. For the combined 92 duplicate analyses of 24 analytes from the two sets of paired samples and two sample digestion procedures, 87 of the duplicate analyses (95%) were within the reported uncertainty, and three of the remainder (3%) were within twice the reported uncertainty (analyses of Al, Be, and Ni for one of the sample pairs). Only two sets of analyses (2%) were not consistent within twice the reported uncertainty, As and Ta for the paired samples FS2229 and FS2232. Overall, these results therefore indicate that the laboratory analyses can be considered reproducible within the reported uncertainties.

COMPARISON OF CHANNEL SAMPLES AND FLOODPLAIN SAMPLES

Significant differences in analyte concentrations are present between the samples of coarse channel sands and the bulk floodplain samples, as summarized in Tables 5 and 6. For nearly all analytes, concentrations are higher in the floodplain deposits than in the channel deposits, as shown for As, Be, and U in Figure 4. This is consistent with the dominance of quartz and sanidine phenocrysts derived from the Bandelier Tuff within the channel deposits and with the higher concentrations of fine-grained sediment in the floodplain deposits that could both have greater mineralogical variability (including higher abundances of clay minerals and

Table 1. Location of Sample Sites and Description of Samples, TA-39.

Sample Number	Sample Location*	Type of Deposit	Sample Depth	Particle Size	Notes
FS2220	Indio Cyn, 6425' (1)	floodplain	0-18"	<2 mm (sand, silt, clay)	bulk sample, gravel removed
FS2221	Indio Cyn, 6425' (1)	floodplain	0-18"	<0.075 mm (very fine sand, silt, clay)	sample split, sieved
FS2222	Indio Cyn, 6425' (1)	floodplain	0-18"	0.25-0.075 mm (fine sand)	sample split, sieved
FS2223	Indio Cyn, 6425' (1)	floodplain	0-18"	<2 mm (sand, silt, clay)	duplicate of FS2220
FS2224	Indio Cyn, 6425' (1)	channel sands	0-6"	<2 mm (mainly coarse sand)	bulk sample, gravel removed
FS2225	Indio Cyn, 6400' (2)	channel sands	0-1"	<2 mm (mainly fine sand)	black (magnetite) sands
FS2226	Indio Cyn, 6387' (3)	mud in channel	0-1"	<2 mm (mainly fine sand, silt, clay)	mud deposits from recent flood
FS2227	Ancho Cyn, 6228' (4)	old floodplain	4.1-4.6'	<2 mm (sand, silt, clay)	bulk sample, gravel removed
FS2228	Ancho Cyn, 6228' (4)	old channel sands	2.6-3.1'	<2 mm (mainly coarse sand)	bulk sample, gravel removed
FS2229	Ancho Cyn, 6295' (5)	floodplain	8-16"	<2 mm (sand, silt, clay)	bulk sample, gravel removed
FS2230	Ancho Cyn, 6295' (5)	floodplain	8-16"	<0.075 mm (very fine sand, silt, clay)	sample split, sieved
FS2231	Ancho Cyn, 6295' (5)	floodplain	8-16"	0.25-0.075 mm (fine sand)	sample split, sieved
FS2232	Ancho Cyn, 6295' (5)	floodplain	8-16"	<2 mm (sand, silt, clay)	duplicate of FS2229
FS2233	Ancho Cyn, 6295' (5)	channel sands	0-6"	<2 mm (mainly coarse sand)	bulk sample, gravel removed
FS2234	Indio Cyn, 6425' (1)	floodplain	0-18"	0.25-2 mm (coarse + medium sand)	sample split, sieved
FS2235	Ancho Cyn, 6295' (5)	floodplain	8-16"	0.25-2 mm (coarse + medium sand)	sample split, sieved

* Elevations refer to approximate stream channel elevations at sample site, as obtained from FIMAD topographic maps. Numbers in () refer to site locations of Fig. 2.

Table 2. Chemical Data for Samples, TA-39, HNO_3 Digestion.*

Sample	Al (ppm)	Al (+/-)	As (ppm)	As (+/-)	Ba (ppm)	Ba (+/-)	Be (ppm)	Be (+/-)	Ca (ppm)	Ca (+/-)	Co (ppm)	Co (+/-)
FS2220	4600	460	1	0.5	53	5.3	0.53	0.05	1200	120	2.2	0.5
FS2221	7300	730	3	0.60	99	9.90	0.89	0.09	1900	190	3.50	0.50
FS2222	6900	690	2	0.50	77	7.70	0.82	0.08	1700	170	3	0.50
FS2223	4400	440	2	0.50	54	5.40	0.56	0.06	1300	130	2.30	0.50
FS2224	740	74	<0.5		8	0.80	<0.08		180	18	0.60	0.50
FS2225	1400	140	1	0.50	14	1.40	0.70	0.08	990	99	6	0.60
FS2226	8400	840	3	0.60	100	10	1.10	0.11	2600	260	3.50	0.50
FS2227	7700	770	2	0.50	71	7.10	0.74	0.07	1500	150	2.70	0.50
FS2228	2300	230	0.90	0.50	32	3	0.17	0.08	770	77	3.10	0.50
FS2229	7800	780	2	0.50	90	9	0.85	0.09	2100	210	3.50	0.50
FS2230	6800	680	2	0.50	90	9	0.82	0.08	2500	250	3	0.50
FS2231	7600	760	3	0.60	95	9.50	0.87	0.09	2400	240	3.80	0.50
FS2232	6200	620	2	0.50	75	7.50	0.67	0.08	1800	180	3.20	0.50
FS2233	930	93	<0.5		8.30	0.83	<0.08		230	23	0.70	0.50
FS2234	3200	320	1	0.50	37	3.70	0.30	0.08	960	96	1.50	0.50
FS2235	4100	410	1	0.50	49	4.90	0.39	0.08	1100	110	2	0.50

Sample	Cr (ppm)	Cr (+/-)	Cu (ppm)	Cu (+/-)	Fe (ppm)	Fe (+/-)	K (ppm)	K (+/-)	Mg (ppm)	Mg (+/-)	Mn (ppm)	Mn (+/-)
FS2220	3.5	0.5	3.5	0.5	6800	680	970	97	920	92	240	24
FS2221	5.80	0.60	7.30	0.70	9400	940	1500	150	1500	150	330	33
FS2222	4.70	0.50	5.60	0.60	9600	960	1400	140	1300	130	350	35
FS2223	3.30	0.50	3.50	0.50	6500	650	990	99	870	87	240	24
FS2224	1	0.50	0.80	0.50	1400	140	180	74	170	17	53	5.30
FS2225	12	1.20	4.40	0.50	57000	5700	220	22	530	53	1200	120
FS2226	5.60	0.60	12	1.20	9600	960	1800	180	1700	170	380	38
FS2227	5.20	0.50	4.30	0.50	8400	840	1600	160	1400	140	220	22
FS2228	5.40	0.50	1.80	0.50	13000	1300	540	54	570	57	240	24
FS2229	5.70	0.60	5.70	0.60	9100	910	1900	190	1500	150	330	33
FS2230	5.90	0.60	7.50	0.80	8400	840	1900	190	1500	150	230	23
FS2231	5.90	0.60	7.30	0.70	9200	920	2200	220	1600	160	300	30
FS2232	4.70	0.50	4.80	0.50	8000	800	1600	160	1300	130	280	28
FS2233	0.80	0.50	0.90	0.50	1400	140	200	20	200	20	46	4.60
FS2234	2.20	0.50	2.70	0.50	4800	480	650	65	590	59	180	18
FS2235	2.50	0.50	3	0.50	5000	500	1100	110	820	82	190	19

* +/- is uncertainty reported by CST-3.

Table 2. (continued)

Sample	Na (ppm)	Na (+/-)	Ni (ppm)	Ni (+/-)	Pb (ppm)	Pb (+/-)	Sb (ppm)	Sb (+/-)	Ta (ppm)	Ta (+/-)
FS2220	120	14	4	2	5	4	<5		<0.3	
FS2221	120	14	7	2	10	4	<5		<0.3	
FS2222	120	14	5	2	10	4	<5		<0.3	
FS2223	95	14	4	2	8	4	<5		<0.3	
FS2224	46	14	<2		4	4	<5		<0.3	
FS2225	68	14	9	2	11	4	<5		<0.3	
FS2226	190	19	6	2	16	4	5	5	<0.3	
FS2227	150	15	4	2	7	4	<5		<0.3	
FS2228	66	14	4	2	5	4	<5		<0.3	
FS2229	100	14	6	2	10	4	<5		<0.3	
FS2230	110	14	7	2	9	4	<5		<0.3	
FS2232	91	14	6	2	8	4	<5		<0.3	
FS2233	34	14	<2		<4		<5		<0.3	
FS2234	75	14	4	2	5	4	<5		<0.3	
FS2235	80	14	4	2	6	4	<5		<0.3	

Sample	Th (ppm)	Th (+/-)	Tl (ppm)	Tl (+/-)	U (ppm)	U (+/-)	V (ppm)	V (+/-)	Zn (ppm)	Zn (+/-)
FS2220	5.2	0.4	0.5	0.3	0.7	0.3	7.2	0.7	31	3.1
FS2221	7.70	0.50	<0.3		0.90	0.30	12	1.20	38	3.80
FS2222	7.10	0.50	<0.3		1	0.30	10	1	44	4.40
FS2223	5.80	0.40	<0.3		0.90	0.30	7	0.70	31	3
FS2224	1.40	0.30	<0.3		<0.3		1.40	0.50	9	1
FS2225	14	1	<0.3		0.80	0.30	66	6.60	300	30
FS2226	6.60	0.50	<0.3		1.60	0.30	11	1.10	48	4.80
FS2227	5.80	0.40	<0.3		0.60	0.30	9	0.90	33	3
FS2228	2.20	0.30	<0.3		<0.3		20	2	47	5
FS2229	8	0.60	<0.3		0.70	0.30	11	1.10	39	4
FS2230	6.90	0.80	<0.3		0.60	0.30	13	1.30	32	3
FS2231	7.10	0.80	<0.3		0.60	0.30	12	1.20	37	3.70
FS2232	6	0.70	<0.3		0.60	0.30	9	0.90	34	3.40
FS2233	0.90	0.30	<0.3		<0.3		1	0.50	9	1
FS2234	3.60	0.40	<0.3		0.50	0.30	5	0.50	24	2
FS2235	4.30	0.50	1.50	0.30	0.40	0.30	5	0.50	24	2

* +/- is uncertainty reported by CST-3.

