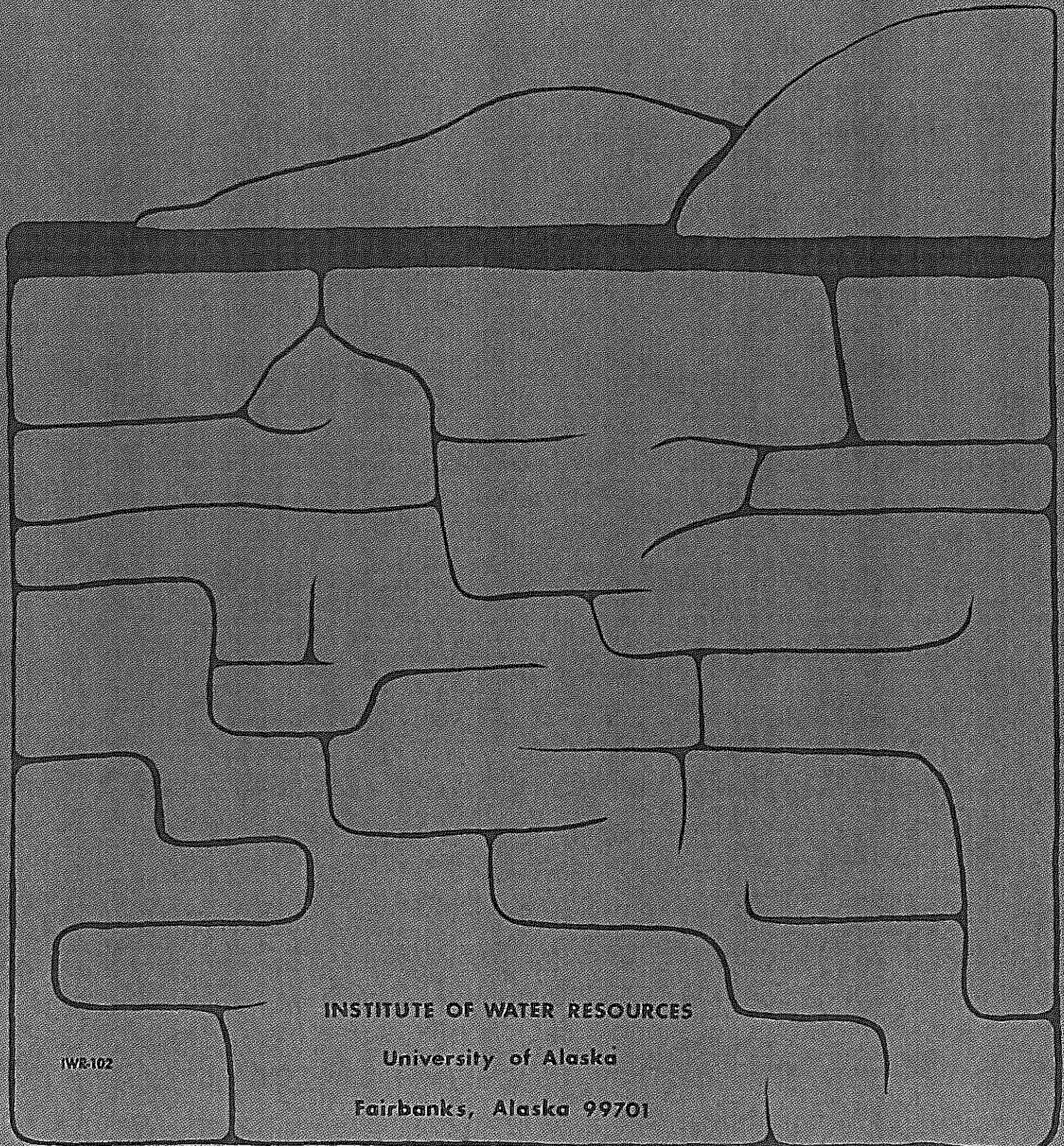


HYDROGEOCHEMISTRY OF THE
CARIBOU-POKER CREEKS
RESEARCH WATERSHED



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IWR-102

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Hydrogeochemistry of the Caribou-Poker Creeks Research Watershed
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ABSTRACT

Bedrock of the Caribou-Poker Creeks Research Watershed dissolves incongruently with a first-order rate constant of about $5 \times 10^{-6} \text{ day}^{-1}$ at 5°C . The resulting solution is potassium-calcium-magnesium rich. The soil-plant environment acts on this solution through sorption of potassium and by evapotranspiration to yield a solution that is relatively depleted in potassium and enriched in calcium and magnesium, but with the same molar ratio of Ca:Mg as the fluid from the rock dissolution. This fluid from the soil-plant reservoir is the dominant contributor of ions to stream waters.

Using the discriminant functions obtained by multiple discriminant analysis

$$D_{\text{PKR}} = 0.572\text{SiO}_2 + 0.240\text{Ca} + 2.89\text{Mg} - 0.384\text{Na} + 0.452\text{NO}_3 - 9.18$$

$$D_{\text{CRB}} = 0.913\text{SiO}_2 + 0.042\text{Ca} + 1.28\text{Mg} + 1.17\text{Na} + 4.63\text{NO}_3 - 7.27,$$

the waters of Caribou Creek and Poker Creek can be distinguished on the basis of chemical composition. In general, Poker Creek waters are slightly more concentrated than Caribou Creek waters.

On the average, $1.4 \times 10^{13} \text{ g H}_2\text{O/year}$ leaves the watershed as surface water. At an average calcium concentration of 14 ppm for the water, 0.1% for the bedrock, and a watershed area of 46 mi^2 , this flow corresponds to a maximum loss of about 17 metric tons of rock per hectare per year.

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INTRODUCTION

The purpose of this study was to interpret hydrogeochemical data for the Caribou-Poker Creeks Research Watershed (see Figures 1 and 2). We attempted to determine: if compositional differences exist between the two streams; the extent to which the chemical composition of the waters of the two streams can be accounted for by interactions with the bedrock; and the hydrogeochemistry of the watershed.

This study is in three parts. The first deals with a statistical analysis of the existing compositional data of the waters from the watershed. The second deals with a laboratory study of the kinetics of bedrock dissolution and the relationship of this study's results to the natural water system. The third uses the data and results of the preceding investigations to interpret the hydrogeochemistry of the watershed. The quantity of data generated in this study was large and could not be included in this report. Only summaries of data and interpretations are presented here. Copies of all data are available from the authors on request.

STATISTICAL ANALYSIS

Univariate Statistics

We used the data of Lotspeich et al. (1976), supplemented by more recent data from Slaughter and Hilgert (unpublished). We used the Biomedical Statistical Programs (Dixon, 1979) to refine the data. Summary statistics for the different chemical variables for the two streams are given in Table 1 and shown in histogram form in Figures 3a-3b. These data show that waters of Caribou Creek are more dilute than those of Poker Creek. The compositions of the two streams are very similar, as can be seen from the Stiff diagrams shown in Figure 4. These were prepared by estimating the HCO_3^- content of the waters from the measured pH and assuming that the anions must balance the cations. From these diagrams, it is clear that the waters of the two streams are dominated by calcium bicarbonate.

