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Geochemical Baselines for Surface Waters and Stream Sediments and Processes Controlling Element Mobility, Rough and Ready Creek and Oregon Caves National Monument and Vicinity, Southwestern Oregon

by

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Introduction

When precipitation falls within a drainage basin, water comes into contact with rock-forming minerals and chemical weathering is initiated. Chemical weathering within a basin involves the congruent dissolution of minerals such as calcite or the incongruent dissolution and transformation of minerals such as plagioclase to clay minerals. These processes release elements to the natural waters of a basin. Therefore, the chemical composition of natural waters evolved within a basin that has not been affected by human influence is determined primarily by the chemical composition of rocks within the basin. Climate (mainly precipitation and temperature) plays a role, particularly in determining the rates of water-rock reactions, but composition of the rocks is the fundamental control.

There are multiple methods for quantifying the composition of rocks within a drainage basin. The approximate major element composition of most rock types can generally be inferred from geologic maps, thereby giving a degree of insight into the expected major element composition of natural waters of the basin in question. However, this is not true for trace elements, which can vary by two or more orders of magnitude within the same rock type. Quantification of rock composition involves sampling and chemically analyzing the rocks themselves or the stream sediments within a drainage basin. Sediments provide a robust sample that is easy to collect and representative of the composition of the rocks, soils, and mechanical weathering products upstream from sampling sites (Plant and Hale, 1994).

The background geochemistry of natural waters is, by definition, the composition of the waters without any input from human activities. Unfortunately, there is probably no place in the world in which the background composition of waters has not been modified to some extent by anthropogenic activities such as agriculture, urbanization, or mining. This input is always superimposed on the natural background geochemistry. Relatively pristine areas, such as National Parks or National Forests, may contain areas which are only minimally affected by human influence. At these sites, geochemical baselines (defined as the chemical composition at a given point in time regardless of human input) can be determined for stream waters and may approximate the true background geochemistry. This information is useful for an understanding of the processes responsible for the chemical composition of waters within a drainage basin. In addition, because water geochemistry is sensitive to changes in the environment, the monitoring of water geochemistry allows us to recognize and quantify changes in the environment of the basin under study.

The purpose of this study is to determine the geochemical baseline for the time of sampling for a wide range of major, minor, and trace elements in selected stream and spring waters in the Rough and Ready Creek drainage basin within the Siskiyou National Forest, Oregon (fig. 1). The determination of these baselines will allow the recognition of any changes in water quality that may be caused by the proposed mining of nickel laterite deposits within the basin. In addition, the study determined baselines (for the time of sampling) of streams, springs, and underground flow in the Oregon Caves National Monument and vicinity and for Grayback Creek (fig. 1). Recent advances in analytical technology, particularly inductively coupled plasma-mass spectrometry, allow for the determination of a wide range of elements at very low detection limits. The determination of geochemical baselines for this study establishes a range of element concentrations in waters at the time of sampling. Stream sediments were also collected at selected sites to provide information on rock composition within the study areas and to provide a baseline for the geochemistry of the stream sediments.

Regional Setting

The study areas lie within the Klamath Mountains geomorphic province of southwestern Oregon and northern California. The Klamath Mountains consist of four north-trending arcuate belts of rocks (Irwin, 1966 and Hotz, 1971). The two study areas fall within the two western most belts called the Western Paleozoic and Triassic Belt, which includes the Applegate Group and associated ultramafic and younger intrusive rocks, and the Western Jurassic Belt which includes the Rogue and Galice Formation and associated intrusives rocks (Ramp and Peterson, 1979). All the layered rocks conform to the regional trend of the Klamath Mountains. These rocks were once sea floor rocks and island-arc volcanic deposits that collided with the continental margin (Allen and Beaulieu, 1976).

Field and Laboratory Methods

Water

Water samples were collected from 17 streams and 3 springs during September 9 - 11, 1997. During this time the weather was stable and no precipitation occurred. Samples were collected by width and depth integration (Edwards and Glysson, 1988) except for sites such as springs where flow was minimal. Temperature, pH, and conductivity were measured at the site. An Orion model SA 250 pH meter with an Orion Ross Shur-Flow glass electrode with a Ag/AgCl junction was used to measure pH. The conductivity was measured using an Orion model 120 conductivity meter. Samples were collected into clean high-density polyethylene bottles. For the dissolved cation analyses, a 30-ml sample was filtered through a 0.45 μm-membrane filter and acidified with ultrapure reagent-grade Ultrex nitric acid to pH < 2. A 15-ml sample was filtered but not acidified for anion analyses, and a 125-ml untreated sample was

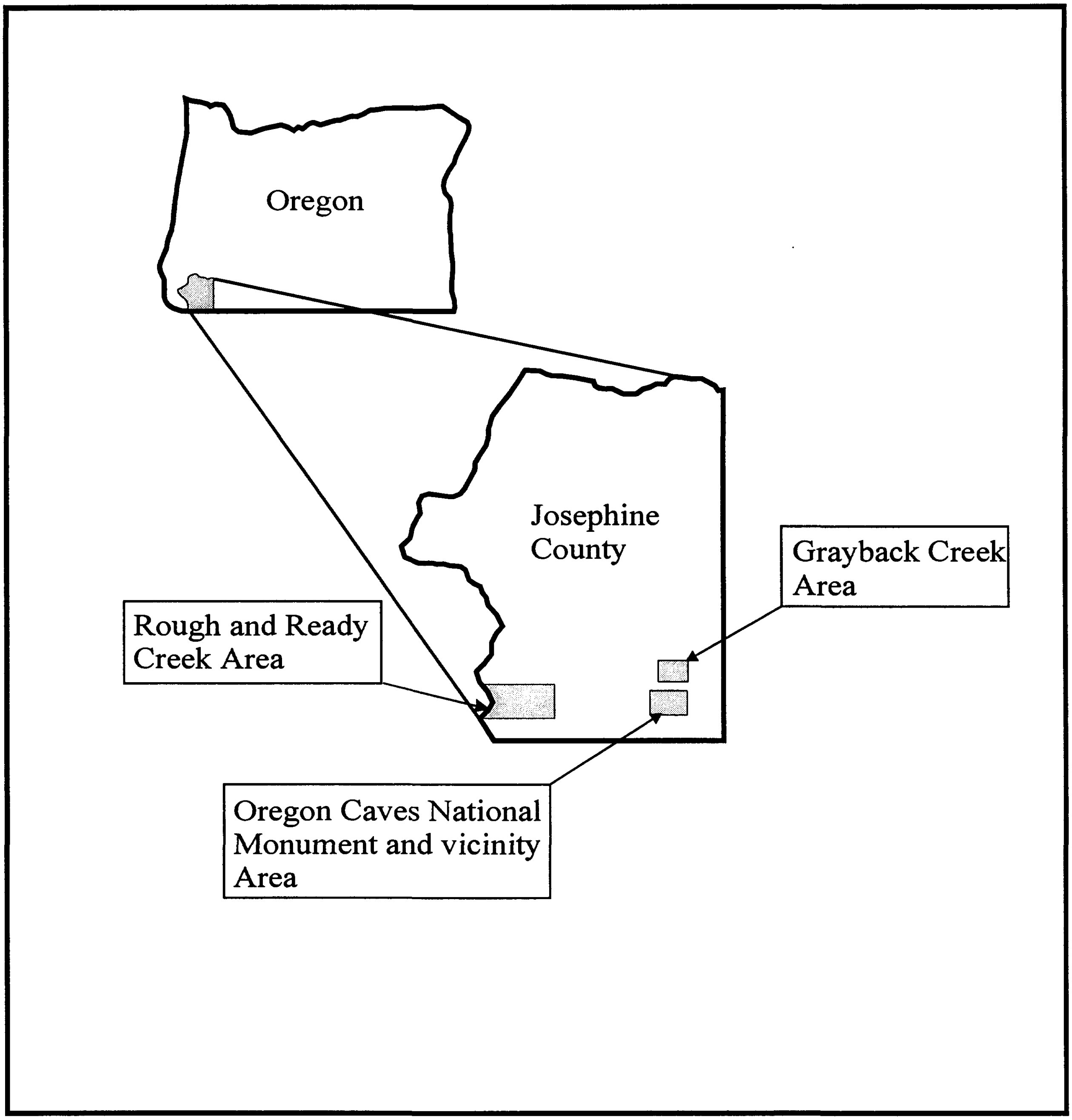

Figure 1. Location map showing the study areas, Southwestern Oregon

collected for alkalinity measurement. The samples were stored in an ice chest after collection and later in a refrigerator and kept cool until analyzed.

