WEATHERING MECHANISMS AND MASS BALANCE IN A HIGH SIERRA NEVADA WATERSHED - - DISTRIBUTION OF ALKALI AND ALKALINE EARTH METALS IN COMPONENTS OF PARENT ROCK AND SOIL, SNOW, SOIL MOISTURE AND STREAM OUTFLOW

Thesis by

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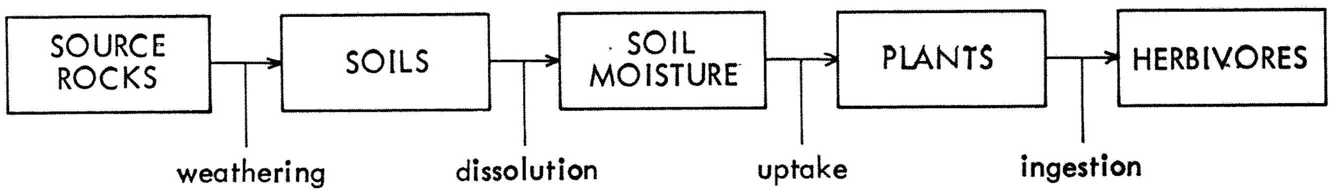
A note to the reader:

This thesis is organized in such a way that an overview of the arguments and data may be made by reading only the Introduction (pp 1-5) and the summary sections at the beginning of each chapter (pp 6-11, 44-48, and 67-72).



Frontispiece: scheme of flow of metals through the Thompson Canyon watershed system: geological and biological portions of the metals "food chain".

ABSTRACT

The alkali metals K, Rb and Cs, and the alkaline earth metals Ca, Sr and Ba were analyzed in the rocks, minerals, soils, snow, stream water and soil moisture films of Thompson Canyon, a glacially scoured watershed in the central crest region of the Sierra Nevada in east central California. The stable isotope dilution method was used.

1. The mass balance of metals entering and leaving the watershed, the denudation rate, and chemical and mineralogical details of the weathering process: In the batholithic source rock, two major minerals, microcline and plagioclase, and one minor mineral, biotite, contain most of the mass of the six metals. Snow is the main source of water to the valley, and contains much lower concentrations of metals than has been previously reported. These metals originate from distant sources. The mass of metals leaving the watershed annually in stream outflow indicates that the watershed is being denuded at a rate of less than 1 cm per 1000 yr, and that the principal process is chemical removal. Ca and Sr are being denuded more rapidly from the batholithic rock than the alkalies or Ba. This is shown by the greater proportion of Ca and Sr in stream water in contrast to the greater proportion of alkalies and Ba in the source rock. Rapid breakdown of plagioclase is responsible for this differential removal. In rock and grus, ratios among metals present in plagioclase (Ca and Sr) and those in K-feldspar (K and Ba) show that plagioclase is preferentially removed as rocks weather and crumble to grus. Rivulets running away from melting snow banks in mid summer dissolve large amounts of Ca and Sr at only short

distances away from the snow banks, and hold these metals for transport out of the watershed. Particles from the snow banks, rich in Rb and Cs, similar in composition to mica, are deposited in soils by the rivulets. Comparison of metal compositions of rock and grus show that mica particles are freed as the rocks break down.

2. Metals in soils: Masses and distribution of the six metals were determined in the soil reservoir. Three soil fractions were analyzed: (1) organic matter (humus), (2) clay (+ silt) size and (3) igneous minerals (sand size). The Rb/K and Cs/K ratios are greater in humus than in whole soil or in the source rocks. On the other hand, Sr/Ca and Ba/Ca ratios are lower in the humus. The metal ratios in humus are similar to those in soil moisture films in subsaturated soils. Area and humus content of soil types show that about 100,000 tons of humus are present in the watershed. The mass of metals in humus is about 100 times greater than that mobilized annually by weathering or present in soil moisture films. Metal composition of the clay fraction is similar to batholithic rock, but richer in Rb and Cs. The igneous mineral fraction shows that soils are not the residue rich in quartz and alkali feldspar which would be predicted from rock composition and data on metal loss from the watershed. Instead, the soils are enriched in plagioclase and depleted in K-feldspar, necessitating a hypothesis that the weathering products of K-feldspar in soils are periodically swept out of the watershed. Data on metals in turbid streams after violent rains support this.

3. Metals in soil moisture films: Soil moisture films may be regarded as the final geological occurrence of metals in a food chain,

because in this form metals are available to the roots of growing plants. A technique was developed for collecting minute samples (300 mg) of moisture from undisturbed soils in the field by rapid blotting onto stacks of cleaned absorbent paper discs. The proportions of metals in soil moisture films are different from those in source rocks. In soil moisture the heavy metal Cs is greatly enriched in the alkali family, and in the alkaline earth family the heavy metal Ba is depleted.

Metal concentrations in soil moisture films collected in the field are quite different from those in soil solutions prepared in the laboratory by traditional methods, and from "exchangeable" and "soluble" ions determined in NH_4^+ acetate buffered solutions: soil moisture films show K/Ca ratios commonly as high as 4, while other traditional methods give values below unity for the same soils. Compared to other types of water, such as phreatic and stream samples, soil moisture films have much higher concentrations of alkalies relative to alkaline earths.

Metal concentrations in soil moisture films vary seasonally, concentrations of alkalies increasing in the autumn near the surface of humus rich soils.

Table of Contents

List of Figures

List of Tables

INTRODUCTION

A new concept is used here to study the biogeochemical distribution of metals. The ease of analytical techniques did not guide the selection of metals measured nor did the ready availability of samples determine the materials analyzed. Instead, abundant nutritious and trace toxic members of two families of metals, the alkalies and the alkaline earths, were selected for study in a food chain. Although absolute metal concentrations were determined, the aim was not to use these data per se, but to compare the depletion or enrichment of a trace toxic metal with its nutritious relative at various trophic levels in the food chain. This study deals mainly with the geologic portion of the food chain.

Three alkali and three alkaline earth metals (K, Rb, Cs and Ca, Sr, Ba) were investigated in rocks, soils, snow, stream waters and soil moisture films in a valley where the geology was known and metal inputs and outputs were measured. Each metal was determined with a high degree of accuracy and reliability, not common in this field of study, by using mass spectrometric isotope dilution analysis under clean laboratory conditions.

Various mass balance studies have been made of watersheds in the past of metals in rocks and stream solutes (Likens and others, 1967; Viro, 1953; Gambell and Fisher, 1966; Cleaves and others, 1970) but use has not been made of the changes in distinctive ratios of such metals among the various component parts of geologic systems. Garrels and Mackenzie (1967) and Cleaves and others (1970) predicted that Ca would be removed in relative excess because of the weathering of plagioclase from igneous rocks. This study confirms that plagioclase is the source of the excess Ca and Sr found in stream outflow. Mass balance information together with metal ratio relationships were used to establish this.

This study is the first to use new techniques of low temperature oxidation and dilute acid leaching to separate and characterize organic matter (humus) as a distinct fraction of soil, and as a readily exchangeable reservoir of metals in the soil, different from the clay minerals which have been widely regarded as the major or sole source of available soil metals.

This study is the first to show that the composition of a soil present in a watershed is different from what would be expected on the basis of rock composition and metal loss considerations. This has required the postulation of a new mechanism of removal of material from developing soils; namely, the periodic washing out of the weathering products of certain types of K-feldspar known to exist in the source rock. Without knowledge of the composition of all of the major minerals of the source rock for all six metals, together with total metal inputs and outputs, the details of the mineral changes and the details of the role of removal mechanisms involving water could not have been understood.

A technique has been devised for collecting small amounts of soil moisture films in the field and analyzing them for trace metals. This is the first time in more than eighty years of the study of the chemistry of soils that the actual compositions of soil moisture films in the field have been analyzed. It was found that the metals in soil solutions obtained in the laboratory using standard procedures were quite different from those present in soil moisture films collected in the field.

This work shows that strong chemical fractionation occurs among the metals as they pass from their origin in the batholithic rocks to the films of soil moisture which provide the nourishment for plants and ultimately the rest of the biological system.

This study of six metals in their natural biogeochemical state can provide a foundation for pollution studies. The biogeochemical distribution of Pb can be predicted by analogy from the natural behavior of its close relative Ba. Gross distortions in the expected distribution of Pb would indicate the extent and modes of industrial Pb pollution.

Field area selected: Thompson Canyon is located in the northern part of Yosemite National Park at an altitude of 3170 m with an area of 12.2 km^2. More than half of the exposed surface of the canyon is bare rock. There are no lakes, although a broad, poorly drained meadow is at the southern end. There are no streams entering the canyon and precipitation is largely by snow. The main stream, draining the melting snow, runs continuously through the summer. The canyon is sparsely forested with lodgepole and whitebark pine and mountain hemlock. Figure 1 is a map of Thompson Canyon.

Analytical and sample handling methods: The mass spectrometric thermal-emission stable isotope dilution method, used for all analyses in this study, is discussed in Chapter I. Some of the techniques

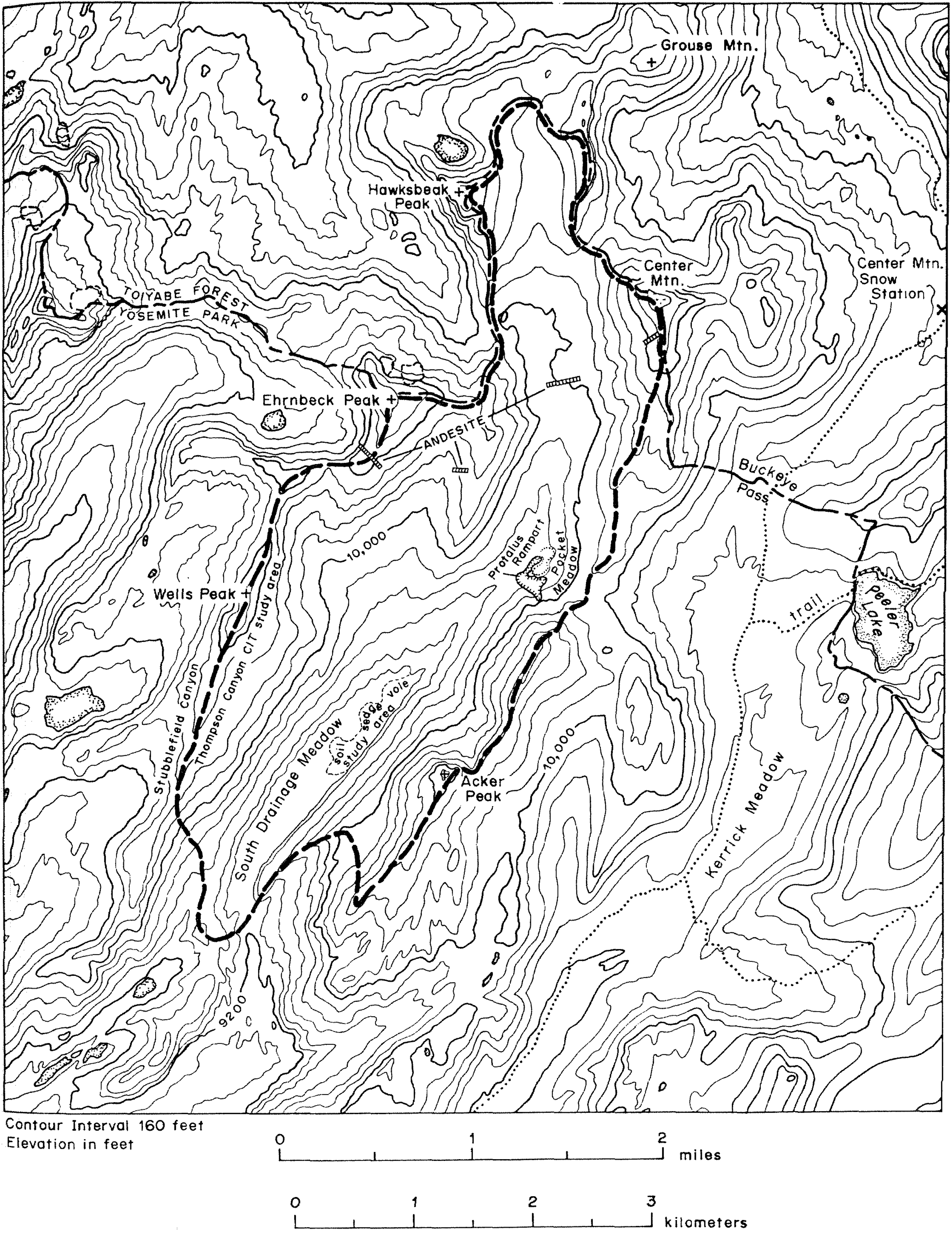


Figure 1: Map of the Thompson Canyon Watershed

Center Mountain is at 119° 29' longitude, 38° 06' latitude.

recently developed for the analysis of alkalies and alkaline earths in lunar materials have been used in this study (Tera and others, 1970). Great care was taken to exclude contamination from the samples during collection in the field and analysis in the laboratory. This care involved the use of ultra-clean collecting devices and transporting containers, a filtered-air clean laboratory, and ultra-high purity reagents and ware (Patterson and Settle, 1975).

I. MASS BALANCE AND DENUDATION AND CHEMICAL RELATIONSHIPS IN THE WEATHERING REGIME

The bedrock of the Thompson Canyon watershed is a quartz monzonite pluton (Cathedral Peak Quartz Monzonite, Broderson, 1962; Calkins, 1930; Bateman and others, 1963). Aplite and pegmatite dikes and small remnants of volcanic ash falls occur within the drainage but their surface exposures are small and they are insignificant with respect to denudation and soil formation considerations.

The manner in which each metal is removed from its igneous environment by weathering and transported by waters through the valley is regulated by the characteristics of the igneous mineral in which each is originally located; therefore the distributions of the six metals among the minerals of the rock were determined (Tables 1 and 2).

Table 1

Average of seven samples of
Thompson Canyon batholithic rock

	weight percent
K	3.3
Rb	0.012
Cs	0.000420
Ca	1.2
Sr	0.051
Ba	0.11
K/Rb	270
K/Cs	7900
Ca/Sr	24
Ca/Ba	10.5
K/Ca	2.8

Table 2

Percent of metal in the whole rock from major minerals

% mineral in rock		K	Rb	Cs	Ca	Sr	Ba
24	microcline	86	80	44	5	26	90
38	plagioclase	6	3	1	73	70	6
3	biotite	8	16	46	1	0	3

As shown in Table 2, most of the mass of K and Rb in the rock is in microcline perthite, although the concentration of Rb is higher in biotite than in microcline. The large ion Cs, however, is sufficiently concentrated in biotite that the rock's Cs is about equally distributed between biotite and the more abundant K-feldspar.

As for the alkaline earth family, the rock's Ca and Sr are almost entirely bound in the plagioclase, whereas the large ion, Ba, resides in microcline.

Metals in addition to those provided by rock enter the watershed with snow or as dry deposition. Rain constitutes less than 5% of the precipitation on the watershed. Dry deposition material was sampled by exposing a horizontal collection plate at times of snow cover and at times when rocks and soils of the canyon were exposed. The metals deposited were analyzed and the annual dry deposition input was calculated from area and exposure times of the collector. Samples representing the entire snowpack were collected and analyzed for the six metals. The mass of the snowpack was measured at the time of maximum accumulation.

Stream runoff was sampled and fluxes measured at several times during the year at the outlet of the watershed. Masses of metals which leave the watershed were calculated from the concentration of the metals in stream runoff, and from the mass of stream runoff. The magnitude of stream bedload transport was determined by capturing transported grains in a mesh basket.

Table 3

Annual mass balance in Thompson Canyon (kg/yr)

	Input from snow	Dry deposition of foreign origin	Stream output (solute and suspended)		Ratios	
					stream output	source rocks
K	447	64	864			
Rb	1.7	0.29	4.0	K/Rb	216	255
Cs	0.27	0.028	0.14	K/Cs	6200	8100
Ca	797	97	4210	Ca/Sr	50	22
Sr	6.0	1.0	83	Ca/Ba	80	9.9
Ba	12.6	2.2	15	K/Ca	0.21	3.1

Table 3 shows that all six metals except Cs undergo a net removal from the watershed; Ca and Sr are present, as solute and suspended material in stream outflow, in great excess over the other metals relative to the proportions in which the metals occur in the source rocks.

It is clear that plagioclase, the reservoir of nearly all Ca and Sr in the rock, is the source of the great bulk of the Ca and Sr removed from the watershed, and that plagioclase is weathered and removed in preference to any other major mineral in the rock. The much lower relative concentrations of the alkalies and Ba in stream runoff show that K-feldspar and biotite in the rock are much more resistant to chemical breakdown in this weathering environment.

A denudation rate for the watershed may be calculated from the metal removal rate and rock and mineral composition data. A layer of rock 0.8 cm thick over the watershed would be depleted of all of its

Ca each 1000 yr under present conditions. A much less thick layer of rock would be depleted of any of the other metals in the same time, so the 0.8 cm/1000 yr for Ca removal may be regarded as the maximum value for denudation by stream removal of solute and suspended matter.

The magnitude of bedload transport from the watershed suggests that the rate of mechanical denudation ranges between a small fraction of that of chemical denudation, and a maximum of near-equivalence: the power of bedload transport varies greatly between years and with times of the season.

Further evidence that plagioclase is readily broken down, and furnishes the excess amounts of Ca and Sr observed to be denuded from the valley by streams, was obtained from a comparison of the compositions of batholithic rocks with their associated gruses. Analysis of four whole batholithic rock samples and their gruses in Table 4 shows that K/Ca in the gruses is higher than in the source rock, indicating that plagioclase has been removed while K-feldspar remains.

Table 4

Comparison of Thompson Canyon rocks and their associated gruses

	composite of four rocks	composite of four gruses
K/Rb	255	260
K/Cs	8,110	9,940
Ca/Sr	22	21
Ca/Ba	9.9	7.9
K/Ca	3.1	3.5

The Ca/Sr ratios are unchanged because both metals are contained mainly in plagioclase. Ca/Ba ratios, however, are lower in gruses because Ba is concentrated in K-feldspar, and this confirms the preferential removal of plagioclase relative to K-feldspar. An additional type of mineralogical fractionation during weathering is suggested by the observation that the K/Cs ratio is higher in grus than in rock, indicating that micas are freed and swept away as the grains of rock separate and grus is formed. It was observed that micas contain nearly one half of the Cs present in the whole rock, but only a small fraction of the K.

A comparison of the compositions of snow bank melt water and rivulet water running away from the snow banks confirms that the weathering products of plagioclase are rapidly and preferentially taken up by stream waters as they course over rock and soils. Analysis of the six metals in these waters, listed in Table 5, shows that concentrations of Ca and Sr in waters dripping from melting snowbanks increase greatly as they run in rivulets away from the snowbanks. The compositions of the rivulets are concordant with those of larger streams which exit the watershed with high concentrations of Ca and Sr.

Table 5

Metals in snowbank meltwater and rivulet water
Parts per 10^9

	Snowbank melt water containing solute and particles	Rivulet water 200 m from snowbank source
K	130	62
Cs	0.096	0.019
Ca	74	445
Sr	1.8	7.0

Centrifugation experiments on these waters suggest that the decrease in Cs shown in Table 5 may result from the deposition of particles rich in Cs from the melt waters as they run over soils. This suggests that micas, freed from rocks crumbling to grus, collect by dry deposition on aging snowbanks and are carried to soils by such running waters. As explained in the next section (II) the soils of the watershed are visibly rich in mica, and are measurably enriched in Cs (K/Cs is 7,900 in whole rock, 2,000 in whole soils, and 880 in material removed from snowbank melt water as it runs over soils).