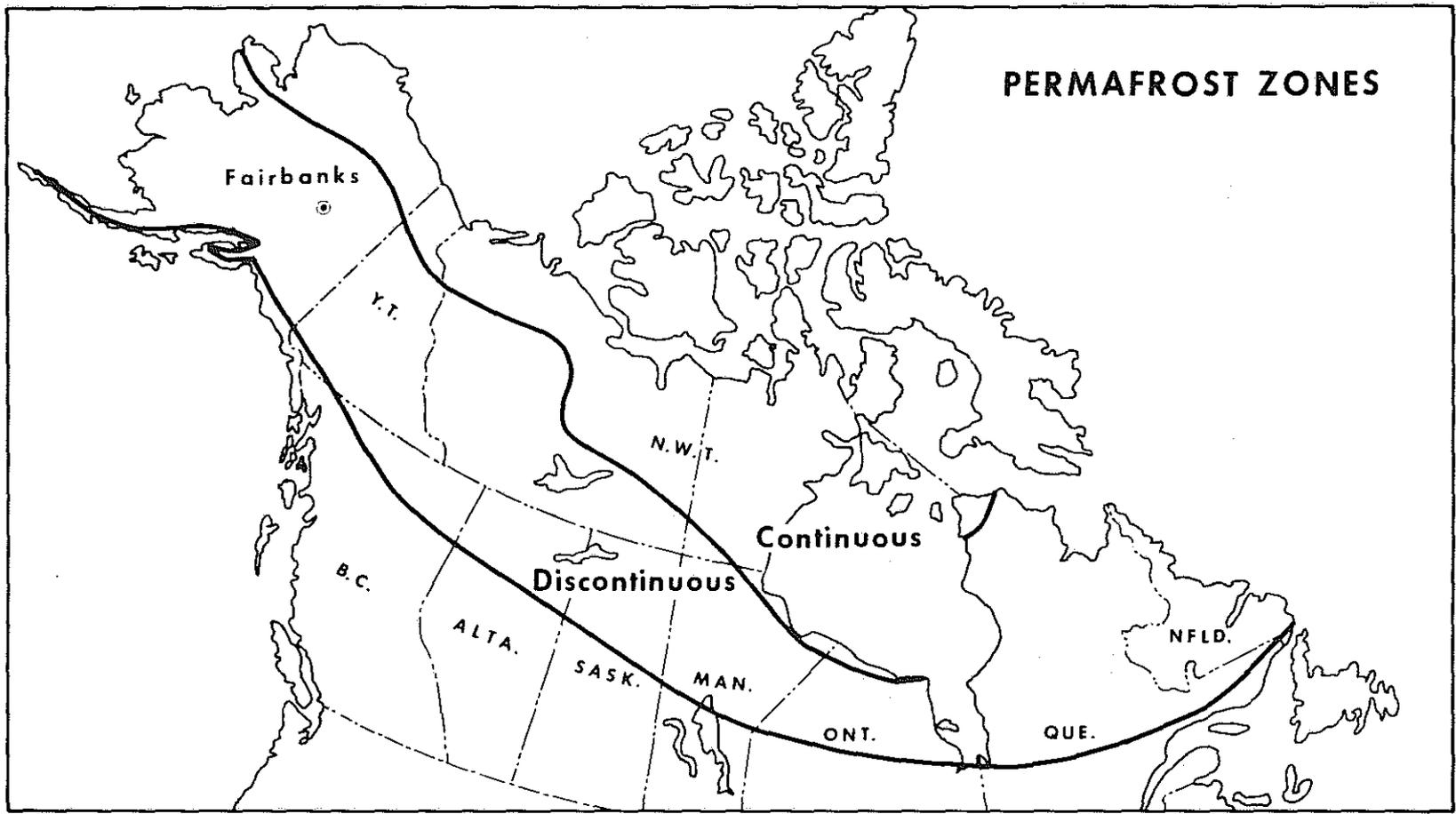


Figure 1. Distribution of permafrost in North America. Note that Fairbanks, which is near the Caribou-Poker Creeks Research Watershed, is almost in the middle of the zone of discontinuous permafrost (Lotspeich and Slaughter, 1981).

VEGETATION MAP OF CARIBOU-POKER CREEKS RESEARCH WATERSHED

VEGETATION TYPES

- A Aspen (*Populus tremuloides*)
- BP White birch (*Betula papyrifera*)
- BN Dwarf birch (*Betula nana*); used for all above-tree-line areas
- PG White spruce (*Picea glaca*)
- PM Black spruce (*Picea mariana*)
- C Sedge (*Carex* sp., *Eriophorum* sp.); commonly includes sparse overstory of black spruce, occasional tamarack (*Larix laricina*)
- S Alder/willow (*Alnus* sp., *Salix* sp.)
- R Riparian species (*Salix* sp., *Betula nana*, *Vaccinium* sp., *Populus balsamifera*, etc.)

DENSITY CLASSES

- 1 High
- 2 Medium
- 3 Low

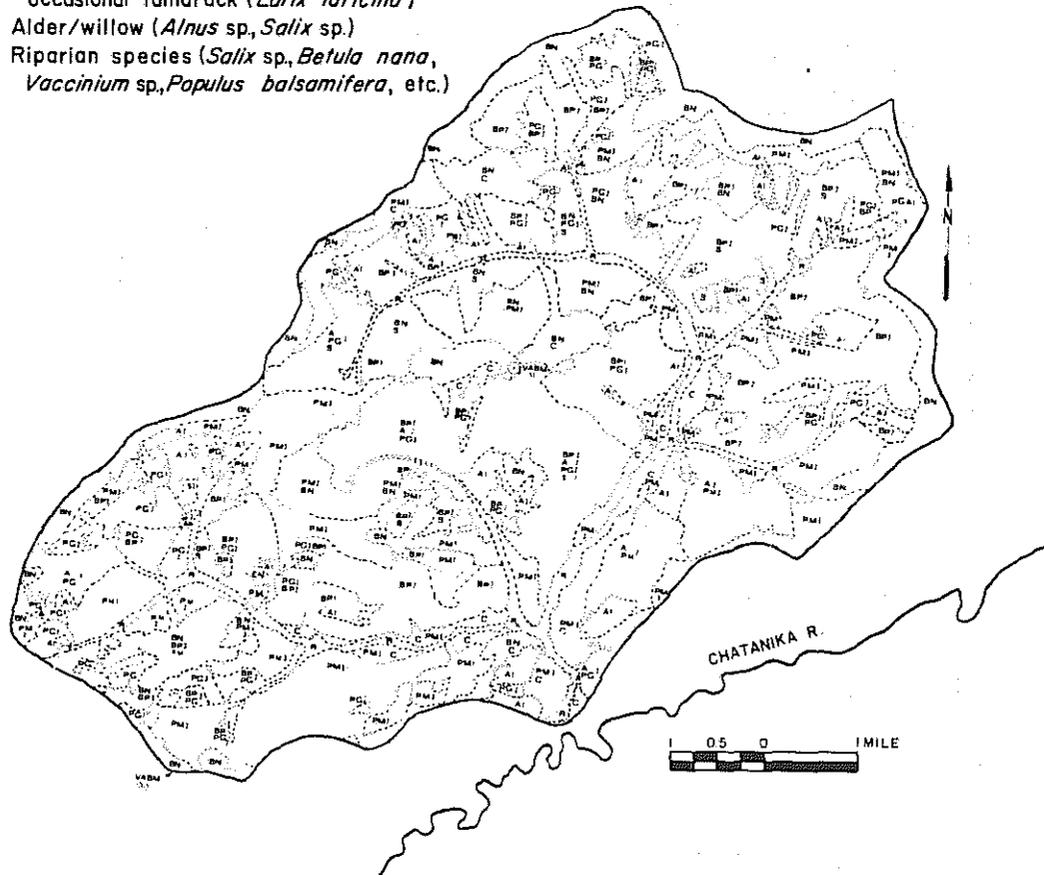


Figure 2. Vegetation map of the watershed (after Vogel and Slaughter, 1972).

