UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

GEOCHEMICAL VARIATION IN A COPPER-BEARING REDBED SEQUENCE OF THE RAVALLI GROUP (BELT SUPERGROUP), NORTHWESTERN MONTANA AND NORTHERN IDAHO

PART A. GEOLOGICAL INTERPRETATION

By

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This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards nor with the North American Stratigraphic Code

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ABSTRACT

This report describes the results of a geochemical survey of a regionally extensive, Cu-bearing redbed sequence in the Ravalli Group (Middle Proterozoic Belt Supergroup) of northwestern Montana and northern Idaho. The survey was based on random sampling in 19 stratigraphic sections. The samples were collected according to a five-level hierarchical sampling scheme designed primarily to ascertain the proportion of geochemical variation which could be viewed as regional or basinwide.

The redbed sequence of this report consists of the Spokane, Grinnell, and St. Regis Formations and their probable lithostratigraphic equivalents. In their type areas, the three formations each exhibit a distinct kind of quartzite. Each quartzite-type decreases in abundance away from its type area, suggesting that the sequence was derived from more than one sediment source. Light REE enrichment in the sequence indicates that all potential sources were continental.

Most of the geochemical variability in the sequence reflects variation in proportion of mudstone (argillite and siltite) from sample to sample. Basinwide, many mud-related elements decrease northeastward because of increase in quartzite in that direction. Geochemical oddities include exceptionally low Sr and As overall, high Nb and Yb in the Helena Embayment (in a distinctive heavy-mineral suite?), locally high Pb in the Rogers Pass area (probably due to hydrothermal activity), locally high Hg on the east side of Glacier National Park, locally high P (in phosphorite), and a highly erratic distribution in Cu, which probably reflects massive diagenetic(?) rearrangement.

Variability in Cu is enormous in these rocks ranging from <1 - 7600 ppm (parts per million). The average (median) concentration is 4 ppm, uncommonly low for muddy sediments. Secondary concentrations appear at about 100 and 1500(?) ppm Cu, both of which represent epigenetic Cu mineralization. Previous work demonstrated the local presence in these rocks of a concentration around 22 ppm, which was believed to represent the original background level for the sequence. Because a 22 ppm mode is vanishingly small in the data of this study, the bulk of the sequence appears to have been pervasively leached of Cu.

Anomalously high Cu is widespread but spotty; about 3 percent of the total volume of the sequence contains high Cu. If that 3 percent reflects lateral transfer from the low-Cu parts of the sequence, it is estimated that a total of about 1400 teragrams (1,400,000,000,000,000 gm) Cu were solubilized, of which as much as a third (450 teragrams) may have been subsequently redeposited in the high-Cu parts of the sequence. Ag and Hg, and possibly ferrous Fe, Mo, and Sn, were enriched along with the Cu.

Geochemical discriminant analysis indicates that most of the rocks in the sequence display a much greater geochemical resemblance to the St. Regis Formation than they do to either the Spokane or the Grinnell Formations; possibly, these latter formations represent eastern variants in a much larger area of St. Regis-type deposition.

INTRODUCTION

This report describes the results of a geochemical survey of a regionally extensive, Cu-bearing redbed sequence in the Ravalli Group (Belt Supergroup) of northwestern Montana and northern Idaho (fig. 1). This survey examined the variability of elements, primarily Cu, in the Spokane, the Grinnell, and the St. Regis Formations and their probable lithostratigraphic equivalents. This sequence comprises a significant part (as much as 50 percent locally) of the Ravalli Group succession and constitutes a widespread regressive unit in the Belt Basin prior to deposition of the middle Belt carbonate unit (Connor and others, 1984, p. 14). I will hereafter refer to this regressive redbed sequence as "the sequence".

Small, subeconomic accumulations of Cu are widely scattered throughout the sequence. These accumulations are most common in intervals of interbedded red and green argillitic rocks; the green strata in these intervals are a preferred locus of Cu accumulation ("green bed-type Cu" of Harrison and Reynolds, 1979, p. 2). The association with red strata, however, is deemed critical to the formation of the deposits, because some view them as a source of the Cu (Walker, 1989).

These deposits collectively constitute a substantial low-grade Cu resource (see Harrison and Reynolds, 1979; Earhart and others, 1981; Lange and Eby, 1981; and Collins and Smith, 1977). At Blacktail Mountain (fig. 1), Connor and others (1981) noted that much of the non-mineralized strata in a green bed-type Cu deposit had an exceptionally low Cu content. They suggested that the mineralized horizons in the deposit obtained their Cu, at least in part, from adjacent Cu-poor strata. A primary goal of the present study was to examine the regional (basinwide) distribution of Cu in these rocks.

A secondary goal was to examine, in general, the total geochemical variability of this widespread, economically interesting sequence. To a large extent, this involved an attempt to determine how much of the variability of a given geochemical constituent could be viewed as basinwide, or regional. The work was reconnaissance in nature and, as such, employed a formal experimental design based on the hierarchical case of the analysis of variance. It is the only geochemical work in the Belt basin to use such a design, and only one of a few attempted to date in studies of large, mineralized areas (see, for example, Lindsey, 1975, or Johnson and others, 1980).

I wish to express my appreciation to R. L. Earhart, whose good-hearted help in both logistical support and sampling in Glacial National Park was especially welcome, and to Pat Hettinger, Mike Pantea, R. C. Severson, and Robert Weir for assistance in sampling. Special appreciation is due the U.S. National Park Service for permission to sample inside Glacier National Park. I also wish to express my indebtedness to the chemical analysts, without whose able laboratory support this work would not have been possible.