EXTENDED DISCUSSION OF MASS BALANCE AND DENUDATION AND CHEMICAL RELATIONSHIPS IN THE WEATHERING REGIME

Analytical method: The stable isotope dilution method was used to determine the mass of each metal in the samples analyzed in this study. In this method, a known amount of an isotopically enriched tracer is equilibrated with the sample. The resultant isotopic ratios are measured on a solid state, thermal emission mass spectrometer and the sample masses calculated from the departure of the measured ratios from known naturally occurring isotopic ratios for each metal.

Sample preparation facilities: Sampling vessels, laboratory ware, and samples were prepared inside a positive pressure, filtered air clean laboratory. Highest purity reagents and water were available for sample preparation.

Rock and mineral sample preparation: Rock samples were finely powdered in a rotary ring mill ("Shatterbox") cleaned with silica sand between samples. Mineral samples were manually crushed very finely in an agate mortar.

Minerals were separated from rock by crushing in a Diamond mortar, serially sieving, and performing separations by heavy liquid, magnetic and hand picking methods. Before crushing, mineral grains were sonically cleaned in water, soaked 30 seconds in 0.1 N HCl, rinsed and vacuum dried.

10 mg samples of very finely powdered rock or mineral material were added to a 30 ml FEP teflon beaker containing 1 ml of concentra-

ted HNO_3 and any statically dispersed clots were then reincorporated by sweeping the walls with the acid drop. 1 ml of 50% HF was added and the vessel covered with a TFE teflon watchglass, allowed to stand at 25° C overnight, then placed for 3 hr in a filtered-N_2-flushed closed TFE oven at 85° C; the watchglass was then removed and the solution allowed to evaporate to a single drop at 65° C (removal of Si as SiF_4 gas); 1 ml HNO_3 was then added and taken to dryness at 180° C, followed by one more ml of HNO_3 going to dryness. The vessel was then removed from the oven and 1 ml of HNO_3 added to dissolve and suspend the residue. 10 ml of water were then added, 0.5 ml at a time, with much swirling and standing, over about a five minute span, thus putting all material into solution. The sample was then poured into an FEP teflon or conventional polyethylene bottle and diluted to about 50 g for convenient removal of aliquots, typically 0.03 g, to be mixed with isotopic spikes.

Water sample vessels and collection methods: FEP teflon bottles with teflon lined screw caps were used for snow and water sample collection. New bottles were degreased with detergent solutions, leached in two successive baths of 100° C analytical reagent grade HNO_3 for several days, followed by a leach bath of at least 3 days in a pH 1 solution of doubly distilled HNO_3 and purest water (Patterson and Settle, 1975). Bottles were carried triply bagged to the field area. During the collection the bottles were touched only with plastic-gloved hands and held so that samples did not contact the outside of the bottles before capture.

Snow and streamwater: Before decanting aliquots, sample bottles were shaken vigorously to assure suspension of any particles. Equilibration of decanted aliquot and isotopically enriched spike solution was then assured by treatment of the mixture exactly as for the rock and mineral sample degestion, taking the spiked sample to dryness with two successive 1 ml additions of HNO_3.

Loading onto filament and ionization: The spiked sample, in a 30 ml beaker (FEP), was dissolved or swept up in a single drop of water. Half of it, by estimate, was then loaded onto an oxidized tantalum filament for ionization in the mass spectrometer. Common failure of Cs, or Rb and Cs, to give a signal necessitated a subsequent analysis on a rhenium filament with a matrix of silica gel and phosphoric acid; in such cases, K was measured in both loads and Rb and Cs were normalized to the K value from the Ta filament load.

Troublesome amounts of organic matter in spiked sample: A high temperature (fuming) evaporation of the spiked sample with 1 ml $HClO_4$, followed by taking to dryness twice with HNO_3, was in some cases necessary to oxidize organic matter (especially with snow and soil moisture samples). After this treatment, sufficient ion beam intensity of Cs was almost never experienced on a tantalum filament, necessitating use of rhenium silica gel loads for determination of that metal.

Mass spectrometer: The machine used was a twelve inch radius of curvature unit with electron multiplier, equipped with expanded scale time-integrating registration on chart paper. Charts were read, and calculations made, by hand.

Spikes and sample/spike ratios: The enriched isotopes in the spikes were ^{41}K, ^{87}Rb, ^{135}Cs, ^{42}Ca, ^{84}Sr and ^{136}Ba. In addition,

^{40}K and ^{48}Ca were present and used as mass fractionation indicators, and ^{137}Cs was present and used to confirm that hydrocarbons were not contributing to the intensity of the ^{135}Cs peak.

Intensity ratios of (main natural isotope from sample)/(enriched tracer isotope from spike) of about unity were considered desirable to give most sensitive results in the calculation. The following form was used:

$$\begin{array}{c}\text{Moles isotope y}\\ \text{in sample}\end{array} = \frac{(\text{measured ratio } \frac{x}{y}) - (\text{ratio } \frac{x}{y} \text{ in spike})}{(\text{ratio } \frac{x}{y} \text{ for metal in nature}) - (\text{measured ratio } \frac{x}{y})} \cdot \begin{array}{c}\text{moles isotope y}\\ \text{in spike}\end{array}$$

<u>Rocks and minerals in Thompson Canyon</u>: The data in Tables 6, 7 and 8 show the complete metals data for Thompson Canyon batholithic rock, the eight mineral phases separated from it, and the material which can be leached from it.

The rock's Ba is contained in both medium-grained groundmass crystals and very coarse, zoned, unevenly distributed euhedral crystals of microcline (Kerrick, 1969).

The presence of considerable quartz in the mineral fraction analyzed as plagioclase can account for the greater Ca content in whole rock than that determined by the summing of metals in minerals.

To determine whether significant quantities of metals are present in amorphous intercrystalline material, a sample of the rock was crushed sufficiently to separate the crystalline grains and then leached 2 hr at room temperature in a 0.1 N HNO_3 solution. As shown in Table 6 , Ca and Sr were the metals most easily removed with respect to their abundances in the rock. They were removed in a ratio very

TABLE 6: METAL CONCENTRATIONS IN MAJOR MINERALS IN A SINGLE SPECIMEN (TC 16, Table 8) OF THOMPSON CANYON WALL ROCK (WEIGHT PERCENT)*

Mineral (% of rock)	K	Rb	Cs	Ca	Sr	Ba
Microcline (fine, high density) (14)	10.7	0.035	0.00045	0.24	0.058	0.3
Microcline (fine, low density) (6)	12.0	0.041	0.00054	0.067	0.0041	0.11
Microcline (v. large, euhedral) (4)	8.65	0.021	0.0008	0.53	0.096	0.65
Biotite (3)	7.1	0.056	0.0045	0.34	0.0058	0.086
Plagioclase (38)	0.44	0.00082	0.000065	2.1	0.085	0.014
Magnetite (2.6)	0.13	0.00028	0.000053	0.38	0.00024	0.0031
Apatite (0.3)	0.010	0.00013	0.000025	39.0	0.035	0.028
Sphene (0.4)	0.083	0.00035	0.000044	17	0.0058	0.0022
Leach (0.5)	1.9	0.010	0.00057	7.3	0.26	0.024

*Quartz is 30 percent in rock, low in all metals; all modes determined in thin section.

TABLE 7: METAL CONTRIBUTIONS FROM MINERALS IN THOMPSON CANYON WALL ROCK

Metal	Calculated fraction of metal in whole rock from each mineral							
	fine, high density M'cline	fine, low density M'cline	large, euhed. M'cline	Biotite	Plagio.	Apatite	Sphene	Leach
K	0.51	0.24	0.12	0.078	0.056	0	0	0.003
Rb	0.48	0.24	0.082	0.16	0.030	0	0	0.005
Cs	0.22	0.11	0.11	0.46	0.0086	0	0	0.0098
Ca	0.033	0.0037	0.019	0.009	0.73	0.11	0.062	0.034
Sr	0.176	0.005	0.083	0.004	0.70	0.002	0	0.028
Ba	0.51	0.080	0.31	0.031	0.064	0.001	0.001	0.001

TABLE 8

Metal in rock: weight percent

	Calculated sum in total rock from mineral concentration and modes	Total, this study (rock TC 16)	Other Thompson Cyn rocks			Other wet chem. and spectrogr. analyses	
			TC 19	glacially quarried cirque rk.	compos- ite of 4 rocks	(*)	(+)
K	2.96	2.9	4.1	3.2	3.3	3.7	3.9
Rb	0.0103	0.011		0.012	0.013		
Cs	0.00029	0.00029		0.00062	0.00040		
Ca	1.10	1.5	1.3	1.3	1.1	3.2	1.0
Sr	0.046	0.054	0.054	0.054	0.048		0.04
Ba	0.083	0.080	0.18	0.099	0.11		0.1

*Analysis by D. Peck, U. S. Geological Survey, 1963 (unpub'd); rock from Cathedral Peak pluton, 20 mi south of Thompson Canyon.

+Analysis of Cathedral Peak-type rocks from other plutons Bateman and others, 1963.

close to the Ca/Sr ratio of the plagioclase. The ratios of Ca/Sr/Ba are 280/10/15 in the rock and 300/10/1 in the material removed by the acid leach. Similar Ca/Sr ratios in plagioclase and leached material suggest that materials removed in the leach do not necessarily represent intercrystalline deposits characteristic of the fresh rock but probably represent removal from slightly weathered plagioclase surfaces.

Metals in snow and streams: The accumulated snowpacks were sampled in early April 1973 and late March 1974 (3.3 m deep in both years) in five discreet, equal vertical divisions, avoiding the top and bottom 2 cm of the pack. The top sample showed the highest, and the bottom sample the lowest concentration for all metals (Table 8, Figure 2). Metal concentrations are approximately one order of magnitude lower than previously reported for snow in mountainous regions of the western United States (Feth and others, 1964). This difference may be due to greater care taken in collecting uncontaminated samples and to the greater reliability of the isotope dilution method at these low metal concentrations. In past studies dirty, surficial snows may have been collected or the snows may have been contaminated during collection, storage, and analysis.

A stepped trench was dug to the bottom of the pack, crosswise to the direction of prevailing wind, and all spoils were thrown down wind. For each increment (bottom fifth sampled first) the vertical upwind face of the trench was scraped back 1-2 cm with a cleaned TFE teflon scraper immediately before sampling. Snow was put into one-liter FEP teflon bottles by means of a cleaned KEL-F teflon corer, or, in harder strata, scraped directly into the bottles with a cleaned KEL-F teflon scoop.

Table 9

METAL CONCENTRATIONS IN ACCUMULATED LATE WINTER SNOWPACKS, 1973 and 1974*

part of snowpack 1973 (vol. %)	K	Rb	Cs	Ca	Sr	Ba	Ca/K ratio	Ca/Sr ratio
Top 20%	14	0.070	0.0082	41	0.30	0.36	2.9	141
Next	13	0.051	0.0063	14	0.13	0.21	1.04	109
Middle	8.0	0.033	0.0035	13	0.11	0.21	1.59	141
Next	7.8	0.028	0.0034	14	0.12	0.15	1.77	115
Bottom	4.5	0.019	0.0019	6.0	0.066	0.13	1.41	95
Average+ (mass weighted)	9.7	0.042	0.0048	18	0.15	0.22	1.84	109
1974								
Top 20%	78	0.36	0.070	231	1.5	2.5	2.95	157
Next	36	0.21	0.041	76	0.69	0.90	2.15	111
Middle	11	0.026	0.0022	5.2	0.067	0.12	0.48	79
Next	23	0.089	0.0082	19	0.171	1.4	0.80	110
Bottom	7.2	0.021	0.0023	8.3	0.048	0.63	1.16	174
Average	35	0.129	0.023	62	0.45	1.0	1.76	137
2 cm top crust of aged snowpack, May 4, 1972	270	1.2	0.092	110	2.1	6.4	0.40	52
Other@ Sierra snow analyses	400			500				

* Concentrations in parts per 10^9; samplings made April 4, 1973 and March 21, 1974

\+ Density of 0.44, Oct. 1972-April 4, 1973; density of 0.36 Oct. 1973-March 21, 1974.

@ Representative values for composite of crest and east slope data; (Feth and others, 1964).

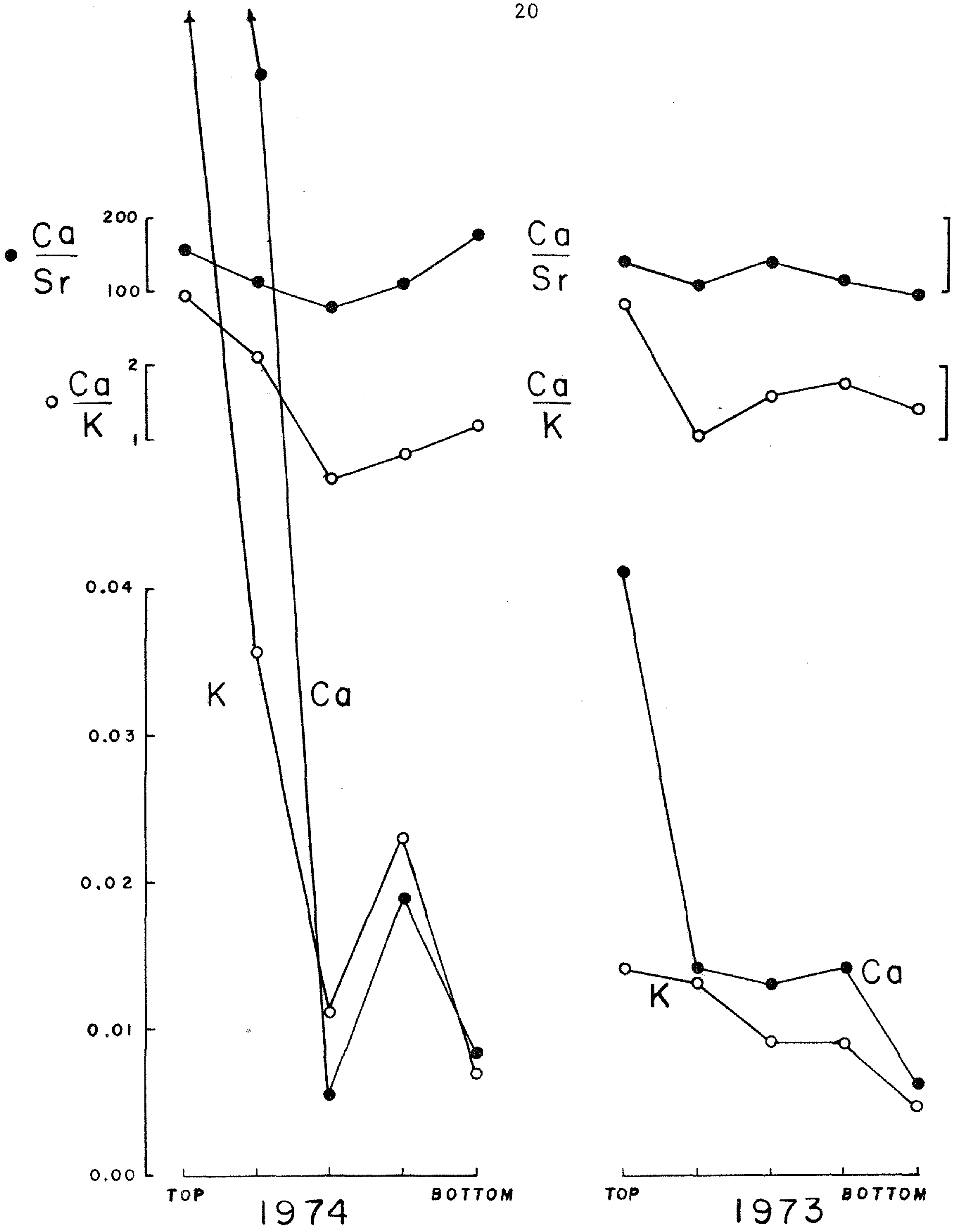


Figure 2:

Metals (Parts Per Million) through the profiles of two years' snowpacks. Both 3.3 m deep, sampled at the time of maximum accumulation (late March-early April)

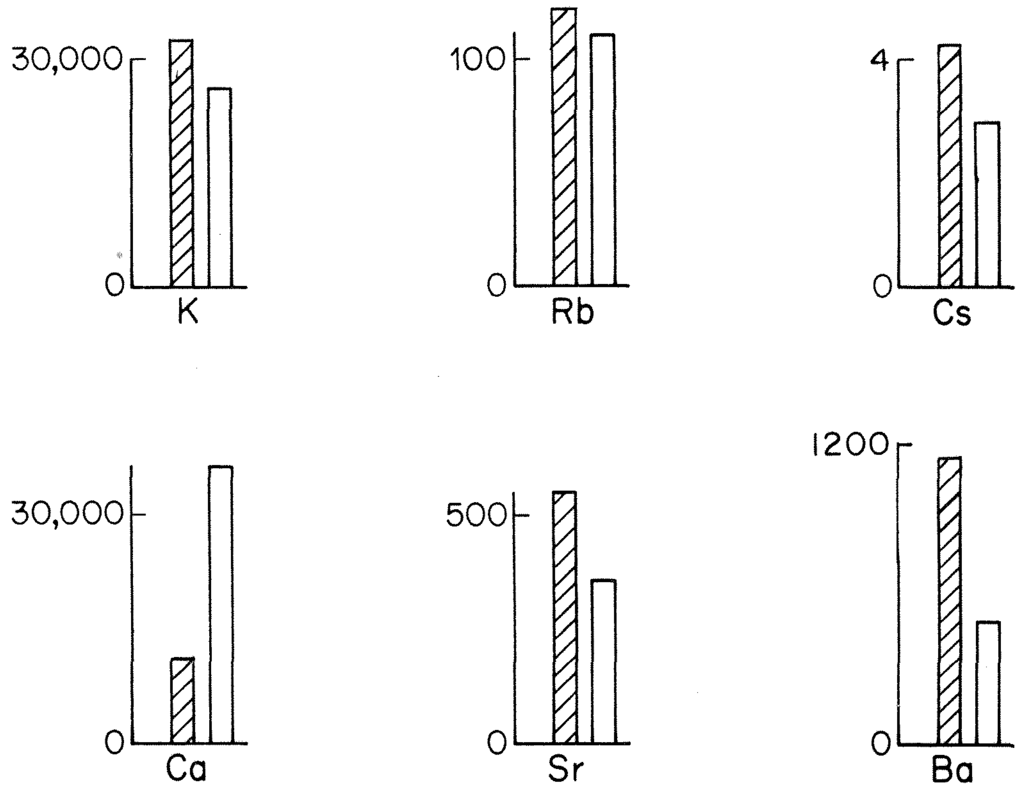


Figure 3: Differences in metal concentration (ppm) between Thompson Canyon batholithic rocks (hachured bars, average of 7 samples) and average crustal rocks (open bars, Poldervaart's data), which allow dusts of foreign and local origin to be distinguished.

The sampler wore a rinsed, hooded polyethylene parka and acid-washed gloves. Samples were aliquoted for analysis after only the shortest possible time in the liquid state, or else acidified to 0.1% HNO_3, to avoid adsorbtion of metals by the walls of the bottles. Hirao acid leached bottles which had held samples and found that wall absorbtion is not a problem over times of only a few days (personal communication).

Samples of the packs from single locales were assumed to be representative of snow over the watershed, due to the deposition of snow and incorporated dusts by atmospheric agencies. The lack of wetness, and fineness of texture between any ice horizons in the profile, suggest that the snowpacks had undergone little melting since early autumn.

The differences in metals composition between Thompson Canyon quartz monzonite and average crustal rocks (Poldervaart, 1964). allow a distinction to be made between silicate dusts that are locally derived and those from distant sources. The Thompson Canyon rocks are slightly high in the alkalies, but low in Ca by more than a factor of two and high in Sr and Ba by nearly a factor of two, as shown in Figure 3.