Table 1. Summary Statistics for the Chemical Composition of (A) Poker Creek and (B) Caribou Creek Expressed in Parts Per Million (ppm).

Variable	Creek	Mean	Std. Dev.	Std. Err. of Mean	Coef. of Variation	Smallest Value	Z-score	Largest Value	Z-score	Range	N
SO ₄	A	6.7	2.9	0.40	0.44	2.5	-1.4	15.6	3.0	13.1	52
	B	8.6	2.9	0.44	0.33	3.8	-1.7	14.4	2.0	10.6	42
SiO ₂	A	6.4	2.3	0.31	0.36	0.60	-2.5	8.9	1.1	8.3	54
	B	6.3	2.2	0.34	0.35	1.2	-2.3	9.4	1.4	8.2	42
Ca	A	11.3	5.0	0.68	0.44	2.4	-1.8	19.4	1.6	17.0	54
	B	14.6	5.9	0.91	0.40	4.4	-1.7	23.8	1.6	19.4	42
Mg	A	2.7	0.89	0.12	0.34	0.75	-2.1	4.3	1.8	3.6	54
	B	3.5	0.99	0.15	0.28	1.7	-1.8	5.1	1.6	3.4	42
K	A	0.57	0.20	0.12	0.65	0.09	-1.4	1.1	2.7	0.84	54
	B	0.67	0.19	0.03	0.28	0.38	-1.6	1.3	3.3	0.92	42
Na	A	1.3	0.86	0.12	0.65	0.09	-1.4	5.7	5.2	5.6	54
	B	1.1	0.63	0.10	0.60	0.11	-1.5	2.2	1.8	2.1	42
Fe	A	0.21	0.21	0.029	0.98	0.030	-0.88	1.2	4.5	1.1	53
	B	0.26	0.27	0.041	1.0	0.010	-0.94	1.2	3.6	1.2	42
PO ₄	A	0.050	0.033	0.004	0.66	0.010	-1.2	0.14	2.7	0.13	54
	B	0.052	0.032	0.005	0.61	0.01	-1.3	0.12	2.2	0.11	42
NO ₃	A	0.42	0.22	0.03	0.53	0.13	-1.2	1.4	4.4	1.3	54
	B	0.36	0.16	0.02	0.43	0.15	-1.4	0.90	3.4	0.75	42
Cl	A	1.3	1.9	0.27	1.5	0.10	-0.60	10.4	4.7	10.3	54
	B	2.9	4.5	0.71	1.6	0.20	-0.60	17.8	3.1	16.3	40
Carbon (total)	A	10.0	4.1	0.66	0.38	3.0	-1.9	21.0	2.4	18.0	40
	B	13.2	4.1	0.70	0.33	3.0	-2.3	22.0	2.2	19.0	40

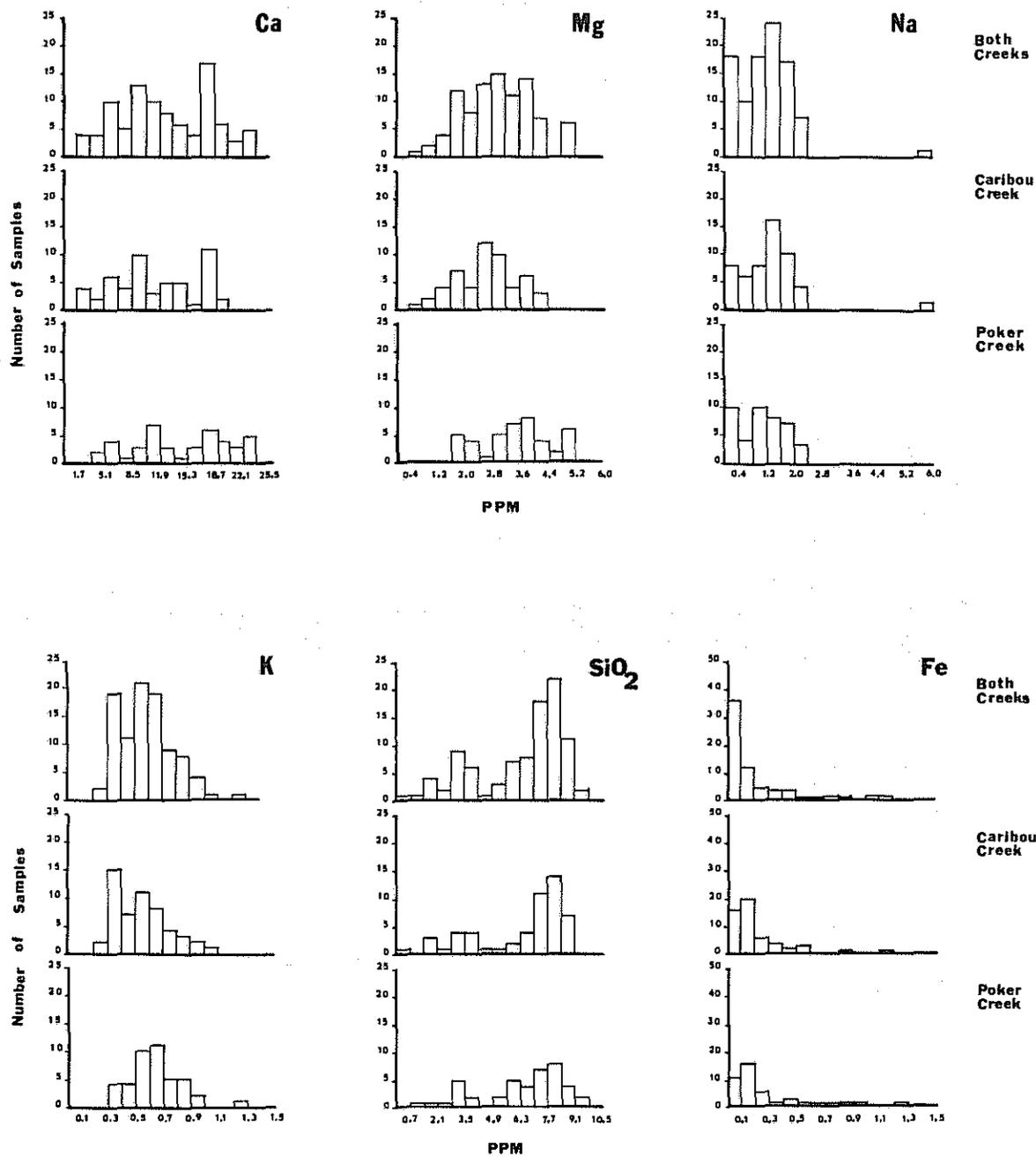


Figure 3a. Histograms of the number of samples versus the ppm of Ca, Mg, Na, K, SiO₂, Fe, Cl, NO₃, SO₄, PO₄ and total carbon for Poker Creek, Caribou Creek and both creeks combined.