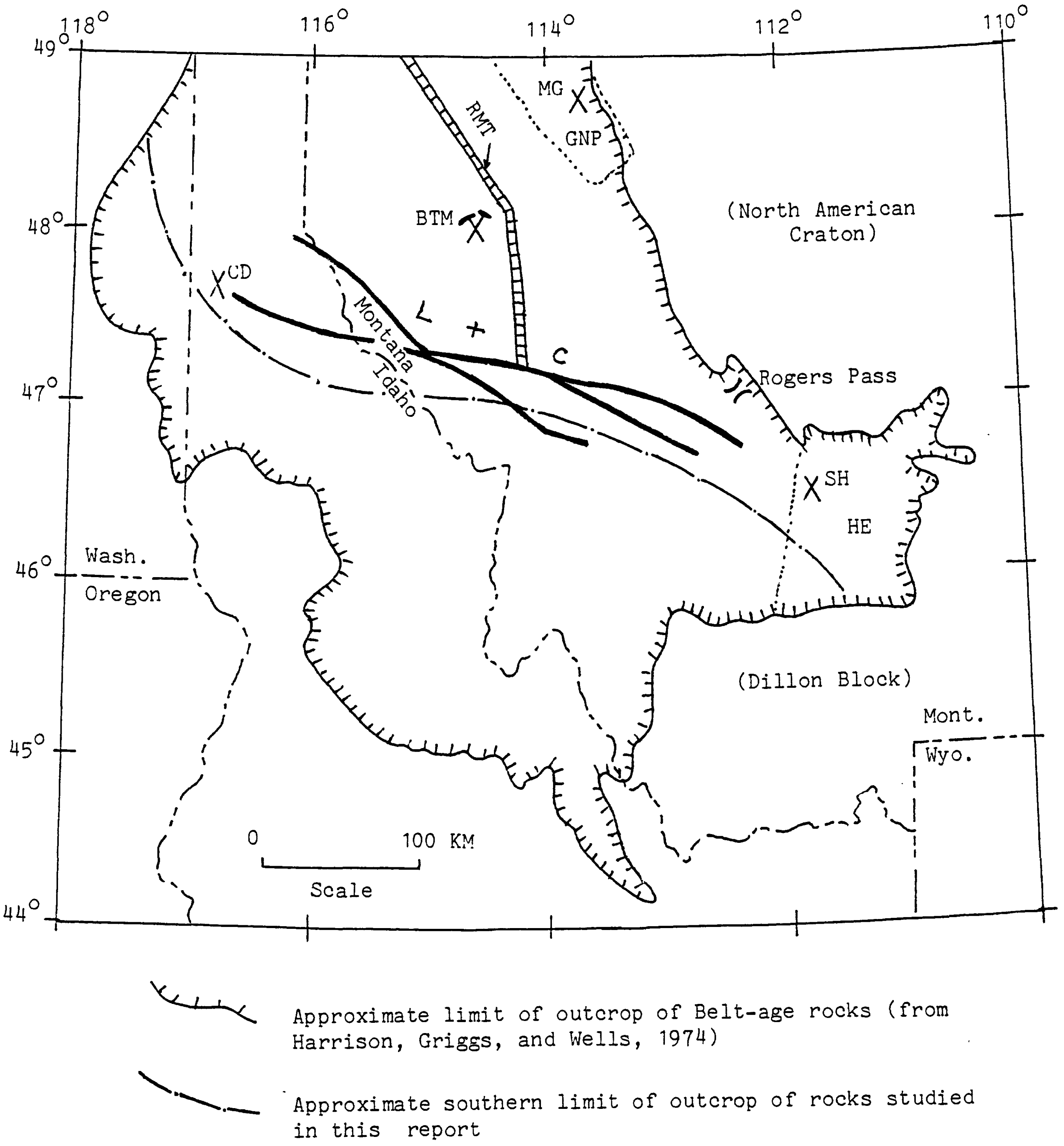


Figure 1. Index map showing distribution of Belt-age rocks. [MG, Mt. Grinnell, type area of Grinnell Formation (Willis, 1902); CD, Coeur d'Alene mining district, type area of St. Regis Formation (Ransome,]905); SH, Spokane Hills, type area of Spokane Formation (Walcott,]899); GNP, Glacier National Park; HE, Helena Embayment; RMT, Rocky Mountain Trench; BTM, Blacktail Mountain; L+C, Lewis and Clark line].

SAMPLING PLAN

This work is based largely on 173 samples collected in a random fashion from 19 relatively well-exposed stratigraphic sections of the sequence spaced over the study area (solid circles, fig 2). A few non-random samples were collected as well from these and one additional stratigraphic section (open circle, section H, fig. 2). In reference to individual samples in this text, sample numbers ending in the letter "R" represent random samples; sample numbers ending in "T" represent samples which were taken as "typical" of some feature in the rocks.

The sampling design underlying the random sample collection was specifically chosen to permit the use of the hierarchical case of the analysis of variance (Krumbein and Slack, 1956). This technique subdivides the total observed variance of a geochemical measurement into parts or components, one of which in this study was defined as "regional" in character; that is, the design purports to assign a stated amount of geochemical variation to lateral (geographic) distance.

