U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

ACID-NEUTRALIZING POTENTIAL OF IGNEOUS BEDROCKS IN THE ANIMAS RIVER HEADWATERS, SAN JUAN COUNTY, COLORADO

by
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Open-File Report 00-165

2000

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

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ABSTRACT

Chlorite found in minor and moderate amounts in 14 igneous rocks from the upper Animas River headwaters near Silverton, in southwestern Colorado has significant acid-neutralizing potential (ANP). Minor calcite is present in four of the 14 igneous rocks studied and ranges from about four to six weight percent. Sulfate and metal rich leachate was prepared from samples of the Yukon and May Day mine waste piles, which are located in the upper Animas River watershed north of Silverton near Cement Creek. The leachates prepared from the mine wastes were used to perform acid neutralization experiments on the igneous rocks sampled. Leach experiments indicate that propylitically altered rocks with no calcite have an average ANP equivalent to 10 weight percent calcite. Chlorite is lower in abundance in post-leach samples when compared with their pre-leach equivalents, which indicates that chlorite is dissolved by the acidic mine waste leachate.

Mineralogical study of 22 stream sediment samples from tributaries and the main stems of Cement and Mineral Creeks show that they are depleted in chlorite, relative to the amounts of chlorite present in the igneous bedrock. The lower abundance of chlorite in fluvial sediments suggests that chlorite is dissolved by acidic stream waters. Because chlorite is relatively soft and easily broken down in the stream environment, physical abrasion will promote dissolution.

INTRODUCTION

The headwaters area of the Animas River near Silverton, in southwestern Colorado has been the focus of many studies related to degraded water quality due to acidity and metal contamination. Cement and Mineral Creeks are major tributaries and major sources of metal contribution to the Animas River (Owen, 1997; Church and others, 1997; Nimmo and others, 1998; Besser and others 1998, Yager and others, 2000; Bove and others; 2000).

This study is an examination of the acid-neutralizing potential (ANP) of the different igneous bedrock units that are predominant in the Animas River headwaters for all drainages north of the mouth of Mineral Creek. These bedrock units are chiefly volcanic rocks that include intermediate composition lava flows, volcaniclastic rocks, caldera-related silicic ash flow tuffs, and intrusive rocks (Burbank and Luedke, 1969; Lipman, and others, 1973; Casadevall and Ohmoto, 1977; Bove, and others, 2000, Yager and others, 2000).

Fourteen samples of typical igneous bedrock units from Cement Creek, Mineral Creek, and Animas River basins in the Silverton area were studied. The sample localities, rock descriptions, and mineralogy are given in Table 1 and their localities are shown on Figure 1.