Two kinds of dust were observed in the snow. The surface layer of the snowpack in the very late spring showed much higher metal concentrations and lower Ca/K and Ca/Sr ratios than in the rest of the snowpack (Table 9). Because the Ca/K and Ca/Sr ratios in local rocks are about 0.5 and 25, respectively, higher values of these ratios in the snowpack indicate that its dusts originated in distant areas underlain by different rock types, whereas the bulk of late season surface dusts are derived locally from Thompson Canyon rocks and soils (Figure 4).

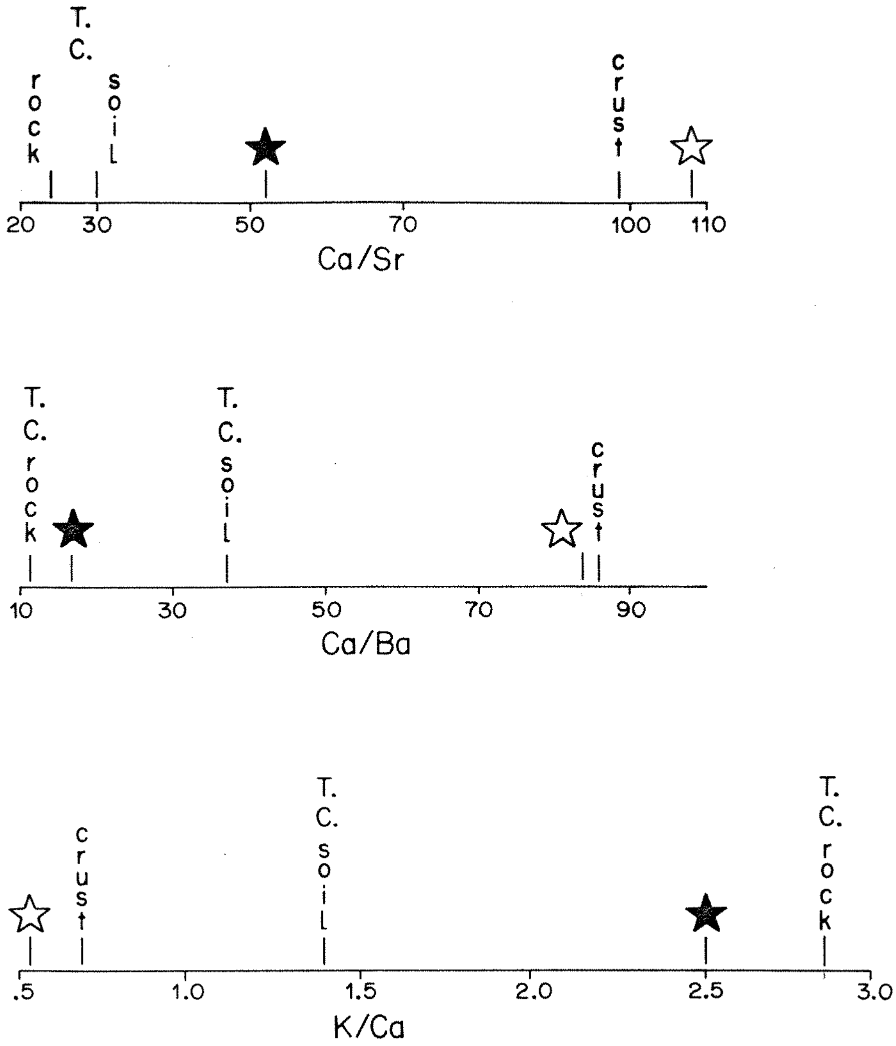


Figure 4: Metal Ratios (weight) in
☆ new fallen snow
★ old snow pack
Thompson Canyon soils
Thompson Canyon rock

Ca/Sr and Ca/K variation through the main mass of the snowpacks of both years vary in harmony with one another, as shown in Figure 2. This indicates simple minor variation in the proportions of local and foreign dusts.

The average annual water balance is summarized in Figure 5. Figure 6 is a drainage map showing stream and snowpack measuring sites. An approximate 50 yr average for Thompson Canyon snowfall was obtained by comparing the mass of two years' snowpacks in the canyon with those at a nearby snow accumulation station which has been monitored for 50 years by the California Department of Water Resources. The ratios between the two locations were used to normalize the measured year in Thompson Canyon to its 50 yr average. Snowpack water content, measured with a standard snow survey core sampling set, was determined on courses on slopes and meadows in upper and lower portions of the watershed. Stream runoff was determined with a Pygmy current meter in uniform channels at the outlet of the watershed. Cross sections were measured immediately prior to each measurement of flow velocity. Data were taken May 5, June 21, July 28, September 3 and October 9, 1973, and June 4, June 13 and July 20, 1974. Part of the integrated curve was taken from a similar Sierra watershed where continuous data were available (Cooperative Snow Investigations, 1948-1952). Because of the presence of high bedrock canyonsides, it is assumed that little water crosses watershed boundaries by subsurface filtration, but rather nearly all is by stream runoff. At the outlet station itself, the canyon is narrower than elsewhere, and the exposure of bedrock is nearly continuous. The mass difference between snow input and stream

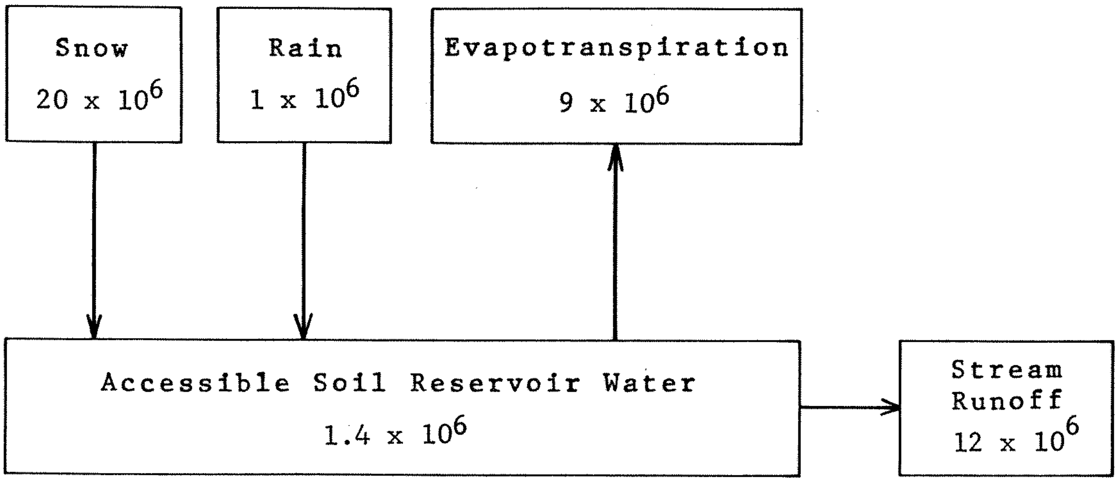


Figure 5: Average annual water balance in Thompson Canyon (metric tons/12.2 km^2 study area)

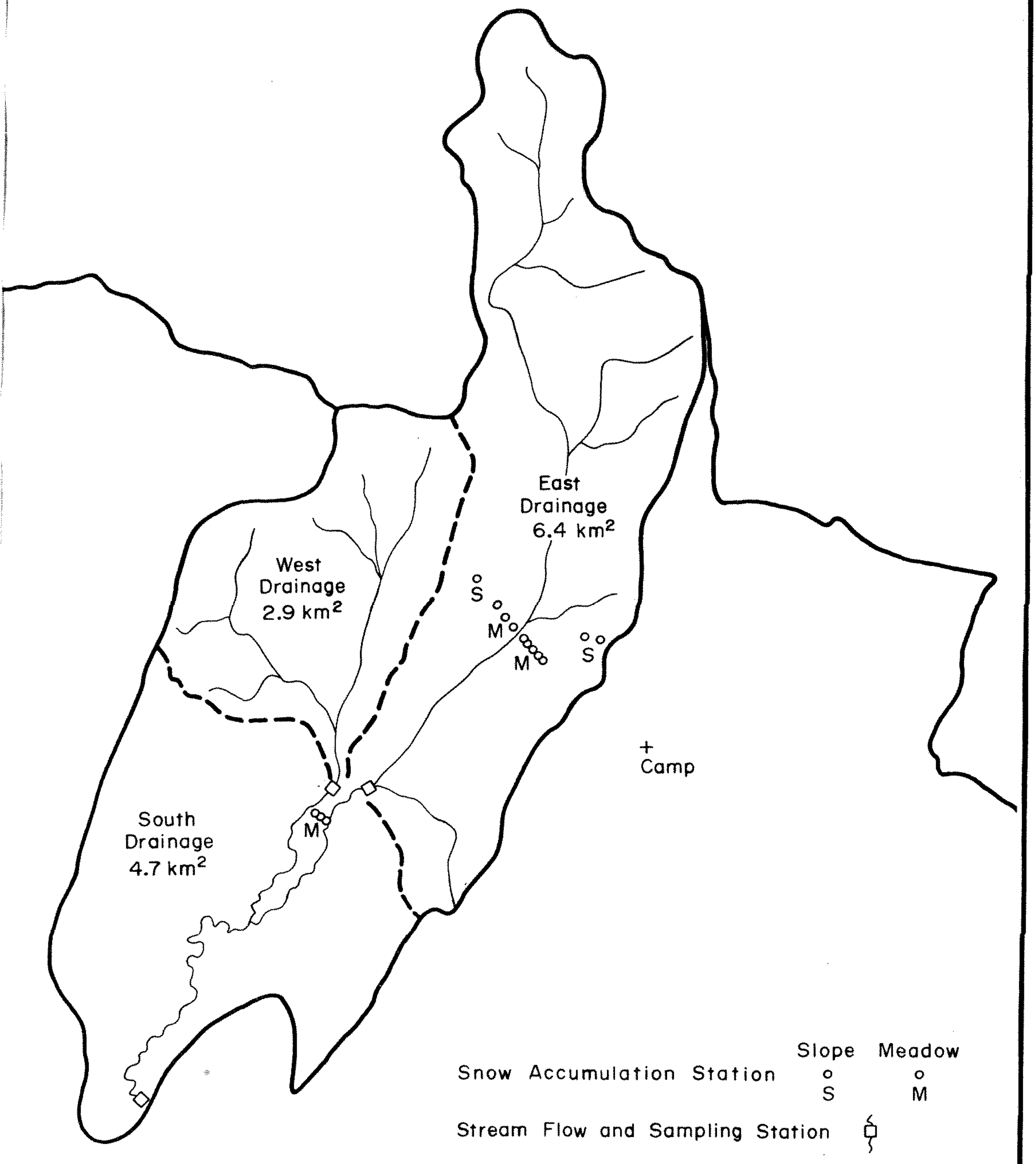


Figure 6: Drainage map of Thompson Canyon, showing stations where stream flux and snowpack accumulation are measured

outflow is approximately the evapotranspiration that would be expected in an area with the proportions of meadow, forest cover, and bare ground of Thompson Canyon (Summary Report of the Snow Investigations, 1956). Summer rain has not been analyzed due to the unavailability of a sample that is definitely not contaminated. Mass of rain is 5% or less of the total water input. The mass of the soil water was estimated from the thickness and extent of the soil blanket and its water content.

Metal concentrations in stream water at the outlet station are given in Table 10 for June and October, 1972, the months of high and low flow, respectively. Other samples, collected in the months of January, May, July and August in various years from 1971 to 1974, vary no more than 10% from the June or October values for any of the six metals. June concentrations were used for metal removal calculations for 1973, and July (1974) concentrations used for the 1974 calculations.

Given the mass balance of H_2O and the metal content of snow and water, the mass of metals entering the drainage annually in snow may be subtracted from the mass removed in stream outflow, yielding the net amount removed from the drainage each year (Table 11).
The proportions of input and output may be compared with figures for other watersheds (Viro, 1953; Likens and others, 1967; Cleaves and others, 1970; Miller, 1963). The data are shown in Table 12.
In 1973 the mass of metals entering Thompson Canyon in snow was small in relation to the output in stream outflow; in 1974 the balance was comparable to that reported in other studies.

TABLE 10 METAL CONCENTRATIONS IN STREAM OUTFLOW*

Metal	June 21 1972	October 9 1972	July 21 1974
K	82	110	62
Rb	0.35	0.44	0.26
Cs	0.012	0.014	0.011
Ca	320	750	380
Sr	6.5	12	7.4
Ba	1.3	1.8	1.2

*Concentrations in parts per 10^9; samples taken at outlet station

TABLE 11 NET METAL OUTPUTS AND ACCUMULATIONS[*]

Metal	Stream output	Input from snowpack	Net output	Input as percent of output	Net mass accumulating annually in the watershed[+]
			1973		
K	980	190	790	20%	9,700
Rb	4.2	0.83	3.4	20	35
Cs	0.14	0.096	0.048	67	1.2
Ca	3,800	360	3,500	9.4	0
Sr	78	3.0	75	3.9	84
Ba	16	4.4	11	28	350
			1974		
K	743	700	43	94	12,000
Rb	3.7	2.6	1.1	71	43
Cs	0.13	0.45	-0.32	340	1.5
Ca	4,600	1,230	3,300	27	0
Sr	88	9.0	79	10	105
Ba	14	21	-6.3	143	420

[*] Values in kg per 12.5 km^2 watershed.

[+] Assuming that source rock weathers uniformly, and all Ca weathered is removed from watershed in stream outflow.

Table 12 ANNUAL METALS BUDGETS FOR VARIOUS AREAS OF THE WORLD (after Likens and others, 1967)

	Input	Output	Net Loss	Input as percent of output	Location	Reference
Ca	2	12	10	17	Finland	Viro, 1953
	8	26	18	31	New Zealand	Miller, 1963
	6	19	13	32	SE USA	Gambell and Fisher 1966
	3.0	8.0	5.0	38	NE USA	Likens and others 1967
	0.29	3.1	2.8	9	Thompson Cyn, 1973	Present study
	0.99	3.7	2.7	27	Thompson Cyn, 1974	Present study
K	2	4	2	50	Finland	Viro, 1953
	8	13	5	62	New Zealand	Miller 1963
	1	6	5	17	SE USA	Gambell and Fisher 1966
	2.5	1.8	-0.7	139	NE USA	Likens and others 1967
	0.16	0.63	0.63	20	Thompson Cyn, 1973	Present study
	0.56	0.03	0.03	94	Thompson Cyn, 1974	Present study

*Expressed in kilograms per hectare.

Dry deposition material entering and leaving the watershed: Dry deposition material was collected for metals analysis and mass measurement by exposing a horizontal plate of FEP teflon of known area for known lengths of time (several days) at different seasons of the year. By exposing the plate in the canyon during early winter when the local ground is covered with snow, aerosols of largely foreign origin were collected. During the summer when the local soil was exposed, a mixture of aerosols was collected in which a major fraction originated from local rocks and soils. The foreign versus local components can be distinguished by comparing key metal ratios in the sample with ratios in dust of known foreign origin (sample collected at White Mountain by T. J. Chow), and with ratios in Thompson Canyon rocks and soils. The early winter sample appeared to be about 85% foreign material. When the ground was fully exposed in summer, the sample was about half local and half foreign dust. The compositions of the metals in the early winter dry deposition sample and in the winter snowpack are the same, indicating a common origin. Results are shown in Table 13.

A layer of dry deposition material 0.04 cm thick would accumulate each 1000 yr in Thompson Canyon (having the density of rock). On the average, slightly more than this quantity may be blown out of Thompson Canyon; dry deposition material from the continents may account for part of the 0.01 cm/1000 yr rate of sediment accumulation estimated by Goldberg (1968). Although the incoming material would be richer in Ca than the material leaving, and the material leaving would be richer in the alkalies, Sr and Ba, the imbalance for any metal is unmeasured and small relative to inputs and outputs by snow and streams, and should

Table 13

COMPOSITION AND ORIGIN OF DRY DEPOSITION AEROSOLS

	Metals in snowpack Oct.-Apr. Thompson Canyon	White Mtn. air filter (foreign dust)	Dry dep'n rock & soil covered by snow (Oct.)	Dry dep'n rock & soil exposed (August)	Average clay + silt in local soils
K/Rb	270	250	220	230	175
K/Cs	1560	3400	2400	2200	840
Ca/Sr	140	130	96	52	29
Ca/Ba	59	74	45	22	15
K/Ca	0.57	0.50	0.67	1.37	1.62

October deposition rate was 64 g Ca/km^2/day

August deposition rate was 41 g Ca/km^2/day

White Mtn. filter represents a one month collection, taken in May, 1973, at 4000 m elevation, 120 km southeast of Thompson Canyon not form part of the mass balance and denudation estimates (see below) of this study.

Denudation: The depths of layers of batholithic rock which would be depleted of each of the six metals in a period of 1000 yr are listed in Table 14. These denudation values are calculated from the composition of the whole batholithic rock, the input of metals with winter snow, and the removal of both dissolved and suspended material in stream runoff. Suspended matter was sampled, digested, and analyzed with stream water. The calculation does not include material removed by stream bedload transport, and it assumes that any imbalance of input and removal of dry deposition material is negligible.

The denudation rate given by Ca, 0.8 cm/1000 yr, is higher than that of any other important metal in the rock and may be regarded as a maximum value for the rate of chemical denudation at the present time. It is clear from the available data of all other studies that Na, if measured in stream outflow water, would yield a denudation rate intermediate between those for K and Ca (Conway, 1942; Feth and others, 1964; Likens and others, 1967; Miller, 1963; Viro, 1953; Garrels and Mackenzie, 1967).

Mechanical removal of material was experimentally determined by capturing transported bedload grains in a mesh basket, assuming that the observed flux (near maximum spring runoff) was operative for 1 mo per season. The resultant rate is 0.01 cm per 1000 yr for 1973, but approximately equal to the power of chemical erosion in 1974 when the maximum velocity of stream flow was higher for part of the melt season than at any measured time in 1973. Calculation of mechanical removal, by stream bedload parameters, using Colby's nomographs (Sediment

TABLE 14 CHEMICAL DENUDATION - - REMOVAL OF BATHOLITHIC ROCK BY STREAM WATERS

	Value (cm per 1,000 yr)	
Metal	1973	1974
K	0.071	0.004
Rb	0.081	0.03
Cs	0.034	-0.2
Ca	0.86	0.83
Sr	0.44	0.44
Ba	0.029	0.000

The values include suspended fine material, but not bedload.
Values for 1974 for K, Rb and Ba are subject to some uncertainty, since input and output masses nearly balance.

Transport Mechanics, 1971) yields a value about ten fold higher than actually measured. The calculation assumes a well-sorted bed material, and the departure of the measured value (poorly sorted actual bedload material) from the calculated value is in the proper direction. Inspection of samples of bedload material shows enrichment of quartz and depletion of plagioclase with respect to abundance in source rock, suggesting that bedload material complements the Ca and Sr which is preferentially removed as dissolved material in streams.

The denudation effects of the violent summer rainstorms, which raise the stream runoff to the spring maximum rate for periods of a few hours and turn the waters roiled and milky (Tables 20 and 25) are modest. Despite the dense appearance, the concentration of Ca, the most abundant of the six metals, barely exceeds 1 ppm in combined solute and suspended material in such flood waters. Assuming one such flood per season, denudation by this agency accounts for only approximately 0.001 to 0.005 cm per 1000 yr.

Due to similar climate, quantity of precipitation, and rock type, similar values for denudation rates taken by this method might be expected in nearby areas. The most recent independent estimate for this high, glacially scoured zone of the Sierra Nevada was Janda's (1966) rate of 2.4 cm per 1000 yr for present, non-glacial conditions. The estimate was made on the basis of reservoir sedimentation studies, and emphasized areas farther south along the crest of the range. The large difference between that estimate and the estimate from this study is to be attributed to differences in elevation, nature of terrain, and possible emphasis by Janda of areas west of the crest of the range.

Garrels and Mackenzie's estimation of the solution denudation rate (1967) in the Sierra, of more than 10 cm/1000 yr, is in error because of their assumption that all precipitation attains the composition of spring waters very different in composition from the stream runoff water actually involved in denudation processes.