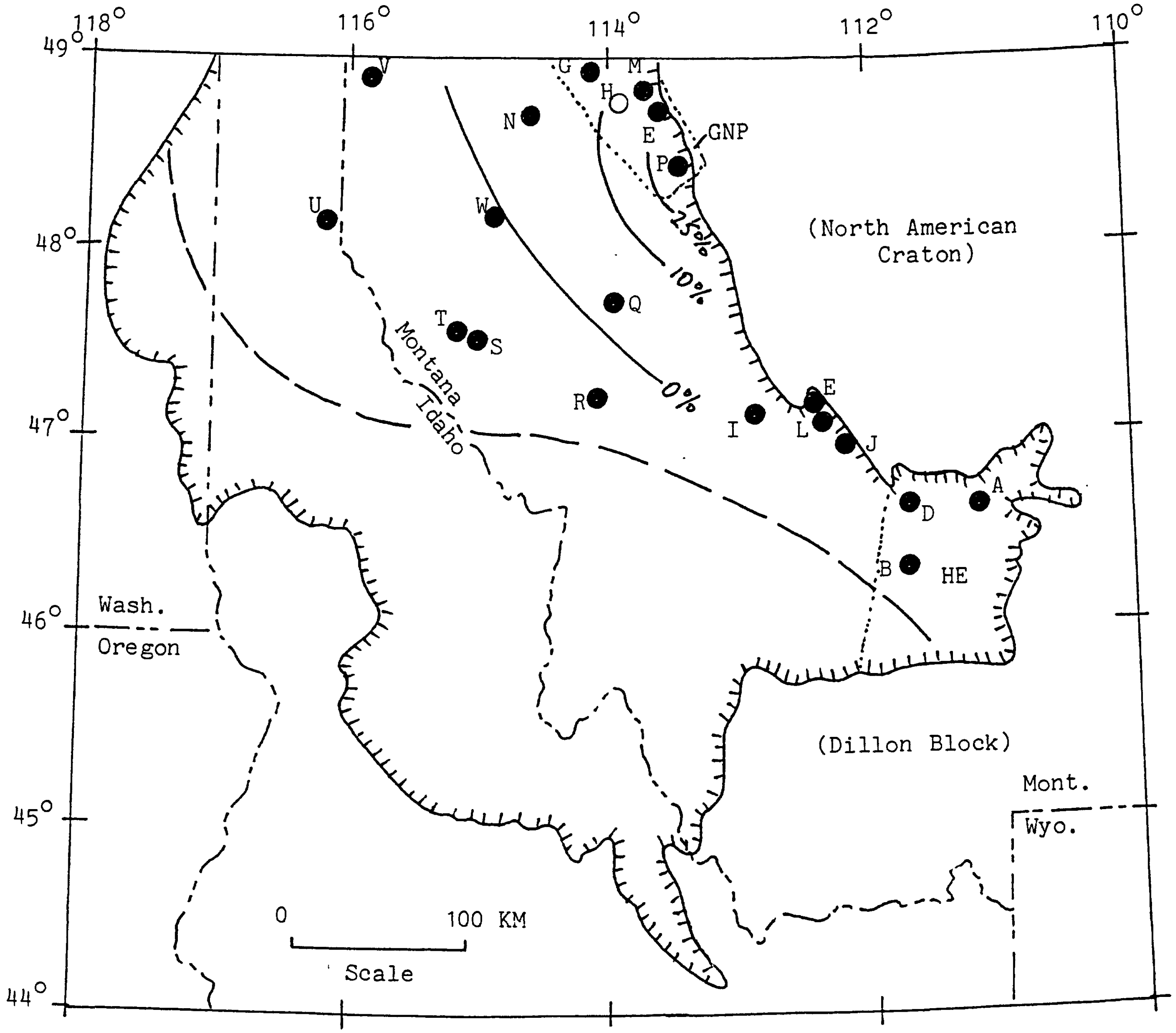
Because all sections in this study lie in thrust blocks of varying size and generally unknown but presumably large throw, there is risk in attempting to equate variation with distance. However, as a realistic palinspastic reconstruction within the basin as a whole is difficult, if not impossible, regional patterns here are of necessity based on spatial relations among the sampled locations where they currently exist rather than at the time of deposition.

Sampling hierarchy

The dividing line between what geographic scale constitutes a regional scale and what does not is technically arbitrary, but in this work limitations on outcrop effectively forced a division at about 50 km. Stratigraphic sections sufficiently exposed for sampling were by happenstance spaced on average about 50 km apart (fig. 2). In terms of the size of the study area (about 400 km from section A, Newlan Creek, to section V, Hoskins Lake), variation at scales greater than about 50 km may reasonably be viewed as regional. Variation at lesser scales then is defined as local.

The sampling scheme in fact was organized into five hierarchical levels; three of which were defined in terms of geographic distance. The first, or regional, level of the sampling hierarchy consisted of eight major areas, labeled 1 through 8 in figure 3. Geochemical differences observed among sample averages in the eight areas clearly represent variation at scales larger than about 50 km.

The second, or next lower, level of the sampling hierarchy consists of two localities within each major area. Most localities consist of a single stratigraphic section but three localities contain a pair of sections: sections F and L in area 3, sections M and E in area 4, and sections S and T in area 7. Ideally, every locality should have a pair of closely-spaced sections but, once again, outcrop limitations prevented this. Geochemical differences observed among averages of the 16 localities define variation at scales from about 10-50 km.