Upon return to the USGS laboratories, alkalinity as HCO_3^-, was determined by titration with H_2SO_4 using an Orion Model 960 autochemistry system, Richard Sanzolone, analyst. The anions sulfate, chloride, nitrate, and fluoride were determined by ion chromatography (IC) (Fishman and Pyen, 1979), Peter Theodorakos, analyst. The cations Mg, Na, Fe, and P were analyzed by inductively coupled plasma - atomic emission spectrometry (ICP-AES) (Briggs and Fey, 1996). The remaining cations were analyzed by inductively coupled plasma - mass spectrometry (ICP-MS) (Meier and others, 1994). Duplicate water samples, blank samples, and USGS Water Resource Division standard reference waters were analyzed with each data set. Elements which were analyzed for, but were below analytical detection for all the samples are shown in Table 1. The chemical analyses of the water samples are shown in Table 2.

Stream Sediments

Stream sediment samples were collected and chemically analyzed from eleven sites within the study areas. The purpose of determining geochemical baselines for sediments was to provide an estimate of the rock composition within the sampled basin. This information, in turn, was used to gain insight into the processes which affected water chemistry within the basin.

Each sediment sample was collected from approximately 100 meters of stream in the vicinity of the location shown on Figs. 2, 4, and 5. The sediment was passed through a 2-mm screen at the sample site, air dried, and transported to the U.S. Geological Survey in Denver, CO for preparation and analysis. In the lab, the samples were sieved to minus-0.18 mm (minus-80 mesh), ground to minus-0.15 mm (minus-100 mesh) and submitted for chemical analysis. The sediment analyses were performed by XRAL, Inc. under contract with the USGS.

The samples were analyzed for forty elements by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using for sample digestion a mixture of hydrochloric, nitric, perchloric, and hydrofluroic acids at low temperature to achieve a total decomposition of all mineral phases in the sample (Briggs, 1996). The samples were also analyzed by ICP-AES for ten elements using a hydrochloric acid-hydrogen peroxide digestion (Motooka, 1996). This digestion solubilizes metals not tightly bound within silicate minerals and, thus, constitutes only a partial dissolution of the sample. The data for each of these methods is shown in Table 3.

Rough and Ready Creek Study Area

Most of the rocks (>90%) within the Rough and Ready Creek watershed consist of serpentinite and partly serpentinized peridotite which make up the Josephine ultramafic sheet.

Table 1. Elements in water samples that were all below level of detection, Rough and Ready Creek and Oregon Cave National Monument and vicinity, Oregon

Element	Lower level of analytical detection in ppb
P	50
Be	0.05
Cu	0.5
Ga	0.02
Ge	0.2
As	0.4
Zr	0.05
Nb	0.02
Cd	0.02
In	0.01
Sn	0.07
Te	0.1
Pr	0.01
Eu	0.005
Tb	0.005
Gd	0.005
Dy	0.005
Ho	0.005
Er	0.005
Tm	0.005
Yb	0.01
Hf	0.05
Ta	0.02
W	0.1
Re	0.02
Au	0.01
Pb	0.05
Bi	0.01
Th	0.01
Tl	0.05

Table 2 . Chemical analyses of waters from Rough and Ready Creek and Oregon Caves National Momument and vicinity

Site	Description	Latitude			Longitude			Temp	pH	Cond	Alkalinity	Ca
		Deg	Min	Sec	Deg	Min	Sec	deg C		uS/cm	mg/l HCO3	mg/l
	Rough and Ready Creek Watershed											
SK04	W. Fork of the Illinois River	42	5	13	123	40	27	18.0	7.95	134	85	3.1
SK05	Rough and Ready Creek	42	5	16	123	40	36	18.7	7.65	195	124	1.5
SK06	South Fork of Rough and Ready Creek	42	5	17	123	45	39	18.6	8.21	120	75	0.85
SK07	North Fork of Rough and Ready Creek	42	5	19	123	45	39	18.3	8.43	175	105	1.6
SK08	Tributary stream	42	5	26	123	45	49	18.7	8.05	248	167	0.6
SK09	Spring	42	5	24	123	45	44	18.7	7.70	201	123	1
SK10	Spring	42	5	11	123	45	11	11.7	7.63	152	99	0.4
SK11	Rough and Ready Creek	42	5	31	123	44	35	20.1	8.40	172	99	1.4
SK12	Tributary stream	42	5	39	123	44	37	19.7	8.53	237	157	0.6
SK13	Tributary stream	42	5	39	123	44	1	18.0	8.52	265	182	1.3
SK14	Rough and Ready Creek	42	5	43	123	42	26	21.1	8.58	180	108	1.5
SK15	Tributary stream	42	5	43	123	42	20	17.6	8.04	277	178	1.8
	Oregon Caves National Momument and vicinity											
SK16	Grayback Creek	42	9	9	123	24	0	12.4	7.90	100	60	9.9
OC01	Surface flow within Oregon Cave	42	5	50	123	24	20	7.8	8.06	289	180	54
OC02	Surface flow within Oregon Cave	42	5	50	123	24	19	7.2	8.10	229	140	42
OC03	Cave Creek at exit form Oregon Cave	42	5	53	123	24	22	5.9	7.95	228	143	37
OC04	Spring	42	5	55	123	24	27	7.1	7.80	243	148	39
OC05	Cave Creek	42	5	54	123	24	34	7.9	8.38	243	148	40
OC06	Noname Creek	42	5	47	123	24	49	10.6	8.62	211	132	34
OC07	Lake Creek	42	6	28	123	24	10	10.1	7.92	91	54	12

Table 2 continued.