Fate of the six metals in the initial stages of weathering: decomposition of the source rock to grus: The four samples of quartz monzonite and their associated gruses discussed above were taken from widely separated locales in the watershed. Complete compositional data are presented in Table 15. Studies in the past, by Dennen and Anderson (1962) and Yamasaki and others (1955), have examined chemical differences between rock and primary weathering product but the results have not been used to gain information about the overall weathering regime of a geological environment.

Differences in composition between snow bank melt water and streamwater: dissolution of plagioclase and deposition of mica in soils: To determine the changes in composition between snow bank melt water and water running away from the snow banks in rivulets over soils and then into major streams, samples were collected in midsummer at three dripping snowbanks at widely separated locales in the watershed and from rivulets at a few tens and at hundreds of meters away.

To distinguish between metals present in the water as solute and those present in particles, the snowbank melt samples were analyzed whole and analyzed again after particle residues were removed by centrifuging. Comparison of the metals contents of snowbank melt and rivulet water is presented in Figures 8 and 9 and Table 16.

Table 15

COMPARISON OF METALS COMPOSITION OF THOMPSON CANYON ROCKS AND THEIR ASSOCIATED GRUSES

(weight percent)

	Composite of four rocks, separate localities	Composite of four gruses, collected with rocks
K	3.3	3.8
Rb	0.013	0.015
Cs	0.00040	0.00038
Ca	1.1	1.1
Sr	0.048	0.053
Ba	0.11	0.14
K/Rb	255	260
K/Cs	8,100	9,900
Ca/Sr	22	21
Ca/Ba	9.9	7.9
K/Ca	3.1	3.5

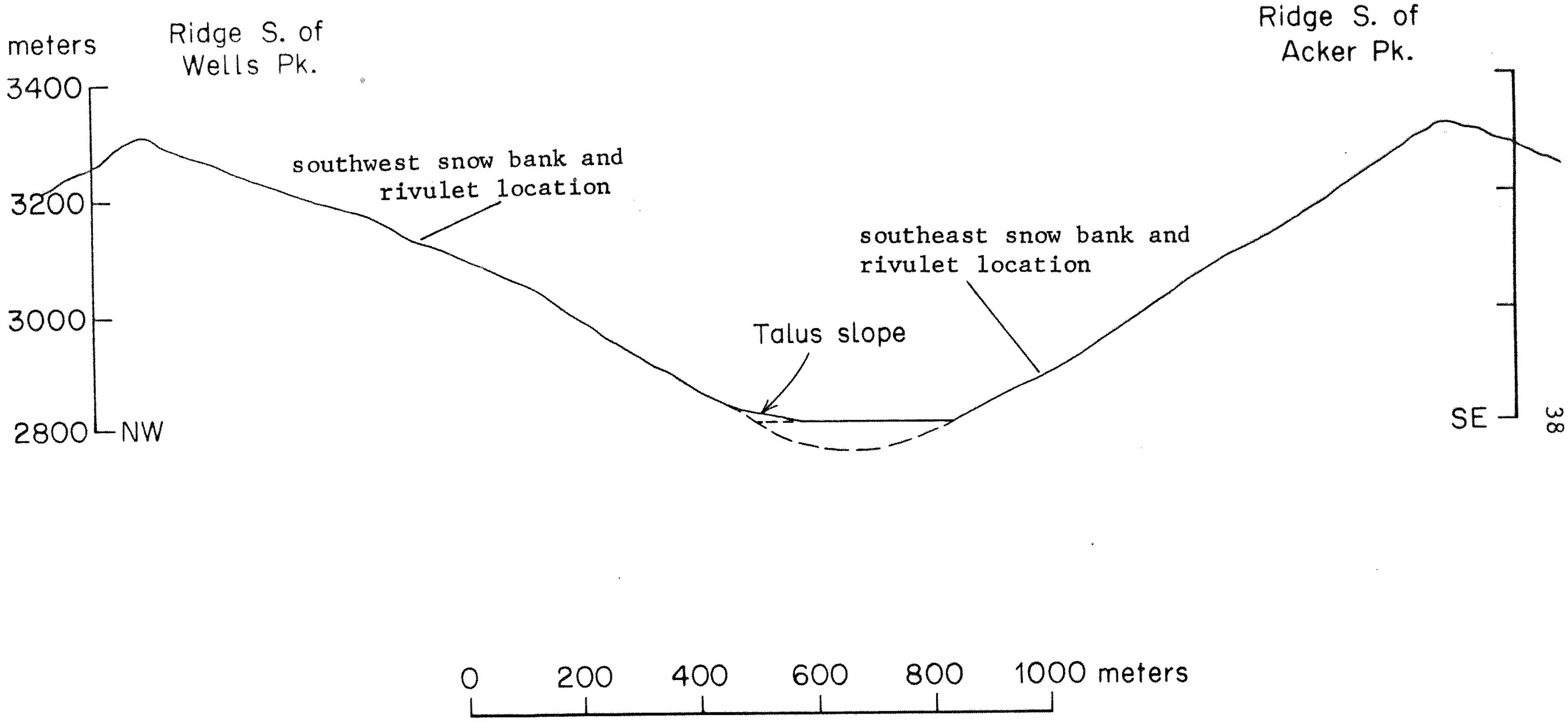


Figure 7: Cross section through the southern meadow of Thompson Canyon, showing snow bank melt and rivulet sampling locations.

The data show the following:

a) Concentrations of Ca and Sr in rivulet water are much higher than in total uncentrifuged snow bank melt waters, indicating that the rivulet waters very rapidly take up these constituents of the weathering plagioclase as they run short distances over rocks and soils.

b) Concentrations of K, Rb and Cs are much lower in rivulet waters than in total snow bank melt samples. The bulk of these metals in the melt is in the form of particles which may be removed by centrifuging. The decrease in alkali concentrations from snow bank to rivulet sampling locations may result from mechanical entrapment of the particles by soils. Changes in K/Rb and K/Cs ratios between snow bank melt and rivulet sampling locations show that the particles are especially rich in heavy alkalies, similar in composition to micas and clays.

The minor variations in metal concentration change patterns among the three snow bank and rivulet systems sampled may be attributed to the different environments of the three systems (location, elevation, exposure), different collection times in the season, and different preceding weather conditions.*

<u>A simplified model of the magnitude of the metal contribution of late season snow bank melt particles to surficial soils</u>:

Rivulets from late season snow banks could deposit appreciable masses

---

* The snow bank and rivulet system on the southeast side of the watershed was sampled July 30, 1973, after a long rainless period; the one on the northeast side after torrential rains on the preceding day, July 31; southwest system August 31, 1973, after a rainless period during which there was some dusting by late summer snow.

Figure 8:

Metal Concentrations in Water Dripping from Snow Banks and in Rivulets Running away from them

The symbol "C" denotes water which has been centrifuged

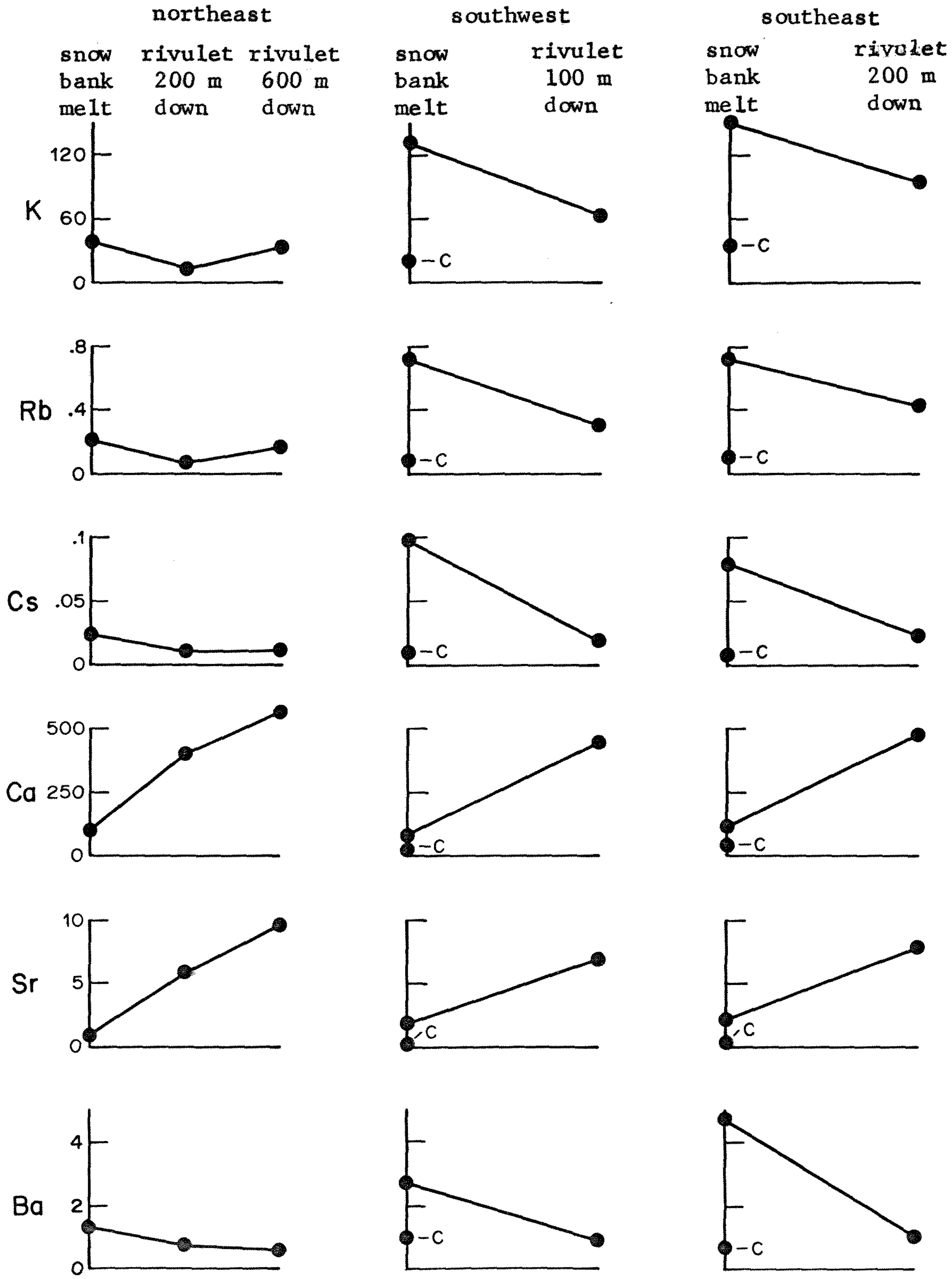


Figure 9:

Metal Ratios in Water Dripping from Snow Banks and in Rivulets *Running away from them*

"C" denotes water with particles removed by centrifuging

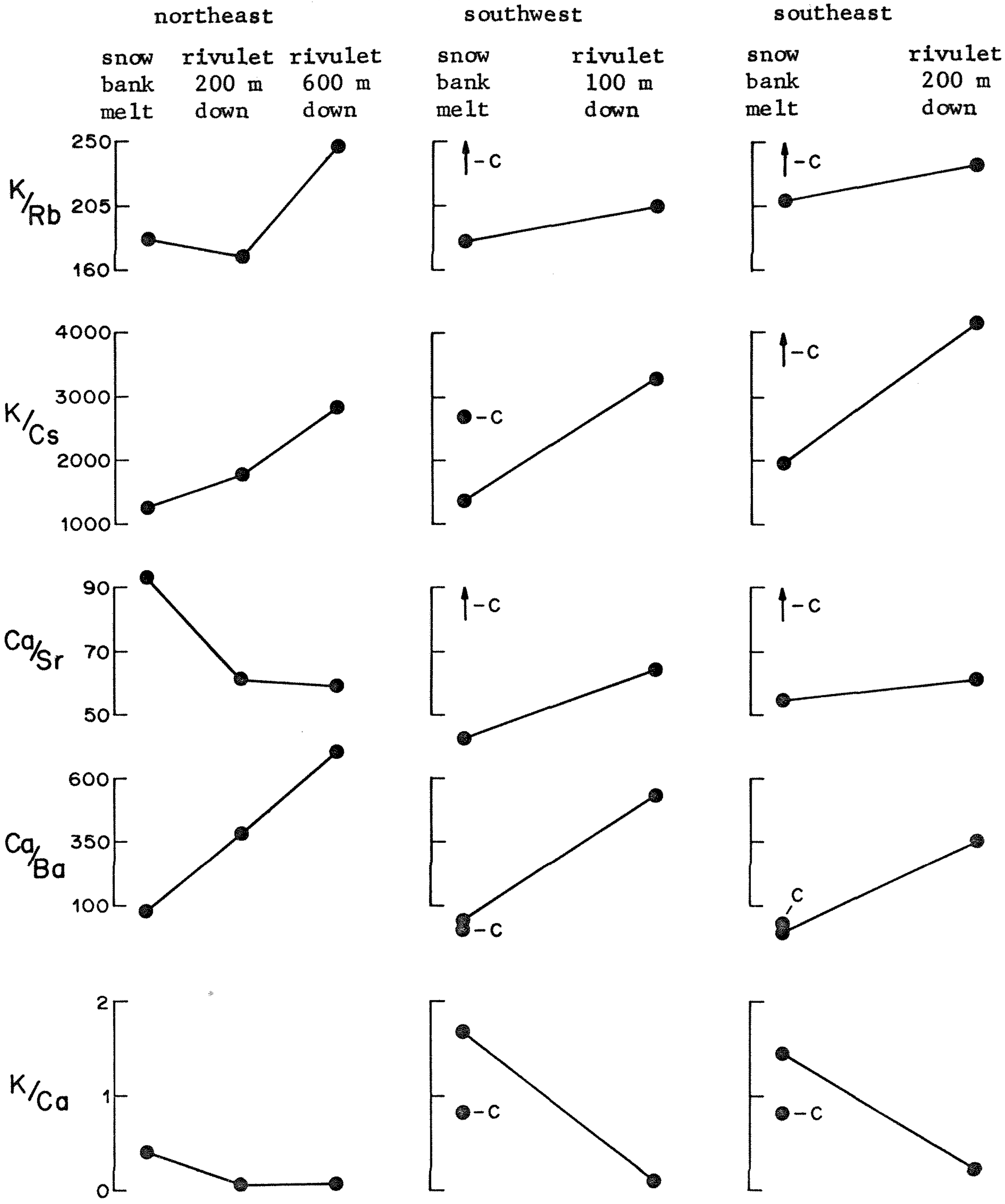


Table 16

COMPARISON OF METALS COMPOSITION IN THE MELTWATER OF MID-SUMMER SNOWBANKS (WHOLE AND WITH PARTICULATES REMOVED BY CENTRIFUGATION) AND IN THE WATER OF SMALL STREAMS DIRECTLY DERIVED FROM THEM

concentrations in parts per 10^9

	Northeast side of watershed			Southeast side of watershed			Southwest side of watershed		
	snow bank melt (whole)	rivulet 200 m down	rivulet 600 m down	snow bank melt (whole)	snow bank melt (centri-fuged)	rivulet 200 m down	snow bank melt (whole)	snow bank melt (centri-fuged)	rivulet 100 m down
K	40	20	35	130	33	62	150	20	96
Rb	0.22	0.12	0.14	0.71	0.094	0.31	0.72	0.069	0.42
Cs	0.024	0.011	0.012	0.096	0.0048	0.019	0.078	0.0074	0.023
Ca	93	360	560	74	39	450	105	15	470
Sr	0.99	5.8	9.5	1.8	0.29	7.0	2.0	0.13	7.7
Ba	1.2	0.95	0.80	2.9	0.59	0.86	4.6	1.1	1.3
K/Rb	180	170	250	180	360	200	208	290	230
K/Cs	1,270	1,750	2,800	1,340	6,900	3,300	1,920	2,700	4,200
Ca/Sr	93	61	59	42	135	64	54	112	61
Ca/Ba	73	370	700	26	66	530	23	13	360
K/Ca	0.43	0.056	0.062	1.70	0.85	0.14	1.4	1.4	0.20

of metals in soils in the time which has passed since the retreat of the glaciers. The following fractions of metals might have been contributed to the top 1 cm of soils in this way:

K:	28%
Rb:	55%
Cs:	45%
Ba:	325%

The basis of the calculation is as follows: assume that 1% of winter snow pack lasts into summer and becomes dusty enough to deliver melt water with the metals content measured in this experiment. Also assume that soils remove the amounts of metals from the meltwater indicated by the composition of the rivulets, that 1/6 of the area of the watershed has soils receiving the metals, and that the glaciers disappeared 10^4 years ago (Adam, 1967).

This mechanism for providing metals to the soils may be less important than air transport of dusts into and out of the soils during the summer, when there is no snow cover. This experiment on snow bank melt and rivulets gives the composition of some dusts which are available to the environment, and shows which metals may be deposited in soils by running water.

The actual composition of the soils of the watershed is very different from the residue of quartz, alkali rich minerals and aluminosilicate minerals which would be predicted from the results of this study to this point, and have been predicted by other workers (Garrels and Mackenzie, 1967). The actual composition of the soil and possible reasons for it are discussed in the following section.

II. METALS IN SOILS OF THE WATERSHED

Soils constitute a complex reservoir of metals in the watershed. The chemical properties of the soil constituents control the availability of metals to the soil solutions and eventually to the plants and animals supported by the soils. The metal compositions of the soil constituents bear a definite relationship to the composition of the rock and its minerals which are the source material of the soil, and to the chemical and physical processes involved in soil development. The six metals have been measured in three fractions of the soil: organic matter (humus); igneous minerals (sand size); and clay (+ silt) size material.

Organic matter may form the most readily available and exchangeable reservoir of metals in these mountain soils. The igneous mineral fraction constitutes the largest reservoir of metals in the soils but its metals are far less available to soil moisture films than those of the other fractions because they are contained within the large mineral grains. However, the composition of this fraction bears the closest relation to the composition of the parent rock, and information about the alteration of this parent material by soil forming processes is most readily obtained by studying this igneous mineral fraction of the soil. Clay (+ silt) makes up a larger reservoir of metals than the organic fraction, but the total surface area of the particles may be much smaller than in the organic fraction, making the main mass of metals less readily exchangeable. Metal compositions of the three fractions from a mid meadow soil are listed in Table 17.

Table 17

Concentrations of metals in three fractions of a mid meadow soil (ppm) (fraction of total metal in whole soil in parentheses)

	Organic matter (humus) (19% of dry soil)		Igneous minerals (sand size) (52% of dry soil)		Clay (+ silt) size (29% of dry soil)	
K	770	(0.83%)	18,900	(60%)	21,000	(39%)
Rb	8.2	(2.2 %)	54	(42%)	126	(56%)
Cs	0.63	(1.5 %)	4.2	(30%)	17	(69%)
Ca	1130	(1.7 %)	15,000	(66%)	13,800	(32%)
Sr	15	(0.70%)	500	(68%)	410	(32%)
Ba	39	(1.7 %)	260	(32%	930	(66%)

Organic matter (humus): Metals were analyzed in the organic matter fraction by ashing the soil in an excited oxygen plasma at room temperature and then leaching it with dilute acid. This method of analyzing organic matter fraction metals separately from clays has not been tried in any past studies. The metals in humus are low in concentration compared to other soil fractions and they are of a distinctive composition. Humus is rich in the heavy alkalies Rb and Cs, similar to soil moisture films (chapter III), suggesting that soil organic matter, despite its small mass, constitutes the major reservoir of metals in the soil available to the biosphere.

The total mass of metals in the readily exchangeable organic reservoir in the soils of the watershed were determined by analyzing the metals in humus in various soil types and by mapping the extent of each type for which the depth and humus content had been measured. As can be seen from Table 18 the mass of metals in humus is about

100 times larger than the reservoir of metals in soil moisture films, and is about 100 times larger than the mass of metals annually removed from the watershed by streams. However, the mass of metals mobilized annually by weathering the source rock could supply the mass of metals in the humus reservoir within a few decades.