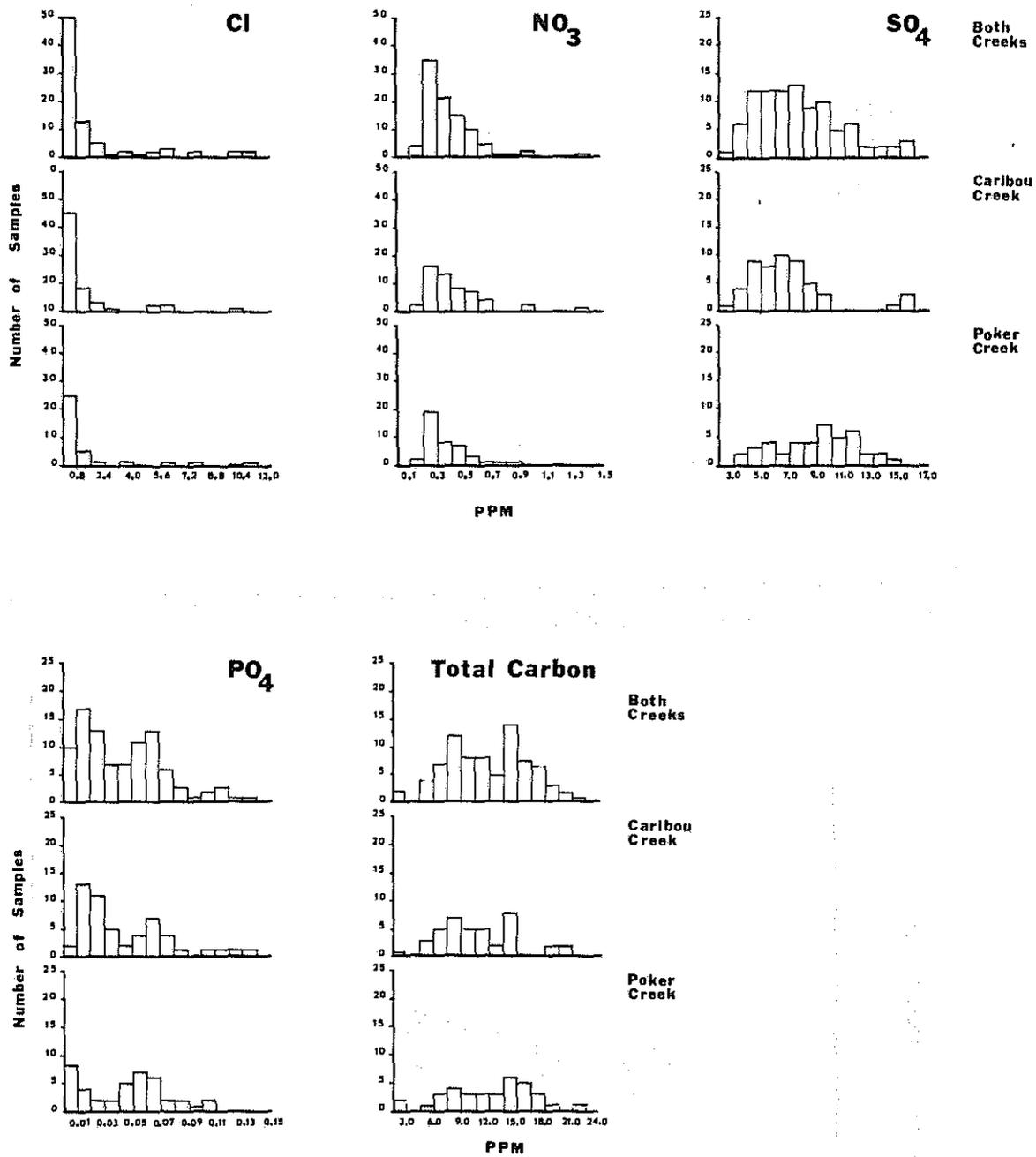


Figure 3b. Histograms of the number of samples versus the ppm of Ca, Mg, Na, K, SiO₂, Fe, Cl, NO₃, SO₄, PO₄ and total carbon for Poker Creek, Caribou Creek and both creeks combined.

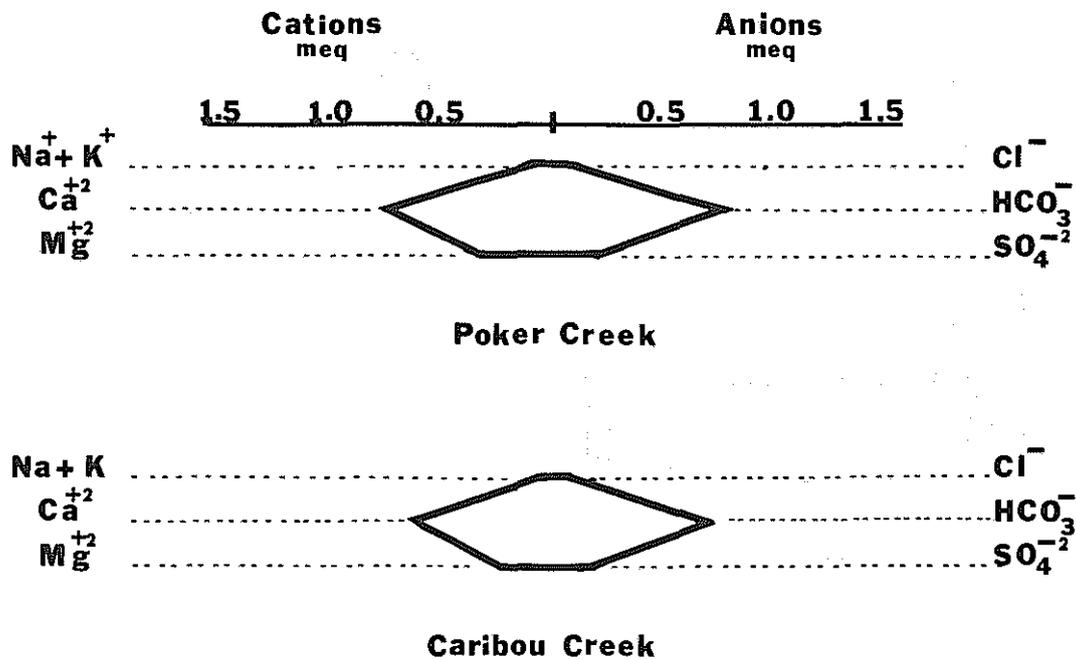


Figure 4. Stiff diagram showing the major-ion composition of Poker Creek and Caribou Creek.

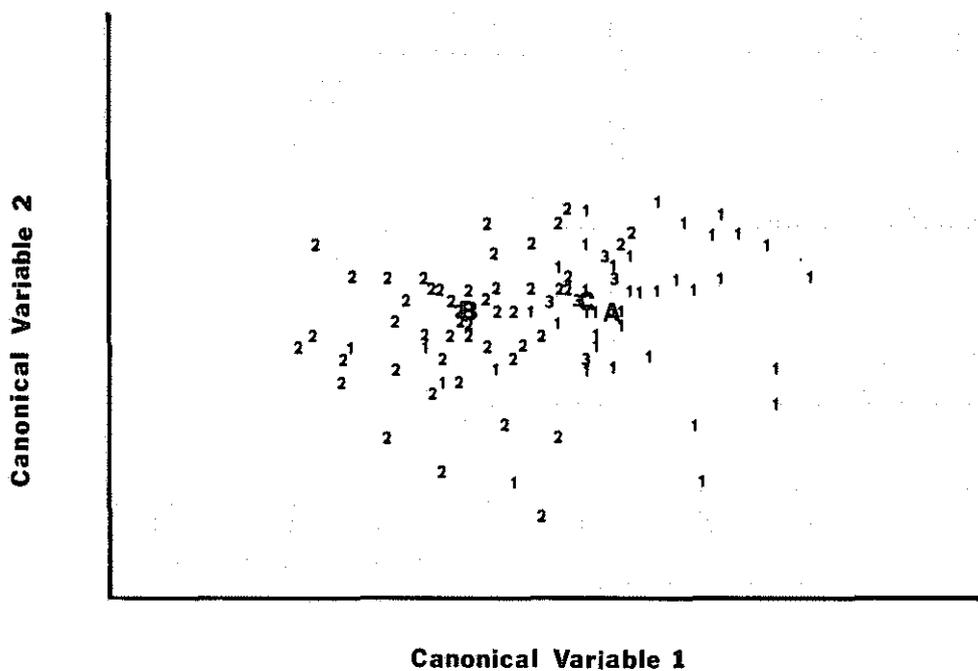


Figure 5. Canonical variate plot showing the best 2-dimensional separation of Poker Creek (1), Caribou Creek (2), Poker Creek below the confluence (3) and the compositional means A, B and C, respectively, of these groups.