Site	Mg	Na	K	SiO2	Sulfate	Chloride	Fluoride	Nitrate	Fe	Mn	Al	Li	Sc
	mg/l	mg/l	ug/l	mg/l	mg/l	mg/l	mg/l	mg/l	ug/l	ug/l	ug/l	ug/l	ug/l
Rough and Ready Creek Watershed													
SK04	12	1.8	330	20	<2	2	<0.1	<0.1	65	12	1.4	< 0.6	3.7
SK05	21	1.2	100	32	<2	3.8	<0.1	0.2	<20	< 0.01	1.9	< 0.6	5.6
SK06	12	1.3	92	21	<2	2.5	<0.1	0.2	<20	< 0.01	1.3	< 0.6	3.8
SK07	17	2.8	160	19	<2	6.6	<0.1	<0.1	<20	1.1	26	< 0.6	3.5
SK08	29	1	41	30	<2	2	<0.1	0.2	<20	0.03	0.50	0.6	4.8
SK09	21	2	84	24	<2	5.4	<0.1	0.2	<20	< 0.01	< 0.2	< 0.6	3.5
SK10	17	<1	48	22	<2	1.1	<0.1	<0.1	<20	0.02	0.3	< 0.6	2.9
SK11	16	2.3	120	19	<2	5.9	<0.1	<0.1	<20	0.04	1.3	0.6	2.6
SK12	27	<1	46	28	<2	2	<0.1	0.4	<20	0.01	< 0.2	< 0.6	4.3
SK13	29	<1	70	28	<2	2.1	<0.1	0.3	<20	0.03	0.3	0.8	4.0
SK14	19	2	92	24	<2	5.3	<0.1	<0.1	<20	0.42	0.79	0.6	3.2
SK15	31	1	320	31	5.8	2.3	<0.1	<0.1	<20	7.7	0.67	1	4.5
Oregon Caves National Momument and vicinity													
SK16	3.6	3.2	890	22	3.1	0.8	0.1	<0.1	<20	0.65	8.4	0.6	3.4
OC01	<1	<1	620	5.0	<2	0.7	0.1	0.2	<20	0.14	2.2	0.6	< 0.7
OC02	<1	<1	620	5.4	<2	1.2	0.1	0.2	<20	0.04	1.2	0.6	< 0.7
OC03	3.1	2	950	20	<2	1	<0.1	0.2	<20	< 0.01	< 0.2	1	3.1
OC04	3.3	2.2	950	18	<2	1.2	<0.1	0.2	<20	< 0.01	1.2	1	2.8
OC05	3.1	2.2	880	17	2.1	1.5	<0.1	0.4	<20	0.05	2.8	1	2.4
OC06	3.4	2.3	1300	18	2.5	1.1	<0.1	<0.1	<20	4.7	4.1	1	2.7
OC07	2.1	2.7	870	17	2.2	0.7	<0.1	<0.1	<20	2.6	22	1	2.7

Table 2 continued.

Site	Ti	V	Cr	Co	Ni	Zn	Se	Rb	Sr	Y	Mo	Ag	Sb
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
Rough and Ready Creek Watershed													
SK04	< 0.3	< 0.3	< 1	0.07	11	< 0.5	0.2	0.14	22	< 0.01	0.3	0.02	0.07
SK05	< 0.3	< 0.3	2	< 0.02	17	4	< 0.2	0.090	8.6	< 0.01	0.2	< 0.01	0.05
SK06	< 0.3	< 0.3	< 1	< 0.02	23	< 0.5	< 0.2	0.16	6.0	< 0.01	0.2	< 0.01	0.04
SK07	4.4	< 0.3	4	< 0.02	11	< 0.5	0.3	0.27	6.6	< 0.01	0.2	< 0.01	0.02
SK08	< 0.3	< 0.3	5	< 0.02	28	< 0.5	< 0.2	< 0.03	1.8	< 0.01	0.1	< 0.01	< 0.02
SK09	< 0.3	< 0.3	4	< 0.02	18	< 0.5	0.3	0.095	3.4	< 0.01	0.1	< 0.01	< 0.02
SK10	< 0.3	< 0.3	5	< 0.02	33	< 0.5	0.2	< 0.03	1.2	< 0.01	0.1	< 0.01	< 0.02
SK11	< 0.3	< 0.3	4	< 0.02	13	< 0.5	< 0.2	0.13	6.0	< 0.01	0.1	< 0.01	< 0.02
SK12	< 0.3	< 0.3	3	< 0.02	15	< 0.5	< 0.2	< 0.03	1.6	< 0.01	0.07	< 0.01	< 0.02
SK13	< 0.3	< 0.3	3	< 0.02	19	< 0.5	< 0.2	0.06	2.5	< 0.01	0.07	< 0.01	< 0.02
SK14	< 0.3	< 0.3	3	0.02	13	< 0.5	0.2	0.13	7.0	< 0.01	0.1	< 0.01	< 0.02
SK15	< 0.3	< 0.3	1	0.2	36	< 0.5	0.3	0.17	12	0.02	0.2	< 0.01	0.02
Oregon Caves National Momument and vicinity													
SK16	< 0.3	1.2	< 1	< 0.02	1.8	< 0.5	0.4	0.66	62	0.02	0.2	< 0.01	< 0.02
OC01	< 0.3	< 0.3	1	0.07	1.4	< 0.5	0.3	0.30	54	< 0.01	0.08	< 0.01	< 0.02
OC02	< 0.3	< 0.3	< 1	0.05	1.0	< 0.5	< 0.2	0.22	43	< 0.01	0.06	< 0.01	< 0.02
OC03	< 0.3	0.4	< 1	0.05	1.1	< 0.5	< 0.2	0.14	67	0.07	0.09	< 0.01	< 0.02
OC04	< 0.3	0.3	< 1	0.05	1.0	< 0.5	0.3	0.20	68	0.02	0.09	< 0.01	< 0.02
OC05	< 0.3	< 0.3	< 1	0.05	1.6	< 0.5	0.4	0.27	66	0.01	0.08	< 0.01	< 0.02
OC06	< 0.3	0.5	< 1	0.06	1.1	< 0.5	0.4	0.42	60	0.02	0.1	< 0.01	< 0.02
OC07	< 0.3	0.5	< 1	0.03	0.4	< 0.5	0.3	0.41	48	0.02	0.2	< 0.01	< 0.02

Table 2 continued.

Site	Cs	Ba	La	Ce	Nd	Sm	U
	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
Rough and Ready Creek Watershed							
SK04	< 0.01	5.9	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK05	< 0.01	2.6	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK06	< 0.01	0.64	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK07	0.02	0.69	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK08	< 0.01	0.70	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK09	< 0.01	0.51	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK10	< 0.01	0.47	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK11	< 0.01	0.56	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK12	< 0.01	0.46	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK13	< 0.01	0.76	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK14	< 0.01	2.6	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
SK15	< 0.01	6.8	< 0.01	< 0.01	< 0.01	< 0.01	< 0.005
Oregon Caves National Momument and vicinity							
SK16	< 0.01	5.0	0.03	0.01	0.01	< 0.01	0.01
OC01	< 0.01	16	< 0.01	< 0.01	< 0.01	< 0.01	0.09
OC02	< 0.01	14	< 0.01	< 0.01	< 0.01	< 0.01	0.15
OC03	< 0.01	18	< 0.01	< 0.01	< 0.01	< 0.01	0.12
OC04	< 0.01	18	< 0.01	< 0.01	< 0.01	< 0.01	0.10
OC05	< 0.01	18	< 0.01	< 0.01	< 0.01	< 0.01	0.11
OC06	< 0.01	18	< 0.01	< 0.01	< 0.01	< 0.01	0.07
OC07	< 0.01	5.5	0.04	0.02	0.02	0.01	0.08

Table 3. Chemical analyses of stream sediments from Rough and Ready Creek and Oregon Caves National Monument and vicinity. (See Table 2 for location coordinates and description of sample sites. Element names followed by /P indicate partial dissolution of samples as discussed in text.)

Site	Al %	Ca %	Fe %	K %	Mg %	Na %	P %	Ti %	Mn PPM	Ag PPM	As PPM
Rough and Ready Creek Watershed											
SK04	5.2	1.3	4.4	0.96	3.5	0.90	0.03	0.36	621	< 2	< 10
SK05	3.6	0.71	5.6	0.86	12	0.70	0.03	0.26	786	< 2	< 10
SK06	2.2	1.7	8.1	0.06	17	0.45	0.02	0.29	1210	< 2	< 10
SK07	1.6	1.1	9.3	< 0.005	18	0.26	0.01	0.15	1190	< 2	< 10
SK08	0.89	0.56	8.4	< 0.005	20	0.09	0.01	0.08	1200	< 2	< 10
SK11	1.7	1.1	7.2	< 0.005	20	0.33	0.01	0.15	1070	< 2	< 10
SK12	0.70	0.51	8.7	< 0.005	21	0.05	0.009	0.05	1320	< 2	< 10
SK13	0.81	0.46	8.2	< 0.005	19	0.04	0.01	0.05	1350	< 2	< 10
SK14	2.3	1.0	7.3	0.24	17	0.34	0.02	0.18	1190	< 2	< 10
Oregon Caves National Monument and Vicinity											
SK16	7.4	4.3	6.6	1.0	3.5	1.9	0.05	0.67	1170	< 2	< 10
OC07	6.3	5.4	6.7	0.65	5.0	1.2	0.05	0.51	1330	< 2	< 10