Table 18

MASS OF METALS IN FLOWS AND RESERVOIRS IN THE WATERSHED

masses in kilograms

	In total soil (excludes deep alluvium	In total humus (10^5 tons dry weight)	Accumulating annually*	Annual output in streams	In all soil moisture films
K	23,800,000	119,000	10,900	850	2,700
Rb	80,000	1,270	39	4	20
Cs	13,000	201	1.4	0.14	2.9
Ca	16,800,000	260,000	0	4,200	640
Sr	520,000	2,700	105	83	1.7
Ba	490,000	7,600	390	15	8.0

* From weathering rock, relative to Ca, assuming that all Ca weathered from the rock is transported out of the watershed.

Igneous minerals (sand size): This fraction was isolated from soil samples after stirring in pure water. The clay, silt and organic material were removed by decantation while still suspended. This material is not the residue of K-feldspar and quartz that would be expected from information on rock composition and metal loss from the watershed (chapter I). Those data indicated that plagioclase is preferentially broken down and removed from weathering rocks and from the watershed. The metal data in Table 19 show instead that K-feldspar has been depleted from the igneous mineral fraction of the mature soils of the watershed. K and Ba (metals concentrated in K-feldspar) have lower concentrations relative to Ca in the soils than in the rock. The slight increase of Ca/Sr ratios in the igneous mineral fraction also attests to the removal of Ca poor K-feldspars which contain moderate amounts of Sr.

Table 19

Metal ratios of Thompson Canyon rock, and of the igneous mineral (sand size) fractions of three Thompson Canyon soils of differing maturity

	Batholithic rock	Least mature soil: perched hill slope	Intermediate maturity soil: forest	Most mature soil: flat (deep) meadow
K/Ca	2.8	2.6	1.4	1.3
Ca/Sr	24	26	28	30
Ca/Ba	11	18	25	58

This discrepancy between the observed composition of the soil and that expected by denudation data necessitates a hypothesis of removal of breakdown products of K-feldspar from the soils at irregular intervals. Data on metals in stream runoff after violent storms support the hypothesis of such occurrences. Such roiled, swollen streams carry larger quantities of constituents of K-feldspar (K and Ba), relative to the Ca from plagioclase, than do streams carrying meltwater at rainless times, as shown in Table 20.

Table 20

Comparison of the metal content of streams under different conditions (parts per 10^9)

	Normal streams during rainless periods	Swollen, roiled stream 1 hr after violent rainstorm
K	62	930
Ca	380	1100
Ba	1.2	27
Ca/Sr	52	37
Ca/Ba	310	41
K/Ca	0.16	0.85

Much more violent storms than those actually observed necessarily occur at irregular intervals.

Clay (+ *silt*) *size fraction*: This fraction was isolated from a vacuum dried sample of soil by passing through a 50 micron mesh sieve. This material is similar to the batholithic source rock, except that it is very rich in Cs, consistent with the deposition of Cs-rich material in soils by snowbank melt waters and the removal of Cs-rich material from rock as it is broken down to grüs. The Ca/Ba ratios of the clay fractions of three soils of different degrees of maturity listed in Table 21 confirm that Ba-rich K-feldspars are breaking down in soils as they mature and that the Ba-rich weathering products are preserved in the clay and silt size material.

Table 21

Ca/Ba ratios in clay (+ silt) fractions of three soils

	least mature soil	intermediate maturity soil	most mature soil
Ca/Ba	31	17	14

EXTENDED DISCUSSION OF METALS IN SOILS OF THE WATERSHED

Separation and nature of the three soil fractions: Three fractions of each of three Thompson Canyon soils were separated for measurement of the six metals: a humus poor forest soil; a humus rich perched hill slope soil; and a humus rich mid-meadow soil.

Organic matter (humus): After sieving to less than 2 mm, the soil was ashed in an excited oxygen plasma at room temperature to put metals from organic matter into soluble form, gently leached with 0.1 N HCl, and particles were removed from the leach solution by centrifuging. The remaining solution was then analyzed for metals.

In the organic matter fraction of the soil the following points are important:

1. In the alkali family, the heavy metals Rb and Cs are very much enriched relative to K.
2. In the alkaline earth family the heavy metals Sr and Ba are depleted relative to Ca.

The humus fraction is of extremely distinctive metals composition, very different from rocks, rock leach solutions, the other two soil fractions (below), or whole soils or minerals. Its metal pattern is similar to that in the films of soil moisture discussed in the next chapter (III). This similarity to the moisture films supported by Thompson Canyon soils (enrichment of heavy alkalies, depletion of heavy alkaline earths) directs special attention toward the humus fraction as a possible active provider of metals to the aqueous solutions and the biological regime associated with the soil.

Table 22

METALS COMPOSITION OF THREE FRACTIONS OF THREE DIFFERENT SOILS

conc. in parts per million of the (dry) material of the fraction

	Forest soil			Flat Meadow (deeply developed meadow soil)			Perched Hill Slope soil		
	Humus (leach of ashed soil)	Clay (and silt size)	Igneous Minerals (sand size)	Humus (leach of ashed soil)	Clay (and silt size)	Igneous Minerals (sand size)	Humus (leach of ashed soil)	Clay (and silt size)	Igneous Minerals (sand size)
K	920	20,000	24,000	760	21,000	19,000	1,240	22,000	38,000
Rb	11.9	112	109	8.1	126	54	7.7	117	145
Cs	2.8	32	6.8	0.64	16.7	4.2	0.76	15.4	6.6
Ca	2,600	12,600	16,800	1,130	12,800	15,100	2,700	13,700	14,400
Sr	18.1	470	610	14.5	410	500	43	320	560
Ba	73	740	660	39	930	260	71	460	800
K/Rb	78	181	220	94	169	350	163	190	260
K/Cs	330	640	3,500	1,190	1,280	4,500	1,640	1,450	5,800
Ca/Sr	143	27	28	78	32	30	64	43	26
Ca/Ba	35	17.1	25	29	13.9	58	39	31	18.1
K/Ca	0.36	1.62	1.41	0.68	1.63	1.25	0.45	1.64	2.6
	(3.6% humus)			(19.1% humus)			(11.9% humus)		

Metal concentrations in the organic matter fraction of soils are lower than in the clay or igneous mineral fractions.

In the past, separate characterizations of the composition of humus and clay fractions has been neglected due to the recognition of the difficulties of physically separating these two soil constituents (personal communications, J. Lagerwerff, E. Epstein). There is evidence that in this study the metals content of each fraction has been successfully segregated and analyzed separately. In the past only the most indirect data have been presented on the metals holding properties of organic matter, gained from comparison of properties of humus rich and humus poor soils, and has concerned apparent exchangeability of metals rather than actual content. The low temperature oxygen plasma ashing may be expected to have put the metals associated with humus into soluble form without damaging the structure or lessening the insolubility of the clay size material. Removal of particulates from the leach solution by centrifugation was thorough. While some minor amounts of metals may have been contributed to the humus leach solution by sesquioxide films, the weathering surfaces of igneous mineral grains, and the exterior of clay particles, the distinctiveness of the metals composition of the humus fraction of the soils points to the uniqueness of the material represented in the leach solution. Past characterizations of metals in humus are discussed by Broadbent (1965) and Kononova, (1961).

Quantitative assessment of the mass of humus in the watershed and the humus as a reservoir of metals: To determine the mass of total humus in the watershed and the mass of each metal in this readily exchangeable soil fraction, soil types have been mapped and areal exposure of each type established over the watershed by field and aerial photo methods. These soils have been cored to depths of several feet to determine the depth of development of actual soil material. Key soils have been analyzed for humus content. From the above, and data on metal concentration in humus in the various soil types, the mass of the six metals associated with humus in the watershed may be established.

Mapping soil and rock types exposed on the surface and measuring the areas of each type: A scheme distinguishing the various types of rock and soil cover material was adopted and mapped on the basis of field and air photo* observation.

The eleven surface cover types distinguished are the following:

Deep meadow: These are flat valley floor areas in the southern portion of the watershed, formed atop alluvial and glacial deposits which may extend to depths of 50 m by topographic projections. They are traversed by meandering stream channels and bear sedges, grasses, rushes and herbs. Soils present have been identified as entisols (Soil Taxonomy, 1974) but histosols and inceptisols may also occur. Wedges of fluvially transported gravel may be present within and may overlie soil profiles. All clay is amorphous, perhaps allophane, ranging to only a 6 per cent upper limit of clay content. Thick layers of highly organic pond sediments are present in the profiles. Organic-bearing surficial deposits are underlain by stream gravels of variable textures, and fine, blue-gray inorganic

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*Air photos in color and black and white, overlapping coverage, for Toiyabe National Forest, ETO 14 through 25, available from U. S. Forest Service Map Sales Division, Ogden, Utah.

glacial discharge deposits.

Sloping meadow: These are open, sloping or rolling areas of moderately to well developed soils, commonly bordering stream courses. Their main extent is in the northern and high western parts of the watershed. They support vegetation similar to, but less profuse than, the deep meadow areas which are less well drained. The soils are variable in depth and stoniness. Humus content is visibly lower than in deep meadows. The soils are underlain at variable depths by deposits of stream gravels and large cobbles.

Large trees, perched soils: These are stepped areas on canyon side slopes whose structure is controlled by joints in the quartz monzonite. Well developed soils exist on the steps (20% of the projected area of this type of terrain), nearly as humus-rich in the upper layers as deep meadow soils. Both large trees (hemlock and lodgepole) and meadow plants are present. Profiles are most commonly terminated at depths of less than 0.5 m by rocks. The remaining 80% of the area is bare rock.

Dense forest: In these smoothly but variably sloped areas soils are developed upon glacial tills (C. Wahrhaftig, unpublished map of the Tower Peak quadrangle) or unsorted alluvial material. Soils are variably stony, and termination of developed soil material by large rocks is common at less than 0.3 m. Organic content is concentrated in a thin top layer a few cm in thickness. Trees are lodgepole and hemlock.

Sparse large trees: These areas are on steeper slopes and at higher elevations than dense forest. Areas of soil development cover only 6% of total area, due to interruption within soil areas by surface boulders and between soil areas by bare rock. Much of the soil surface is covered by pebble pavement. Trees are lodgepole and hemlock. Cobbles and larger rocks commonly occur at depths of 0.2 m, but the soil layers themselves may be well sorted and free of pebbles.

Sparse trees and bare rock: These areas are similar to regions of sparse large trees, but they are at higher elevations and on steeper slopes, with a lower fraction of areas of developed soils. The trees are stunted lodgepole and white pine.

Bare rock: These areas are at the highest elevations and most severely exposed to the elements, and developed soils are not common. The small organic content used in the calculations represents interstitial organic substances in the degraded rock and the humic content in depressions filled with grus.

Dense willows: Steep perenially wet slope areas bear dense thickets of willow. Very humus rich (to more than 6% organic carbon) soils are developed locally within such units although the soils are shallow (commonly 0.2 m) and may have large stones distributed through them. Close field inspection shows that such high-organic soils cover only about one third of such dense willow areas, the remainder being similar to areas of sloping meadow in organic content.

Sparse willows: These areas are present on slopes which are less moist and less steep than those supporting dense willows. Most soils, and most vegetation other than willows, in such areas are similar to those in sloping meadows.

Alluvial fans: Regions of minor areal extent grading into deep meadow are present on the west side of the south portion of the watershed. They are treated in calculations involving organic matter as areas of sloping meadow.

Hummocks: These areas, of minor extent, are stream dissected regions probably similar in past times to sloping meadow. They are present only in the north central portion of the watershed and are treated as sloping meadow.

Examination of soil profiles: Holes were dug by shovel in 21 selected soil locations, to a maximum depth of 0.7 m, for examination and sampling of profiles, and for determination of downward limits or organic matter content. In addition, auger corings were made at 23 locations, to a maximum depth of 3.8 m, for the same purposes (samples taken by auger were used only for organic content determinations, not for metals analysis).

Analysis of soil samples for organic carbon content: 18 selected soil samples were analyzed for organic carbon content by the acid dichromate method (Soil Survey Laboratory Methods, 1972) by L. Grant of the U. S. Soil Conservation Service Laboratory, Riverside, California.

Determination of the mass of organic material in the soils of the watershed and in each soil type: From an evaluation of the depth of developed soil, and the vertical distribution of organic content, in the 44 (shovel dug plus auger cored) described soil profiles, for each soil type a depth was determined for which the laboratory determined organic carbon content was a true average. Fractions of rock and soils, and their respective organic carbon contents, were combined to yield for each soil type (each surficial exposure type) a mass of organic carbon per unit surface area.

Organic carbon values were multiplied by 1.8 to yield organic matter (humus) values (Broadbent, 1965, pp. 1397-1400).

Mass of organic matter in soil of the entire watershed is given in Table 23, with mass of organic matter in each soil type, and areal extent of each soil type.

The estimate of mass of humus in the soil types, and the estimate of mass of metals in this humus reservoir (Table 24, below) are subject to some error. The acid dichromate method, by which the fraction of organic matter was assessed, may remove more or less mass from a soil than represents degraded organic material properly regarded as humus. This does not affect the assessment of mass of metals from humus because masses of metals contributed by humus are recorded for weights of whole soil. In addition, an incorrect depth of development, or fraction of organic matter, accepted for any soil type may be a source of error.

Mass of the metal reservoir in humus in the watershed: Of the three soil fractions investigated, humus may be able to most rapidly and completely exchange the bulk of its metals with soil solutions and thereby provide them to the roots of growing plants. For this reason the mass of metals in this humus reservoir in the soils of the watershed has been estimated, from an integration of the masses of humus in the various soil types and the metal concentrations in their humus fractions. The metal masses, for the watershed and for each soil type, are shown in Table 24.

	Area of soil type over the watershed (km^2)	Mass of organic matter (kg) per m^2	Mass of organic matter over the whole watershed (kg)
Deep meadows	0.31	140	42 x 10^6
Sloping meadows	1.3	19.3	25 "
Dense willows	.49	24	11.7 "
Sparse willows	.52	19.3	10.0 "
Bare rock	6.3	.89	5.6 "
Dense forest	1.1	23	26 "
Sparse large trees	.26	2.5	0.64 "
Large trees and perched soils	.56	13.1	7.3 "
Sparse trees and bare rock	1.3	.77	1.0 "
Alluvial fans	.08	19.3	1.5 "
Hummocks	.01	19.3	.19 x 10^6
	12.2 km^2		131.3 x 10^6 kg

Table 23 Non-living organic matter: total mass and distribution by soil types

Table 24

MASS OF METALS IN THE ORGANIC MATTER (HUMUS) FRACTION OF ALL SOIL OF EACH TYPE

masses in kilograms

	K	Rb	Cs	Ca	Sr	Ba
Deep (flat) meadows	32,000	350	27	48,000	620	1,640
Sloping meadows	23,000	270	46.0	50,000	440	1,500
Dense willows	14,200	89	8.8	32,000	500	820
Sparse willows	8,500	100	18	19,000	165	570
Bare rock	5,200	67	16.	14,500	100	410
Dense forest	24,000	310	74	67,000	470	1,900
Sparse large trees	590	8	1.8	1,700	12	50
Large trees and perched soils	9,000	57	5.6	20,000	31	520
Sparse trees and bare rock	830	10	1.7	1,800	16	60
Alluvial fans	1,300	15	2.7	2,800	25	90
Hummocks	250	30	0.5	600	5	20
Total	119,000	1,270	200	260,000	2,700	7,600

Relationship of the mass of metals in humus* to the mass of other reservoirs and flow rates in the watershed is discussed above and presented in Table 18.

Clay (+ silt) size fraction of the soils of the watershed: To isolate the finest fraction of the soil, small amounts (15 mg) of non-ashed soil were passed through a 50 micron, acid cleaned, stainless steel mesh. The samples were then prepared, spiked and analyzed as all rock and mineral samples (Chapter I).

The metal ratios of this fine fraction show a much greater similarity to the ratios of local Thompson Canyon rocks than to those of material of distant origin (White Mountain air filter, winter dry deposition, snowpack metals, Table 12). The effects of foreign aeolian transport contamination of the soils in Thompson Canyon are probably less pronounced than those reported by Marchand (1974) for soils in the White Mountains, a more arid region with abundant carbonate source material.

Low K/Rb and K/Cs ratios in this clay (+ silt) size fraction indicate the presence of large amounts of the biotite of the local batholithic rocks (Table 6). This is consistent with the evidence for

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* To compute the mass of metals in humus (Table 23) for each of the eleven soil types, the concentrations of metals found in the humus of one of the three soil samples in Table 22 was used (or a combination). The correspondence is as follows: Deep Meadow soil type--mid-meadow soil sample humus metal concentrations; Bare Rock, Dense Forest, Sparse Large Trees, and Sparse Trees soil types- -forest soil sample; Dense Willows and Large Trees and Perched Soils soil types- - perched hill slope soil sample; Sloping Meadow, Sparse Willows, Alluvial Fans, and Hummocks soil types- - average of mid-meadow soil and forest soil samples.

preferential removal of micas from batholithic rock as it crumbles to grus, and the evidence of removal by soils of particles similar to mica from rivulet waters running away from melting snow banks.

Igneous minerals (sand size) fraction of soils of the watershed: The igneous mineral fraction is similar in composition to batholithic rock, but the details of the metal abundance data indicate that a portion of the K-feldspar of the rock is missing from some soils.

The perched hill slope soil (Table 22) is in a less stable erosional setting than forest or meadow soils and is likely to be younger and less mature. Of the three soils, its igneous mineral fraction is closest in composition to the quartz monzonite wall rock of the watershed: K/Ca, Ca/Sr and Ca/Ba ratios in the igneous mineral fraction of the perched soil distinctively identify the batholithic rock as the source material.

The igneous mineral fractions of the forest and meadow soils, which seem likely to be older due to their stable position in the watershed, show successively different K/Ca, Ca/Sr and Ca/Ba ratios (Table 19). The changes in these ratios point to the removal of two distinct types of K-feldspar which exist and were analyzed in the batholithic rock (the very large euhedral type, and the fine, high density type, Table 6). These K-feldspars are rich in K and Ba, contain some Sr, and are poor in Ca. Their removal would be consistent with the low K/Ca, high Ca/Sr and high Ca/Ba seen in the forest and meadow soils.

Such K and Sr depletion from soils has been reported elsewhere. In the data comparing soil and parent rock (syenite) tabulated by Webber and Jellema (1965) for glaciated regions in Quebec, the same relationship appears. No such clear pattern appears in the data reported by Short (1961). for two soils, one developed on a Ca poor granite, one on a K poor granodiorite (both different from Thompson Canyon rocks). Details of composition of constituent minerals in rock or soil, or any Ba data, are not available in the work of either Webber and Jellema or Short.

The K, Ba and Sr depletion suggests the possibility of a preferential weathering of certain types of K-feldspar in the low pH, reducing environment of the near-surface soil, with periodic removal of the weathering products. Such K-feldspar removal would be in contrast to the observed, continuous, preferential breakdown of plagioclase into soluble or suspendable products in the oxidizing, high pH environment of exposed rock, grus and primitive soils. Evidence for the continuous breakdown of plagioclase is discussed at length in Chapter I.

Measurement of the metals in the waters of roiled, milky streams during and after violent summer thundershowers suggests that K-feldspar and mica, or their weathering products, are swept into the streams at such times and removed from the watershed. Complete data are presented in Table 25. High K/Ca, Ba/Ca (and Sr/Ca) ratios in the turbid streamwater suggest removal of Ca-poor K-feldspar or its breakdown products, and high Rb/K and Cs/K ratios suggest removal of micas. This is in contrast to rainless times when the constituents of plagioclase dominate the metals in streamwaters.