Table 3. Chemical Data for Samples, TA-39, HF Digestion.*

Sample	Al (ppm)	Al (+/-)	As (ppm)	As (+/-)	Ba (ppm)	Ba (+/-)	Be (ppm)	Be (+/-)	Ca (ppm)	Ca (+/-)	Co (ppm)	Co (+/-)
FS2220	61000	6100	8.20	1.60	222	22	3.20	0.32	3800	380	2.30	0.50
FS2221	57000	5700	5.30	1	370	37	3.80	0.38	4900	490	4	0.50
FS2222	62000	6200	5.30	1	270	27	4.40	0.44	4300	430	3.80	0.50
FS2223	61000	6100	6.30	1.30	240	24	3.50	0.35	4000	400	2.60	0.50
FS2224	51000	5100	6.20	1.20	130	13	1.10	0.11	2000	200	0.70	0.50
FS2225	11000	1100	4.80	1	32	3.20	1.60	0.16	3400	340	<0.5	
FS2226	63000	6300	8.60	1.70	300	30	5.30	0.50	4900	490	3.40	0.50
FS2227	69000	6900	10.40	2.10	340	34	4	0.40	6100	610	3.90	0.50
FS2228	63000	6300	7.50	1.50	290	29	1.50	0.15	8100	810	7	0.70
FS2229	60000	6000	8	1.60	330	33	3.60	0.36	4900	490	3.50	0.50
FS2230	56000	5600	9.10	1.80	410	41	3.20	0.32	5800	580	3.80	0.50
FS2231	59000	5900	5.90	1.20	380	38	3.60	0.36	5500	550	3.90	0.50
FS2232	61000	6100	3.60	0.70	310	31	3.40	0.34	4700	470	3.30	0.50
FS2233	48000	4800	2.10	0.40	120	12	0.91	0.09	1800	180	1	0.50
FS2234	61000	6100	3	0.60	180	18	2.40	0.24	3400	340	1.50	0.50
FS2235	59000	5900	2.50	0.50	210	21	2.90	0.29	3500	350	2	0.50

Sample	Cr (ppm)	Cr (+/-)	Cu (ppm)	Cu (+/-)	Fe (ppm)	Fe (+/-)	K (ppm)	K (+/-)	Mg (ppm)	Mg (+/-)	Mn (ppm)	Mn (+/-)
FS2220	8.30	0.80	5.10	0.50	13000	1300	27000	2700	1700	170	420	42
FS2221	18	1.80	12	1.20	17000	1700	23000	2300	2700	270	490	49
FS2222	12	1.20	9.60	1	17000	1700	27000	2700	2500	250	580	58
FS2223	9.90	1	6	0.60	14000	1400	29000	2900	1900	190	430	43
FS2224	1.10	0.50	1	0.50	4900	490	26000	2600	470	47	180	18
FS2225	83	8.30	<0.5		110	11	3600	360	3000	300	13000	1300
FS2226	14	1.40	15	1.50	16000	1600	26000	2600	2600	260	540	54
FS2227	15	1.50	7.60	0.80	17000	1700	27000	2700	3300	330	450	45
FS2228	23	2.30	2.60	0.50	52000	5200	25000	2500	2500	250	1300	130
FS2229	15	1.50	8.70	0.90	16000	1600	26000	2600	2700	270	460	46
FS2230	23	2.30	13	1.30	19000	1900	22000	2200	3100	310	420	42
FS2231	17	1.70	13	1.30	18000	1800	24000	2400	3100	310	480	48
FS2232	14	1.40	8.10	0.80	15000	1500	24000	2400	2500	250	430	43
FS2233	2.50	0.50	1.20	0.50	4100	410	24000	2400	530	53	130	13
FS2234	4.40	0.50	3.40	0.50	8500	850	25000	2500	1000	100	290	29
FS2235	7.50	0.80	4.80	0.50	11000	1100	26000	2600	1600	160	330	33

* +/- is uncertainty reported by CST-3.

Table 3. (continued)

Sample	Na (ppm)	Na (+/-)	Ni (ppm)	Ni (+/-)	Pb (ppm)	Pb (+/-)	Sb (ppm)	Sb (+/-)	Ta (ppm)	Ta (+/-)
FS2220	19000	1900	5	2	11	4	<5		6	0.40
FS2221	15000	1500	11	2	20	4	<5		4.70	0.30
FS2222	18000	1800	6	2	16	4	<5		5.30	0.30
FS2223	20000	2000	7	2	13	4	<5		4.20	0.30
FS2224	20000	2000	<2		<4		<5		1.20	0.20
FS2225	2700	270	47	5	50	5	14	5	15	0.90
FS2226	18000	1800	7	2	27	4	<5		5.70	0.30
FS2227	18000	1800	8	2	14	4	<5		4.40	0.40
FS2228	20000	2000	14	2	<4		<5		2.60	0.30
FS2229	16000	1600	8	2	12	4	<5		4.30	0.40
FS2230	14000	1400	10	2	13	4	<5		4	0.40
FS2231	14000	1400	8	2	13	4	<5		4.40	0.40
FS2232	16000	1600	14	2	13	4	<5		4.60	0.50
FS2233	18000	1800	<2		4	4	<5		0.90	0.20
FS2234	21000	2100	2	2	8	4	<5		3	0.30
FS2235	19000	1900	5	2	10	4	<5		3.20	0.30

Sample	Th (ppm)	Th (+/-)	Tl (ppm)	Tl (+/-)	U (ppm)	U (+/-)	V (ppm)	V (+/-)	Zn (ppm)	Zn (+/-)
FS2220	13	0.30	0.50	0.20	3.90	0.20	16	1.60	64	6.40
FS2221	17	0.30	0.70	0.20	5.70	0.30	33	3.30	70	7
FS2222	18	0.40	0.70	0.20	5.60	0.30	25	2.50	88	8.80
FS2223	13	0.30	0.50	0.20	4	0.20	19	1.90	66	6.60
FS2224	3.90	0.20	0.20	0.20	1.10	0.20	2.70	0.50	25	2.50
FS2225	130	4	0.30	0.20	4	0.20	450	45	2500	250
FS2226	18	0.40	0.90	0.30	7.20	0.40	25	2.50	89	8.90
FS2227	15	0.60	0.80	0.20	4.70	0.40	27	2.70	72	7.20
FS2228	9.40	0.40	0.40	0.20	1.50	0.20	84	8.40	210	21
FS2229	15	0.60	0.80	0.20	4.30	0.30	27	2.70	69	7
FS2230	16	0.60	0.80	0.20	4.90	0.40	41	4.10	68	6.80
FS2231	15	0.60	0.80	0.20	4.30	0.30	33	3.30	73	7.30
FS2232	15	0.60	0.80	0.20	4.30	0.30	26	2.60	65	6.50
FS2233	3.30	0.20	0.30	0.20	0.70	0.20	4	0.50	34	3.40
FS2234	8.80	0.40	0.50	0.20	2.50	0.20	9	0.90	43	4.30
FS2235	10	0.40	0.60	0.20	3	0.20	14	1.40	52	5.20

* +/- is uncertainty reported by CST-3.

Table 4. Chemical Data for Samples, TA-39, Deionized Water Leachate.*

Sample	Cl (ppm)	Cl (+/-)	SO_4 (ppm)	SO_4 (+/-)
FS2220	<2.5		<5	
FS2221	<2.5		10	5
FS2222	<2.5		5.9	5
FS2223	<2.5		<5	
FS2224	<2.5		<5	
FS2225	<2.5		<5	
FS2226	<2.5		<5	
FS2227	8.4	2.5	35	5
FS2228	10.3	2.5	26.5	5
FS2229	<2.5		<5	
FS2230	<2.5		<5	
FS2231	<2.5		<5	
FS2232	<2.5		<5	
FS2233	<2.5		<5	
FS2234	<2.5		<5	
FS2235	<2.5		<5	

* +/- is uncertainty reported by CST-3.

ferric oxyhydroxides) and larger amounts of adsorbed trace elements. These differences indicate that the most precise evaluation of the presence or absence of contaminants within sediment samples and their possible concentrations should consider the geomorphic setting and associated particle size of the sediment samples. Specifically, lower natural concentrations of Be, U, and other analytes should be expected in the channel sands than in the floodplain deposits, and concentrations of these elements within potentially contaminated channel sediments could be compared to their concentrations in similar coarse-grained background samples and not to the full data set.