Multivariate Statistics

We used principal components analysis to examine relationships among the chemical variables, multiple discriminant analysis to distinguish compositionally between the two streams, and cluster analysis followed by multiple discriminate analysis to seek and analyze compositional groupings in the data.

Principal components analysis. We performed a principal components analysis of the complete data set of 102 samples and ten variables for the natural waters, and for a reduced data set of five variables for the natural waters and for solutions from the rock dissolution experiments. The correlation matrix for the 102-sample, 10-variable set of natural waters is shown in Table 2a. The correlation coefficients show only moderate relationships among the variables, in that many of the correlation coefficients are statistically significant, but the linear relation among such variables is not pronounced.

The eigen values and cumulative proportion of the variance explained by the different eigen vectors are shown in Table 2b, where it can be seen that three factors or eigen vectors account for 62% of the variance of the data set. The variable loadings on these three factors after rotation are shown in Table 2c. The variance of sodium and nitrate is poorly mapped by these three factors; five factors would be required to show these variables. Factor 1 consists of the variables Ca, K, Mg, SO_4 , and Na. Factor 2 consists of SiO_2 with an antipathetic relationship to Cl, while Factor 3 maps the behavior of Fe. These factors indicate that the alkalis, alkaline earths and sulfate behave as a group, and that SiO_2 and Fe behave independently of the major ions.

The relationships among the variables are not particularly well defined in that expected geochemical relationships were not revealed. We conclude that -- although there are moderate correlations among the variables, and these correlations were enhanced by the principal components analysis -- the analysis did not reveal any fresh insight into the compositional relationships among variables. This should not be interpreted as an indictment of the technique; principal components analysis simply yielded little new information.

Table 2. Summary of Principal Components Analysis of Poker Creek and Caribou Creek Waters.

Table 2a. Correlation Matrix.

	SO ₄	SiO ₂	Ca	Mg	K	Na	Fe	PO ₄	NO ₃	Cl
SO ₄	1.									
SiO ₂	-.02	1.								
Ca	0.56	0.21	1.							
Mg	0.46	0.36	0.48	1.						
K	0.27	0.32	0.49	0.53	1.					
Na	0.21	-0.0	0.51	0.21	0.33	1.				
Fe	-.04	-.34	-.05	-.09	0.17	0.02	1.			
PO ₄	-.34	-.05	-.26	-.24	0.03	-.14	0.31	1.		
NO ₃	0.22	0.22	0.27	0.37	0.12	0.28	-.22	-.23	1.	
Cl	0.17	-.47	0.18	0.03	-.05	0.11	0.08	-.10	-.03	1.

Table 2b. Eigen Values and Eigen Vectors.

Eigen Vector	Eigen Value	Cumulative Proportion of Total Variance
1	3.1	0.31
2	1.7	0.48
3	1.4	0.62
4	0.91	0.71
5	0.73	0.71
6	0.67	0.79
7	0.54	0.91
8	0.37	0.94
9	0.32	0.98
10	0.24	1.0

Table 2c. Sorted and Rotated Factor Loadings.

Variable	Factor 1	Factor 2	Factor 3
Ca	0.83	0.	0.
K	0.76	0.30	0.29
Mg	0.72	0.	0.
SO ₄	0.64	0.	-0.30
Na	0.61	0.	0.
SiO ₂	0.	0.85	0.
Cl	0.	-0.79	0.
Fe	0.	-0.26	0.78
PO ₄	0.	0.	0.72
NO ₃	0.36	0.	-0.48

Principal components analysis was carried out on a five-variable set of natural-water samples from Poker Creek and Caribou Creek, and for the rock-dissolution data. In both cases, three eigen vectors were obtained that accounted for more than 90% of the variance in the rock-dissolution data and 85% of the variance for the natural waters. A two-factor solution was rejected because the variance of K and Mg was not sufficiently accounted for.

The eigen vectors for Poker Creek waters and for the dissolution of Poker Creek rocks show that magnesium was the main variable comprising a single factor. For the Caribou Creek rocks and water, magnesium was strongly associated with potassium on a single factor. A possible explanation for these loadings is that the bedrock of Poker Creek may be dominated by chlorite, whereas the Caribou Creek bedrock may be dominated by muscovite.

In the natural waters for both drainages, the association Ca-Na-K is evident, suggesting feldspar weathering. Silica appears as the main variable on a single factor, implying that there is little relationship between the behavior of silica and the other variables. These differences are discussed further in the section dealing with multiple discriminant analysis.

Multiple discriminant analysis. The purpose of this analysis was to determine if the waters of Poker Creek and Caribou Creek could be distinguished from one another on the basis of their chemical composition.

Training groups consisting of all samples from each of the two drainages were selected. Summary statistics for these samples and for a group of samples from below the confluence of Poker Creek and Caribou Creek are shown in Table 3. These groups were used in a stepwise multiple discriminant analysis (BMDP 7M; Dixon, 1979) in which a linear function of the chemical variables was derived that minimizes the within-group variance and maximizes the between-group variance.

The discriminant functions derived are:

$$D_{PKR} = 0.572SiO_2 + 0.240Ca + 2.89Mg - 0.384Na - 0.452NO_3 - 9.18$$
$$D_{CRB} = 0.913SiO_2 + 0.042Ca + 1.28Mg + 1.17Na - 4.63NO_3 - 7.27$$

For a given sample, if D_{PKR} is less than D_{CRB} , the sample is assigned to Poker Creek. On the basis of these functions, 81% of the Poker Creek samples and 80% of the Caribou Creek samples were assigned to the correct drainage.

Table 3. Summary Statistics of the Training Groups Used in the Discriminant Analysis of Poker Creek and Caribou Creek Waters (parts per million).

Variable	Poker Creek		Caribou Creek		Confluence		All Samples	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
SO ₄	8.6	2.9	6.7	2.9	7.6	2.1	7.5	2.9
SiO ₂	6.3	2.2	6.4	2.3	5.0	2.1	6.3	2.3
Ca	15.	5.9	11.	5.0	13.	6.7	13.	5.4
Mg	3.5	1.0	2.7	0.9	3.1	0.3	3.0	0.9
K	0.7	0.2	0.6	0.2	0.6	0.07	0.6	0.2
Na	1.1	0.6	1.3	0.9	1.2	0.8	1.2	0.8
PO ₄	0.05	0.03	0.05	0.03	0.07	0.04	0.05	0.03
NO ₃	0.4	0.16	0.4	0.2	0.3	0.03	0.4	0.2

The six samples from below the confluence of the two streams were assigned to Poker Creek, reflecting the greater flow and compositional dominance of this stream.