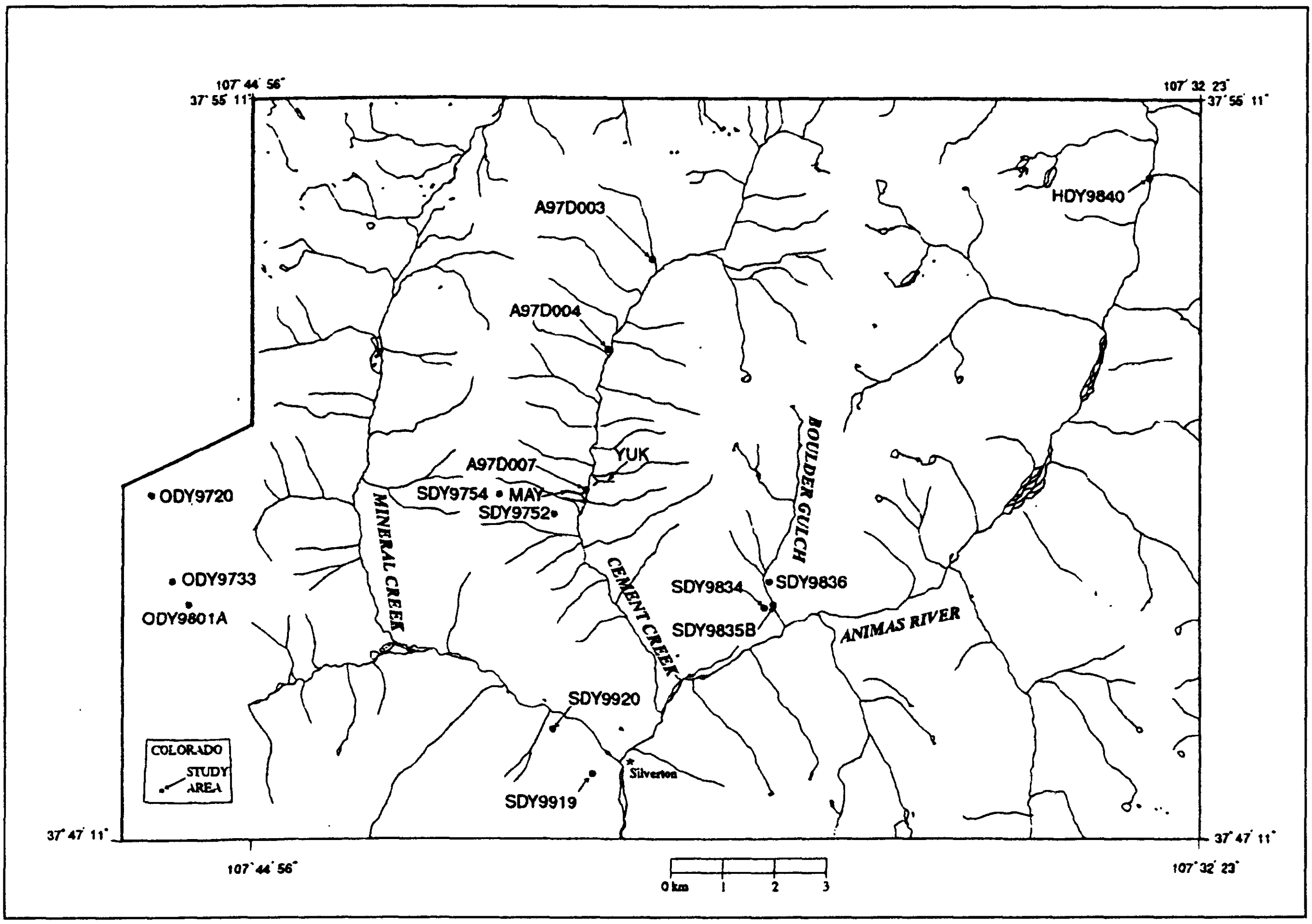

Figure 1. Localities of igneous bedrock samples in the Silverton area of the Animas River watershed, Colorado. MAY and YUK are wastepiles from the May Day and Yukon mines.
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Table 1. Locations of igneous rock samples with names of units and rock types sampled, minerals by XRD, and intensities of 100 (hkl) quartz/200 (hkl) chlorite peaks for unexposed and leached samples, respectively.

Sample	Lat.	Long.	Rock unit	Location	Rock type	XRD Intensity quartz100/ chlorite200 unexposed	Minerals by XRD in addition to quartz and plagioclase [listed in order of abundance] trpy=trace pyrite in heavy concentrate	XRD Intensity quartz100/ chlorite200 LEACHED
				Mineral Creek	**Drainage**			
SDY9920	37 48 22.9	107 40 59.4	Sultan Mtn. stock	Near North Star mine waste pile	monzonite porphyry	4.6	orthoclase, biotite, chlorite trpy	6.5
ODY9801A	37 49 34.4	107 45 48.9	San Juan Formation	Cirque, headwater of Red tributary	dacite/andesite porphyry lava	1.2	chlorite, calcite, epidote, mica	1.02
ODY9720	37 50 42.9	107 46 21.4	San Juan Formation	Near Ophir Pass road	volcaniclastic mudflow	1.4	chlorite, epidote, orthoclase, trace mica	2.29
ODY9733	37 49 49.4	107 46 2.2	San Juan Formation	Above cirque N. of Red tributary headwaters	dacite/andesite porphyry lava	1.6	chlorite, epidote, trace mica	1.94
				Cement Creek	**Drainage**			
A97D003	37 53 18	107 39 52	Silverton volcanics	Roadcut between Dry & Prospect Gulch	dacite lava	1.8	orthoclase, epidote, chlorite	1.94
A97D004	37 52 21	107 40 25	Silverton volcanics	Near mouth of Fairview Gulch	dacite lava	2.4	orthoclase, epidote, chlorite	3.56
A97D007	37 50 53	107 40 39	Silverton volcanics	Roadcut between Ohio & Topeka Gulch	dacite lava	0.96	orthoclase, epidote, chlorite	1.18
SDY9752	37 50 37.2	107 41 3.8	Silverton volcanics	Ridge southwest above Topeka Gulch	dacite lava	2.1	calcite, epidote, chlorite, orthoclase	2.6
SDY9754	37 50 48.6	107 41 47.6	Silverton volcanics	Ridge southwest above Topeka Gulch.	dacite lava	2	chlorite, epidote, orthoclase, calcite trpy	2.56
				Animas River	**Drainage**			
HDY9840	37 54 18.3	107 33 22.4	Picauyune Megabreccia Member, Sapinero Mesa Tuff	1.7 mi.(2.8km) N of Eureka	andesite lava megabreccia	0.93	orthoclase, epidote, chlorite, calcite, amphibole, trpy	1.39
SDY9834	37 49 42.3	107 38 15.7	Silverton volcanics	N of Mayflower mill tailings	dacite/andesite porphyry lava	1.2	chlorite, orthoclase, epidote trpy	1.12
SDY9836	37 49 58.9	107 38 12.4	Silverton volcanics	10,360 ft. in Boulder Gulch	volcaniclastic	1.6	chlorite, epidote, trace mica	1.98
SDY9835B	37 49 44.3	107 38 8.9	Silverton volcanics	Mouth of Boulder Gulch	dacite lava	0.59	chlorite	0.69
SDY9919	37 47 55.6	107 40 26.7	Sultan Mtn. stock	0.5 mi (0.8 km) S of Silverton	Monzonite porphyry lava	3.3	orthoclase, hornblende, chlorite trace mica, pyrite	4.6