During the violent thundershowers, rills and roostertails of water

Table 25

COMPARISON OF METALS CARRIED BY STREAMS LEAVING THE WATERSHED

1) AT A NORMAL, RAINLESS TIME

2) AT A TIME WHEN STREAMS ARE SWOLLEN AND TURBID IMMEDIATELY AFTER A SUMMER THUNDERSHOWER

	outlet stream: rainless period	outlet stream after violent thunder storm time: 16:45	outlet stream after violent thunder storm time: 18:10
K	62	270	930
Rb	0.26	1.5	7.1
Cs	0.011	0.10	0.65
Ca	380	630	1100
Sr	7.4	14	30
Ba	1.2	4.7	27
K/Rb	240	180	132
K/Cs	5,600	2,600	1,430
Ca/Sr	52	46	37
Ca/Ba	310	133	41
K/Ca	0.16	0.44	0.85

Concentrations in parts per 10^9

Includes solute and suspended matter, but not bedload

Collections made in July, 1973

have been observed on slopes in places where melt water channels have not been cut, indicating that the areas swept by flow during such storms are greater than the areas swept by water during normal gentle snow melt conditions. More violent storms than those actually observed, capable of producing conditions of true sheet wash, or overland flow necessarily occur at irregular intervals. Janda (1966) discusses evidence for frequency of major storms. Emmett (1970) discusses the hydraulics of overland flow on hill slopes.

Any argument is very weak that the discrepancy between the observed K-depleted composition of Thompson Canyon soils and the expected Ca-depleted composition may be explained by the original development of Thompson Canyon soils on materials from external sources, or materials different from the wall rocks of the watershed. There are several reasons for this: 1) The watershed is at the crest of the range and glacial material could not have easily come downhill from other locations. 2) Thompson Canyon is in the middle of the Cathedral Peak pluton, with wide margins of rock similar or identical to the wall rock of the canyon. 3) Almost all of the volcanic cover was probably swept away in the earlier of several Pleistocene glaciations. 4) The grain sizes of most of the igneous mineral fraction in soil are too coarse to be of volcanic origin. 5) It is improbable that a foreign parent material could coincide, in the values of several metal ratios, with the composition of Thompson Canyon rock with a single known mineral (K-feldspar) removed.

This initial information, indicating the existence of specific chemical differences between whole parent rock and the rock-derived fraction of soil, which is associable with specific changes in proportions of identifiable mineral species, clearly suggests directions for future work in this nearly overlooked area.

Other possible reservoirs of heavy metals in soil: Olson and Skogerboe (1975) have reported that the majority of Pb in some very polluted urban soils exists in the form of authigenic $PbSO_4$ crystals which may be separated from the soil by precipitation in heavy liquid. To determine whether Pb and the chemically similar metal Ba occur in such sulfate or other heavy mineral reservoirs in Thompson Canyon soils, two whole soils were analyzed by emission spectrography for Pb and Ba, and the analysis was repeated for a high-density separate from each soil (0.7% and 1.1% of whole soil).

Ba concentration is 5-10 fold lower in the high density fractions than in the whole soils (520 and 470 ppm in whole soils versus 51 and 86 ppm in dense separates). Pb concentrations remain constant between whole soil and high-density separate at about 20 to 23 ppm. This information suggests that the bulk of Ba and Pb in soils may be associated with alkali feldspar as it is in the batholithic rock, or with other phases in the low density fraction of the soil, and that enrichment of these metals in a dense crystalline phase distinct from humus, clay, or igneous minerals is not important in the more pristine soils of Thompson Canyon.

Mass of developed soil in the watershed and mass of rock weathered since the glacial retreat: There is a striking broad agreement, perhaps within a factor of two, between mass of rock material weathered, indicated by stream metals output data, and observed mass of soil in the watershed. As discussed in Chapter I the Ca removed from the watershed in stream water represents a denudation rate of batholithic rock of about 0.8 cm/1000 yr. The other constituents of the rock are much less rapidly removed than Ca and presumably remain behind in the watershed after weathering, representing approximately 8 cm of rock over the watershed since the glacial retreat (10^4 yr). This minimum amount of rock weathered would place 65 cm of primitive, organic-free material on the deep meadows of the watershed, or 14 cm on a larger area including sloping meadows.*

There is in fact somewhat more developed soil material in the meadows than could be provided by the <u>minimum</u> mass of weathered rock indicated by data on metal removal by streams. However, the closeness in composition of rock and derived grus (Chapter I) suggests that a large mass of rock may be turned to granular material before a major share of its Ca is dissolved away. More information on the mass of rock turned to granular material in relation to the mass of dissolved Ca could be obtained from a measurement of the composition, and long-term monitoring of the mass, of the material leaving the drainage as stream bedload. A bedload of large mass relative to material removed in solute, and of composition similar to the batholithic rock, would indicate that large masses of rock are turned to granular material without extensive alteration. A small bedload mass, rich in quartz and alkali feldspar (complementing the plagioclase-derived Ca in stream solute), would indicate that only moderate amounts of rock are turned

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*Rock density 2.6, soil density 1.8; deep and sloping meadows 0.3 and 1.3 km^2, respectively, in a 12.2 km^2 watershed.

to granular material in the watershed as the rocks are chemically leached. Measurement in the two runoff seasons to date have indicated that weathered rock carried as bedload is either smaller than or equivalent to the masses represented by solute (Chapter I).

III. METALS IN SOIL MOISTURE FILMS

Films of moisture surrounding soil particles constitute the final phase in the geological occurrence of metals, because in this form the metals are available to the roots of growing plants. Proportions of metals in soil moisture films can be expected to be different from those in source rocks because the metals have been fractionated along the pathways from rocks to soils by differential mineral weathering, solution chemistry, and mechanical transport of mineral grains.

Attempts at determining metal concentrations in films of water in soils at normal (subsaturated) moisture content have been plagued by a two sided problem: ordinary analytical techniques require large amounts of moisture for trustworthy analysis, but the collection methods involved in taking large samples alter the composition of moisture films which exist in undisturbed soils. A technique for sampling very small amounts of moisture from undisturbed soils in the field was developed, in which soil moisture was rapidly blotted onto stacks of specially cleaned absorbent paper. The small amounts of sample collected by this method are readily analyzed by the stable isotope dilution technique.

The proportions of metals in soil moisture films were observed to be different from those in batholithic source rocks. The major features of this difference are as follows. In the alkali family

Cs is greatly enriched relative to K. In the alkaline earth family Ba is depleted relative to Ca. In addition, the alkalies are generally enriched relative to alkaline earths. These features are shown in Table 26.

Table 26

METAL ENRICHMENTS AND DEPLETIONS IN ROCKS AND SOIL MOISTURE FILMS

	7 whole rocks	4 mid meadow soil moisture films
K/Cs	7900	630
Ca/Ba	10.5	27
K/Ca	2.8	4.0

In the flow of metals from rocks to soil moisture films, soils are an intermediate phase. Whole soils take intermediate compositions as the changes in proportions of metals in each family progress from rocks to soils to soil moisture films. However, the proportions of metals in soil moisture films tend to parallel those in the organic matter fraction of soils, which might be expected because the surface area of this phase is probably far greater than that of any other in the soil.

Compositions of soil moisture films are also quite different from those of phreatic and stream waters. Metal concentrations in soil moisture samples taken near the soil surface range to 1000 times higher than those in phreatic water (below the water table) or stream samples collected at the same location. Soil moisture is the only type of water in the watershed which has an excess of alkalies over alkaline earths. Stream water, phreatic water, and snow all contain more alkaline earths than alkalies. Samples of each water type are compared in Table 27.

Table 27

METALS IN MID MEADOW SOIL MOISTURE FILMS COMPARED TO PHREATIC WATER AND STREAM WATER FROM THE SAME LOCALITY (parts per 10^9)

	4 mid meadow soil moisture films	Phreatic water	Stream water
K	7000	11	62
Rb	71	0.17	0.26
Cs	11	0.005	0.011
Ca	1740	530	380
Sr	32	13	7.4
Ba	64	6.5	1.2
K/Rb	98	66	238
K/Cs	630	2300	5600
Ca/Sr	54	41	52
Ca/Ba	27	82	310
K/Ca	4.0	0.022	0.16

Soil solutions obtained by traditional methods in the laboratory possess different concentrations and proportions of metals than those found in soil moisture films collected in the field by the method developed in this study. Table 28 shows that the concentrations of both K and Ca are greatly increased in soil moisture films obtained in the laboratory relative to the field sample. On the other hand the concentration of Cs declines. The differences become much more pronounced if the soil is dried at elevated temperatures. Concentrations of metals in soil moisture films collected in the field in this study are generally much lower than those reported for soil solutions obtained in the laboratory by traditional methods (Bradford and others, 1971).

Table 28

FIELD AND LABORATORY SOIL MOISTURE FILMS OBTAINED BY BLOTTING FROM THE SAME SAMPLE OF SOIL (1500 g)

Parts per 10^9

	Field Sample (taken in July)	(Soil dried (by vacuum) and rehydrated to field moisture content, allowed to stand 2 hr	Soil oven dried @100° and rehydrated to field moisture content, allowed to stand 2 days
K	4,200	12,600	30,600
Cs	14	1.3	0.78
Ca	1,910	2,100	38,000

Other parameters traditionally used for evaluating availability of metals in soils give very different results from those obtained here by sampling soil moisture films in the field. For example, a standard determination of cations in the soil sample exchangeable with NH_4^+ gave a K/Ca ratio of 0.23, while this ratio in the soil moisture film collected in the field was 4.1. Even on soils developed on very K rich, Ca poor parent material, such as true granite, Ca is by far the most available ion in traditional "soluble" and "exchangeable" extracts made in the laboratory (R. Arkley, unpublished data), while in soil moisture films sampled in Thompson Canyon in the field, from soils developed on only moderately alkali rich material, K dominates strongly over Ca.

If traditional laboratory methods of obtaining soil solutions had been used in this study, the true relationships among the metals within and between the alkali and alkaline earth families in the various phases of the geological system would not have been perceived.

Soil moisture films were collected at different times in the summer, at different soil depths, and for different soil types. The metals data are summarized in Table 29, and they show that metal concentrations are much higher in soil moisture films collected from humus rich zones near soil surfaces than from the more mineralic zones at depth. In the soil moisture films in humus rich zones at shallower depths the concentrations of alkalies generally increase in the autumn. In the more mineralic zones at depth the opposite trend is observed in some soils. An example is given in Table 29.

Table 29

VARIATION IN SOIL MOISTURE FILM COMPOSITION WITH SOIL DEPTH AND TIME OF SEASON (PERCHED HILL SLOPE SOIL)

Parts per 10^9

		Late July	Latest September
5 cm depth	K	9,300	20,000
(humic soil)	Cs	2.7	8.9
30 cm depth	K	2,600	1,030
(less humic soil)	Cs	1.2	0.56

Evaluation of seasonal relationships among the compositions of soil moisture films and the uptake of metals by plants is dependent upon the determination of the masses of metals in soil moisture films above the water table in meadow soils, and the masses in the sedge plants supported by the meadow soils. Preliminary estimates suggest that these two reservoirs of metals are of comparable mass.

III. EXTENDED DISCUSSION OF METALS IN SOIL MOISTURE FILMS

The method of collection of soil moisture films from undisturbed soils in the field: Small samples approximating the composition of true soil moisture films (pellicular water, Tolman, 1937) can be obtained in the field by placing a dry absorbent material such as cellulose acetate filter paper in contact with the soil for a short time to allow the soil moisture film to quickly partition itself between soil and paper. Two reports in the literature mention this extraction method, but results have not been reported (Gardner and others, 1937, Intern. Atom. Energy Agency Lab. Report, 1964). This study presents results of analysis of such extracts of soil moisture, taken in the field, from subsaturated alpine soils.

In sampling soil moisture in the field, a flat space was cleared in the soil, a porous plastic (Nuclepore) filter placed on the soil, and a stack of six 4-cm filter paper discs, specially cleaned and weighed, was pressed tightly against the plastic filter for only a few seconds by the thumb of the sampler, covered with an acid cleaned polyethylene glove. The stack was then inserted into a teflon bottle and tightly sealed for reweighing and analysis in the laboratory. The filter discs were leached with 20 ml of 0.1 N HCl for several hours at 55° C in a quartz centrifuge tube, centrifuged to precipitate fibers, and aliquots of this solution removed with a pipette, isotopically spiked, and analyzed for metals.

Seventeen such samples were taken in the field from various soils of Thompson Canyon through the summer season of 1974.

Differences in metal proportions among source rocks, soils and soil moisture films: The changes in metal proportions in both alkali and alkaline earth families from rocks to soils to soil moisture films are plotted in the form of K/Cs and Ca/Ba ratios in Figure 10. In the alkali family Cs is strongly enriched relative to K going from rocks to soils to soil moisture films, and in the alkali family Ba is depleted relative to Ca from rocks to soils to soil moisture films.

Definite phenomena and mechanisms can be cited to account for these changes in proportions between rocks and soils. The soils are richer than the rocks in the heavy alkalies Rb and Cs (relative to K) partly because they contain abundant mica which is rich in Rb and Cs. Mica is visible in the soils as fine golden sparkling particles. It is made available to the soils as mica flakes are freed from the other more equant grains of rock during the formation of grus, and emplaced in the soils in part by deposition of particles from snow melt rivulets (Chapter I). The soils may be poorer than the rocks in the heavy alkaline earths Sr and Ba (relative to Ca) because of preferential removal of microcline from the soils. In the source rock microcline contains very little Ca, some Sr and much Ba.

The differences in metals proportions of the soil moisture films from those of soils are an extension of the same trends of fractionation that are observed between rocks and soils. The soil moisture films correspond well to the Rb- and Cs-rich humus and clay of soil which are expected to be readily exchangeable with aqueous solutions. The humus fraction may be much better able to exchange its metals than the clay

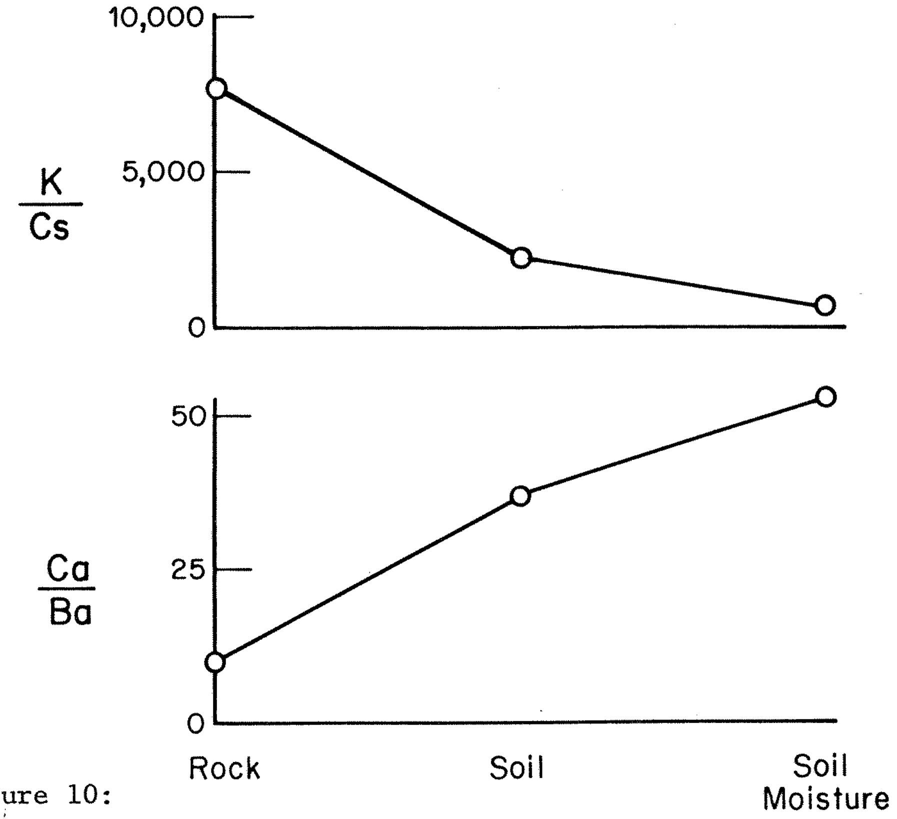

Figure 10:

The trend toward enrichment in the heaviest metal in the alkali family (Cs), and depletion of the heaviest alkaline earth (Ba), moving through the 'geological foundation of a food chain'.

(+ silt): a simplified calculation suggests that humus may have about 500 times more surface area per unit weight. The calculation assumes that humus particles are separate entities with molecular weights of about 50,000 (Broadbent, 1965) and unit density, and that clay (+ silt) particles have a size of 0.0001 cm and a density of two.

Hirao and Patterson (1974) discuss further changes in proportions of metals which take place in the biological system which is supported by the Thompson Canyon watershed.

Samples collected in the field at different times through the summer: suggested trends: Soil moisture films were sampled in the field in 1974 in Thompson Canyon at early, intermediate and late times in the summer, on distinct soil types and at different soil depths.

Soils selected were 1) a humus rich soil in the center of the broad deep meadow, sampled in a single near-surface zone containing sedge roots; 2) a soil perched on a narrow hill slope terrace, humus rich near the surface but less deeply developed than the meadow soil: this soil was sampled at both 5 cm (growth zone of shallow herb and sedge roots) and 30 cm depths (deeper rooted plants such as large lupine); 3) a soil on the boundary of conifer forest and meadow, less humus rich than the other soils at both near-surface and deep sampling levels: this soil supported both conifers and meadow plants. (Organic matter contents of the five soils sampled for moisture are as follows: mid meadow, 19%; near-surface perched soil, 7.1%; deep perched soil, 2.7%; near-surface forest-meadow soil, 6.3%; deep forest-meadow soil, 3.3%.)

The soil moisture metals data for the seasonal sampling of the various near-surface and deep soils are presented in Tables 30 and 31 and in Figure 11.

The major features of difference between the soil moisture films collected near the soil surface (5 cm, humus rich zones) and those collected at greater depths (30 cm, mineralic zones) are that 1) the metal concentrations are much higher in the near-surface samples and 2) the alkalies are more abundant relative to the alkaline earths in the near surface samples.

In soil moisture films taken near the surface in humus rich soils the concentrations of alkalies rise in the autumn (mid meadow and perched soils). In samples taken at greater depth below surface the alkali concentrations decrease in the autumn (perched soil)*.

Due to the variation in metals concentrations in duplicate field samples (plotted in Figure 11 for June and July mid meadow soils, and discussed below) the trends must be regarded as strongly suggested but not certain.

<u>Reasons for variations in metals in soil moisture with soil type and time of season</u>: Three possible factors influencing the seasonal

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*The very earliest season samples (June 14) were taken under conditions where the soils were in direct contact with water flowing from melting snow (near-surface perched soil) or awash for hours each day due to diurnal stream overflow (mid meadow soil). For this reason, the June 14 samples are not likely to be properly a part of any smoothly changing pattern through the growing season. The July, August and September samples for both meadow and perched soils were collected under consistent conditions (same apparent soil moistness, never immediately after a rain). The forest-meadow boundary soil is not considered valid for a seasonal-variation interpretation due to too few data (one very early in the season) and poor duplication of sampling location.