Table 5. Summary of Background Sediment Analyses, TA-39, HNO_3 and Deionized Water Digestion.

Element	Coarse Channel Sands, Average (ppm)*	Bulk Floodplain Deposit, Average (ppm)**	Minimum Value in Data Set (ppm)***	Maximum Value in Data Set (ppm)***
Al	835 ± 134	5750 ± 1768	740 a	8400 c
As	<0.5	1.8 ± 0.4	<0.5 a	3 c, e, f
Ba	8.2 ± 0.2	68 ± 21	8 a	100 c
Be	<0.08	0.65 ± 0.15	<0.08 a	1.1 c
Ca	205 ± 35	1600 ± 495	180 a	2600 c
Cl	<2.5	<2.5	<2.5	10.3 i
Co	0.65 ± 0.07	2.8 ± 0.8	0.6 a	3.8 f
Cr	0.9 ± 0.14	4.3 ± 1.3	0.8 a	5.9 e, f
Cu	0.85 ± 0.07	4.4 ± 1.2	0.8 a	7.3 e
Fe	1400 ± 140	7650 ± 1273	1400 a	57000 d
K	190 ± 14	1365 ± 544	180 a	2200 f
Mg	185 ± 21	1148 ± 357	170 a	1700 c
Mn	50 ± 5	273 ± 46	46 a	1200 d
Na	40 ± 8	102 ± 8	34 a	190 c
Ni	<2	5 ± 1.4	<2 a	9 d
Pb	<4	7.8 ± 1.8	<4 a	16 c
Sb	<5	<5	<5	5 d
SO_4	<5	<5	<5	26.5 i
Ta	<0.3	<0.3	<0.3	<0.3
Th	1.2 ± 0.4	6.3 ± 1.1	0.9 a	14 d
Tl	<0.3	<0.3	<0.3	1.5 g
U	<0.3	0.7 ± 0.1	<0.3 a	1.6 c
V	1.2 ± 0.3	8.6 ± 2.1	1 a	66 d
Zn	9 ± 1	34 ± 4	9 a	300 d

* Samples FS2224 and FS2233. Uncertainty is 1σ.
** Samples FS2220, FS2223 (duplicate), FS2229, and FS2232 (duplicate). Uncertainty is 1σ.
*** a = coarse channel sands; b = bulk floodplain deposit; c = mud deposit; d = black sands; e = very fine sand to clay separate of floodplain sample; f = fine sand separate of floodplain deposit; g = coarse to medium sand separate of floodplain deposit; h = 3000 year old floodplain deposit; i = 1200 year old coarse channel sand.

Table 6. Summary of Background Sediment Analyses, TA-39, HF Digestion.

Element	Coarse Channel Sands, Average (ppm)*	Bulk Floodplain Deposit, Average (ppm)**	Minimum Value in Data Set (ppm)***	Maximum Value in Data Set (ppm)***
Al	49500 ± 2121	60750 ± 354	11000 d	69000 h
As	4.2 ± 2.9	6.8 ± 0.6	2.1 a	10.4 h
Ba	125 ± 7	276 ± 63	32 d	410 e
Be	1.0 ± 0.1	3.4 ± 0.1	0.91 a	5.3 e
Ca	1900 ± 141	4350 ± 636	1800 a	8100 i
Co	0.9 ± 0.2	3.0 ± 0.7	<0.5 d	7 i
Cr	1.8 ± 1.0	11.8 ± 3.8	1.1 a	83 d
Cu	1.1 ± 0.1	7.0 ± 2.0	<0.5 d	13 e, f
Fe	4500 ± 566	14500 ± 1414	4100 a	****
K	25000 ± 1414	26550 ± 2121	3600 a	29000 b
Mg	500 ± 42	2200 ± 566	470 a	3300 h
Mn	155 ± 35	435 ± 14	130 a	13000 d
Na	19000 ± 1414	17750 ± 2475	2700 d	21000 g
Ni	<2	8.5 ± 3.5	<2 a	47 d
Pb	<4	12 ± 0.4	<4 a, i	27 e
Sb	<5	<5	<5	14 d
Ta	1.1 ± 0.2	4.8 ± 0.5	0.9 a	6 b
Th	3.6 ± 0.4	14 ± 1.4	3.3 a	130 d
Tl	0.3 ± 0.1	0.7 ± 0.2	0.2 a	0.9 e
U	0.9 ± 0.3	4.1 ± 0.3	0.7 a	7.2 e
V	3.4 ± 0.9	22 ± 6	2.7 a	450 d
Zn	30 ± 6	66 ± 1	25 a	2500 d

* Samples FS2224 and FS2233. Uncertainty is 1σ.
** Samples FS2220, FS2223 (duplicate), FS2229, and FS2232 (duplicate). Uncertainty is 1σ.
*** a = coarse channel sands; b = bulk floodplain deposit; c = mud deposit; d = black sands; e = very fine sand to clay separate of floodplain sample; f = fine sand separate of floodplain deposit; g = coarse to medium sand separate of floodplain deposit; h = 3000 year old floodplain deposit; i = 1200 year old coarse channel sand.
**** Highest Fe value should be in magnetite-rich black sand, but the reported value is believed to be in error because it is less than the Fe in the other samples and less than the Fe in the black sand sample from the HNO_3 digestion.

ANALYSES OF BLACK (MAGNETITE-RICH) SANDS

One sample of relatively clean black (primarily magnetite, Fe_3O_4) sand from Indio Canyon was analyzed to examine the natural elemental concentrations within these heavy mineral deposits. Field measurements of one black sand deposit near a TA-39 firing site had indicated above-background radioactivity, and laboratory X-ray florescence (XRF) analyses of a sample from this site confirmed high concentrations of uranium (217 ppm; Essington, 1995). It was thus hypothesized that such black sands may concentrate some anthropogenic heavy metals such as uranium as a "placer" deposit; and that selective sampling of black sands could provide an additional tool to examine the transport of high-density contaminants away from firing sites.

The sampled black sands from Indio Canyon (sample FS2225, Tables 2 and 3) have very high concentrations of many elemental species, including the highest concentrations of Fe, Mn, Sb, Th, V, and Zn from the HNO_3 digestion and Cr, Mn, Ni, Sb, Th, V, and Zn from the HF digestion (the low reported value of Fe in the HF digestion is believed to be due to laboratory error). Notably, although the concentration of uranium in the black sands was higher than in the typical channel sands, it was within the range of analyses from the floodplain samples. This result indicates that anthropogenic uranium may be present where concentrations of uranium in black sands exceed

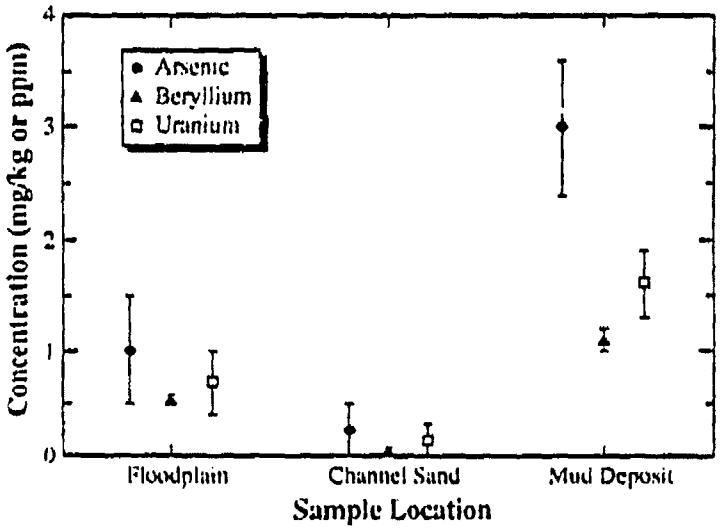

Fig. 4. Comparison of the concentrations of As, Be, and U between floodplain deposits (sample FS2220), active channel deposits (sample FS2224), and mud deposits (sample FS2226) in Indio Canyon. Concentrations obtained using HNO_3 digestion (Table 2).

the range of background floodplain samples, and thus supports the hypothesis that depleted uranium particles from firing sites can be concentrated in black sands by surface water due to sorting of sediment particles by their respective densities.