MINERALOGY OF IGNEOUS ROCKS

Most rocks sampled are propylitically altered. The mineralogy of the propylitic assemblage is variable, but often consists of chlorite, epidote, (±)calcite, (±)pyrite, and opaque oxides. The primary magmatic mineral phases are preserved in various stages of alteration. Although quartz and sodic plagioclase are abundant in these igneous rocks, these minerals have negligible ANP. Calcite which has a high ANP,was detected in four of 14 samples in amounts ranging from 4 to 6 weight percent. Chlorite is present in all samples and probably has significant ANP, but the amount present varies about 6-fold, based on the variations observed for relative XRD intensities of the 002 (hkl) peak. Study of the mafic minerals for Boulder batholith rocks in Montana showed that biotite plus chlorite concentrates, and tremolite plus chlorite concentrates have high ANP, but it could not be shown unequivocally, that chlorite is the dominant ANP contributor (Desborough and others, 1998). Kwong and Ferguson (1997) and Jambor and Blowes (1998) suggested that chlorite is a significant ANP mineral but provided no quantitative evidence of the ANP of chlorite.

METHODS FOR BEDROCKS

Bedrock samples were sawed to obtain unweathered slabs that were crushed and pulverized using tungsten carbide lined vials and tungsten carbide balls. Pulverized rocks were dry sieved to the <325 mesh (<0.044mm) size fraction. About 20-50 grams was obtained from each sieved sample. A three-gram split was analyzed for mineralogical characterization using X-ray diffractometry methods (Table 1). A one-gram split was exposed to an acid-sulfate- and metal-saturated leachate from the May Day and Yukon mine wastes, MAY and YUK (fig. 1), without agitation in side-by-side experiments. The ANP was calculated in terms of weight percent equivalent calcite based on the increase of pH of the leachate. This calculation is based on the millimoles per gram of H^+ neutralization, which is converted to weight percent calcite by a multiplication factor of 50. For example, if one gram of material in 1 L of pH = 3, raised the pH of the solution to a pH of 4, .0009 moles or 0.9 millimoles of H^+ was consumed. The following calculation illustrates this example:

$$0.9 \times 50 = .045 \text{ grams or } 4.5 \text{ weight percent } CaCO_3 \text{ (Calcite)}$$

This procedure was followed to obtain the weight percent calcite equivalent data (Table 2) for each sample exposed to the MDYU leachate.

Mine waste Leachate preparation

MDYU leachate was prepared by mixing mine wastes obtained from the May Day and Yukon waste piles, with deionized water in the laboratory in ratios of 1:16-1:20 (waste:water) for 48 hours. The leachate, aggregating 49 L, was filtered with 0.45 micron cellul.ose nitrate filters to obtain an acid- sulfate-, metal- rich solution. The concentrations of selected elements and sulfate are given in Appendix 1. The May Day and Yukon wastes mineralogy and leachate characteristics are described by Desborough and others, (1999). Both wastes are adjacent to Cement Creek about 5 km upstream from the confluence of Cement Creek with the Animas River (Figure 1).