VARIATION THROUGH THE GROWING SEASON IN THE METALS COMPOSITION OF SOIL MOISTURE FILMS:
WELL-DEVELOPED SOILS IN MID MEADOW AND ON A HILL SLOPE PLATFORM

concentrations in parts per 10^9

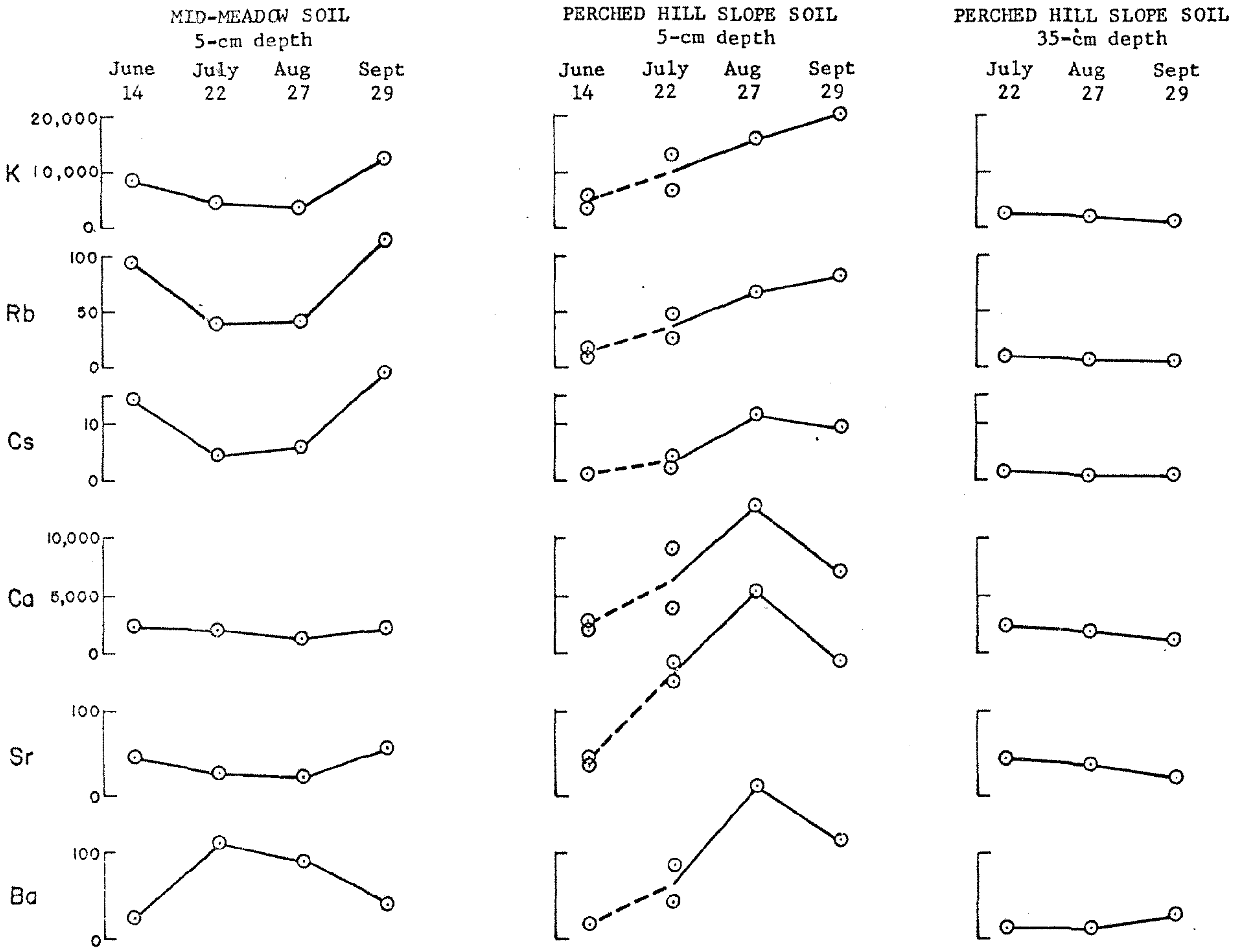


TABLE 30

SEASONAL VARIATION IN THE COMPOSITION* OF SOIL MOISTURE FILMS: WELL-DEVELOPED SOILS IN MID MEADOW AND ON A HILL SLOPE PLATFORM: 5 cm depth

	Mid-meadow soil, supporting herbs and sedges				Soil perched on hill slope platform, supporting herbs					
					Duplicates taken side-by-side on the ground		Duplicates stirred in container in field			
	June 14	July 22	Aug 27	Sept 29	June 14		July 22		Aug 27	Sept 29
K	8,200	4,200	3,300	12,100	3,000	5,100 155	6,100	12,400	15,500	19,900
Rb	94	37	39	114	10	15.5	24	45	92	104
Cs	14	4.3	5.8	19	0.54	0.38	1.8	3.6	11.2	8.9
Ca	2,100	1,910	1,030	1,950	1,940	2,600	3,600	8,900	12,500	6,700
Sr	39	26	23	41	30	41	131	153	240	155
Ba	19	110	88	38	15	15	38	82	178	111
K/Rb	87	115	85	106	296	329	249	273	169	192
K/Cs	600	900	580	630	5,600	13,400	3,300	3,500	1,390	2,200
Ca/Sr	53	72	46	48	66	63	27	58	52	43
Ca/Ba	11	17	12	52	133	168	95	108	70	60
K/Ca	4.0	3.0	3.2	6.2	1.55	1.97	2.5	1.39	1.24	3.0

* Metal concentrations in parts per 10^9

TABLE 31

SEASONAL VARIATION IN THE COMPOSITION OF SOIL MOISTURE FILMS*

	Soil perched on hill slope platform supporting herbs (see table __ for 5-cm depth)			Soil on forest-meadow boundary supporting herbs with conifers nearby			
	30 cm depth			5 cm depth		30 cm depth	
	July 22	Aug 27	Sept 29	June 14	Sept 29	June 14	Sept 29
K	2,600	2,300	1,030	22,000	5,300	1,220	1,210
Rb	8.4	6.7	5.2	124	20	5.9	2.4
Cs	1.2	0.70	0.56	4.6	2.1	1.8	0.56
Ca	2,500	2,000	1,390	5,800	2,200	2,400	2,400
Sr	42	38	24	105	51		35
Ba	18	13	27	73	66		98
K/Rb	300	340	199	178	260	210	500
K/Cs	2,200	3,200	1,850	4,800	2,500	1,030	2,100
Ca/Sr	58	54	56	56	44		67
Ca/Ba	136	158	50	80	34		24
K/Ca	1.04	1.11	0.75	3.8	2.4		0.51

* Metal concentrations in parts per 10^9

soil moisture film composition are the following: 1) metal uptake and release of metals by the standing crop of plants; 2) uptake and release of metals by humus and clay in soils, in response to temperature, pH or other physical factors; 3) through-flow of solutions with different metals content.

As for effects due to the growth of plants, the mass of metals in soil moisture films above the water table in mid meadow is comparable to the mass of metals in the leaves of the standing crop of sedge (Patterson and others, 1973). Metal ratios in sedge leaves vary strongly with time of season, but it is unknown whether these variations represent only internal redistribution of metals between leaves and the large root systems of these plants. Strong effects from through-flow of soil solutions of variable composition are unlikely in the poorly drained Thompson Canyon soils except in the earliest snowmelt part of the season. As for the possibility of effects of pH and temperature on release of metals by humus and clay, pH was found to be between 4 and 5 at all times of the season for all soils. Average soil temperatures may rise measurably in mid season. Lengths of time necessary to replace metals in soil moisture films from the humus and clay reservoirs are completely unknown.

Correlations of metal patterns in soil moisture films with the tissues of growing plants and with traditional "ion exchange" properties of soils: Higher values of K/Ca ratios in moisture from near surface humus rich soil zones than from deep zones at the same site is a preliminary hint of compositional correlation between the soil moisture films of each zone and the tissues of plants which locate their roots in those zones: leaves of shallow rooted sedges correspond to the high values (more than unity) of K/Ca ratios in soil moisture films near the soil surface, whereas the tissues of the more deeply rooted conifers are reported to have much lower K/Ca ratios (Patterson and others, 1973), corresponding to the low ratios (near or less than unity) in soil moisture from the deep zone of the perched soil or forest-meadow boundary soil. Conifer roots are present in the deep sampling zones of both of these soils. This correspondence suggests that the compositions of indigenous plant xylems and soil moisture films may be positively related under natural conditions.

Data available at present on the compositions of laboratory prepared soil solutions and exchangeable cation characteristics may be less relevant than commonly assumed for making proper correlations between metal compositions of tissues of growing plants and the soil solutions actually available to them. The exchangeable cation characteristics of the mid meadow soil are listed in Table 32.

Table 32

EXCHANGEABLE CATIONS IN MID MEADOW SOIL COMPARED WITH METALS IN SOIL MOISTURE FILMS

K/Ca in exch. bases	K/Ca in soil moist. films
0.12	4.1

Exchangeable bases (with NH_4^+ pH 7, meq/100 g air dried soil)	Na	1.3
	K	0.11
	Ca	0.95
	Mg	0.23
total exchangeable cations at pH 7		21.0

Exchangeable cation data measured by U.S. Soil Conservation Service, Riverside, Calif.

The new method of sampling soil moisture films in the field: comparison with traditional methods of "soil solution" sampling, and tests for reliability: The sampling method developed and used in this study potentially offers insights not available earlier into the actual composition of soil moisture as it exists in undisturbed soils in the field. In order to confirm that this is true, it is necessary to show that the method is capable of yielding reproducible, accurate metals data on solutions sampled, and to compare the results from the new method with those from traditional sampling methods which are suspected of altering the composition of soil solutions by laboratory operations on the soils.

Differences in metals content of soil moisture films sampled in the laboratory from those sampled in the field: A soil moisture sample was collected in the field after thoroughly stirring the soil (1500 g sample). This same sample, a humus rich mid meadow soil, was brought to the laboratory and additional soil moisture film samples were collected from it. The methods of soil treatment and soil moisture collection used in the laboratory are described below, and the results of the metals analysis of the samples. Data are shown in Table 33.

1. Storing the soil frozen (-10^{o} C) for several weeks, thawing, allowing to stand 2 hr, and sampling by the same blotting technique used in the field. Results are the following:

   a. Metal concentrations increased about two fold over those in the soil moisture sample collected in the field.
   b. Cs is depressed relative to the other metals, compared to the field sample.

Table 33

VARIOUS SAMPLING AND SOIL TREATMENT METHODS:
EFFECT ON METALS COMPOSITION IN THE MOISTURE FILM OF A SINGLE SOIL

	Sampled in field by blotting with filter paper (late July, 1974, mid-meadow)	Laboratory Samplings			
		Frozen, thawed, sampled by blotting	Vacuum-dried, rehydrated, sampled by blotting	Vacuum-dried, rehydrated, sampled by centrifug'n	Oven-dried (100° C) rehydrated, sampled by blotting
K	4,200	11,600	12,600	13,400	31,000
Rb	37	124	68	101	127
Cs	14	8.3	1.3	1.8	0.78
Ca	1,910	2,900	2,100	3,000	38,000
Sr	26	73	48	76	910
Ba	110	126	67	149	840
K/Rb	115	94	183	133	241
K/Cs	900	1,400	9,600	7,400	40,000
Ca/Sr	72	40	44	40	41
Ca/Ba	17	23	32	20	50
K/Ca	3.0	4.0	5.9	4.5	0.81

2. Vacuum drying the soil (equivalent to air drying) after thawing and rehydrating the sample to its original field moisture content, with the usual blotter sampling.

    a. The heavy metals in each family are depleted relative to the light ones, compared to the metal proportions in the field sample and the sample which was frozen and thawed without drying. Cs is relatively depleted many fold compared to either of the two samples.

    b. K and Ca, the light metals in each family, are present in nearly the same concentrations as those in the sample frozen and thawed only.

3. Vacuum drying and rehydrating, as described above, but with the sample collected by pipette after separating a supernatant layer by centrifuging: Cs is strongly depleted, as it was in 2. above, the concentrations of K and Ca are the same as in 1. and 2. above and Sr and Ba are the same as in 1. For a soil in a given condition, this sampling method does not give greatly different results from the blotting method.

4. Oven drying the soil at 100° C and rehydrating to the original field moisture content, and using the blotting technique, after allowing the soil to stand two days:

    a. Total metal concentration rises several fold over that of other soil treatment methods.

    b. Concentrations of alkaline earths rise as a group to overshadow the alkalies.

    c. In the alkali family Rb and Cs are depleted relative to K.

> The K/Cs ratio in the oven dried sample is about fifty times higher than in the field sample.

The soil is obviously greatly altered by the oven drying. The soil has a burned odor, and after rehydration appears much wetter than before drying.

Vacuum drying and especially oven drying may alter the abilities of organic matter and clay to donate or retain metals when in contact with solutions. McKenzie (1963) has shown that certain cations (K^+, Rb^+, Pb^{++}, in montmorillonite; Cs not investigated) may be rendered non-exchangeable if the clay containing them is dried, even without the application of heat. There is no published data on the effect of drying upon the exchange properties of organic matter.

Sampling reproducibility: To test reproducibility, duplicate sample collections were made in the field by each of two methods:

1. Two soil moisture film samples were taken in rapid succession directly from the cleared soil surface in the field, only a few cm apart (in June).
2. A soil sample (1500 g) was thoroughly stirred in a cleaned polyethylene pan and two samples were collected from it in rapid succession (in July).

The data are shown in Table 30, for the near surface sample of the perched hill slope soil.

For some of the six metals, the variations in the duplicates are considerable fractions of the total masses. The differences must be attributed to the control of physical constituents of the soil very close to the sampling blotter. The individual analyses in each duplicate have been plotted separately in Figure 11 (seasonal variation in metals in soil moisture films). If "error bars" were assigned to all of the other single points in the seasonal variation plot, of length determined by the spreads between the duplicate points, the seasonal trends for some metals would be less distinctive.

Analytical reproducibility is discussed below.

Investigation of the possibility of preferential retention of metals within the filter paper disc stack during sampling: In the method of sampling soil moisture films in the field reported by Hinkley and Patterson (1973) the bottom filter paper disc in the stack was in direct contact with the soil and was discarded in order to eliminate soil particles sticking to the bottom disc. If any metals were preferentially retained by the bottom disc, through which the sample first passed during collection, an erroneously low value would be reported for them.

To test this possibility, the following experiment was done during a sample collection in the field: the bottom disc was discarded, but the next-to-bottom disc was removed from the stack and analyzed separately from the upper discs. The results, shown in Table 34, strongly suggest that the alkaline earths, especially the heavy ones, will be preferentially retained by the bottom paper discs through which the moisture sample first passes, but the alkalies are less strongly affected. Furthermore, the retention gradient through the stack would be expected to vary with metal concentration, mass and pH of the sample collected, so a correction could not be practically applied.

Two approaches were taken to eliminate this problem of preferential

Table 34

PREFERENTIAL METAL RETENTION THROUGH A STACK OF CELLULOSE ACETATE FILTER PAPER DISCS USED TO SAMPLE SOIL MOISTURE FILMS

Calculated concentrations in soil moisture in upper seven discs and single next-to-bottom disc of the stack (ppm)

	K	Rb	Cs	Ca	Sr	Ba
Upper 7 discs in stack	8.8	0.045	0.0021	3.7	0.060	0.037
Single next-to-bottom disc	11.2	0.066	0.0020	10.2	0.20	0.24

Comparative masses of metals in the upper seven discs and the single next-to-bottom disc of the stack (nanograms)

	K	Rb	Cs	Ca	Sr	Ba
Upper 7 discs in stack	62,000 (85%)	320 (83%)	14.6 (88%)	26,000 (72%)	420 (67%)	260 (52%)
Single next-to-bottom disc	11,200 (15%)	66 (17%)	2.1 (12%)	10,200 (28%)	200 (33%)	240 (48%)

retention of metals through the disc stack. One was the discontinuation of the practice of discarding the bottom disc, by adopting the use of a non-absorbent porous plastic filter disc (Nuclepore) between the disc stack and the soil. The other was the development of a new technique for cleaning the absorbent cellulose acetate paper. The technique was developed to lower the contribution of the paper to the analytical blank, but it incorporates a final step which may leave the exchange sites on the paper largely filled with NH_4^+, making them unavailable for the retention of metals.

Cleaning procedure for the absorbent paper: Whatman #40 ashless cellulose acetate filter paper discs (5.5 cm) were batch cleaned by leaching 25 hours in each of three successive 55^o baths of 25% HCl solutions of increasing purity (analytical reagent grade, G. Frederic Smith distilled, National Bureau of Standards distilled), with moderately thorough water rinses (to pH 4 or 5) between each acid bath. Highest purity rinse water was sucked through a few discs at a time on a Buchner funnel. The discs were vacuum dried between each acid bath. The HCl leachings were followed by similar baths, with rinsing and drying, in 0.5% highest purity HF, and in 1% NH_4Cl at pH 7. The final rinse, after the NH_4Cl, was very sparing, intended to leave some NH_4^+ on the paper.

Part of this sequence was suggested by E. E. Dickey of the Institute of Paper Chemistry in Appleton, Wisconsin.

This cleaning sequence, with the HF and NH_4^+ steps, reduces the previously troublesome Ba analytical blank about ten fold, compared to that from a simple HCl cleaning sequence (Hinkley and Patterson, 1973).

It is to be observed that F^- is a smaller ion than Cl^- or NO_3^- and may have superior abilities to dislodge metals from the paper. NH_4^+ is nearly the same size as K^+, Ba^+ Pb^+ and may be able to swamp exchange sites on the paper ordinarily occupied by the metals.

The 40 micron pore size Nuclepore plastic filter discs were cleaned in the same way as the papers.

Analytical reproducibility, and reliability of the soil moisture sampling and analytical method: The accuracy of the soil moisture sampling and analysis method was tested by comparing analyses of a metals stock solution which was sampled in two ways. The first analysis was of a sample blotted onto papers through a Nuclepore plastic filter. The other was of a sample taken directly from the bottle. The stock solution was similar in the concentrations of the six metals and in pH to soil moisture. Results of the two analyses are presented in Table 35, and show the following to be true

1. The metal concentrations for the two sampling and preparation methods match within at most a few percent of the values, showing that the method of soil moisture sampling does not distort metal abundances. This small variation in metal values for two very different chemical procedures may be taken as a generous upper limit on analytical variability for samples which are chemically prepared in the same way.

2. There is no preferential retention or fractionation of the metals as the solution passes through the Nuclepore plastic filter.

3. Metals are totally removed from the cellulose acetate paper when samples are leached from it by warm dilute HCl prior to analysis.