In addition to uranium, many other analytes are also present in higher concentrations in the black sands than in other sediments in these canyons. As an example, Figure 5 shows the elemental concentrations for the black sands and the bulk sediment samples collected within the active channel deposits in Indio Canyon. These differences in elemental concentrations indicate the importance of mineralogy in influencing trace element distributions in heterogeneous sediments. The ratio of the elemental concentration in the black sands to the concentration in nearby channel deposits varies greatly between elements, and these ratios (HNO_3 digestion) in decreasing order are: V (47) > Zn (33) > Mn (23) > Be (17) > Cr (12) > Th (10) > Ni (9) > U (5) > As (4) > Pb (3). The higher concentrations in the magnetite-rich sands occur as a result of ionic substitution of the trace

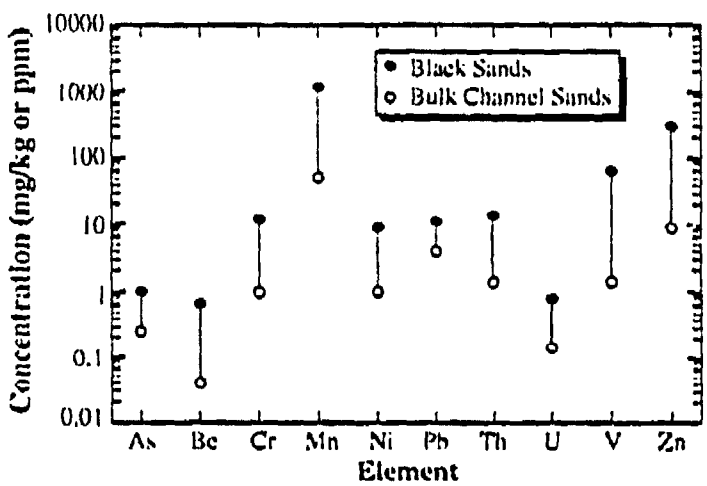

Fig. 5. Comparison of the concentrations of selected elements in black, magnetite-rich sands (sample FS2225) and nearby active channel sands dominated by quartz and sanidine crystals (sample FS2224) in Indio Canyon. Concentrations obtained using HNO_3 digestion (Table 2).

elements with one or more major elements within the mineral lattice during primary crystallization (Bloss, 1971) and/or adsorption onto secondary alteration products such as ferric oxyhydroxides (Rai and Zachara, 1984).

COMPARISON OF DIFFERENT SIZE FRACTIONS WITHIN FLOODPLAIN SAMPLES

Two large samples of floodplain deposits, one each from Ancho and Indio Canyons, were separated into three different size fractions to further examine the relation of particle size to elemental variability. A comparison of the elemental concentrations in these separates with the coarse channel sands (Tables 7 and 8) reveals several notable points. Concentrations of most analytes progressively increase from the coarse channel sands to the fine sand separate, although element concentrations in the fine sands are generally indistinguishable from the very fine sand, silt, and clay fraction. These variations support the general increase in trace element concentration with decreasing grain size as indicated by the comparison of the channel sands with the bulk floodplain deposits. The similarity of the two finer size separates, however, suggests either that they are mineralogically similar or that they have similar adsorptive properties. Specifically, the percentage of clay minerals in these samples is unknown, and it is possible that they have very low clay contents, being dominated by very fine sands and silts that are geochemically similar to the fine sand fractions. For example, grain size analysis of a texturally similar floodplain

Table 7. Summary of Different Size Fractions, TA-39, HNO_3 and Deionized Water Digestion.

Element	Coarse Channel Sands, Average (ppm)*	Coarse and Medium Sand, Average (ppm)**	Fine Sand, Average (ppm)***	Very Fine Sand, Silt, Clay, Average (ppm)****
Al	835 ± 134	3650 ± 636	7250 ± 495	7050 ± 354
As	<0.5	1 ± 0.5	2.5 ± 0.7	2.5 ± 0.7
Ba	8.2 ± 0.2	43 ± 8	86 ± 13	95 ± 6
Be	<0.08	0.35 ± 0.06	0.85 ± 0.04	0.86 ± 0.05
Ca	205 ± 35	1030 ± 99	2050 ± 495	2200 ± 424
Cl	<2.5	<2.5	<2.5	<2.5
Co	0.65 ± 0.07	1.8 ± 0.4	3.4 ± 0.6	3.3 ± 0.4
Cr	0.9 ± 0.14	2.4 ± 0.2	5.3 ± 0.9	5.9 ± 0.1
Cu	0.85 ± 0.07	2.9 ± 0.2	6.5 ± 1.2	7.4 ± 0.1
Fe	1400 ± 140	4900 ± 141	9400 ± 283	8900 ± 707
K	190 ± 14	875 ± 318	1800 ± 566	1700 ± 283
Mg	185 ± 21	705 ± 163	1450 ± 212	1500 ± 150
Mn	50 ± 5	185 ± 7	325 ± 35	280 ± 71
Na	40 ± 8	78 ± 4	115 ± 7	98 ± 31
Ni	<5	4 ± 2	6.0 ± 1.4	6.0 ± 1.4
Pb	<4	5.5 ± 0.7	9.5 ± 0.7	8.5 ± 2.1
Sb	<5	<5	<5	<5
SO_4	<5	<5	<5.5	<7.5
Ta	<0.3	<0.3	<0.3	<0.3
Th	1.2 ± 0.4	4.0 ± 0.5	7.1 ± 0.5	7.3 ± 0.6
Tl	<0.3	<0.9	<0.3	<0.3
U	<0.3	0.45 ± 0.07	0.80 ± 0.28	0.75 ± 0.21
V	1.2 ± 0.3	5 ± 0.5	11 ± 1	13 ± 1
Zn	9 ± 1	24 ± 2	41 ± 5	35 ± 4

* Samples FS2224 and FS2233: bulk channel samples, dominated by coarse sand. Uncertainties are 1σ.
** Samples FS2234 and FS2235: 0.25-2.0 mm fraction. Uncertainties are 1σ.
*** Samples FS2222 and FS2231: 0.75-0.25 mm fraction. Uncertainties are 1σ.
**** Samples FS2221 and FS2230: <0.75 mm fraction. Uncertainties are 1σ.

Table 8. Summary of Different Size Fractions, TA-39, HF Digestion.

Element	Coarse Channel Sands, Average (ppm)*	Coarse and Medium Sand, Average (ppm)**	Fine Sand, Average (ppm)***	Very Fine Sand, Silt, Clay, Average (ppm)****
Al	49500 ± 2121	60000 ± 1414	60500 ± 2121	56500 ± 707
As	4.2 ± 2.9	2.8 ± 0.4	5.6 ± 0.4	7.2 ± 2.7
Ba	125 ± 7	195 ± 21	325 ± 78	390 ± 28
Be	1.0 ± 0.1	2.7 ± 0.4	4.0 ± 0.6	3.5 ± 0.4
Ca	1900 ± 141	3450 ± 71	4900 ± 849	5350 ± 636
Co	0.9 ± 0.2	1.8 ± 0.4	3.9 ± 0.1	3.9 ± 0.1
Cr	1.8 ± 1.0	6.0 ± 2.2	15 ± 4	21 ± 4
Cu	1.1 ± 0.1	4.1 ± 1.0	11 ± 2	13 ± 1
Fe	4500 ± 566	9750 ± 1768	17500 ± 707	18000 ± 1414
K	25000 ± 1414	25500 ± 707	25500 ± 2121	22500 ± 707
Mg	500 ± 42	1300 ± 424	2800 ± 424	2900 ± 283
Mn	155 ± 35	295 ± 50	530 ± 71	455 ± 50
Na	19000 ± 1414	20000 ± 1414	16000 ± 2828	14500 ± 707
Ni	<2	3.5 ± 2.1	7.0 ± 1.4	11 ± 1
Pb	<4	9.0 ± 1.4	15 ± 2	17 ± 5
Sb	<5	<5	<5	<5
Ta	1.1 ± 0.2	3.1 ± 0.1	4.9 ± 0.6	4.4 ± 0.5
Th	3.6 ± 0.4	9.4 ± 0.9	17 ± 2	17 ± 1
Tl	0.3 ± 0.1	0.6 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
U	0.9 ± 0.3	2.8 ± 0.4	5.0 ± 0.9	5.3 ± 0.6
V	3.4 ± 0.9	12 ± 4	29 ± 6	37 ± 6
Zn	30 ± 6	48 ± 6	81 ± 11	69 ± 1

* Samples FS2224 and FS2233: bulk channel samples, dominated by coarse sand. Uncertainties are 1σ.
** Samples FS2234 and FS2235: 0.25-2.0 mm fraction. Uncertainties are 1σ.
*** Samples FS2222 and FS2231: 0.75-0.25 mm fraction. Uncertainties are 1σ.
**** Samples FS2221 and FS2230: <0.75 mm fraction. Uncertainties are 1σ.

deposit overlying the sampled prehistoric channel sands in Ancho Canyon indicate the presence of only 8% to 9% clay-sized particles, compared with 26% to 44% silt and 47% to 66% sand (Bw1 and Bw2 horizons of Longmire et al., 1995, Ancho Canyon site; Reneau and McDonald, 1996, pp. 71–72). Alternatively, because chemical dispersants were not used to disaggregate clays, it is possible that the coarse size fractions include aggregates of silt and clay or thin clay coatings on larger sediment particles. The higher analyte concentrations in the coarse and medium sand separates compared with the channel sands suggest that the latter are perhaps better sorted, containing a higher percentage of quartz and sanidine crystals from the Bandelier Tuff, and also suggest that the coarse and medium sand separates may provide an analog with less well sorted channel deposits (with a higher content of fine sediment).