We interpret these results to mean that significant, though subtle, compositional differences exist between the two streams. The most important variable distinguishing the two streams is magnesium, followed by nitrate, sodium, calcium, and silica in that order. The selection of magnesium as a major variable agrees with the selection of magnesium as a major variable in the principal components analysis. The best two-dimensional plot for the samples is shown in the canonical-variate plot of Figure 5, where the 1s are Poker Creek samples, 2s are Caribou Creek samples, 3s are from below the confluence of the two streams, and A, B and C are the respective means of the three groups.

Cluster analysis. Using cluster analysis, we examined the data for the natural waters for compositional groupings. Although both cluster analysis and discriminant analysis are used in examining structural groupings in a data set, the two analyses proceed from different premises. In discriminant analysis, the structure is recognized beforehand; i.e., we know at the start that there are two groups of samples, those from Poker Creek and those from

Caribou Creek. The problem addressed by discriminant analysis is that given these two groups of samples, can they be discerned in the variables measured? No structure is assumed beforehand in cluster analysis. The question is posed "Here is a set of variables measured on a number of samples; what similarities exist among samples?" Stated another way, can groupings of samples be found that have like compositions?

We performed a Q-mode cluster analysis (Parks, 1970) coupled with a dendrograph routine of McCammon and Wenninger (1970). These methods calculate the pairwise similarity coefficients among the samples based on all the measured variables, and group the samples in order of decreasing similarity, showing the groupings graphically in the form of a dendrograph. Figure 6 is the dendrograph for the pre-1978 analyses of Poker Creek and Caribou Creek using ten chemical variables. At least six compositional groups are evident. Three and two compositional groups are evident at lower levels of similarity. In none of these groups are the samples from the two drainages clearly separated; samples from both drainages are present in all groups.

We examined the chemical variables responsible for the clustering by means of multiple discriminant analysis. We found that all the variables were used in the clustering, and the variables selected in decreasing order of importance (discriminating power) are Ca, K, Mg, PO₄, NO₃, Fe, SO₄, SiO₂, Cl, and Na. The canonical plot of the six groups shown in Figure 6 is linear, suggesting a continuous, gradational compositional change among the water samples in the different cluster groups. The reason for this strong linearity is not clear. If we examine the composition of the two extreme groups, 5 and 3, and the midgroup, 2, (Table 4) we see that -- with the exception of the minor constituents -- the major ions decrease in concentration in going from 5 to 2 to 3. Samples with the highest concentrations are clustered in group 5; those with the lowest are clustered in group 3; those with average concentrations are clustered in group 2; and those in other groups are transitional to these. The samples in the most dilute group (3) came from two locations, C1 and C3, and were collected mainly during June 1971 and June 1972. These localities are adjacent in the southwest part of the watershed. The samples in this "dilute" group may represent the effect of late snowmelt coupled with rain.

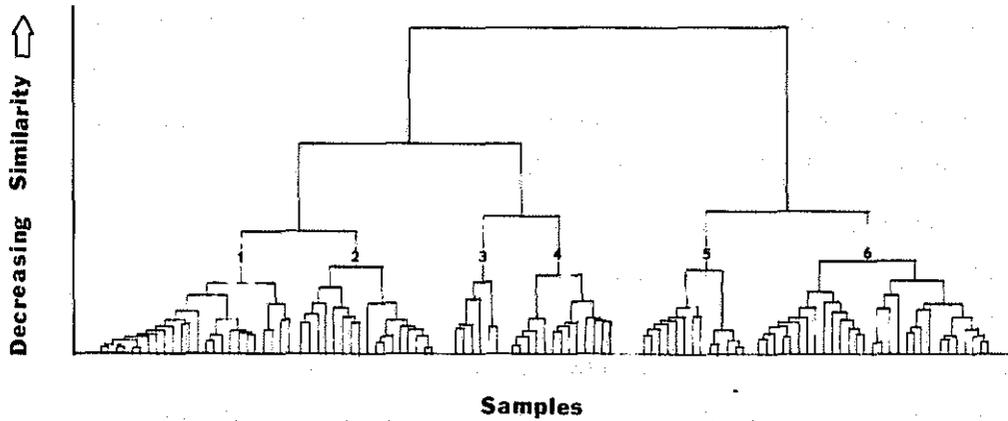


Figure 6. Dendrograph showing the results of the cluster analysis of Poker Creek and Caribou Creek waters.

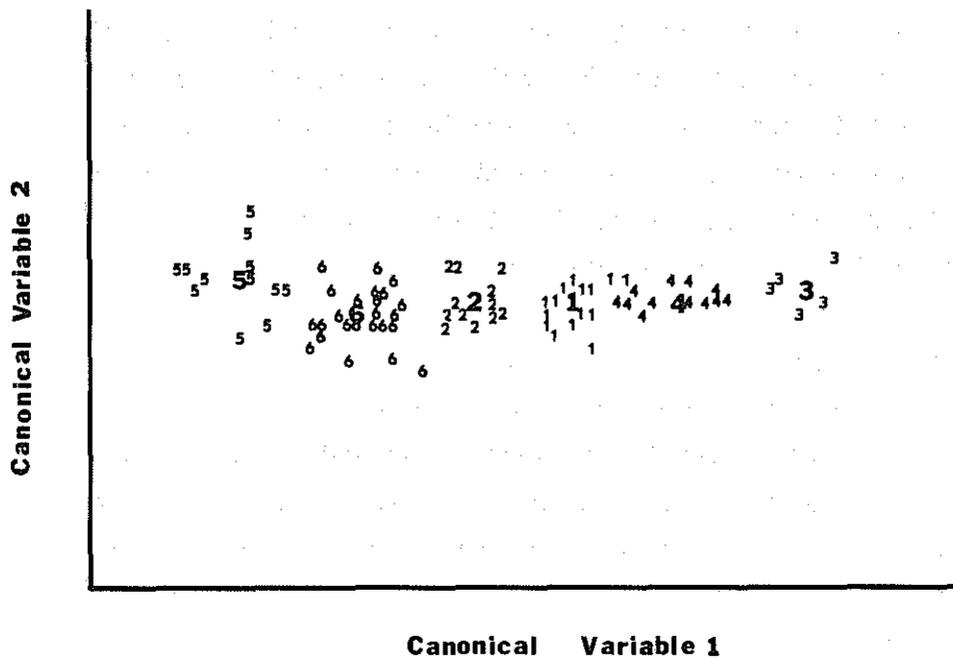


Figure 7. Canonical variate plot from the discriminant analysis of the 6 cluster-analysis groups shown in Figure 5.

The samples from group 5 are from both drainages with both CM and Pm localities dominant. The samples were collected in the winter months of 1974. Assuming that no differences in laboratory procedures had occurred since 1971, we speculate that this compositional grouping represents extreme low-flow conditions dominated by groundwater discharge.

Table 4. Composition of Several Cluster-Analysis Groups.