X-Ray diffraction of unweathered bedrocks and leached bedrocks

Chlorite abundances in both unweathered and leached samples was determined by measuring the relative intensities of the 100 (hkl) quartz peak and the 200 (hkl) chlorite peaks. The ratio of the 100 quartz peak/002 chlorite peak are given in Table 1. The chlorite peak intensity ratios for both the unweathered and leached samples are shown in Figure 2, which indicates that the abundance of chlorite in the leached samples is reduced due to dissolution in the acidic leachate. Ten samples without calcite were leached twice and the mean reduction in the 200 chlorite peak intensity is 19 percent. Four of these ten samples without calcite were leached a third time; for these, the mean reduction in the 200 chlorite peak intensity, relative to the 100 quartz peak intensity is 20.8 percent. It is not possible to determine the chemical composition of the chlorites because of their fine grain size. The fine grain size of these rocks also precludes physical separation of high purity chlorite concentrates.

XRD peak intensities were used for semiquantitative evaluation of changes in mineral concentrations because peak intensity is a function of concentration. The mean calcite equivalent of the samples without calcite is about 2 weight percent (table 2) and for these about 20 percent of the chlorite was consumed by the acid. Thus for the corresponding ANP of two weight percent calcite equivalence, the ten calcite-free samples would have an average of 10 weight percent calcite equivalent ANP. For those samples with calcite (marked with a bold **C**) in Table 2, after the first 48-hour exposure to the leachate, the solution pH values ranged from only 3.36-4.93. Thus, all of the calcite in these samples was probably dissolved in the first exposure (Table 2). If all of the calcite had not been consumed in the first exposure, the final leachate pH should have been 6.0-7.0, or higher.

Table 2. Acid-neutralization potential (ANP) of igneous bedrocks determined by exposing one gram of the < 0.044 mm fraction of pulverized rock to 1 L of MAY-YUK leachate of pH = 3.2 for 48 h. Each exposure used fresh MAY-YUK leachate.[n.e. = not exposed] Samples with XRD-detectable calcite are indicated with a –**C**

Sample	First Exposure	Second Exposure	Third Exposure	Total or sum
	ANP in weight percent calcite equivalent			
SDY9920	1.15	0.7	n.e.	1.85
ODY9801A**C**	3.34	0.7	0.05	4.1
ODY9720	1.1	0.15	0.2	1.45
ODY9733	1.6	0.55	n.e.	2.15
A97D003	1.4	0.5	n.e.	1.90
A97D004	1.4	0.6	0.2	2.2
A97D007	1.4	0.55	n.e.	1.95
SDY 9752**C**	3.5	1.8	0.6	5.9
SDY9754**C**	3.4	1.25	0.55	5.2
HDY9840**C**	2.2	1.2	0.55	3.95
SDY9834	1.2	0.75	0.60	2.55
SDY9836	1.5	0.75	n.e.	2.25
SDY9835B	1.3	0.85	0.55	2.7
SDY9919	1.1	0.9	n.e.	2.0