Stratigraphic sections:
A. Newlan Creek
B. Limestone Hills
D. Avalanche Creek
E. Baring Creek
F. Green Mountain
G. Long Bow Lake
H. Dutch Lakes
I. Arrastra Creek
J. Gladstone Creek
L. Rogers Pass
M. Mount Grinnell
N. Coal Creek Canyon
P. Rising Wolf Mountain
Q. North Crow Creek Canyon
R. Lamoose Creek
S. Weeksville
T. Thompson River
U. Clark Fork
V. Hoskins Lake
W. Meadow Peak

Figure 2. Location of sampled stratigraphic sections. Solid circles denote sections used in the hierarchical analysis of geochemical variance. [Percentage contours estimate distribution of Grinnell-type quartzite]

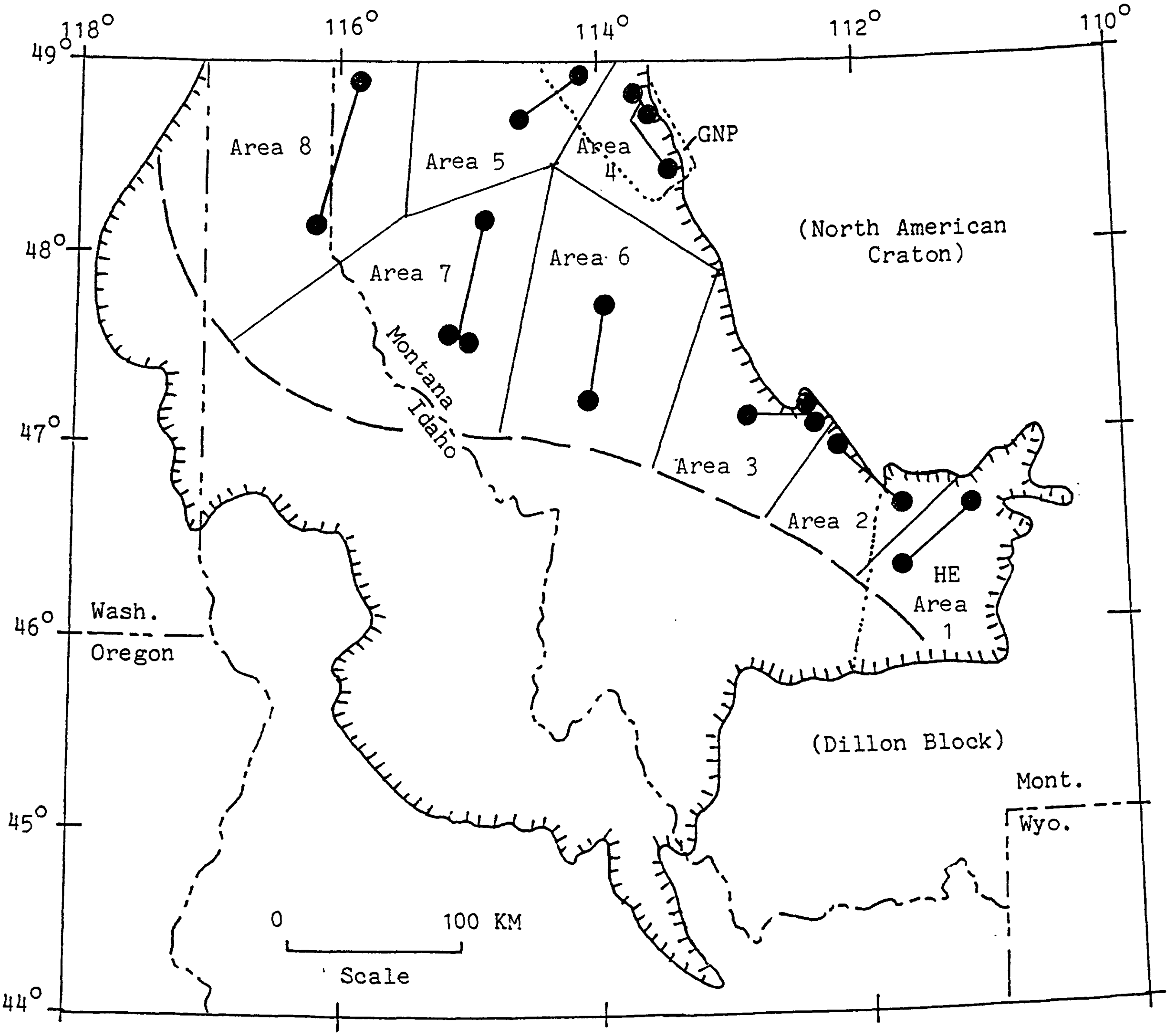


Figure 3. Hierarchical sampling design. The eight numbered areas represent the top level of the sampling hierarchy; each area is represented by a doublet or triplet of stratigraphic sections. [See text for explanation of hierarchy]

The third level of the sampling hierarchy consists of the closely-paired sections (identified above) in areas 3, 4, and 7. Geochemical differences observed among these three section pairs, then, define variation at very short scales, in effect at distances less than about 10 km.

Lastly, two still lower and non-geographic levels of the hierarchy were defined. The fourth level consists of the samples themselves, in the sense that geochemical differences observed among the samples define the variation across layering; that is, stratigraphic variation. The fifth, and bottom, level consists of sample splits (analytical replicates) dispersed through the sample suite. Geochemical differences observed among the splits define variation arising from the laboratory procedures; that is, analytical error.

The magnitude of the geochemical difference observed at each level of the hierarchy provides insight on where in the design "important" variation occurs. Geochemical variation at the second through fifth levels is of particular use in evaluation of efficient sampling strategies (see appendix).

Variance Components

The five levels of the sampling hierarchy define five components of geochemical variance, as follows:

Level	Source of variation		Component definition
	Between:	Within:	
1	Areas	study area	variation at scales >50 km
2	Localities	areas	variation at scales 10-50 km
3	Sections	localities	variation at scales 0-10 km
4	Samples	sections	stratigraphic variation
5	Analyses	samples	analytical error

Mathematically, the hierarchy is defined as:

$$X(ijklm) = M+A(i)+B(ij)+C(ijk)+D(ijkl)+E(ijklm) \qquad (1)$$

where X(ijklm) is the mth analysis of the lth sample in the kth section in the jth locality in the ith area of the study area. The terms to the right, except for M, are deviations about mean values each associated with one of the five levels of the hierarchy. M is the grand mean for all samples in the study. In effect, equation (1) states that each measurement reported by the laboratory (X) may be viewed as the adjustment of a constant (M) by five values, whose magnitudes and signs depend on where in the sampling plan that measurement fell (which area, which locality, etc.).