Table 35

COMPARISON OF TWO ANALYSES OF A SOLUTION SIMILAR TO SOIL MOISTURE

1. Directly from the stock bottle
2. Absorbed onto cellulose acetate paper through Nuclepore plastic filter

	(1) Direct	(2) Through plastic filter onto cellulose acetate paper
K	675	700
Rb	156	163
Cs	0.782	0.780
Ca	2577	2623
Sr	84.0	88.7
Ba	230	234
K/Rb	4.32	4.30
K/Cs	864	898
Ca/Sr	30.7	29.6
Ca/Ba	11.2	11.2
K/Ca	0.262	0.267

Concentrations in parts per 10^9; solution buffered to pH = 5 by NH_4Cl; NH_4^+ was 0.1 N

Appendix

DESCRIPTION AND CATALOG OF SOIL PROFILES

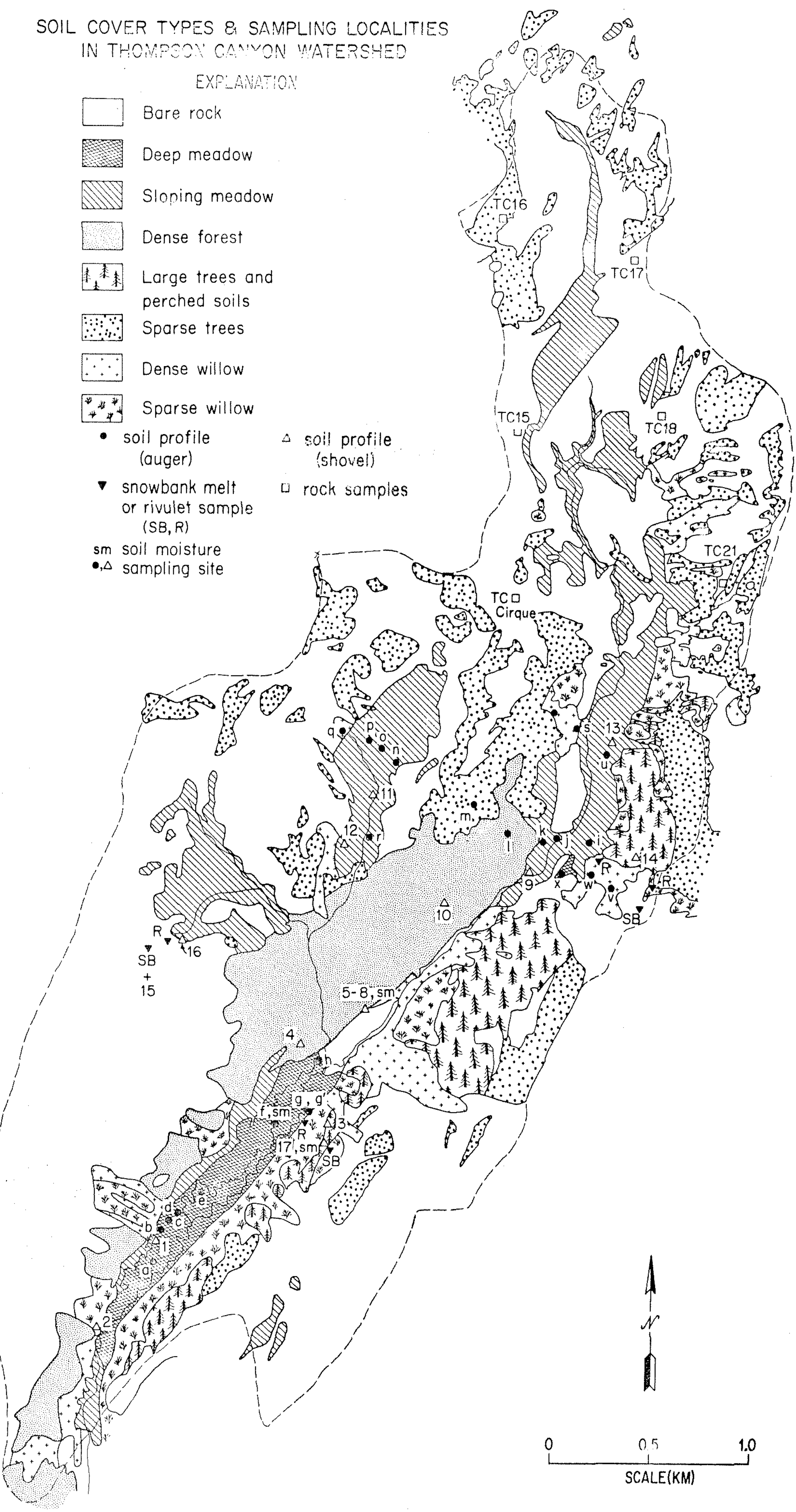
The numerals and lower case letters which identify samples correspond to localities on the map (following sheet)

Soil profiles described from the walls of shovel-dug holes, or from the spoils:

1. Profile extends to 78 cm. Entire profile is unstratified sandy loam, excepting a zone of 1 cm thick ashfall layers which interfinger over 4 cm, at a depth of 38 cm. Easily-sheared rust-colored splotches are randomly distributed through the profile below 21 cm. Abundant fine gold mica sparkle is conspicuous below about 23 cm. Plant roots are less abundant below about 43 cm than higher in the profile. Low hairy sedges and asters grow on this soil. 4 meters to the west, soil is grussy on the surface and without plants. 4 meters to the east is a depression where high sedge grows. Water table is not present in this profile (July).

2. Profile extends to 50 cm. This locality is very near the west wall of the drainage. Rocky, poorly-developed soil, about one third or more or which is poorly-sorted, stream-rounded cobbles in various stages of saprolitization, most altered at depth. Topmost 3 cm are moderately organic-rich. Slightly-reddish brown coarse-sandy soil, less organic-rich, to 36 cm. Rust-red, crumbly, coarse, organic-poor soil below 36 cm. Terminated by large cobbles at 50 cm. No water table in this profile (July).

3. Profile to 81 cm. Top 5 cm are forest litter. Underlying the forest litter, a 3 cm thick layer of medium-grained white-gray sand


SOIL COVER TYPES & SAMPLING LOCALITIES
IN THOMPSON CANYON WATERSHED
EXPLANATION
Bare rock
Deep meadow
Sloping meadow
Dense forest
Large trees and perched soils
Sparse trees
Dense willow
Sparse willow
● soil profile (auger)
△ soil profile (shovel)
▼ snowbank melt or rivulet sample (SB, R)
□ rock samples
sm soil moisture
●,△ sampling site
TC16
TC17
TC15
TC18
TC21
TC Cirque
q
p
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n
11
12
r
m
l
k
j
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13
u
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14
R
x
w
v
R
SB
9
10
R
SB
16
15
5-8, sm
4
h
g, g'
f, sm
R
3
17, sm
SB
e
d
c
b
1
a
2
N
0
0.5
1.0
SCALE (KM)

is sandwiched in a 5 cm organic-rich black layer. Red-brown, rock-free soil, sandy and organic-poor, unstratified, is present below 8 cm. Large hemlock roots extend to a depth of 48 cm, with fine roots below. Soil has fruity or organic chemical odor after storage. Unsorted rocks become abundant at 80 cm.

4. Profile to 50 cm. In a small clearing in the forest, on gravel-armored ground. 5 cm of dark brown soil at top, organic-rich and with specks of charcoal. Light reddish brown to tan below 5 cm, very dry. Rock-free to 50 cm, at which depth some rocks appear. Unstratified below 5 cm. This is the forest soil of which three fractions were analyzed for metals.

5-8. Profile to 36 cm. In a meadow-like strip (not shown on map) on the very edge of the forest. Top 6 cm is organic-rich, rooty soil. Between 6 and 13 cm the soil is sandy and organic-poor, decreasing smoothly in organic content with depth. Below 33 cm soil is sandy and very organic-poor. No conifer roots extend below 33 cm. Mid-summer water table may be near the bottom of the profile. "Forest-meadow boundary" soil moisture samples were taken on this soil.

9. Profile to 68 cm. Near the forest edge, in the sloping meadow. An irregular, 1 cm thick organic-rich layer at the surface. Gray-brown moderately organic soil extends to about 30 cm, making an irregular contact (15-30 cm) with an underlying red-brown layer mottled by darker brown, becoming increasingly rocky near 68 cm, but with developed soil extending deeper. No stratification in the profile except as mentioned. Charcoal flecks, bark fragments and

conifer roots are distributed through the profile. No distinct mica glitter in this profile.

10. Profile to 25 cm. This profile may be typical of soils in forests on steep, smooth (unledged) slopes. Top 3 cm is undecomposed forest litter, underlain by 5 cm of tightly packed forest humus which is dry, crusty, only partly decomposed. Between 8 cm and 18 cm is gray-brown, moderately organic soil, with an ashfall layer present at about 12 cm. Below 18 cm is tan, more sandy, organic-poor soil. Unsorted rocks are distributed through the profile.

11. Profile to 40 cm, with unsorted rocks distributed through the profile. Soil is sandy and red-tan-brown through the profile, with a 4 cm moderately-organic layer at the top, organic-poor below. No mica glitter. Large cobbles at 40 cm.

12. Profile to 56 cm, rock-free except for cobbles at bottom. Top 38 cm is brown with moderate organic content, somewhat richer in organics in topmost 5 cm. The thickest, least mixed ashfall layer seen in the watershed is present near 38 cm, up to 4 cm thick. Soil supports bilberry, Solidego, grasses. Site is between willow clumps, in the lowest portion of the meadows of the west drainage.

13. Profile to 62 cm, through tan-brown sandy soil of moderate organic content, slightly richer at the top of the profile. Rockiness increases below 56 cm, but developed soil may extend deeper. Little mica glitter. Ashfall layer is present at 18 cm. Soil supports bilberry, hair grass, clumps of sedge.

14. Profile to 28 cm, through perched but sloping soil near a large clump of hemlocks. At surface is 1-3 cm of forest litter and partly decomposed humus. Below is dry medium-brown to tan stony soil, with fewer charcoal fragments than observed in other forest soils. Moderate amounts of mica glitter, no ashfall layer. Cobbles at 28 cm.

15. Profile to 30 cm Very mineralic soil, annually covered by snow until middle-late summer.

16. Profile to 30 cm through black, moderately organic soil with rocks of all sizes through profile.

17. Profile to 43 cm, at site of "perched hill slope soil moisture" collection. Top 12 cm is very dark, moist, rooty, organic-rich soil. From 12 cm to about 40 cm is dark, sandy, moderately organic-rich sticky soil, with thick lupine roots, cobbles irregularly distributed near 40 cm. This is the 'perched hill slope soil' of which 3 fractions were analyzed for metals.

Soil profiles described from auger-cored holes, while the soils were in the auger bit or after removal.

a. To 130 cm, in mid-meadow, in a slight depression. Top 12 cm is silty and sandy, moderately organic-rich loam. Between 12 and 42 cm is pink, pebbly (rounded) stream-deposited alluvium, becoming extremely red in color near 40 cm, with rusty deposits which may be scraped from the frets in the pebbles with the fingernails. Below 42 cm, a 3 cm thick stratum finer and less pebbly than the above, tan and without red color. Below 45 cm, a 5 cm thick stratum of brown-gray clay-textured material (contaminated glacial discharge material?), with possible dark layers laced through it; no reduced-organic odor or taste; very slightly gritty. Below 50 cm, a thick deposit of water-logged loose grussy soil, less pebbly than above.

b. To 175 cm. The high- to moderately-organic sticky topsoil becomes more loamy but is still sticky at 16 cm. An ashfall layer is present at 33 cm, underlain by a sticky clay-textured (glacial discharge?) layer with mica sparkles. Near 50 cm, the loam appears to be more organic, with reddish clots. A light, sandy lens appears at about 50 cm, becoming pure tan in color, and coarser, at 63 cm, and dirty brown and coarse and poorly sorted at 76 cm. Between 88 cm and 140 cm material is wet tan grus, without red stains, with large black mica flakes, becoming more poorly sorted and more pink and with quartz pebbles near 140 cm. Poorly rounded, barley-colored pebbles and grus below 140 cm.

c. To 250 cm. Soil is loamy and organic to 15 cm, grainier but still brown and rooty at 23 cm. Lighter color at 33 cm. Heavy, clay-textured soil with mica sparkles between 33 cm and 81 cm. Coarse tan sand begins at 81 cm, with sparkles. Light gray clay-textured material with sparkles, probably glacial discharge, at 96 cm, continuing to 170 cm. Pure white, well-sorted medium grained quartz and feldspar sand at 170 cm. Water table broken through at 170 cm, rises to 152 cm. Pebbles with relict orange stains dilute the white sand below 180 cm, continuing to 250 cm. No significant organic matter present below 81 cm, probably none present for some distance above that.

d. To 230 cm. Top organic-rich layer is only 5-8 cm thick, with grainy, coarse, dark brown soil below that, grading into sandy, coarse light brown material by 63 cm. 1 cm layer of well-sorted gray sand at 68 cm, overlying a possible layer of (1 cm) of low-density organic or clay-textured material (pond sediment?). Below this is coarse brown soil to 81 cm. A 5 cm layer of the fine organic or clay-textured material appears at 81 cm. Poorly sorted light gray sand begins at 86 cm, which grades downward to a more brown color. Tan, wet, grussy material appears at 120 cm. Sand with admixture of clay-textured material appears as a horizon at 175 cm, which grades downward into light gray, finer sand. Color changes to tan below 215 cm. Material below 175 cm may be glacial discharge.

e. To 275 cm. Topmost soil is organic-rich and sticky, continuing to 36 cm, but with a 1 cm red horizon, also organic-rich, at 13 cm. Soil becomes abruptly sandier at 36 cm, becoming sandier and lighter in color gradationally to 71 cm, at which depth there is an abrupt change to very light tan, better-sorted, finer material. At 92 cm the fine gray clay-textured *material (less micaceous than elsewhere)* appears, continuing to 152 cm; this is probably glacial discharge material. Below 152 cm the gray material coarsens with sand and gravel but the distinctive light color is unchanged. A 3 cm thick zone of fossilized peaty amber roots may be present in this material at 188 cm, and a darker layer of sticky, rooty soil at 195 cm. Possible wedges of brown clay-textured material, some with roots, at greater depth, as thick as 10 cm, near 230 cm depth. Nature of contacts between light gray and fine brown material is uncertain. Light gray material becomes more gravelly near 260 cm, with a 5 cm band of unsorted, crunchy, coral-colored sand at 270 cm.

f. To 196 cm. Dark brown, organic-rich soil to 25 cm, underlain by a lighter brown crunchy sandy soil. Dark, fine, clay-textured material which is probably pond sediment appears at 50 cm. A 5 cm layer of peaty, tan, preserved roots at 68 cm. The rootiness and micaceous sparkle of the "pond sediment" material vary randomly with depth. A 5 cm thick layer of crunchy, medium-coarse, medium-brown sand or sandy soil appears at 170 cm, underlain by another 5-8 cm of more "pond sediment" material, with more sand (grayer in color) below that. Crunchy, pea- to nut-sized gravel, mixed in auger bit with brown mud, appears at 180 cm. Mid-meadow soil moisture was taken very near this locality.

g. To 76 cm. This locality is 6 meters out into the meadow from in-place wall rock of the canyon. Very black, organic, somewhat rooty soil at the surface, becoming black, organic loam by 13 cm. Thin (3 cm) wedges of gray-tan sand appear at 20 cm, becoming coarser and sandier below that, changing to fine, organic-poor loam by 30 cm, with fossil roots and wood and one or two 1 cm thick wedges of clean tan or salmon fine sand. Crunchy, mineralic, salmon-tan sand appears at 45 cm, poorly sorted, to coarse size. By 60 cm the sand has changed to pea- to walnut-sized poorly sorted gravel, very clean.

g'. To 84 cm. Only 2 meters out into the meadow from the rock of the canyon wall. Coring was made in a gravel-covered patch to avoid the large surface cobbles nearby. Top 5 cm is organic-rich rooty soil, underlain by red-tan, coarse, sandy, poorly-sorted, moderately organic soil to 48 cm, at which depth it changes to fine or medium grained well-sorted clean sand. Pea- to walnut-size gravel at 50 cm and below. No cobbles.

h. To 150 cm. Top 5 cm is organic-rich black material, underlain to a depth of 60 cm by poorly sorted sand, similar to "construction sand" excepting a distinctive orange color. 60-68 cm is dark, clay-textured "pond sediment" material, underlain by fine, well-sorted, fairly clean tan sand, which becomes coarser and dirtier with depth. A very poorly sorted, very muddy gravel is present below 93 cm, with some rounded pebbles to 3 cm near 150 cm.

i. To 116 cm. Soil is sandy, organic-poor, medium brown loam throughout the profile, free of all rocks near top, with 1 cm pebbles becoming abundant near 50 cm. Pebbles of sizes up to 4 cm are present near 116 cm, where auger is stopped by a rock. Grasses and herbs in area.

j. To 215 cm. Willow clumps near this locality, with stunted lodgepoles, sedges and grasses, less bilberry than elsewhere in the sloping meadow. Topmost material is darker, wetter, more organic-rich and stickier than at locality i. At 31 cm the material changes to coarse, poorly sorted, organic-poor, mineralic, silty, wet soil. At 120 cm there is a rapid gradational change to much lighter, tan-gray coarse sandy material (glacial discharge?), probably devoid of organic matter. This sandy material is distinctly darker than the similar-textured barley-colored material in the lower deep meadow. Material becomes very much less cohesive near 180 cm.

k. To 195 cm. Vegetation at this locality is similar to that at j, but with more bilberry. Top material is very dark brown and organic-rich, with no large mineral grains, and only slightly moist in late summer. At 26 cm, soil becomes medium brown, grainier, much less organic-rich, and at 55 cm becomes rust-brown, grainy and sandy. It becomes gradationally redder, wetter and sandier to 140 cm, where there is an abrupt change to very clean sand with black large mica flakes, gray-tan, medium grain size, poorly sorted. Sand becomes coarser downward, with some pebbles to 1 cm in size near 195 cm where auger is stopped by rock. Bottom material lacks cohesiveness as in j.

l. To 30 cm. Slope in this region is about 15°, gentler than on east side of canyon. About 35% of the surface area is large and small boulders, the remainder is soil with 1-2 cm of forest litter, underlain by dry, dusty and grainy soil appearing to be organic-poor. Abundant poorly-rounded stones, which make it difficult to dig through the dull-brown, dry, loamy soil, are present through the profile. This locality is in a clearing, common to this part of the forest, containing about six surface cobbles of about 30 cm diameter per square meter of ground.

m. To 30 cm. This locality is in "sparse trees", at higher elevation than is l. The proportion of surface boulders to soil is the inverse of that at l, 65% boulders here. Soil is rocky and similar to that at l.

n. To 30 cm. This locality is sloping meadow, rather near the poorly-defined edge of forest soils. Vegetation is hair grass, bilberry, Solidego, small lupine, with willows nearby. The soil is fine-textured medium brown loam, very dry in late summer. Unrounded pebbles of 1 cm diameter are present through the profile. Rocks block the auger at 30 cm.

o. To 53 cm. This locality is nearer the axis of the west drainage than n, and soil is more moist. The soil is slightly less organic-rich by appearance than corresponding soils in the northeast drainage of Thompson Canyon, but here the organic content declines markedly by 13 cm depth, rather than by about 28 cm as in the northeast. Soil has some rust-brown layers but is still brown and loamy at 53 cm where the auger is stopped by rocks.

p. To 68 cm. Tan, dry, powdery soil, less organic-rich in appearance than n or o. 1 cm pebbles are present, but the soil is all fine. Ashfall layer is present at 50 cm.

q. To 140 cm. Top 5 cm is dry black soil, low-density and extremely organic-rich. Between 5 and 30 cm is black, mucky, extremely organic-rich material, continuing mucky and somewhat less organic-rich to 120 cm, with very black, anoxic organic layers 1 cm thick near 60 cm. Soil becomes sandy, sticky, organic-poor at 120 cm.

r. To 60 cm. In lowest elevation portion of the sloping meadows of the west drainage area. Vegetation and soil nearly identical to that at n.

s. To 60 cm. This dense-willow soil lacks the dry organic top layer seen in the soil at q, and is somewhat less organic-rich in the top 10 cm. Soil becomes less organic, and brown in color at 56 cm.

t. To 36 cm. This locality is a higher-elevation portion of the same willow area which contains locality s. The topmost 20 cm are intermediate in organic content between q and s, but the organic matter may be less fully decomposed than in the two other willow soils. There are surface boulders over about half of the total area of this willow region, in effect diluting the high organic content.

u. To 36 cm. Dry, medium-light brown loamy soil, very similar to soil at locality n and related profiles. Auger stopped by rocks at 36 cm.

v. To 60 cm. 1 cm or more of litter on top, though this material was not present everywhere in this willow area. 5 cm of rooty, spongy peat, underlain by black, chunky, organic-rich soil to 28 cm depth. Below 28 cm, soil changes to medium brown, very grainy (medium-to-coarse) organic-poor soil, becoming harder and poorer in organic material with depth, until auger is stopped by hardness at 60 cm.

w. To 60 cm. This locality is a grassy clearing in the center of dense willows. Topmost 1-3 cm are organic-rich and rooty, but with small sandy lenses present even in that small thickness. Moderately organic-rich soil to 13 cm, becoming gradationally sandier and browner until auger is stopped by rocks.

x. To 60 cm. This locality is in the center of the small flat area designated as 'deep meadow' in the northeast drainage. Top 1-2 cm are organic-rich, dark-brown soil, underlain by fine sandy medium brown organic-poor loam to 11 cm. 11-18 cm is coarse reddish brown sand, coarsening and turning to gravel gradationally with depth.

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