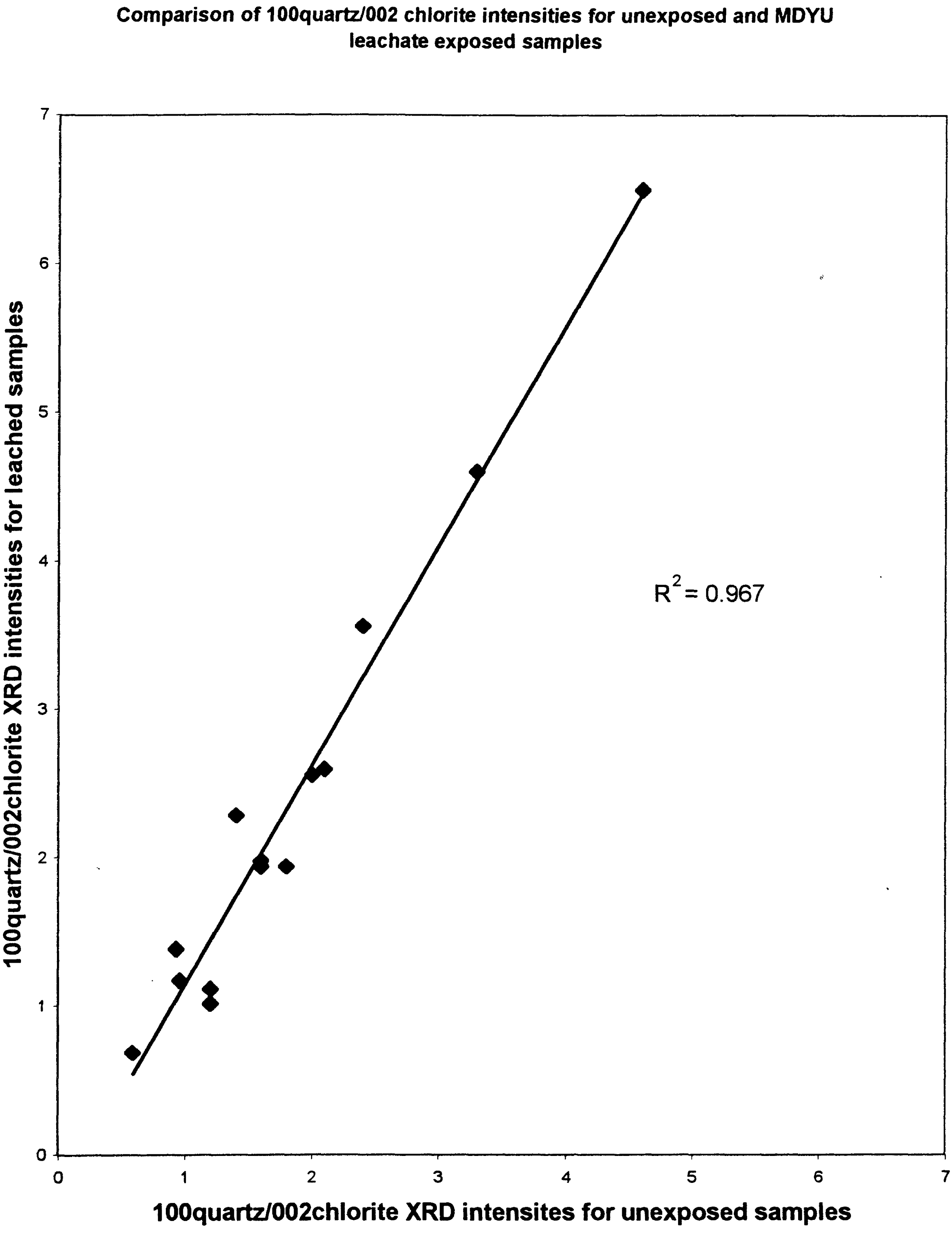

Figure 2 XRD intensity ratios of 100 (hkl) quartz/ 002 (hkl) chlorite for 14 igneous rocks before and after two or three exposures to the MAY-YUK leachate. If there were no chlorite dissolution the best-fit line would extend diagonally from zero to seven.