If statistical assumptions of independence and homogeneous variance in the data are met, the total variability of a given geochemical measurement may be subdivided into the five components of variance described above:

$$V(X) = V(A) + V(B) + V(C) + V(D) + V(E) \qquad (2)$$

where V(X) is the total variance, and the terms on the right are the components. In geochemical studies generally, and in this one in particular, the measurement X is commonly transformed to Log X; the components thereby become logarithmic components. With the log transformation, the right hand skew common in many trace element distributions may be reduced which in turn helps insure the assumptions of independence and homogeneous variance.

Sample collection and analysis

A sample consisted of about 1 kg of chips taken from as much as 15 cm of section; a 10-cm thickness was common. All samples were collected from outcrop and obvious weathering rinds removed. The only tools used in the collection were a geologic pick and, if necessary, a steel chisel. I intended this work to be based on 10 randomly selected samples from each of 19 stratigraphic sections. However, due to unforeseen problems, not all 19 sections ended up with a full complement, and the geochemical examination was ultimately based on only 173 random samples.

Together with the non-random samples, a total of 251 rock samples were submitted for chemical analysis. All samples were submitted to the Denver laboratories of the U.S. Geological Survey in a randomized sequence in order to effectively transform any time-dependent drift in analysis into random errors. Such a procedure guards against subsequent attempts to explain laboratory drift as a geologic phenomenon. Thirty-eight sample splits were randomly dispersed through the suite, and their analysis was used to estimate the degree of analytical error (table 1).

A number of elements were looked for but detected in only a very few or none of the analyses (table 2). One of these elements was gold, which was not detected at 0.1 parts per million in 16 samples of siliceous Grinnell quartzite from the eastern side of Glacier National Park.

The analyses, the analytical methods, short sample descriptions and identification of sample locations within sections appear in Part B of this report (Connor, 1991).

Finally, a continuing problem in geochemical data evaluation is a condition known as left-censoring. When the concentration of an element in one or more samples of a suite falls below the limit of analytical determination, the data for that element is said to be left-censored, and special handling may be required for evaluation. Techniques are available for producing reasonable estimates of the mean and variance of left-censored distributions (Miesch, 1967), but none are available for estimating the individual censored values. Rather, it has become conventional to simply assume small but sensible concentrations for the censored values where evaluation techniques, such as the analysis of variance, require completely numeric data. In this work, such substitution was made on those variables where less than one-third of the values were left-censored (variables with more than one-third censoring were not subjected to the analysis of variance). The substituted values were set equal to 0.7 of the lower limit of analytical determination.

Table 1.--Estimated error of geochemical analysis.

Variable	Error variance	Geometric error	Number of analyses
		X-Ray fluorescence	
SiO2	0.1746	0.42(1)	76
Log Al_2O_3	<.0001	<1.02	76
Log $FeTO_3$(2)	<.0001	<1.02	76
Log MgO	.0002	1.03	74
Log CaO	.0007	1.06	76
Log Na_2O	.0002	1.03	70
Log K2O	<.0001	<1.02	76
Log TiO_2	.0030	1.13	76
Log P_2O_5	.0018	1.10	70
Inductively coupled argon plasma-atomic emission spectrometry			
Log Ba	.0070	1.21	76
Log Be	.0047	1.17	64
Log Ce	.0040	1.16	76
Log Co	.0309	1.50	72
Log Cr	.0016	1.10	76
Log Cu	.0541	1.71	74
Log Dy	.0347	1.54	42
Log Er	.0124	1.29	4
Log Ga	.0049	1.17	76
Log La	.0088	1.24	76
Log Li	.0052	1.18	76
Log Mn	.0012	1.08	76
Log Nb	.0218	1.40	62
Log Nd	.0081	1.23	76
Log Ni	.0017	1.10	74
Log Pb	.0236	1.42	60
Log Pr	.0188	1.37	20
Log Sc	.0012	1.08	74
Log Sm	.1061	2.12	24
Log Sn	.0171	1.35	12
Log Sr	.0009	1.07	76
Log Th	.0293	1.48	68
Log V	.0019	1.11	74
Log Y	.0077	1.22	74
Log Yb	.0155	1.33	62
Log Zn	.0026	1.12	72

Table 1.--Cont.

		Atomic Absorption	
Log As	.0024	1.12	56
Log Hg	.0079	1.23	56
Log Sb	.0122	1.29	56
		Ion selective electrode	
Log Cl	<.0001	<1.02	2
		Potentiometric titration	
Log FeO	.0003	1.04	56
		Neutron activation	
Log U	.0004	1.05	56

(1) Standard error
(2) Total Fe as Fe_2O_3

Table 2.--Elements looked for but rarely detected.