Variable	Group 5	Group 2	Group 3
SO ₄	9.9	7.2	4.5
SiO ₂	7.6	6.5	2.9
Ca	20.3	11.6	5.6
Mg	4.2	3.3	1.3
K	0.84	0.63	0.39
Na	2.1	1.0	0.84
Fe	0.23	0.26	0.18
PO ₄	0.04	0.05	0.05
NO ₃	0.59	0.39	0.22
Cl	1.2	1.8	1.3

We postulated that the concentration of ions in the streams should be inversely related to discharge, since high discharge means that the flow is the result of snowmelt or rain -- both of which are deficient in dissolved constituents. We plotted the discharge of Poker Creek and Caribou Creek versus time for the period 1971-1977 (U.S. Geological Survey, 1971-1977). Flow generally increases into the summer with occasional storm-event peak flows. As the summer ends, flow tends to decrease, and by October the flow shows a steady decrease until the following spring breakup. The lowest flows occur in late winter (generally April) before the first thaws.

Comparison of the discharges from streams in the watershed could not be made on an absolute basis because of the large difference in flow volume among

the streams. To circumvent this problem, we normalized the discharge of the different streams (tributaries of Poker Creek and Caribou Creek) to their average discharge. The discharge was converted to standard scores (units of standard deviation about the mean). The concentrations of the different ions were then compared for all the streams at the same relative discharge level. We found little variation in the concentration of the dissolved ions with variation in discharge. We conclude that discharge alone cannot account for the compositional differences observed in the data.

ROCK DISSOLUTION STUDIES

Bedrock Dissolution

The purpose of these experiments was to obtain data on the effect of bedrock on the composition of the waters in contact with the rock. Samples of bedrock were taken from available outcrops, which were very scarce in the two drainage basins. Caribou Creek is represented by a rock sample taken from Haystack VABM and Poker Creek by a sample from Poker VABM (see Figure 2). These samples simply represent material from the two drainages available for study. The chemical compositions of the two samples are given in Table 5. Analyses were performed by Skyline Labs, Inc., of Denver, Colorado. Both samples are greenschist facies, chloritic, quartz-mica schists. The rocks are silica rich and calcium deficient relative to the average shale, which is the sedimentary precursor of these metamorphic rocks.

Table 5. Chemical Composition of Bedrock Samples (%).

Sample Drainage	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	MnO
Poker Creek	72.6	11.5	1.4	5.7	2.3	0.15	0.74	2.3	0.21
Caribou Creek	69.7	16.7	1.7	3.7	2.1	0.15	0.95	2.8	0.12

For the dissolution experiment, we followed a procedure similar to that described by Hawkins and Nelson (1976). Seventy-two crushed rock samples, 2.5 g each, were immersed in 50 ml of distilled water for increments of time ranging from five to 30 days at 30°C, 40°C, and 50°C. The experiments were run in duplicate, and the leachates were analyzed for Na, K, Mg, Ca and SiO₂ using atomic absorption spectrometry. It was found that the concentrations of all ions were generally higher in the leachates from the Poker Creek rock than from the Caribou Creek rock.

The analytical data were used to distinguish between the natural waters of Caribou Creek and Poker Creek based on differences in the composition of solutions obtained by leaching bedrock samples from the two drainages. Multiple discriminant analysis was used. Caribou Creek and Poker Creek rock-dissolution data were used as training groups for the derivation of the discriminant function, which was then used to classify the natural waters of the two drainages. The variables Mg, Na, and K were selected by the stepwise procedure for the discriminant function. From the discriminant functions derived, all solutions from the rock-dissolution experiments were correctly assigned to the proper group and -- most importantly -- 74% of the natural water samples of Poker Creek and 62% of those for Caribou Creek were correctly assigned to the proper drainage. We interpret these results to mean that the bedrock composition exerts a significant effect on the chemical composition of the waters draining the areas, and that bedrock differences contribute to the difference in chemical composition observed for the two streams.

Kinetic Data

Following Hawkins and Nelson (1976), the rock-dissolution data were used to derive rate constants for the dissolution of bedrock under assumed natural conditions. The estimated rate constants for K and SiO₂ at 5°C are 3.8×10^{-6} day⁻¹, and 7.3×10^{-6} day⁻¹, respectively. Water must be in contact with bedrock for about 200 days to reach observed stream-water concentrations at 5°C. This estimate is probably within a factor of 3 to 5 of the correct value and is similar to those found by Hawkins and Nelson for the dissolution of a metagraywacke.

An important result of the kinetic study is that -- based on the rock dissolution data -- the rocks studied probably aren't the immediate source for all the dissolved constituents in the streams. The calcium content is far too low, and an unusually long period of leaching would be required to yield calcium concentrations similar to those observed in the streams. While a calcium content of about 5% in the rocks would yield a solution of the requisite concentration, the high calcium concentration probably results from interactions of precipitation with vegetation and soil.

HYDROGEOCHEMISTRY OF THE WATERSHED

The composition of the waters draining the watershed are distinctly different from the solutions resulting from the bedrock-dissolution experiments. The natural waters are more concentrated and are dominated by calcium. The rock-dissolution solutions are enriched in potassium and are deficient in calcium. Table 6 presents data on the composition of precipitation.

Table 7 is a summary of data from Van Cleve (unpublished), Lotspeich et al. (1970) and this study. Figure 8 is a ternary plot of the mole percentages of calcium, magnesium and potassium in the various fluids and bedrock listed in Table 7. The near coincidence of the soil extracts, aspen runoff, and exchangeable cations in the soil is striking, as is the proximity of the Poker Creek and Caribou Creek waters to these points. Note especially that these points are at about the same Ca-Mg ratio as the rock-dissolution data, but they are potassium deficient with respect to the dissolution data. Note finally that the bedrock clearly dissolves incongruently, inasmuch as the bedrock composition point is far removed from that for solutions arising from its dissolution.

It seems that the natural fluids resulting from the decomposition of the rock and mineral soil are initially potassium rich. Potassium is an essential nutrient and is also preferentially sorbed in most ion-exchange reactions, so plants and soils tend to retain potassium. The remaining solution is relatively depleted in potassium, and is relatively more concentrated in Ca

Table 6a. Elemental Contribution from Rain (from Van Cleve, unpublished).

Element	Average Concentration (ppm)
Ca	0.40
Mg	0.02
K	0.07
Na	0.02

Table 6b. Elemental Contribution from Snow (this study).

Element	Average Concentration (ppm)	Standard Deviation	Number of Samples
Ca	0.383	0.205	9
Mg	0.020	0.009	8
K	0.105	0.026	8
Na	0.405	0.065	9

Table 7. Average Concentrations of Calcium, Magnesium, and Potassium in Natural Waters, Soil Extracts, Vegetation Runoff, Rock-dissolution Solutions and Rocks.