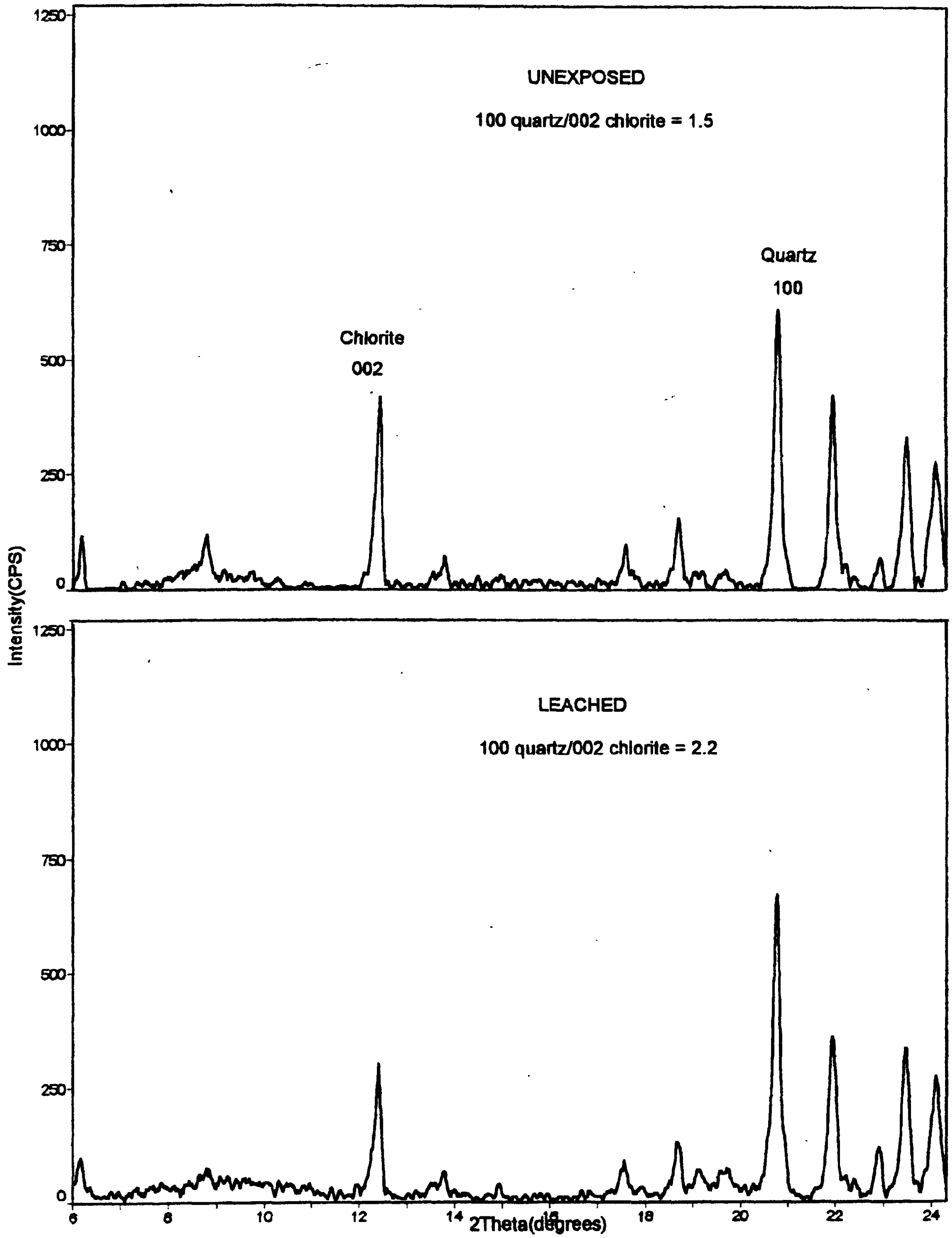

Figure 3. Comparison of X-ray diffraction peaks for unexposed igneous rock (ODY9720) with those of the same rock after three exposures to the MAY-YUK leachate. Note the lower intensity of the chlorite 002 peak in the leached sample.

STREAM SEDIMENTS

Stream sediment samples were collected from 25 sites in Cement Creek, Mineral Creek, and upper Animas River watershed in September, 1999. These samples were obtained from submerged sediments and were sieved on site using stream water to remove the > 2mm fraction. The < 2 mm material from each site ranged from about 200-500 g. Stream pH was measured at the time of collection. Samples were air dried at room temperature for about two weeks and then half of each was mechanically dry sized for 7 minutes before wet sizing in tap water (pH = 7-7.5) for about 3-5 minutes. Wet sizing was done to remove highly soluble salts that might be present. After wet sizing, the sized fractions were air dried at room temperature for several days. The < 0.090 mm fractions were analyzed by XRD to determine mineralogy (Table 4). One dry-sized < 0.090 mm fraction, and one wet-sieved < 0.090 mm fraction were each exposed to deionized water (pH = 5.0 $\pm$0.1) in a ratio of one gram of solid : 800 ml of liquid at rest for 24 h, at which point the pH was measured; results are shown in Table 4.

For seven of the eight samples collected from streams with a pH less than 4.0, both the washed and unwashed sediments reduced the pH of the deionized water leachate. Three of the seven samples contained schwertmannite (Table 4) and they generated the most acid when leached by deionized-water. For the seventeen samples from streams with a pH greater than 4, the unwashed fraction raised the pH of the deionized water leachate more than did the washed samples. We suspect this was due to small particles of chlorite that were removed from the washed samples.

The XRD intensity ratio (quartz 100/chlorite 200) data from the unwashed sediments (table 4) differs substantially from the same ratios of fresh samples. Mean values of 12 units for stream sediments is six times greater (table 3) than the mean (1.8) of the 14 fresh rocks (table 1). We interpret these data to indicate a loss of chlorite by dissolution caused by the acidic waters and the physical abrasion in the stream environment. The contrast in the relative abundance of chlorite with respect to quartz for Cement Creek and Mineral Creek sediments and fresh rocksis shown on Figure 4.