Site	Au PPM	Ba PPM	Be PPM	Bi PPM	Cd PPM	Ce PPM	Co PPM	Cr PPM	Cu PPM	Eu PPM	Ga PPM
Rough and Ready Creek Watershed											
SK04	< 8	449	< 1	< 10	< 2	32	35	843	25	< 2	11
SK05	< 8	312	< 1	11	< 2	19	69	620	17	< 2	< 4
SK06	< 8	43	< 1	17	< 2	5	111	2280	3	2	< 4
SK07	< 8	24	< 1	11	< 2	< 5	121	4570	10	3	< 4
SK08	< 8	19	< 1	14	< 2	< 5	153	1260	< 2	< 2	< 4
SK11	< 8	28	< 1	15	< 2	< 5	110	1680	3	< 2	< 4
SK12	< 8	15	< 1	12	< 2	< 5	173	1680	< 2	< 2	< 4
SK13	< 8	22	< 1	12	< 2	< 5	163	1940	< 2	2	< 4
SK14	< 8	162	< 1	12	< 2	7	106	2100	7	< 2	< 4
Oregon Caves National Monument and Vicinity											
SK16	< 8	421	< 1	20	< 2	35	26	95	32	2	11
OC07	< 8	333	< 1	19	< 2	33	31	120	33	2	4

Site	Ho PPM	La PPM	Li PPM	Mo PPM	Nb PPM	Nd PPM	Ni PPM	Pb PPM	Sc PPM	Sn PPM	Sr PPM
					Rough and Ready Creek Watershed						
SK04	< 4	17	26	< 2	13	17	432	14	15	22	87
SK05	< 4	10	19	< 2	25	10	1500	16	14	13	76
SK06	< 4	< 2	6	< 2	38	< 9	2250	19	18	16	56
SK07	< 4	< 2	4	< 2	48	< 9	2310	16	12	< 5	31
SK08	< 4	< 2	4	< 2	43	< 9	3380	15	12	< 5	7
SK11	< 4	< 2	4	< 2	40	< 9	2150	15	14	< 5	38
SK12	< 4	< 2	3	< 2	48	< 9	2950	14	12	< 5	6
SK13	< 4	< 2	3	< 2	42	< 9	2980	12	13	< 5	6
SK14	< 4	3	9	< 2	41	< 9	1940	19	14	< 5	44
					Oregon Caves National Monument and Vicinity						
SK16	< 4	17	12	< 2	9	25	76	18	32	74	317
OC07	< 4	16	9	< 2	13	24	53	12	45	49	207

Site	Ta PPM	Th PPM	U PPM	V PPM	Y PPM	Yb PPM	Zn PPM	Ag/P PPM	As/P PPM	Au/P PPM	Bi/P PPM
Rough and Ready Creek Watershed											
SK04	< 40	< 6	< 100	139	9	1	86	< 0.08	< 1	0.1	< 1
SK05	< 40	< 6	< 100	112	8	< 1	71	< 0.08	< 1	< 0.1	< 1
SK06	< 40	< 6	< 100	167	7	< 1	84	< 0.08	< 1	< 0.1	< 1
SK07	< 40	< 6	< 100	122	3	< 1	101	< 0.08	< 1	0.1	< 1
SK08	< 40	< 6	< 100	72	2	< 1	69	< 0.08	< 1	< 0.1	< 1
SK11	< 40	< 6	< 100	92	4	< 1	66	< 0.08	< 1	0.1	< 1
SK12	< 40	< 6	< 100	71	< 2	< 1	58	< 0.08	< 1	0.2	< 1
SK13	< 40	< 6	< 100	64	< 2	< 1	65	< 0.08	< 1	0.1	< 1
SK14	< 40	< 6	< 100	111	5	< 1	78	< 0.08	< 1	< 0.1	< 1
Oregon Caves National Monument and Vicinity											
SK16	< 40	< 6	< 100	264	19	2	87	< 0.08	< 1	0.1	< 1
OC07	< 40	< 6	< 100	289	21	2	84	< 0.08	< 1	< 0.1	< 1

Site	Cd/P PPM	Cu/P PPM	Mo/P PPM	Pb/P PPM	Sb/P PPM	Zn/P PPM
Rough and Ready Creek Watershed						
SK04	0.2	21.5	0.3	4.0	< 1	67.5
SK05	0.1	20.7	0.4	4.0	< 1	59.3
SK06	< 0.05	9.5	0.2	< 1	< 1	39.2
SK07	< 0.05	17.9	0.2	< 1	< 1	69.3
SK08	< 0.05	5.8	0.2	< 1	< 1	47.7
SK11	0.06	9.9	0.1	2.0	< 1	43.8
SK12	< 0.05	5.7	0.1	< 1	< 1	43.4
SK13	< 0.05	6.8	0.2	1.0	< 1	45.1
SK14	0.07	14.2	0.2	3.0	< 1	59.7
Oregon Caves National Monument and Vicinity						
SK16	0.05	27.2	0.2	2.0	< 1	36.3
OC07	< 0.05	27.2	0.1	1.0	< 1	23.3

The ultramafic rocks were originally mostly peridotite which varied in composition from pyroxenite to dunite (Ramp and Peterson, 1979). The remaining rocks are quartz diorite and related rocks, which occur in the southwestern part of the South Fork of Rough and Ready Creek drainage basin (Ramp and Peterson, 1979). Most of the ultramafic rocks are serpentinized and highly sheared near fault boundaries. Iron and nickel-rich red lateritic soils are developed on the ultramafic rocks. These deposits formed by chemical weathering of peridotite and possibly serpentinite (Hotz, 1964). Olivine and orthopyroxene minerals are readily weathered to hydrated ferric oxides and clays. The lateritic soils occur on nearly flat lying to gently slopping surfaces on broad ridgecrests, in saddles and on lower shoulders, terraces, and benches (Hotz, 1964). Accumulations of lateritic soils range from a few feet to a few 10's of feet thick and have an average Ni content of <1%. The age of the lateritic soils is probably Miocene or younger (Hotz, 1964). The rugged terrain, which makes it difficult to transport the ore, the low grade of the nickel content, and the low volume of the reserves imply that the iron- and nickel-rich lateritic soils within the Rough and Ready Creek drainage are probably marginal in value for ore deposits compared to world-wide averages for nickel ore deposits (see figs. 189 and 190, p. 254, Singer, 1986).

Samples of 9 stream waters, 2 spring waters, and 8 stream sediments were collected within the Rough and Ready Creek watershed (fig. 2). The West Fork of the Illinois River above the junction with Rough and Ready Creek was also sampled for both stream water and sediments (fig. 2). The samples were collected September 9 and 10, 1997. During this time, the weather was stable and no precipitation occurred. The streams were in low flow, near the lowest flow of the season, and all waters were clear.

The waters can be classified as to dominant cation and anion. All the sites are Mg-HCO_3^- dominant waters, mainly because of the peridotite and sepentinite rocks that underlie the watershed. The rock composition determines the geochemistry of the waters that evolve in the watershed. The minerals that compose the rocks are mainly serpentine, olivine, and pyroxene. Serpentine is a stable mineral but olivine and pyroxene will readily weather to serpentine, clay and hydrated iron or aluminum oxides, releasing elements, particularly Mg, Fe, Si, and trace metals Ni and Cr to the waters of the basin.