MUD DEPOSIT

One sample of a one-day-old mud deposit from a flood in Indio Canyon (sample FS2226, flood of August 24, 1994) was collected as a possible fine-grained end member of natural sedimentary deposits in this environment. This deposit has the highest concentrations analyzed for several elements, including Al, Ba, Be, Ca, Mg, Na, Pb, and U for the HNO_3 digestion and Ta, Tl, and U for the HF digestion (Tables 2 and 3). Comparisons of concentrations of As, Be, and U in the mud deposit with channel and floodplain deposits are shown in Figure 4. For several analytes, the mud deposit exceeded element concentrations in the fine floodplain fractions taking into account the analytical uncertainties. These analytes are Be, Cu, Pb, and U for both the HNO_3 and HF digestion and also Na for the HNO_3 digestion. Some of the

elements that are high in the partial (HNO_3) digestions may reflect the presence of dissolved components that had been deposited at this site by evaporation, followed by precipitation and/or adsorption of solutes onto silt- and clay-sized sediments. Another possible complication with this deposit is that the proximity of State Road 4 may be responsible for the anomalous presence of certain elements derived from automobile exhaust, such as lead. The high concentrations of other elements, such as uranium, may be more likely due to their adsorption onto silt- and clay-sized particles, although part of the uranium and other elements may be anthropogenic, dispersed from the TA-39 firing sites (see discussion in Longmire et al., 1995, concerning possible anthropogenic uranium in surface horizons of some mesa-top soils).

COMPARISON OF MODERN SEDIMENT SAMPLES AND PREHISTORIC SAMPLES

Samples of prehistoric sediments exposed in a stream bank along the main fork of Ancho Canyon were analyzed to test the hypothesis that prehistoric sediments could provide a reasonable local background in areas where adequate local background samples could not otherwise be obtained from active channels and floodplains because of the possibility of contamination by Laboratory operations. Alternatively, these samples may be more comparable to sediments penetrated at depth in a core hole than to surface samples because of postdepositional geochemical changes associated with prolonged contact with shallow groundwater or moisture within the vadose zone. Erosion of the sampled stream bank along the main drainage of Ancho Canyon exposed a section of coarse channel sands and gravels overlying an older floodplain deposit, shown schematically in Figure 3. Radiocarbon dating of charcoal contained within these sediments provided ages of about 1200 yr for the channel sands and about 3200 yr for the underlying floodplain deposit (Reneau and McDonald, 1996, p. 69), demonstrating their prehistoric age.

Analyses from the prehistoric sediment deposits (samples FS2227 and FS2228) were compared to both the modern bulk channel and floodplain deposits and to appropriate size fractions from the separated floodplain deposits to ensure that possible natural variability within the modern deposits were being considered (Tables 9 and 10). The prehistoric channel sands were thus compared with the medium and coarse sand fractions of the floodplain deposits, and the prehistoric floodplain deposits were compared with the fine-sand-to-clay fractions of the modern floodplain deposits.

This comparison indicated that for most elements the modern and prehistoric samples could not be distinguished, but that for some elements significant differences exist that suggest postdepositional elemental mobility over the last 1000 to 3000 yr. The old channel sand deposit in particular differed from both the modern channel deposits and also the medium and coarse sand fraction of the floodplain deposits (Fig. 6) with higher concentrations of Co, Cr, Fe Mn, V, and Zn in both the HNO_3 and the HF digestions, Ba, Ca, Mg, and Ni in only the HF digestion, and Cl and SO_4 in the deionized water leachate. As compared to the finer fractions of the recent floodplain deposits, the old floodplain deposits had higher concentrations of Na in the HNO_3 digested fraction and Cl and SO_4 in the deionized water leachate.

The differences seen between the modern and the prehistoric deposits suggest which elements may be naturally higher in subsurface samples collected from boreholes due to solute transport, mineral precipitation, and adsorption processes. Notably, some elements that are potential contaminants of concern at TA-39, such as Be and U, are similar between the recent and the old deposits, suggesting that natural concentrations of Be and U in the subsurface may be similar to those in young deposits. However, because of the small size of

Table 9. Comparison of Modern and Old Deposits, TA-39, HNO_3 and Deionized Water Digestion.

Element	Coarse Channel Sands, Average (ppm)*	Old Channel Sands (ppm)**	Bulk Floodplain Deposit, Average (ppm)***	Old Floodplain Deposits (ppm)****
Al	835 ± 134	2300 a	5750 ± 1768	7700
As	<0.5	0.9	1.8 ± 0.4	2
Ba	8.2 ± 0.2	32 a	68 ± 21	71
Be	<0.08	0.17 a	0.65 ± 0.15	0.74
Ca	205 ± 35	770 a	1600 ± 495	1500
Cl	<2.5	10.3 b, c	<2.5	8.4 b
Co	0.65 ± 0.07	3.1 b	2.8 ± 0.8	2.7
Cr	0.9 ± 0.14	5.4 b	4.3 ± 1.3	5.2
Cu	0.85 ± 0.07	1.8 a	4.4 ± 1.2	4.3
Fe	1400 ± 140	13000 b	7650 ± 1273	8400
K	190 ± 14	540 a	1365 ± 544	1600
Mg	185 ± 21	570 a	1148 ± 357	1400
Mn	50 ± 5	240 b	273 ± 46	220
Na	40 ± 8	66	102 ± 8	150 b
Ni	<2	4	5 ± 1.4	4
Pb	<4	7	7.8 ± 1.8	7
Sb	<5	<5	<5	<5
SO_4	<5	26.5 b	<5	35 b, c
Ta	<0.3	<0.3	<0.3	<0.3
Th	1.2 ± 0.4	2.2 a	6.3 ± 1.1	5.8
Tl	<0.3	<0.3	<0.3	<0.3
U	<0.3	<0.3	0.7 ± 0.1	0.6
V	1.2 ± 0.3	20 b	8.6 ± 2.1	9
Zn	9 ± 1	47 b	34 ± 4	33

* Samples FS2224 and FS2233. Uncertainties are 1σ.
** Sample FS2228: a = beyond range of modern channel sands, but within range of medium to coarse sand separate of banks; b = beyond range of medium to coarse sand separate of floodplain deposits; c = maximum value from this data set.
*** Samples FS2220, FS2223 (duplicate), FS2229, and FS2232 (duplicate). Uncertainties are 1σ.
**** Sample FS2227: a = beyond range of modern bulk floodplain deposits, but within range of fine sand to clay separates of floodplain deposits; b = beyond range of fine sand to clay separates of floodplain deposits; c = maximum value from this data set.

the data set (only one sample each of prehistoric channel and floodplain deposits), these inferences should be considered preliminary.

The comparison of modern and prehistoric deposits suggests that the use of prehistoric sediment samples as a local sediment background in potentially contaminated canyons may be defensible in some circumstances, although care should be used in such an approach. Specifically, we expect that the older the deposit, the greater the chance for significant changes in chemistry due to postdepositional migration of certain elements, and information on the age and potential alteration of sampled sediments would thus be useful. However, this may only be a significant concern for a limited number of analytes, and the use of procedures that exclude outliers from the background data set before summary statistics are calculated can minimize the effects of postdepositional elemental mobility on the calculation of a sediment background.

ARSENIC AND BERYLLIUM IN SEDIMENTS

Arsenic and beryllium are of special concern at the Laboratory in evaluations of possible contamination because their concentrations in soils

Table 10. Comparison of Modern and Old Deposits, TA-39, HF Digestion.

Element	Coarse Channel Sands, Average (ppm)*	Old Channel Sands (ppm)**	Bulk Floodplain Deposit, Average (ppm)***	Old Floodplain Deposits (ppm)****
Al	49500 ± 2121	63000 a	60750 ± 354	69000 c
As	4.2 ± 2.9	7.5	6.8 ± 0.6	10.4 a
Ba	125 ± 7	290 b	276 ± 63	340
Be	1.0 ± 0.1	1.5 a	3.4 ± 0.1	4
Ca	1900 ± 141	8100 b, c	4350 ± 636	6100 a
Co	0.9 ± 0.2	7 b, c	3.0 ± 0.7	3.9
Cr	1.8 ± 1.0	23 b	11.8 ± 3.8	15
Cu	1.1 ± 0.1	2.6 a	7.0 ± 2.0	7.6
Fe	4500 ± 566	52000 b, c?	14500 ± 1414	17000
K	25000 ± 1414	25000	26550 ± 2121	27000
Mg	500 ± 42	2500 b	2200 ± 566	3300
Mn	155 ± 35	1300 b	435 ± 14	450
Na	19000 ± 1414	20000	17750 ± 2475	18000
Ni	<2	14 b	8.5 ± 3.5	8
Pb	<4	<4	12 ± 0.4	14
Sb	<5	<5	<5	<5
Ta	1.1 ± 0.2	2.6 a	4.8 ± 0.5	4.4
Th	3.6 ± 0.4	9.4 a	14 ± 1.4	15
Tl	0.3 ± 0.1	0.4	0.7 ± 0.2	0.8
U	0.9 ± 0.3	1.5	4.1 ± 0.3	4.7
V	3.4 ± 0.9	84 b	22 ± 6	27
Zn	30 ± 6	210 b	66 ± 1	72

* Samples FS2224 and FS2233. Uncertainties are 1σ.
** Sample FS2228; a = beyond range of modern channel sands, but within range of medium to coarse sand separate of floodplain deposits; b = beyond range of medium to coarse sand separate of floodplain deposits; c = maximum value from this data set.
*** Samples FS2220, FS2223 (duplicate), FS2229, and FS2232 (duplicate). Uncertainties are 1σ.
**** Sample FS2227; a = beyond range of modern bulk floodplain deposits, but within range of fine sand to clay separates of floodplain deposits; b = beyond range of fine sand to clay separates of floodplain deposits; c = maximum value from this data set.

routinely exceed action levels established by the EPA (0.32 ppm for As and 0.14 ppm for Be, using HNO_3 digestion) (Longmire et al., 1996). As a result, the evaluation of As and Be in soils at the Laboratory currently uses local background values to establish action levels, and background values thus play a key role in the decision-making process. The analytical data obtained in this study similarly show that concentrations of As and Be in the sediment samples exceed the previously established action levels, although their concentrations in sediments are generally less than that observed in local soils.