Table 3. Locations of stream sediments, pH of stream water, pH of deionized water after exposure to <0.090 mm washed and unwashed stream sediments, mineralogy of stream sediments, and intensity ratio of quartz100/chlorite200.

Sample	Lat.	Long.	Location	stream pH	washed pH=5, 24h <0.090 mm leach ratio 1:800	unwashed pH=5, 24h <0.090 mm leach ratio 1:800	XRD intensity quartz100/ chlorite200 FRESH	Minerals, in addition to quartz and plagioclase 7A=7 Angstrom peak, probably chlorite SCH = schwertmannite [listed in decreasing order of abundance]
			Mineral Creek Drainage					
S1	37 53 40	107 42 50	Red Mtn. Pass, E.of HWY 550	3.01	3.95	3.72	10.2	mica, 7A, SCH
S2	37 53 41	107 42 51	Red Mtn. Pass, W.of HWY 550	6.5	5.59	6.41	11.5	mica, 7A
S3	37 53 32	107 43 05	Head of Mineral Creek	6.7	6.23	6.52	11.3	mica, chlorite
S4	37 53 07	107 43 22	Porphyry Gulch	6.7	6.31	6.38	6.7	mica, 7A
S5	37 52 22	107 43 40	Mill Creek, W. of HWY 550	6.8	6.36	6.42	9.2	mica, 7A
S16	37 52 35	107 43 23	Min. Crk., Chattanooga	4.93	5.5	5.88	9.3	mica, pyrite, 7A
S17	37 51 25	107 43 21	Browns Gulch	3.4	4.87	4.89		mica, pyrite
S18	37 51 45	107 43 27	Min. Crk., 4WD crossing	5.91	5.8	5.91	11.5	mica, chlorite, pyrite
S19	37 51 03	107 43 33	Min. Crk., Burro Bridge	6.02	5.93	6.09	12.3	chlorite, mica, pyrite
S20	37 50 52	107 43 27	Trib. E.of HWY 550 Ophir Pass Rd	3.08	4.67	4.6		mica
S22	37 49 17	107 43 14	Mineral Crk., Campground	4.62	4.75	5.06	10.2	mica, pyrite, 7A
			Cement Creek Drainage					
S6	37 53 18	107 39 52	Dry Gulch	3.15	5.71	6.25	27.1	mica, pyrophyllite, 7A
S7	37 53 00	107 40 05	Prospect Gulch	2.97	4.67	4.1	21.2	mica, pyrophyllite, 7A, SCH
S8	37 52 37	107 40 16	Georgia Gulch	5.03	5.5	6.39	9.5	mica, chlorite
S9	37 52 06	107 40 30	Cement Creek	3.81	4.74	4.47	14.2	mica, 7A, SCH
S10	37 51 50	107 40 32	Minnesota Gulch	5.31	5.69	6.39	9.4	mica, chlorite
S11	37 51 33	107 40 35	Porcupine Gulch	6.04	5.91	6.41	13.7	mica, chlorite
S12	37 51 05	107 40 35	Ohio Gulch	3.09	4.68	4.76	16	mica, 7A, pyrite
S13	37 50 55	107 40 34	Cement Creek	4.02	4.66	4.87	17.3	mica, 7A, pyrite
S14	37 50 45	107 40 44	Topeka Gulch	4.79	5.18	5.69	14.2	mica, 7A, pyrite
S15	37 50 08	107 40 35	Cement Creek	4.07	4.71	4.98	18	mica, 7A, pyrite
S21	37 49 05	107 39 43	Cement Crk. Mem. Park	3.95	4.57	4.84	16.8	mica, chlorite, pyrite
			Animas River Drainage					
S23	37 49 01	107 39 03	Animas R. Bridge	6.5	5.96	6.22	10.2	mica, 7A, pyrite
S24	37 49 24	107 35 18	Cunningham Creek	6.7	6.31	6.42	8	mica, 7A, pyrite
S25	37 51 45	107 34 01	Minnie Gulch	7.01	5.87	5.88	15.4	Na-plag., mica, 7A