Material	Ca(ppm)	Ca(mMol)	Mg(ppm)	Mg(mMol)	K(ppm)	K(mMol)
Aqueous phase recycled to forest floor (Van Cleeve, unpublished)	23.1	0.58	3.0	0.12	3.1	0.08
Average of 25 soil extracts (Lotspeich et al., 1970)	43.6	1.09	5.57	0.23	4.26	0.11
Average of 20 water samples from unburned drainages, Fortymile area (Lotspeich et al., 1970)	15.6	0.39	5.37	0.22	1.76	0.05
Average of all Poker Creek and Caribou Creek waters	13.6	0.34	3.07	0.13	0.63	0.02
Average of Poker Creek and Caribou Creek waters, low-flow	20.1	0.50	3.54	0.15	0.80	0.02
Average rock dissolution solutions	3.04	0.08	0.54	0.02	3.29	0.08
Average bedrock		2.68*		32.9*		53.1*

* mMol/100 g rock

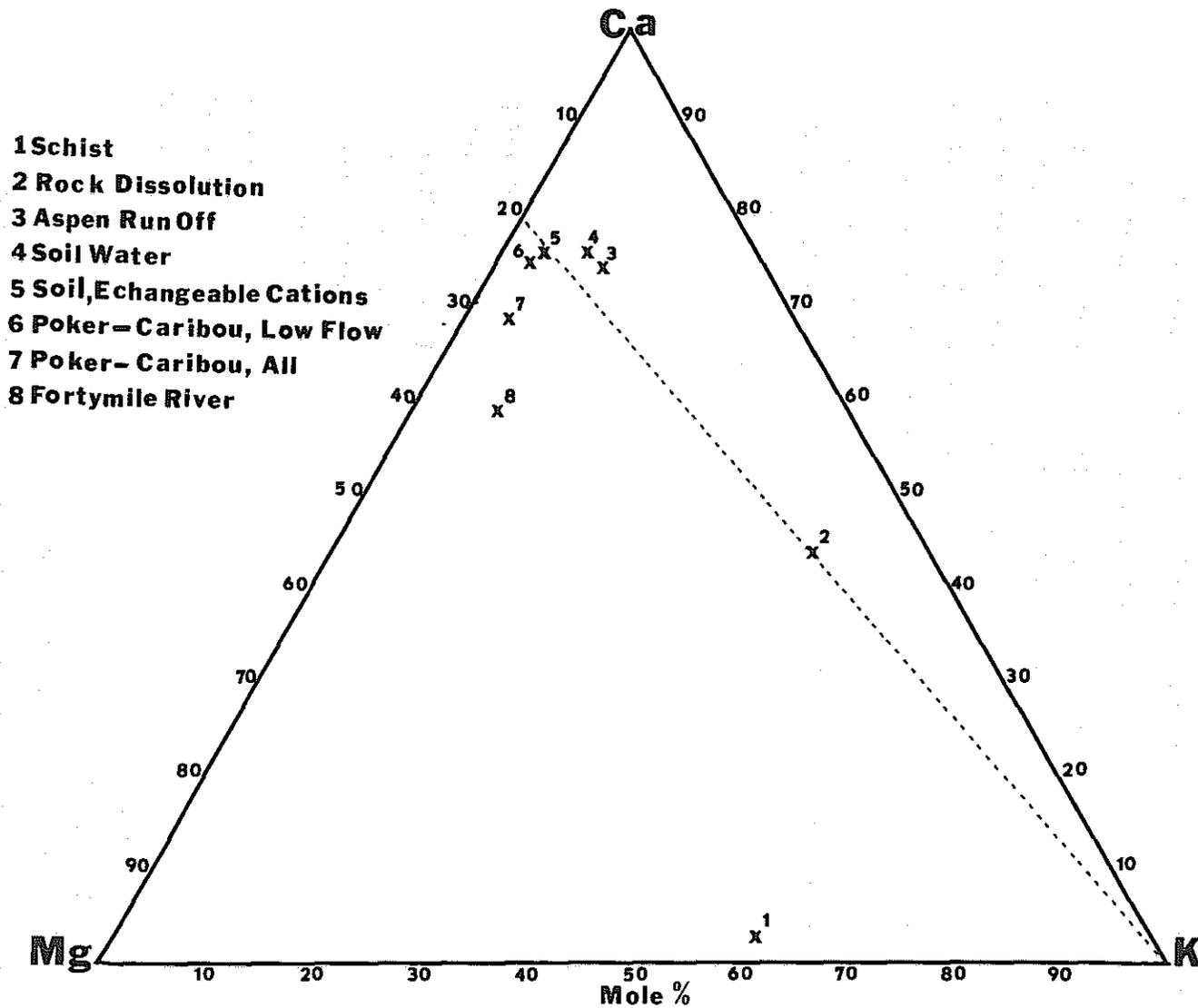


Figure 8. Ternary plot of the mole ratios of K, Mg and Ca for various natural waters and solutions from laboratory experiments. The dashed line on the diagram represents compositions with a fixed Ca/Mg ratio and varying K content.

and Mg because of the selective removal of K, and because of the effect of evapotranspiration. The Ca-Mg ratio remains the same in this fluid as in the original "mineral" solution. The concentrated residual solution infiltrates and runs off, imparting a characteristic composition to the stream and groundwater. The water may subsequently become enriched in magnesium relative to calcium as indicated by the compositional shift from the Poker Creek and Caribou Creek "low-flow" data point, to the point for all the Poker Creek and Caribou Creek data, to that for the Fortymile waters. The essential feature of the soil-plant reservoir is that it serves to retain potassium and concentrate the original "mineral" solution through evapotranspiration. We can infer from this model that if the soil-vegetation reservoir were perturbed (e.g., through fire or disturbance of the soil), the result should be a leakage of potassium to the surface waters. Such a "K-leakage" was observed by Lotspeich et al. (1970) in burned areas of the Fortymile region. The leakage is short lived rather than permanent as Johnson and Needham (1966) discuss.

CONCLUSIONS

With the exception of the ions contributed by precipitation (Tables 6a and 6b), the bedrock and mineral soil are the ultimate sources for the dissolved constituents in the streams.

Based on the average flow of the streams for the period 1971 to 1977, about 1.4×10^{13} g/yr of water leave the watershed each year. The average calcium concentration of this water is 14 mg/l, the area of the watershed is about 12,000 hectares (46 mi²), and the calcium content of the bedrock is 0.1%. Using these data, about 17 metric tons of rock per hectare per year are chemically removed from the watershed.

The rock and mineral soils dissolve incongruently with a first-order rate constant of about 5×10^{-6} day⁻¹ (K and SiO₂ combined). The resulting solution is potassium-calcium-magnesium rich, and the molar ratios of ions in solution are different from the corresponding molar ratios of the parent rock. The plant-soil environment affects this solution primarily through

potassium sorption and evapotranspiration. This results in a fluid that is relatively depleted in potassium, and enriched in calcium and magnesium -- yet this fluid has the same molar ratio of Ca to Mg as the original "mineral" solution. This fluid is the dominant contributor of ions to the stream waters.

The primary effect of a disturbance of the soil-plant reservoir is leakage of potassium to the stream. Contrary to expectations, the volume of discharge has little effect on the concentration of ions in the stream.

Multiple discriminant analysis was particularly useful in separating Poker Creek waters from Caribou Creek waters on the basis of their composition. Using rock-dissolution data as training groups, it was also possible to discriminate between the two natural waters. We conclude that there are differences in bedrock composition and "chemical maturity" -- i.e., loss of K, increased Ca and Mg, and increased Mg/Ca in the drainages of the two streams sufficient to imprint subtle but distinctive chemical signatures on the waters of the two drainages.

Cluster analysis revealed compositional groupings in the data that were apparently related to the location of the samples and the time of sampling. Differences between the two streams were not evident from the results of this method.

Principal components analysis permitted a reduction in the dimensionality of the data set but revealed neither unsuspected nor particularly useful relationships among the variables.

Finally, continued long-term measurements of the quantity and composition of precipitation, surface water, groundwater and fluids in the soil-plant reservoir are needed to refine the geochemical interpretations presented here.

ACKNOWLEDGEMENTS

This work was supported by a grant from the U.S. Forest Service. We thank C. Slaughter and J. Hilgert of the Forest Service for their support and data. We thank K. Van Cleve of the University of Alaska for his data and for

the use of his laboratory. We thank L. Burns of Stanford University for her initial work on this project.

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