The pH values of waters ranged form 7.63 to 8.58 with a mean of 8.16 and conductivity ranged from 120 to 277 μS/cm with a geometric mean of 196 μS/cm (Table 2). Alkalinity, which indicates the capacity of the waters to buffer acid from sources such as acid-mine drainage or acid rain, ranged from 75 to 182 ppm as HCO_3^- with a geometric mean of 124 ppm, indicating that the waters within the watershed have good buffering capacity.

Rock composition is the fundamental control determining the geochemistry of the waters in the watershed. The concentrations of elements that may be a concern for aquatic and public

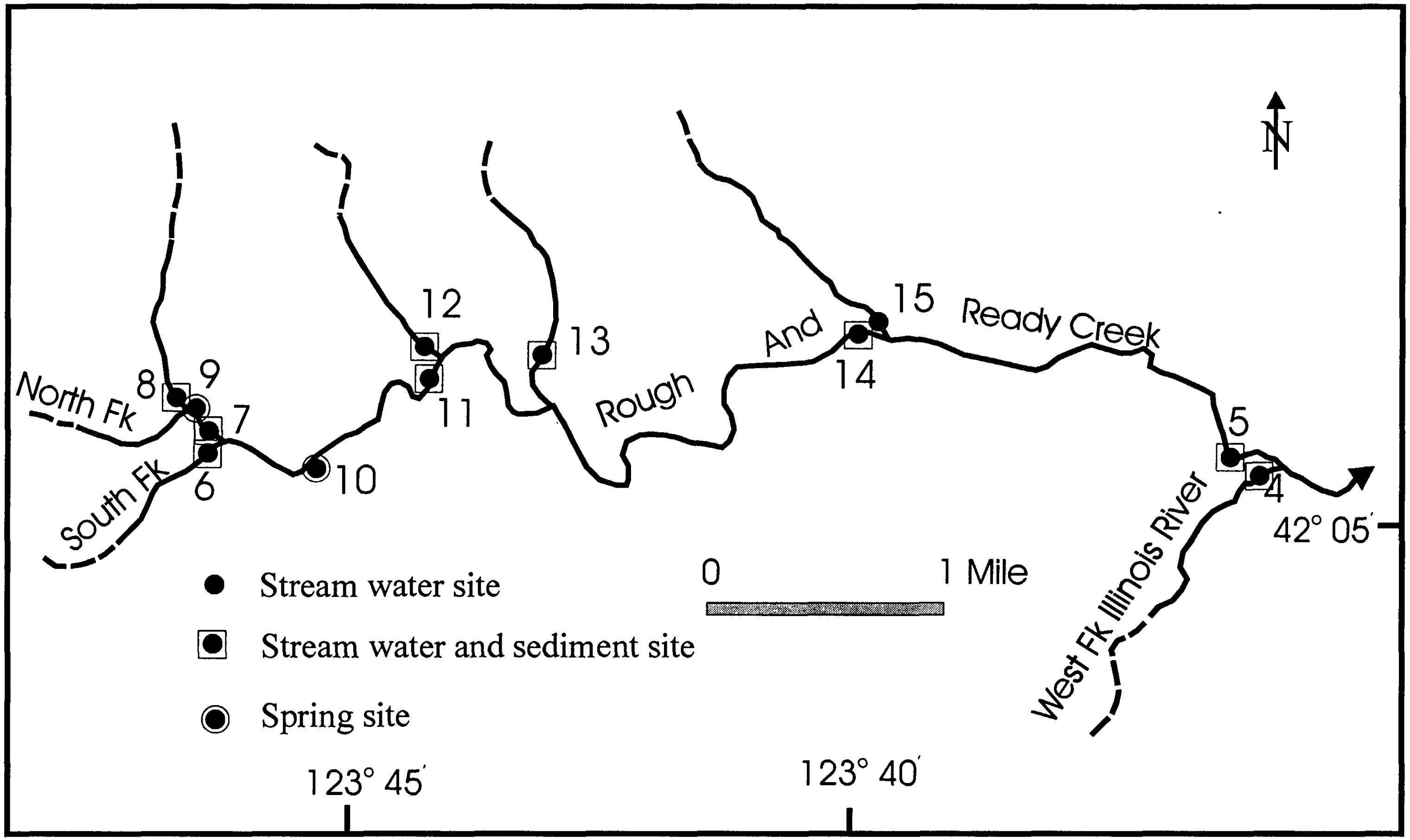

Figure 2. Map showing locations of water and stream sediment samples, Rough and Ready Creek. All sites prefixed with "SK".

health are generally low, particularly for Cu, Zn, As, Co, Se, Sb, Mo, U and nitrate. The only exception is Ni which ranged in concentration from 11 to 36 ppb, with a geometric mean of 19 ppb. The elevated concentrations of Ni compared to average fresh water (Table 4) is due to chemical weathering of Ni-bearing minerals within the watershed. In addition, Cr which ranged in concentration from <1 to 5 ppb is slightly elevated in concentration compared to average fresh water (Table 4). The concentrations of Ca, Na, K, sulfate, F^- and Cl^-, are low and Mg and SiO_2 are high in waters in the watershed, compared to average fresh water (Table 4). The distribution of pH, conductivity, alkalinity, Ni and Mg are shown in fig. 3. Sulfate concentrations are low with a range of <2 to 5.8 ppm. These low values indicate that sulfide minerals are absent or in minimal quantities in the drainage basin. Mn, and Al concentrations are generally low compared to average fresh water (Table 4). The only Fe concentration above the detection limit of <20 ppb occurs at site SK04 (West Fork of the Illinois River) with 65 ppb.

In summary, the water chemistry of the Rough and Ready watershed is influenced by the rock composition that underlies the basin. Sampled waters within the watershed are high in concentrations of Mg and Ni and low in Ca as well as many other elements, compared to average fresh water. High alkalinities of the waters within the watershed indicate good capacity for buffering acid generation from possible sources such as acid rain and acid-mine drainage. Overall the quality of waters in the Rough and Ready Creek watershed is good compared to most water quality standards.

Chemical Modeling of the Waters

To gain understanding of processes such as speciation of elements and identification of minerals that may control the concentration, mobility, and attenuation of elements in the stream waters, chemical modeling of the stream waters was carried out using PHREEQC (Parkhurst, 1995). The modeling program assumes mineral-solution equilibrium. For some chemical reactions, particularly with slow kinetics, this may not be the case. The dominant cations and anions in the stream and spring waters are Mg^{2+}, Ca^{2+}, Na^+, K^+, $Al(OH)^{4-}$, H_4SiO_4, $HCO3^-$, SO_4^{2-}, and Cl^-. At five sites $MnCO_3^0$ is dominant and at the remaining sites, Mn^{3+} is dominant.

Saturation indexes were calculated for a suite of minerals to determine if concentrations of trace metals in water were controlled by mineral phases. The saturation index is a convenient means of expressing saturation states of minerals (Barnes and Clark, 1969) where:

$$SI=\log_{10} IAP/K_T.$$

In the expression, SI is the saturation index, IAP is the ion activity product, and K_T is the

Table 4. Background of elements (in ppb) in freshwater compared to the geometric mean concentration of the Rough and Ready watershed.