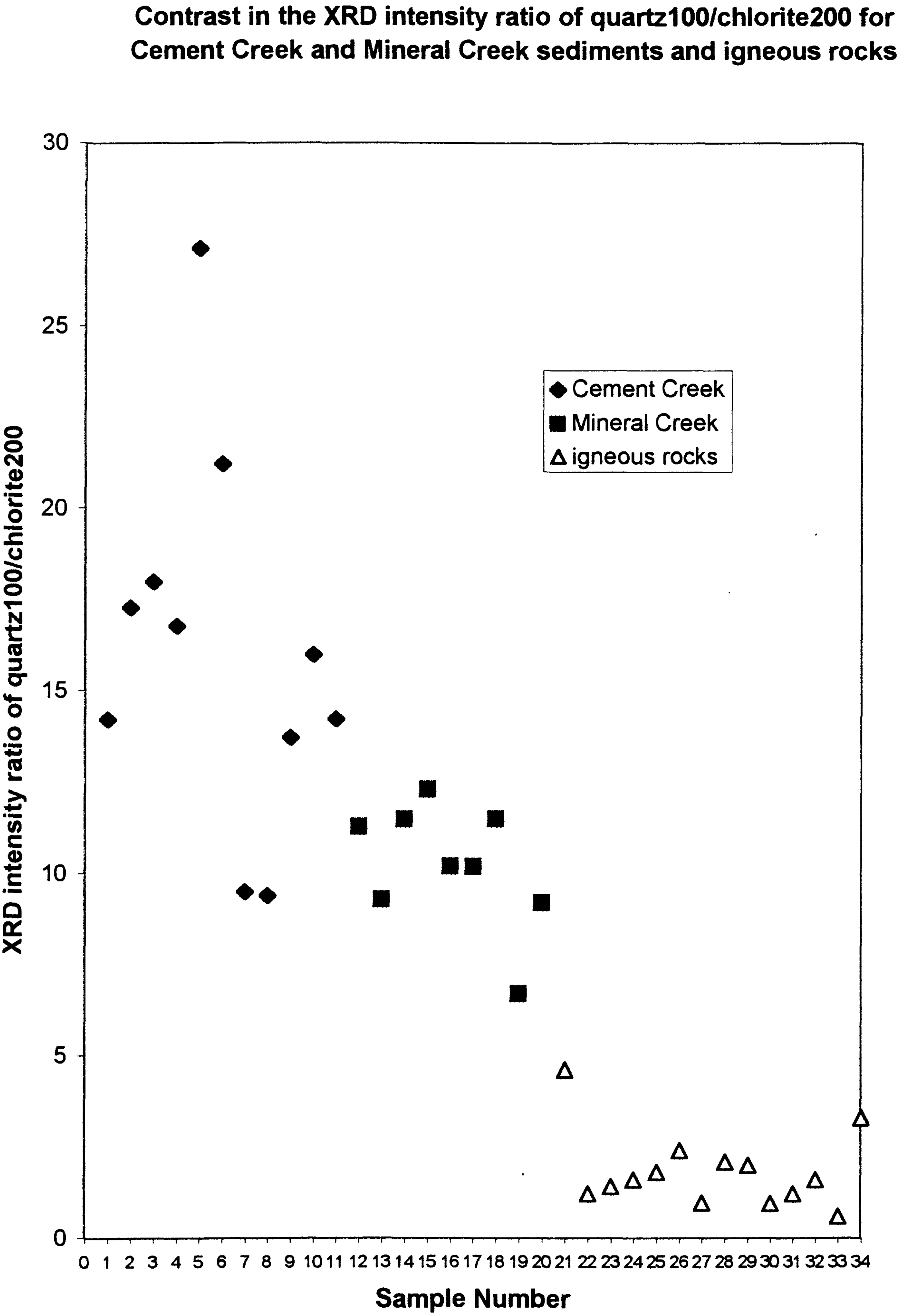

Figure 4. Relations of XRD intensity ratios of quartz100/chlorite200 for Cement Creek sediments (nos. 1-11) Mineral Creek sediments (nos. 12-20) and igneous rocks (nos. 21-34).

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Appendix I. Selected dissolved metals and sulfate in acidic (pH=3.2) MAY-YUK leachate determined by inductively coupled-plasma atomic emission spectroscopy (ICP/AES).

Na	Mg	Al	Si	K	Ca	Fe	Cu	Zn	Cd	Pb	Sulfate
milligrams L^{-1}											
0.66	3.3	7.9	2.5	0.46	21	6.4	0.4	1.7	0.01	0.44	140