The concentrations of As and Be are generally strongly correlated with Fe concentration in soils at the Laboratory (Longmire et al., 1995, 1996; McDonald et al., 1996), and these elemental relationships are also present in the sediments collected within Ancho and Indio Canyons. Figures 7 and 8 are bivariate plots of As versus Fe and Be versus Fe for these sediments, showing high regression coefficients (r^2) of 0.84 and 0.95, respectively. These plots are useful in defining the background concentrations of As and Be as they relate to Fe concentration. Outliers to these bivariate plots may indicate contamination as opposed to natural variations in background concentrations of these analytes.

COMPARISON WITH BACKGROUND SOILS

The background sediment samples from Ancho and Indio Canyons were compared with background

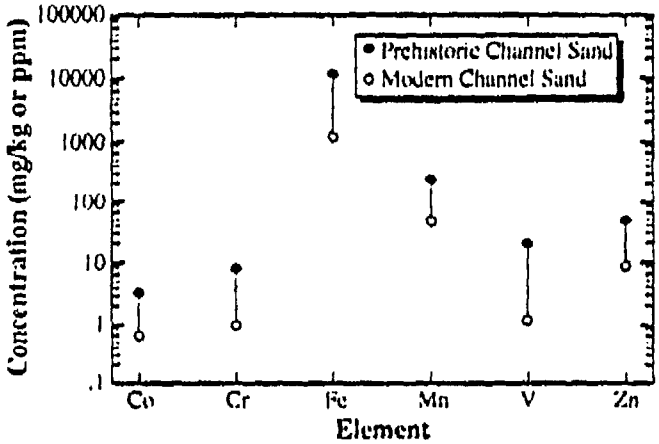

Fig. 6. Comparison of the concentrations of selected elements in prehistoric sands (sample FS2228) and active channel sands (samples FS2224 and FS2233). Concentrations obtained using HNO_3 digestion (Table 2).

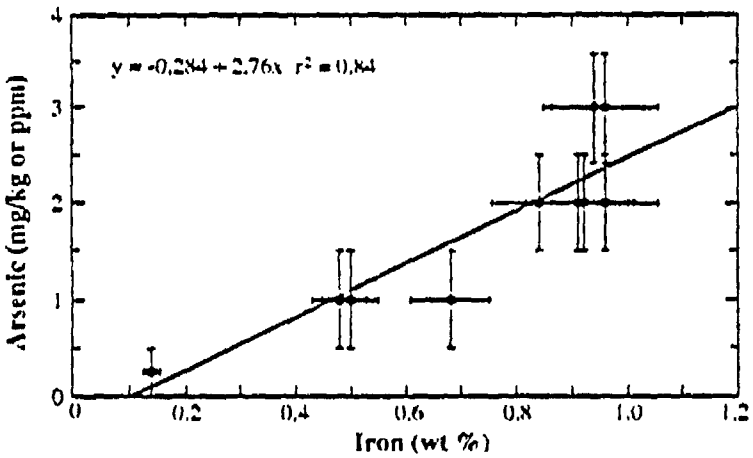

Fig. 7. Plot of As versus Fe for background sediment samples in Ancho and Indio Canyons (excluding samples FS2223, FS2225, FS2228, and FS2232). Concentrations obtained using HNO_3 digestion (Table 2). Error bars indicate reported analytical uncertainties.

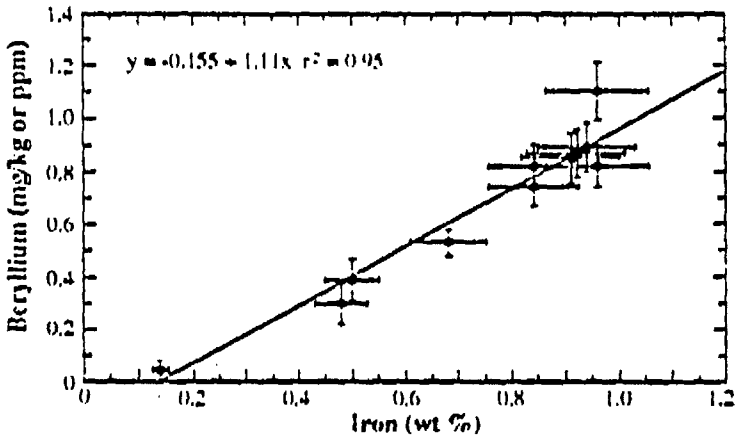

Fig. 8. Plot of Be versus Fe for background sediment samples in Ancho and Indio Canyons (excluding samples FS2223, FS2225, FS2228, and FS2232). Concentrations obtained using HNO_3 digestion (Table 2). Error bars indicate reported analytical uncertainties.

soils data from the Laboratory (Longmire et al., 1996) to evaluate if the sediment chemistry was similar to certain parts of the soil data set. In general, elemental concentrations in the sediments are most similar to soil samples that contained low concentrations of iron. In the soils, iron concentration is generally correlated with the percentage of clay-sized particles in each sample (Longmire et al., 1996), and the lower elemental concentrations present in the TA-39 sediments are consistent with their relatively low iron content. For example, bivariate plots of As versus Fe and Be versus Fe for background soils and sediments collected at the Laboratory are shown in Figures 9 and 10. Arsenic, beryllium, and iron concentrations in the sediments are most similar to concentrations within A and C horizons or within weakly developed B horizons in soils, although the A and C horizons show a greater range of As and Be concentrations. We thus infer that either the dominant source for the sampled sediments is erosion of soils containing low concentrations of iron or that much of the fine-grained Fe-rich component of the soils is winnowed out of the sediments during transport in floods, being carried downstream towards the Rio Grande. The differences between the sediment data set and the soils data set, including the greater range of values in the A and C soil horizons, indicate that it is not appropriate to apply UTLs developed for Laboratory soils to sediment samples.

PRINCIPAL COMPONENTS ANALYSIS

Patterns within the background chemical data set can be examined using a principal components analysis (PCA) (Everitt and Dunn, 1991). PCA helps to simplify the presentation and evaluation of a large multivariate data set by reducing its dimensionality. This simplification enables us to further evaluate, both qualitatively and quantitatively, the factors controlling the variability within the sediment data, and also the differences and similarities between the background soil data of Longmire et al. (1995) and the background sediment samples of this report.

The set of measured concentrations for a single sample constitutes one observation that is a vector in a 21-dimensional space, where each element listed in Table 2 corresponds to a dimension. After eliminating Cl and SO_4 (which are mostly below detection level), the black sand and prehistoric channel samples (which are distinctly different from the other samples), and also some of the major elements (Ca, K, and Mg) in order to minimize problems with singularities in the covariance matrix, there are still 16 dimensions, which are not easily visualized. However, virtually all (98.5%) of the variability among the remaining 14 observations occurs in a two-dimensional subspace of this 16-dimensional space. A projection of the observations onto this subspace (Fig. 11) is very

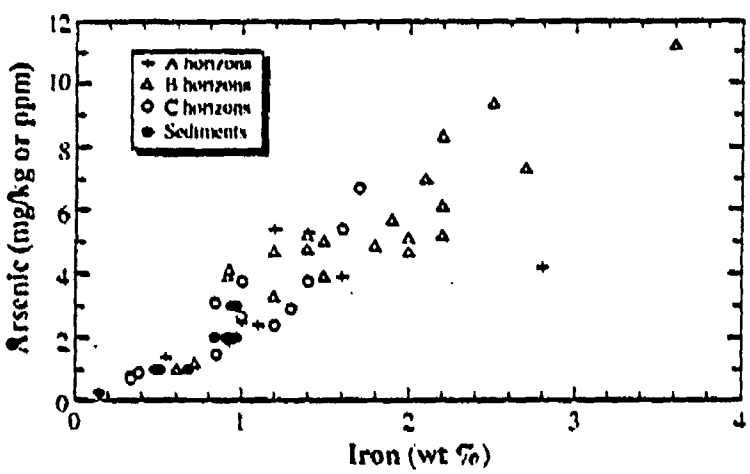

Fig. 9. Plot of As versus Fe for background sediment samples in Ancho and Indio Canyons (excluding samples FS2223, FS2225, FS2228, and FS2232), and the A, B, and C horizons of background soils at the Laboratory (Longmire et al., 1996). Concentrations obtained using HNO_3 digestion (Table 2).