[Data given in parts per million except where noted as percent (%); ratio is number of analyses where element was determined to total number of analyses]

Element	Lower limit of determination	Ratio
Inductively coupled argon plasma-atomic emission spectrometry		
Ag	2	3:289
Bi	10	12:289
Cd	2	0:289
Er	4	6:289
Eu	2	2:289
Gd	10	8:289
Ge	10	0:39
Ho	6	1:289
Mo	2	7:289
Ta	40	0:289
Tb	20	0:289
Atomic absorption		
Au	.1	0:14
Ion selective electrode		
Cl, %	.01	3:63

GEOLOGIC SETTING

The redbed sequence of this report includes the Spokane Formation of Walcott (1899, p. 207), the Grinnell Formation of Willis (1902, p. 322-323), and the St. Regis Formation of Ransome (1905, p. 281-282). In 1979, when I initiated this study, I adopted as a region-wide sampling framework the view of Harrison (1972, fig. 5) that the Spokane, in which he included Willis' Grinnell, and the St. Regis Formations were probable lateral equivalents, most likely representing the eastern and western facies, respectively, of a fine-grained redbed sequence in the Ravalli. Harrison later (1984, written communication) agreed to reinstitution of the name Grinnell, which unit I view here as a third, northeastern facies of the sequence. I use the term Grinnell in the restricted sense of Whipple and others (1984). Together, I believe that these three formations constitute a large regional package of reddened muddy sediment and, as such, they represent a major regressive event in the Ravalli Group (Connor and others, 1984).

I took as the upper boundary of the sequence the top of the dominantly red (or purple) strata in the Ravalli. In eastern exposures this boundary coincides pretty much, but not exactly, with the base of the overlying Empire Formation; in the west it coincides pretty much with the base of the overlying Wallace Formation. The lower boundary is more variable because less was known, at the time of sampling, of the lateral relations among formations beneath the sequence. In eastern exposures, I took the lower boundary as the base of dominantly red (or purple) strata in the Ravalli, which coincides pretty much, but not exactly, with the top of either the Greyson or Appekunny Formations; in western exposures, I took the lower boundary as the contact of the St. Regis with the underlying Revett Formation. Where the Greyson, Appekunny, or Revett Formations are absent or difficult to recognize, the lower boundary was taken on the basis of a color change from gray or green below to purple or red above.

I recognize that these boundaries may be neither physically contiguous nor temporally consistent. Nevertheless, the sequence as a whole appears to form a compositionally coherent interval of regional extent. I suspect that most Belt workers would agree that large parts, of these three formations are lithostratigraphically correlative.

The Spokane Formation in its type area (Spokane Hills, fig. 1) is about 1500 m thick and consists of red and green argillite, silty argillite, and siltite, with minor quartzite and carbonate near the base. The Grinnell Formation in its type area (Mt. Grinnell, fig. 1) is about 900 m thick and consists largely of interlayered red argillitic siltite and white quartzite. The St. Regis Formation in its type area (the Coeur d'Alene Mining District, (fig. 1) is about 240 m thick and consists largely of interlayered and interlaminated purple and green argillite, siltite, and quartzite. All these rocks were metamorphosed to the greenschist facies in pre-middle Cambrian time (Harrison, 1974). Mica crystallinity clearly increases from east to west. Neoformed chlorite and white mica are ubiquitous, and metamorphic biotite is common west of the Rocky Mountain Trench.

Each formation in and near its type area contains a distinctive kind of quartzite. Spokane-type quartzite is thin-bedded, tabular, medium- to coarse-grained, and calcareous. Grinnell-type quartzite is thin- to thick-bedded, lenticular, medium- to coarse-grained, locally conglomeratic, and commonly crowded with red mud chips. St. Regis-type quartzite is laminated to thin-bedded, tabular, very fine-grained, and locally vitreous.

Each quartzite type decreases in abundance away from its type area. Grinnell-type quartzite, for example, uniformly decreases fan-like from a point near section P (fig. 2). This pattern strongly suggests a major source for Grinnell sediment on the North American Craton. In contrast, Boyce (1973) interpreted the St. Regis Formation as the closing phase of deposition on the northeastward prograding Revett prism.

A conspicuous lack of Grinnell-type quartzite in the Spokane in the Helena Embayment suggests that if the Spokane source is cratonic (as is generally assumed), it is apparently a distinctly different part of the craton from that which provided sediment to the Grinnell. Spokane-type quartzite is restricted to the lower part of the Spokane Formation in the Helena Embayment, which is consistent with an eastern or southern source, perhaps the Dillon block (fig. 1).

Average Y/Yb ratios from all parts of the sequence are sufficiently large (8-12) to indicate a strong enrichment in the light end of the rare earth element (REE) suite in these rocks. This enrichment in turn suggests that all sediment sources, wherever they lay, were continental.

DISTRIBUTION OF ELEMENTS

Geochemical summary

A summary of element distributions in the sequence appears in table 3, where observed ranges and selected percentile concentrations in 173 random samples are listed for 45 elements and rock-forming oxides.

The 50th percentiles (medians) collectively constitute the average geochemistry of the sequence. Probable (expected) ranges in element concentration for the sequence may be reasonably taken as the 95 percent range, which is defined as the difference between the 2.5th and 97.5th percentiles. Accordingly, the 97.5th percentile in table 3 readily serves as a threshold against which to judge anomalously high concentrations in the sequence. For example, a sample containing more than 62 parts per million Cu (the 97.5th percentile) must be viewed as highly anomalous. Similarly, the 2.5th percentile concentration may serve as a threshold for judging anomalously low concentrations.

The average chemistry of the sequence is that of shale; at 66 percent SiO_2 and 14 percent Al_2O_3, this chemistry suggests an original composition of about 1/3 quartz and 2/3 clay. Consequently, the distribution of many elements, particularly the trace elements, mirrors the distribution of original mud in the sequence. Major exceptions include CaO (in carbonate), Na_2O (in albite), and P_2O_5 (in apatite).

Table 3.--Distribution of elements.