Element	Background (Freshwater)	Rough and Ready Creek Watershed
	Data from Forstner and Wittmann (1979)	
Al	<30	0.7
Cr	0.5	2.7
Fe	<30	<20
Mn	<5	0.05
Ni	0.3	19.1
Zn	10	<0.5
	Data from Livingstone (1963)	
Ca	15	1.0
Mg	4.1	21
Na	6.3	1.3
K	2.3	0.89
SiO2	13.1	25
SO4	11.2	<2
HCO3	58.4	124
Cl	7.8	3.1

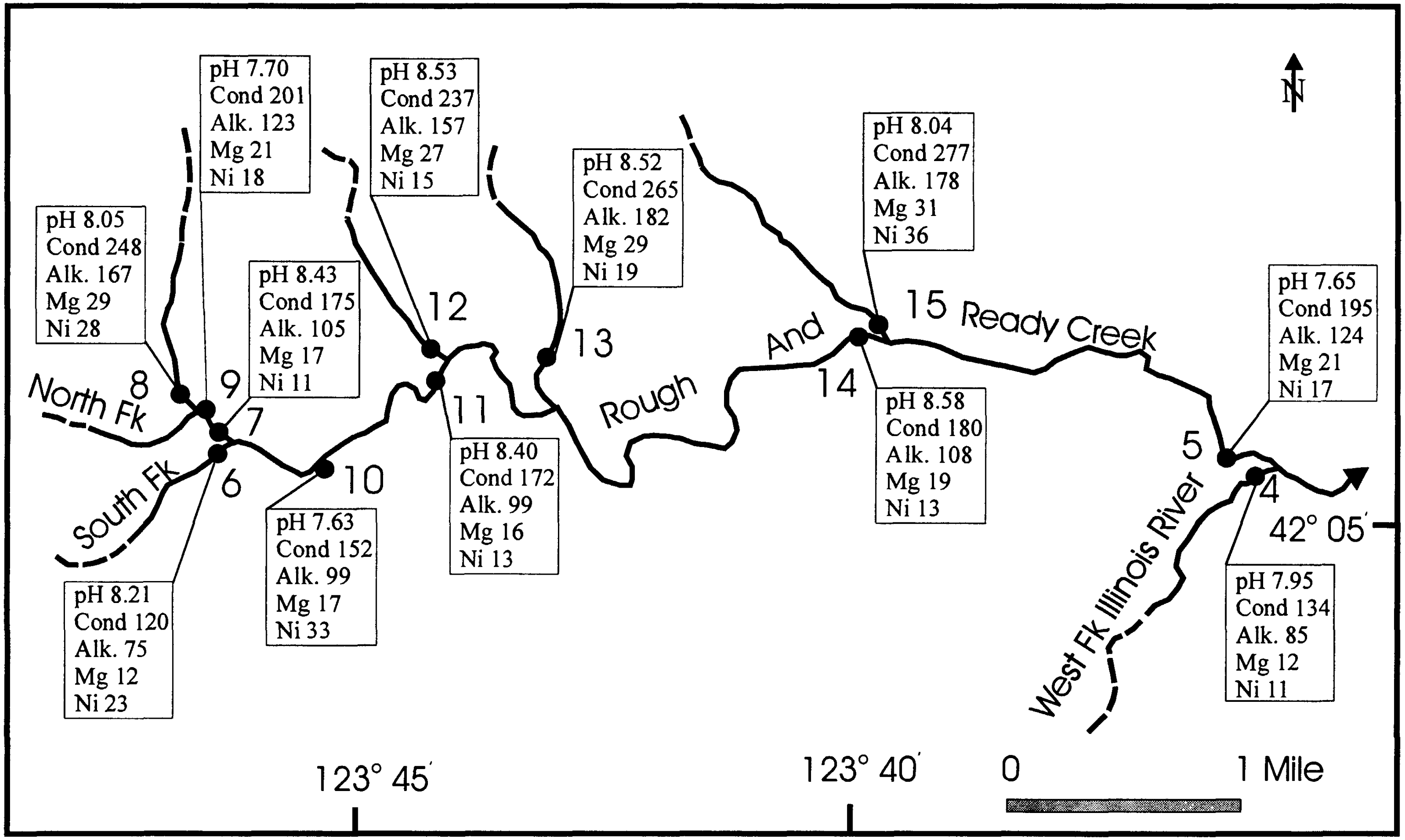

Figure 3. Map showing distribution of selected elements or species in water, Rough and Ready Creek. Conductivity (Cond) in uS/cm, alkalinity (Alk.) as ppm HCO3, Mg in ppm, and Ni in ppb. All sites prefixed "SK".

equilibrium constant of the dissolution reaction at the temperature in question. Mineral phases are supersaturated at SI>0, saturated at SI=0, and undersaturated at SI<0.

All the waters are undersaturated with respect to calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), except for sites SK13 and 14 which are saturated or slightly supersaturated with respect to dolomite (Table 5). At sites SK13 and 14, waters are slightly supersaturated with respect to sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$). At these two sites, either dolomite or sepiolite may control the Mg concentration of the waters. Sepiolite is commonly found as a secondary mineral in the vicinity of serpentinite masses. All the waters are slightly undersaturated with respect to chalcedoney (SiO_2), suggesting that chalcedoney is controlling the concentration of silica concentrations in the waters. Gibbsite ($Al(OH)_3$) is undersaturated at most of the sites, except sites SK07 and 5. This suggests that the alteration of silicate minerals to gibbsite is continuing in much of the watershed.

Possible Impact on Water Quality on Rough and Ready Creek Due to Mining

A proposal has been made to mine Ni-bearing laterite from the Rough and Ready Creek watershed. Laterite is usually a reddish material composed of secondary oxides of iron and aluminum, which is a residual or the end product of weathering. Therefore, the material is chemically stable. The mining of the laterite should present no problem to the chemical quality of waters within the watershed.

If mining occurs within the watershed, access roads will be constructed and serpentinite may be used as a road material. Serpentinite is a rock consisting of chemically-stable serpentine-group minerals with minor chlorite and talc. The use of serpentinite as road material will not have significant effect on the chemical quality of the waters within the watershed. It is possible that the minerals will break down to smaller sizes, and the potential exists to transport this fine material to streams within the basin during rainstorms.

If possible, the use of peridotite as road material should be avoided. Peridotite contains minerals such as olivine that are not chemically stable and will alter and release elements such as Ni to the waters of the watershed. Crushing of the perdiodite for road material will expose fresh surfaces to oxidation and dissolution and increase the release of Mg, Si, Fe, Ni, and other elements to the waters of the basin. The type of elements that will be released to the waters of the basin will be similar to what is currently being released by normal chemical weathering, but the amount will be significantly increased, particularly in the first several years after the road material is first exposed to the surface environment. Even if peridotite is used as road material, the concentrations of these elements in the watershed should not exceed water quality standards.

Table 5. Saturation indexes for selected mineral phases

Site	Calcite	Dolomite	Chalcedoney	Gibbsite	Sepiolite
Rough and Ready Creek Watershed					
SK04	-1.09	-1.34	-0.29	-0.36	-2.72
SK05	-1.55	-1.69	-0.11	0.03	-2.89
SK06	-1.44	-1.46	-0.26	-0.68	-1.53
SK07	-0.83	-0.38	-0.30	0.41	-0.53
SK08	-1.45	-0.95	-0.04	-0.95	-0.84
SK09	-1.68	-1.78	-0.19	-1.07	-2.93
SK10	-2.33	-2.89	-0.12	-0.39	-3.60
SK11	-0.92	-0.48	-0.33	-0.95	-0.68
SK12	-1.00	-0.07	-0.10	-1.94	0.90
SK13	-0.64	0.32	-0.12	-1.60	0.75
SK14	-0.68	0.06	-0.20	-1.39	0.62
SK15	-0.98	-0.47	-0.03	-0.76	-0.86
Oregon Caves National Monument and vicinity					
SK16	-0.86	-1.99	-0.11	0.76	-3.76
OC01	0.38	-2.05	-0.68	0.26	-8.66
OC02	0.21	-1.44	-0.67	-0.01	-6.78
OC03	-0.01	-1.05	-0.07	-0.86	-4.10
OC04	-0.10	-1.21	-0.08	0.30	-4.58
OC05	0.49	-0.06	-0.13	0.04	-2.41
OC06	0.64	0.42	-0.18	-0.18	-1.33
OC07	-0.83	-2.30	-0.16	1.29	-4.44

Oregon Caves National Monument and Vicinity

Water samples were collected from 7 streams and 1 spring in the Oregon Caves National Monument and vicinity and Grayback Creek (fig. 4 and 5). Stream sediments were collected from Lake Creek (OC07) and Grayback Creek (SK16). Samples at site SK16 were collected on September 10, 1997. The remaining samples were collected on September 11, 1997. During this period, the weather was stable and no precipitation occurred. All the streams were in low flow stage.