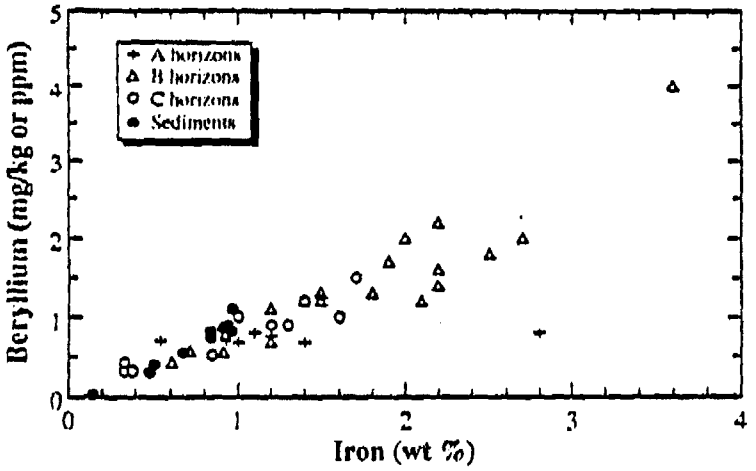

Fig. 10. Plot of Be versus Fe for background sediment samples (from active channels and floodplains) in Ancho and Indio Canyons (excluding samples FS2223, FS2225, FS2228, and FS2232), and the A, B, and C horizons of background soils at the Laboratory (Longmire et al., 1996). Concentrations obtained using HNO_3 digestion (Table 2).

useful in determining what is controlling the variability among the samples.

In Figure 11, the x-axis (first principal component) corresponds to the direction in the 16-dimensional space along which the observations vary most (89% of the total variability). This first component separates the finest and intermediate size fractions (with higher concentrations of most elements) from the coarser fractions of the floodplain samples and clearly isolates the channel sand samples (with relatively low concentrations) on the left side of the figure. Because the PCA calculation was done without rescaling the observations, this first principal component reflects primarily variation in concentrations of the major elements, aluminum and iron.

It would also appear from Figure 11 that the bulk Ancho Canyon floodplain samples had more fine and medium material than the bulk Indio Canyon samples. The Ancho Canyon bulk samples plot on the right with the finer fractions, but the Indio Canyon samples are farther left. Overall, this first dimension of the PCA shows that size fractionation is the principal controlling factor in determining differences among the samples included in this study.

The second dimension, plotted on the y-axis of Figure 11, separates the two principal locations, Ancho and Indio Canyons. For this data set, the difference in chemistry between the sample sites in these two canyons is apparently the second most important factor in controlling the variability in chemical concentrations.

The projections of the two samples excluded from the calculation of the principal components in Figure 11, the prehistoric channel sand sample and the black magnetite sand sample, are way off scale on this plot, demonstrating how different they are from the remainder of the samples.

When principal components analysis is performed using data for the background soil samples of Longmire et al. (1995), the first two dimensions capture about 96.5% of the total variability and serve principally to separate the B horizon data from the A and C horizon data (Fig. 12). The lower left-hand corner of this plot is occupied exclusively by samples identified as coming from the A and C horizons, although some samples from these horizons are scattered farther up and to the right. When the sediment samples are projected onto these principal components, the sands and coarse fractions wind up within this lower left-hand

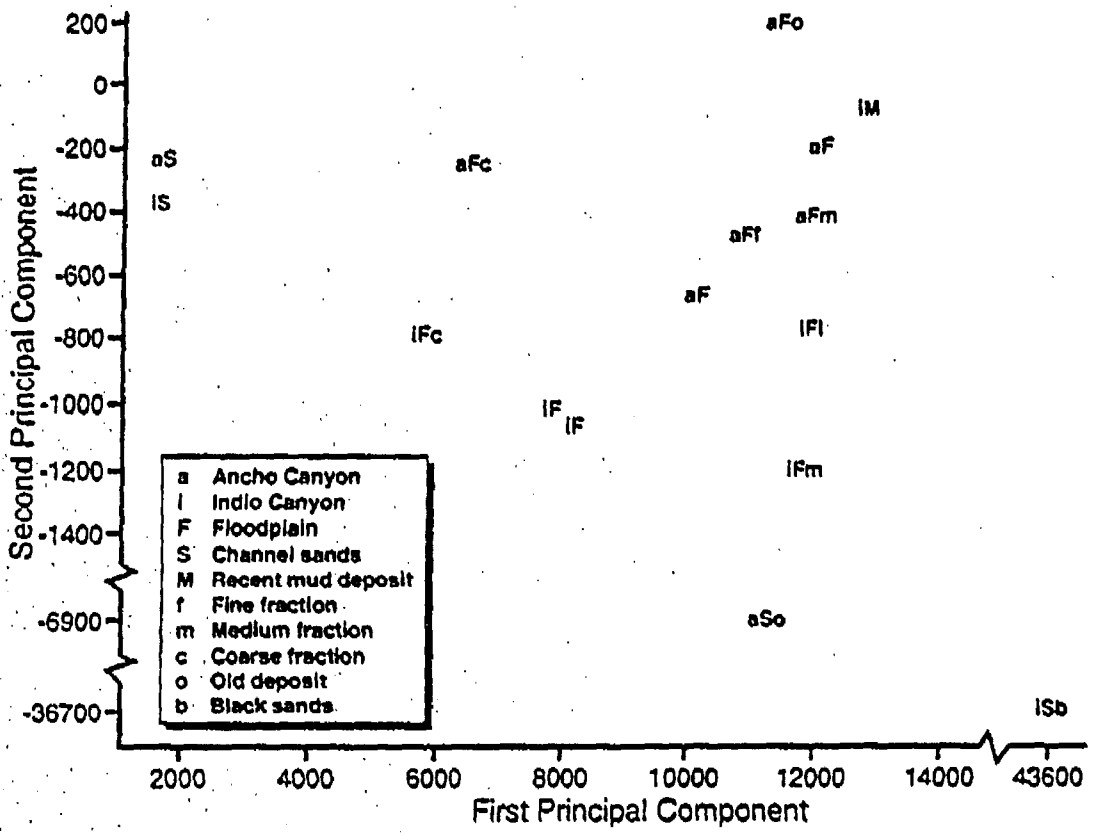

Fig. 11. Sediment samples from Ancho and Indio Canyons displayed in a coordinate system defined by their first two principal components. Note the breaks in the x and y axes that indicate the locations of the black sand sample and the prehistoric channel sample, which have extreme values in this data set. See text for discussion.

corner, and the remaining samples (excepting, again, the prehistoric channel sands and the magnetite sands) are nearby. Overall, these plots further indicate that the sediment samples are most similar to soils from the A and C horizon, although the sediment samples are also similar to some of the B horizon samples, and the greater range for the A and C horizons limits their applicability as a substitute for sediment samples.

SUMMARY STATISTICS FOR BACKGROUND SEDIMENT SAMPLES

Summary statistics for the sediment data are presented in Tables 11 and 12. In view of the fact that the sample location is the second most important explanatory factor for the variation in observed concentrations, as shown by the principal components analysis, the sediment data discussed in this report should be considered strictly preliminary. Two sample areas are probably insufficient to represent the variability that will be encountered when more background sediment locations from other parts of the Pajarito Plateau are added.

This caveat should be borne in mind when using the statistics shown in Tables 11 and 12, which include medians, means, standard deviations, minima, maxima, and (0.95,0.95) UTLs based on the 16 sediment samples. The UTLs are calculated following procedures discussed in EPA (1989), and indicate values that have a 95% statistical confidence of exceeding the 95th percentiles of the true distributions. The statistics were calculated based on values from all samples, excluding outliers in the data set that would inflate the estimate of the mean by more than 10%, or, in the