[Data are in parts per million, except where noted as percent (%); Ratio is number of samples in which constituent was determined to total number of samples analyzed]

Constituent	Ratio	Minimum	Percentile					Maximum
			2.5	5	50	95	97.5	
Ag	1:173	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	4.0
Al_2O_3 %	173:173	1.2	2.5	4.5	14	16	17	19
As	39:39	.40	.40	.40	1.9	7.1	7.4	10
Ba	173:173	91	190	250	570	1400	1500	2600
Be	154:173	<1.0	<1.0	<1.0	2.0	3.0	3.0	4.0
Bi	8:173	<10	<10	<10	<10	10	10	10
CaO %	172:173	<.020	.050	.060	.56	5.8	7.2	12
Ce	173:173	5.0	14	24	68	110	120	130
Cl	2:39	<100	<100	<100	<100	100	100	200
Co	170:173	<1.0	2.0	3.0	11	20	22	25
Cr	173:173	2.0	6.0	8.7	34	50	52	62
Cu	147:148	<1.0	1.0	1.7	4.0	25	62	1400
Dy	74:173	<4.0	<4.0	<4.0	<4.0	10	10	13
Er	3:173	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	5.0
$FeTO_3$ %(1)	173:173	.15	.48	.94	4.1	5.8	6.0	7.9
FeO %	39:39	.060	.060	.060	.78	2.3	2.5	3.3
Ga	168:173	<4.0	<4.0	6.0	17	25	26	31
Gd	6:173	<10	<10	<10	<10	<10	10	10
Hg	31:39	<.010	<.010	<.010	.010	.020	.020	.030
K_2O %	173:173	.29	.85	1.1	3.8	6.1	6.4	7.8
La	173:173	4.0	7.3	12	34	55	61	75
Li	173:173	3.0	9.0	11	43	80	87	120
MgO %	172:173	<.10	.50	.55	2.7	5.1	6.0	8.7
Mn	148:148	53	67	83	350	1200	1600	4800
Mo	4:173	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	4.0
Na_2O %	161:173	<.15	<.15	<.15	1.3	2.5	2.6	3.2
Nb	128:173	<4.0	<4.0	<4.0	8.0	13	15	19
Nd	173:173	6.0	8.3	9.7	34	51	55	64
Ni	170:173	<2.0	2.0	4.7	16	22	24	27
P_2O_5 %	160:173	<.050	<.050	<.050	.12	.19	.22	.65
Pb	147:173	<4.0	<4.0	<4.0	10	33	45	160
Pr	26:173	<10	<10	<10	<10	14	20	20
Sb	39:39	.20	.49	.68	.90	1.6	1.6	1.8
Sc	168:173	<2.0	<2.0	3.0	12	17	17	21
SiO_2 %	173:173	52	57	58	68	86	90	96

Table 3.--Cont.

Sm	31:173	<10	<10	<10	<10	30	30	30
Sn	21:173	<4.0	<4.0	<4.0	<4.0	5.0	6.0	11
Sr	173:173	6.0	12	17	44	96	110	170
Th	156:173	<4.0	<4.0	<4.0	11	18	20	22
TiO_2 %	172:173	<.020	.070	.14	.52	.64	.66	.71
U	39:39	.93	.93	1.3	3.3	5.3	5.4	7.4
V	170:173	<2.0	5.3	11	46	71	75	89
Y	171:173	<2.0	3.0	4.0	15	35	42	49
Yb	143:173	<1.0	<1.0	<1.0	2.0	4.0	4.0	5.0
Zn	164:173	<20	<20	<20	70	110	120	130

(1) Total Fe as Fe_2O_3

Components of geochemical variation

The sampling design in this work was tailored specifically to estimate five components of geochemical variation for each geochemical measurement. Three of these components, V(A), V(B), and V(C), represent variation at decreasing geographic scales. A fourth, V(D), estimates the amount of stratigraphic (across layering) variation, and the fifth, V(E), estimates the amount of analytical (laboratory) variation. These components, as percentages of total logarithmic variance, are given in table 4.

Also shown in table 4 are two indices, v(m) and N(d), useful in assessing 1) stability in geochemical map patterns and 2) minimum sampling requirements, respectively. Specifically, N(d) estimates the minimum number of random samples needed from a stratigraphic section in future regional geochemical work. See the appendix for a detailed discussion of either index.

Regional variation

Regional variation (component V(A)), although generally small in percentage terms, is statistically significant for 16 constituents. This variation represents geochemical differences among the eight areas of the study (fig. 3); these differences, as medians, are listed in table 5.

Much of this regional variation arises solely because of exceptionally low (or, in the case of Hg, high) element concentrations in the samples of area 4, which consists of the Grinnell Formation on the east side of Glacier National Park. If area 4 is excluded from consideration and the analysis of variance rerun, regional differences for Al_2O_3, Cr, Hg, Na_2O, Nd, Sc, Sr, TiO_2, V, and Zn become non-significant. That is, regional variation in these 10 constituents arises solely from low (relatively) concentrations in area 4. The low concentrations in turn reflect the simple fact that the rocks there contain less mud (Al_2O_3, Cr, Sc, Sr, TiO_2, V, and Zn) and plagioclase (Na_2O) than the rest of the sequence.

The high Hg in area 4 is a mystery; just possibly, it reflects upward leakage of Hg from organic-rich shales (Cretaceous) which lie beneath the underlying Lewis thrust fault. Nd is neither particularly high nor low in area 4 and the non-significance of Nd following exclusion of area 4 may be a statistical fluke arising from the reduced "degrees of freedom".

Elements As, Ba, Ce, Cu, Nb, and Yb continue to exhibit significant regional variation even if area 4 is excluded from the analysis (table 5), and their regional patterns, including the data from area 4, are mapped in figures 4A-F. The distribution of Cu, which is believed to reflect massive post-depositional rearrangement, is discussed at length in a later section entitled The special case of copper. The remaining elements are briefly discussed here.