Most of the rocks in the Oregon Caves National Monument and vicinity are Triassic Applegate Group metavolcanics and metasediments (Ramp and Peterson, 1979). The metavolcanics consist of pillow lavas, flow breccias, and tuffs which were intruded by diabase and gabbro dikes (Ramp and Peterson, 1979). The metasedments include argillite, slaty siltstone, chert, tuffaceous sediment, quartzite conglomerate, and marble (Ramp and Peterson, 1979). The caves occur in marble lenses. Sites OC01 and OC02 are from within and near the back of the cave where flowing water enters the cave. Site OC03 is from Cave Creek at the exit of the cave. Site OC04 is a spring along Cave Creek near the contact of the marble with other metasediments and metavolcanics. Site OC05 is Cave Creek below the Oregon Caves Chateau, a historic hotel located within the drainage of Cave Creek, below the exit from the cave. Site OC06 is along No Name Creek, a tributary to Cave Creek. The No Name Creek watershed is underlain by Applegate Group metavolcanics and metasediments. Site OC07 is Lake Creek above the junction with Panther Creek. The Lake Creek watershed is underlain mainly by a granodiorite pluton and provides the water supply for Oregon Caves National Monument. Site SK16 is Grayback Creek below the junction with Mossback Creek. Grayback Creek watershed is underlain by metasediments and metavolcanics of the Applegate Group and by younger intrusive rocks which range in composition of quartz diorite to more mafic rocks.

The chemical analyses of the waters from the Oregon Caves National Monument and vicinity are shown in Table 2. The geochemistry of the waters demonstrate the effect of rock composition on the type of water that will evolve within a watershed. This can be shown by comparing the chemical composition of waters at various sites. Comparing sites OC01 and OC02, waters collected within Oregon Caves, to site OC03, Cave Creek at the cave exit, elements that increase in concentrations at the exit are Mg, Na, K, SiO_2, Li, Sc, V, Sr, and Y. Elements that decrease in concentrations at the exit are Mn, Al, Rb, and Ca. Conductivity and pH also decrease. Waters at sites OC01 and OC02, are mainly in contact with carbonate rocks. Cave Creek at the exit contains a mixture of waters in contact with both carbonate and other types of rocks. These other rock types are probably Applegate Group metavolcanics and metasediments. Chemical modeling shows that sites OC01 and OC02 are supersaturated with

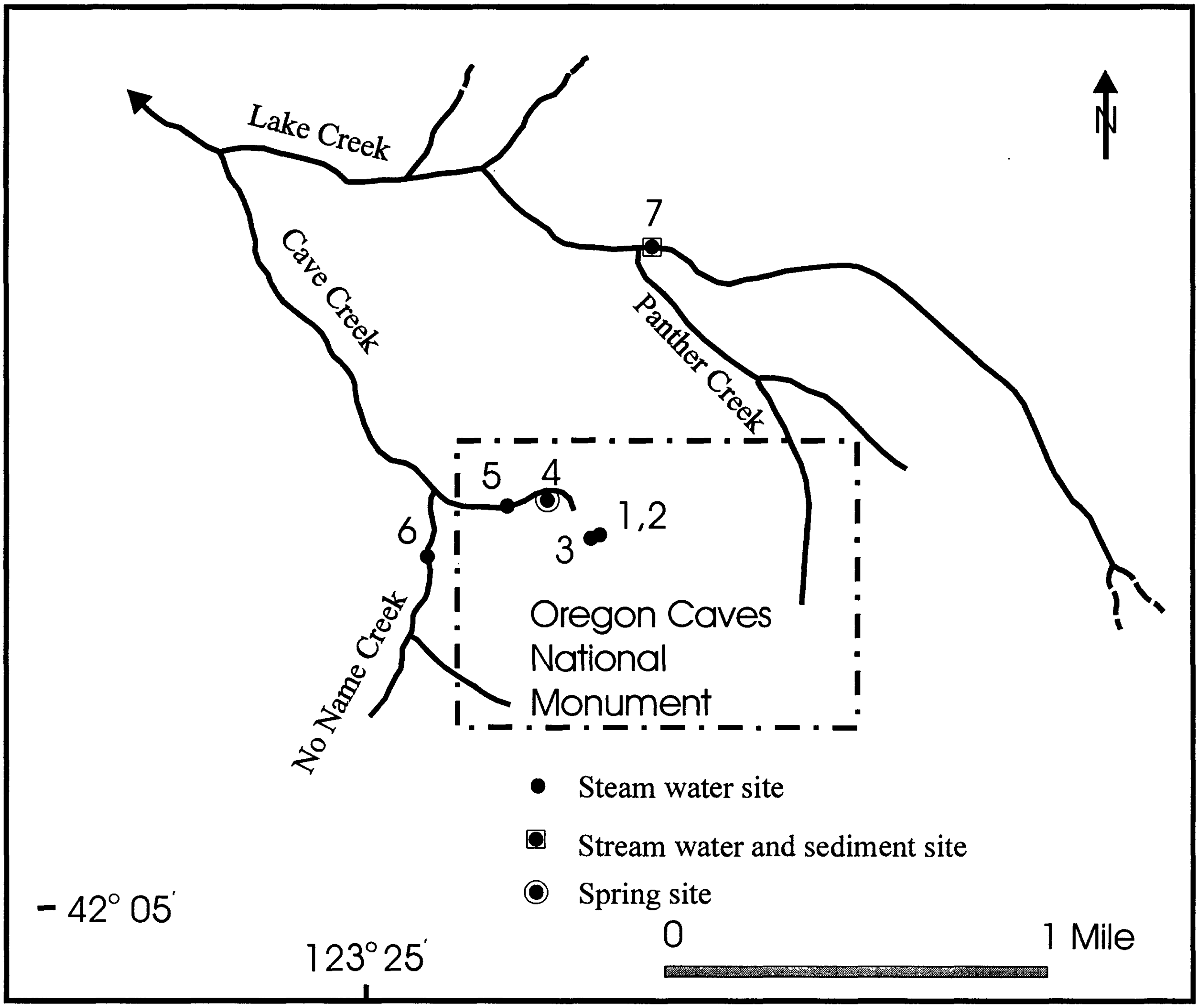

Figure 4. Map showing locations of water and sediment samples (prefixed OC), Oregon Caves National Monument and vicinity