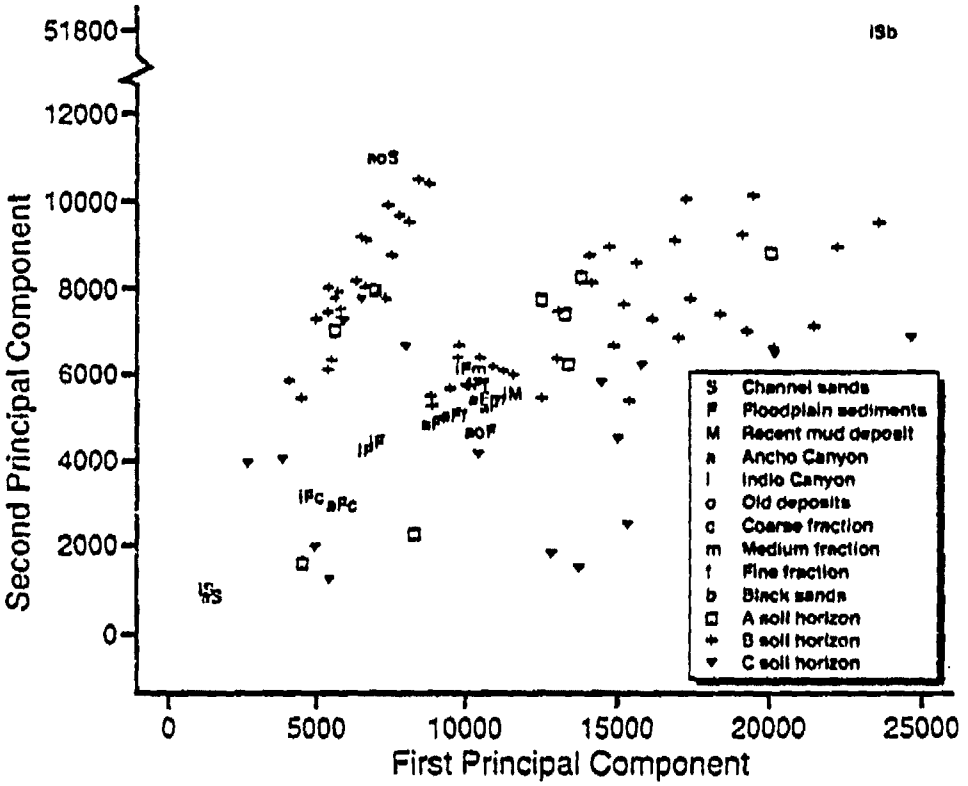

Fig. 12. Background soil samples of Longmire et al. (1995) and sediment samples of this report displayed in a coordinate system defined by the first two principal components of the background soil data set. Note the break in the y axis and the extreme location of the black sand sample.

case of potassium, an anomalously low value. These outliers are presented in Table 13, and include values for the black magnetite-rich sands, the recent mud deposit, and the prehistoric channel deposits. The summary statistics for some of the radioactive isotopes in Table 12 use the whole-sample values in Table 11 and correction factors that are presented in Table 14. The UTLs in Tables 11 and 12 are up to 50% larger than the maximum values observed, as a result of the small sample size, and will require revision as more background sediment samples are obtained.

IMPLICATIONS FOR SAMPLING AND INTERPRETATION OF DATA

The data set discussed in this report is limited by its small sample size and thus may not be representative of the full range of background sediment chemistry present at TA-39. In addition, this data set is not intended to be representative of all sediments on the Pajarito Plateau because the sampled canyons drain areas entirely within the Bandelier Tuff. For example, additional variation will undoubtedly occur in the canyons that head in the Sierra de los Valles and drain areas including Tschicoma Formation dacite. However, the results of this study suggest several implications for the collection of samples and the interpretation of analytical data that should allow improved evaluations of potential contamination in sediments at the Laboratory.

First, because of the dependence of sediment geochemistry on grain size and mineralogy, notes on the characteristics of each sample (such as the general grain size or the presence of black sands) can be valuable in understanding variations in the analytical data and should be routinely made in the field by the sampling team. Second, the correlations that are present between iron and other metals can be used as an additional test for possible deviations from background, such as for

Table 11. Summary Statistics for Background Sediment Samples.*

Analyte	Number of Outliers	Minimum Value (ppm)	Median Value (ppm)	Mean Value (ppm)	Standard Deviation (ppm)	Maximum Value (ppm)	utl95**
Al	0	740	5400	5020	2670	8400	11700
As	0	<0.5	2	1.65	0.91	3.0	3.94
Ba	0	8	62.5	59.5	32.4	100	141
Be	0	<0.08	0.68	0.59	0.32	1.1	1.40
Ca	0	180	1400	1450	747	2600	3340
Co	1	0.6	3	2.57	1.01	3.8	5.16
Cr	1	0.8	4.95	4.15	1.80	5.9	8.77
Cu	1	0.8	4.35	4.21	2.20	7.5	9.85
Fe	2	1400	8400	6970	2850	9600	14400
K	0	180	1250	1170	664	2200	2850
K TOTAL	1	22000	25500	25400	1800	29000	30000
Mg	0	170	1110	1030	509	1700	2310
Mn	1	46	240	241	97.2	380	490
Na	0	34	93	96.3	39.0	190	195
Ni	0	<2	4.5	4.81	2.07	9	10.0
Pb	1	<4	7.5	7.13	2.61	11	13.8
Th	1	0.9	5.9	5.24	2.28	8	11.1
Th TOTAL	1	3.3	15	12.7	4.68	18	24.7
U	1	<0.3	0.6	0.58	0.27	1.0	1.29
U TOTAL	1	0.7	4.15	3.61	1.55	5.7	7.62
V	1	1.0	9.5	8.91	4.82	20	21.3
Zn	1	9	33.5	32.0	11.7	48	62.1

* Statistics presented for results of HNO_3 digestion procedures, except for K TOTAL, Th TOTAL, and U TOTAL, which were obtained from HF digestion procedures and are used for calculation of UTLs for specific radioactive isotopes (Table 12). Statistics were calculated after outliers presented in Table 13 were deleted, and analyses below the detection limit (DL) were considered as 1/2 DL. No values are presented for Cl, Sb, SO_4, Ta, and Tl because of the small number of analyses above DL (0-4).

** utl95 is a (0.95,0.95) UTL, computed using estimated mean and standard deviation and normal assumptions (i.e., selecting a "k-factor" appropriate for a sample of size 16 [0 outliers, k = 2.523], 15 [1 outlier, k = 2.566] or 14 [2 outliers, k = 2.614]. Then utl95 = mean + [k*standard deviation]).

Table 12. Estimated Summary Statistics for Selected Radioactive Isotopes in Background Sediment Samples.*

Isotope	Number of Outliers	Minimum Value (pCi/g)	Median Value (pCi/g)	Mean Value (pCi/g)	Standard Deviation (pCi/g)	Maximum Value (pCi/g)	utl95**
^{40}K	1	18.0	21.3	20.8	1.48	23.7	24.6
^{231}Pa	1	0.01	0.06	0.06	0.02	0.09	0.12
^{226}Ra	1	0.25	1.42	1.29	0.55	2.02	2.71
^{228}Ra	1	0.36	1.64	1.39	0.51	1.97	2.70
^{228}Th	1	0.36	1.64	1.39	0.51	1.97	2.70
^{230}Th	1	0.25	1.42	1.29	0.55	2.02	2.71
^{232}Th	1	0.36	1.64	1.39	0.51	1.97	2.70
^{234}U	1	0.25	1.42	1.29	0.55	2.02	2.71
^{235}U	1	0.01	0.06	0.06	0.02	0.09	0.12
^{238}U	1	0.23	1.34	1.21	0.52	1.90	2.55

* Statistics estimated using whole-sample values presented in Table 11 and correction factors presented in Table 14 (for ^{40}K, ^{232}Th, ^{238}U, ^{235}U, and ^{234}U), or assumption of secular equilibrium with next higher parent isotope in decay chain (for ^{231}Pa, ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{230}Th). Statistics were calculated after outliers presented in Table 13 were deleted.

** utl95 is a (0.95,0.95) UTL. See footnote to Table 11.

Table 13. Outliers in Background Sediment Data Set.*

Sample Number	Sample Description	Analyte	Concentration (ppm)
FS2225	black magnetite-rich sands	Co	6
		Cr	12
		Fe	57000
		K TOTAL	3600
		Mn	1200
		Th	14
		Th TOTAL	130
		V	66
		Zn	300
FS2226	recent mud deposit	Cu	12
		Pb	16
		U	1.6
		U TOTAL	7.2
FS2228	prehistoric channel sands	Fe	13000
		V	20

* Outliers only calculated for HNO_3 digestion, except for values labeled "TOTAL", which were obtained using HF digestion. Outliers identified as values that would inflate the estimate of the mean by more than 10%, except for the K TOTAL value for sample FS2225, which was anomalously low in comparison to the other samples.

Table 14. Correction Factors used to Estimate Concentrations of Selected Radioactive Isotopes.*

Isotope	Specific Activity (pCi/g)	Natural Abundance (%)	Correction Factor (pCi/g per ppm)
^{40}K	6.99×10^{6}	0.0117	8.1736×10^{-4}
^{232}Th	1.09×10^{4}	100	1.092×10^{-1}
^{234}U	6.23×10^{6}	0.0057	3.55×10^{-1}
^{235}U	2.16×10^{6}	0.710	1.53×10^{-2}
^{238}U	3.36×10^{4}	99.28	3.34×10^{-1}

* Whole-sample values of K, Th, and U presented in Table 11 were multiplied by these correction factors to provide estimates of activity in background sediment samples. Values from Installation Work Plan for Los Alamos National Laboratory Environmental Restoration Project.

high values that may lie beyond the background data set but still would be consistent with the natural elemental trends. Third, selective sampling of certain types of deposits (such as black magnetite-rich sands where dense particles like depleted uranium may be concentrated) may be useful in examining the transport of specific contaminants. Finally, sediments in the subsurface sampled in core holes may have significantly higher concentrations of certain elements than surface sediment due to postdepositional alteration associated with migrating water, and selection of appropriate background samples for comparison needs to be made accordingly.

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