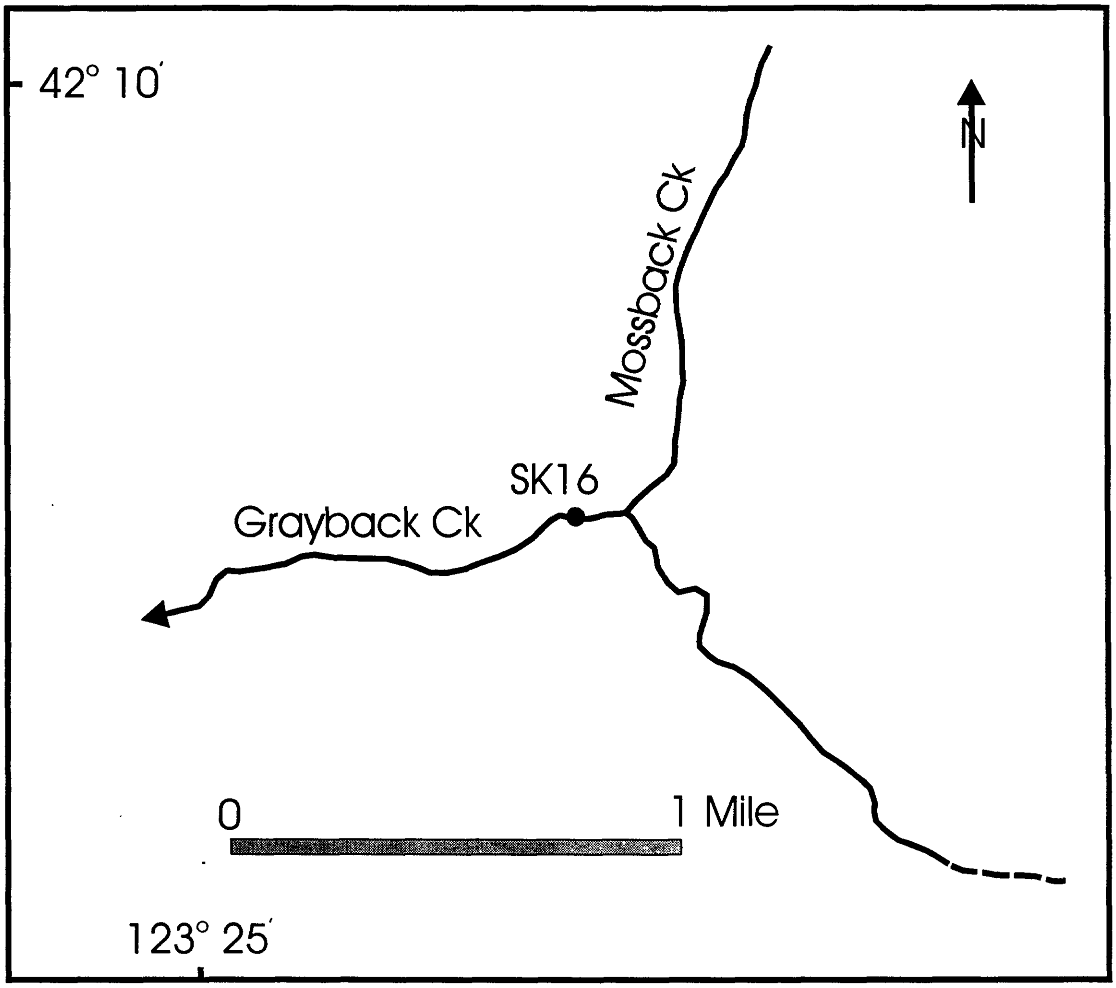

Figure 5. Map showing location of stream water and sediment sample from Grayback Creek

respect to calcite (Table 5). Calcite should precipitate at these sites. The mixed water at site OC03, at the exit of the cave, is near saturation with respect to calcite, which should not dissolve or precipitate at this site. Chalcedony (amorphous silica) is undersaturated at sites OC01 and OC02, but near saturation at site OC03, further suggesting that site OC03 contains water that was in contact with silicate rocks.

Water from site OC04, a spring, is similar to Cave Creek at site OC03, suggesting that the water at the spring is a mixture of waters in contact with marble and metavolcanics and metasediments. The water at the spring is slightly undersaturated with respect to calcite and chalcedony (Table 5).

The water from Cave Creek site OC05, below the Oregon Caves Chateau, compared to OC03 or OC04, contains slightly greater concentrations of Ca, alkalinity, nitrate, Mn, Al, Ni, Rb and slightly less concentrations of SiO_2, Sc, V, and Y. Values of pH are also slightly higher at site OC05 (Table 2). The water at site OC05 has been in contact with marble along the streambed after leaving the cave, and probably has dissolved minor calcite, which increases the pH and accounts for the differences in many of the other species. The water of site OC05 is supersaturated with respect to calcite (Table 5). The increase in concentrations of nitrate, Mn, and Al below the Oregon Cave Chateau may be due to the presence of the chateau's leach field above site OC05.

The water from No Name Creek, OC06, compared to Cave Creek, contains greater concentrations of K, SO_4, Mn, Al, and Rb and less concentrations of alkalinity, Ca, Sr, and nitrate. No Name Creek contains a mixture of waters in contact with both marble and more silicious metasediments and metavolcanics. The water at this site is supersaturated with respect to calcite and dolomite and near saturation with respect to chalcedony (Table 5).

The water from Lake Creek, site OC07, is higher in concentrations of Al, La, Nd, and Sm and lower in concentration of alkalinity, Ca, Mg, Ni, Sr, Ba, nitrate, and conductivity, compared to Cave Creek or No Name Creek. The chemistry of the water, in particular La, Nd, and Sm, suggests that the water is in contact with more felsic intrusive rocks compared to other sites in the study area. The Lake Creek watershed is underlain by granodiorite, and the sediment data show elevated concentrations of Ca, K, Na, La, Nd, and Sn, typically high in areas underlain by felsic rocks. The water is undersaturated with respect to calcite, suggesting the absence of marble in the watershed, and slightly undersaturated with respect to chalcedony (Table 4). The watershed provides the water supply for the Oregon Caves National Monument. The water quality of the inorganic chemistry of the watershed is excellent. The alkalinity is lower compared to Cave Creek. The lower alkalinity, which is a measure of buffering capacity of the water, indicates that if the watershed is impacted by processes which generate acid, such as acid-rain, the waters of the watershed could deteriorate and quickly become acidic.

The water from Grayback Creek, site SK16, has low pH and conductivity values and is low in concentrations of alkalinity and Ca and highest in Mg, Na, SiO_2, SO_4, V, Ni, and Rb compared to the other waters in the study area. The water chemistry indicates that the waters are in contact with mixed rocks ranging from intermediate composition to mafic rocks. The stream sediment data is similar to that of Lake Creek. The waters at this site are undersaturated with respect to calcite, suggesting an absence of marble in the watershed, and slightly undersaturated with respect to chalcedony (Table 5).

Conclusions and Summary

Temperature, pH, conductivity, alkalinity, and 65 elements or species were determined for waters collected from 17 streams and 3 springs in southwestern Oregon. Because of the low sensitivity of the ICP-MS analyses, these results provide a geochemical baseline, for the time of sampling, for a wide range of elements at low sensitivities, many documented for the first time for this area. Stream sediments were collected and chemically analyzed from 11 of the water sampling sites to provide an estimate of the composition of rocks upstream from the sites. The water chemistry of these sites demonstrate the importance of rock composition in the type of waters that will evolve in a watershed. In the Rough and Ready Creek watershed, the waters in contact with the underlying ultramafic rocks are high in Mg and Ni and low in most other cations. In Oregon Caves National Monument, waters in contact with marble are high in Ca and alkalinity and low in most other cations. Other waters in the vicinity are mixtures of waters in contact with marble, metasediments, metavolcanics, and younger intrusive rocks. The water chemistry at these sites reflects these mixtures of rocks within the watershed..

In most cases, the water chemistry in both study areas indicates that there is minimal input from anthropogenic sources. One exception is Cave Creek, site OC05, which is below Oregon Caves Chateau. Nitrate at this site is elevated in concentration above that at site OC03, Cave Creek above the Chateau, probably because of the leach field for the chateau. The concentration of nitrate at site OC05 is still low and does not pose a health concern.

Mining of Ni-bearing laterite and the building of access roads in the Rough and Ready Creek watershed should not pose a water quality problem to the watershed, particularly if peridotite rocks are not greatly disturbed. Disturbing peridotite rocks will increase chemical weathering and increase the amounts of Mg and Ni released to the watershed.

Because of the minimal input from anthropogenic sources in the two study areas, the geochemical baselines establish an approximation of background geochemistry of stream and spring waters for the time of year in which the sampling was done, mainly low flow period. Because water chemistry is sensitive to changes in the environment, these results can be used to compare with future water chemistry in order to determine if change has taken place in the watersheds.

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