At an average of 1.9 ppm (table 3), As overall seems low in rocks as muddy as these. Its highest values appear, however, in areas near the Lewis and Clark line (fig. 4A). Because As is a volatile element commonly associated with hydrothermal activity, these highs might reflect some kind of

Table 4.--Components of logarithmic geochemical variance.

[*, component significantly different from zero at the 0.05 probability level. (V(D) and V(E) not tested for significance); v(m) and N(d) shown only where V(A) is significant, see appendix for definitions of v(m) and N(d)]

		Percent of total logarithmic variance						
Element or oxide	Total Log V(X)	Between areas V(A) (>50 km)	Within areas V(B) (10-50 km)	Between sections V(C) (0-10 km)	Between samples V(D) (Strat)	Between analyses(1) V(E) (Lab)	v(m)	N(d)
Al_2O_3	0.0346	11*	<1	3	86	<1	2.1	11
As	.1885	28*	14	<1	57	1	2.9	5
Ba	.0578	16*	5	<1	67	12	2.6	8
Be	.0481	5	<1	12	73	10		
CaO	.4015	13	15*	<1	72	<1		
Ce	.0516	5*	<1	11	76	8	.6	
Co	.0847	<1	15*	<1	49	36		
Cr	.0596	7*	2	<1	88	3	1.4	19
Cu(2)	.1217	26*	5	<1	25	44	4.9	4
FeO	.1426	<1	<1	23	77	<1		
$FeTO_3$(3)	.0710	<1	7*	2	91	<1		
Ga	.0388	1	<1	2	84	13		
Hg	.0343	28*	<1	25	24	23	2.3	45
K_2O	.0559	<1	<1	16*	84	<1		
La	.0524	3	<1	16*	65	17		
Li	.0686	<1	10	<1	82	8		
MgO	.0912	<1	23*	<1	77	<1		
Mn	.1437	<1	17*	<1	82	1		
Na_2O	.1342	43*	24*	<1	31	<1	3.2	2
Nb	.0664	19*	<1	7	42	33	3.1	7
Nd	.0466	8*	<1	14	61	17	.9	
Ni	.0623	<1	7	<1	90	3		
P_2O_5	.0447	<1	10	<1	86	4		
Pb	.1231	12	2	20*	46	19		
Sb	.0595	<1	30	<1	49	21		
Sc	.0537	3*	5	<1	90	2	.4	
SiO_2(4)	72.01	13	10*	<1	77	<1		
Sr	.0572	29*	14*	<1	55	2	3.0	4
Th	.0679	<1	<1	27*	30	43		
TiO_2	.0640	14*	<1	<1	79	5	3.6	12

Table 4.--Cont.

U	.0582	<1	<1	68*	31	1		
V	.0878	7*	3	<1	89	2	1.2	23
Y	.1341	20	<1	40*	34	6		
Yb	.0772	20*	<1	20*	40	20	1.8	
Zn	.0542	4*	<1	6	85	5	.6	

(1) Error variance (from table 1) as percentage of total variance
(2) This analysis excludes five anomalously high samples (>62 ppm Cu)
(3) Total Fe as Fe_2O_3
(4) Simple variance, not logarithmically transformed

Table 5.--Geochemical comparison of eight areas.

[Data are given as medians; values are in parts per million except where noted as percent (%); areas 1, 4, and 8 contain the type areas of the named formations]

	Areas							
Constituent	1 (Spokane)	2	3	4 (Grinnell)	5	6	7	8 (St. Regis)
Al_2O_3 %	13	14	14	12*	14	13	14	13
As	3.6	1.6	3.5	1.4	.40	2.7	2.0	.70
Ba	390	620	440	410	620	700	730	690
Ce	73	67	72	62	67	56	72	68
Cr	35	33	37	22*	37	32	32	35
Cu	10	3.0	4.0	4.0	3.0	2.0	3.0	2.0
Hg	.01	.01	.01	.02*	.01	.01	.01	.01
Na_2O %	.87	1.3	1.4	.28*	1.2	1.6	1.7	1.4
Nb	10	7.0	10	7.0	4.0	8.0	5.0	4.0
Nd	44	31	35	32*	30	25	33	30
Sc	12	12	13	9*	13	11	11	11
Sr	40	45	37	21*	46	49	52	48
TiO_2 %	.53	.51	.55	.39*	.55	.46	.51	.47
V	50	45	46	37*	52	50	43	44
Yb	3.0	2.0	2.0	1.0	2.0	1.0	2.0	2.0
Zn	70	70	90	50*	80	70	80	50

* If area 4 is excluded from the analysis of variance, differences among the remaining seven areas are not significant

regionally extensive hydrothermal impact in or near the line. The highest As concentration seen in this study (14 ppm As) was measured in sample JC1J15T, a Cu-mineralized argillite from section J, also suspected of being hydrothermally enriched.

The element Ba generally increases westward, for reasons unknown (fig. 4B). The highest Ba found in this study was in a dolomitic siltite (sample JC0F12T) in section F. It contained 7500 ppm Ba, about 1.3 percent normative barite. Connor and McNeal (1988) found elevated Ba in mineralized quartzite beds of the sequence in this general area.

The pattern of Ce, like the pattern of Ba, defies easy interpretation (fig. 4C). In fact, this pattern is likely spurious as is discussed in the appendix. The highest Ce found in this study was 550 ppm in sample JC0G01T in section G, a quartzite also high in the REE La (250 ppm), Pr (50 ppm), and Nd (170 ppm). These highs presumably reflect the presence of REE-bearing minerals in the sample. (The highest concentrations of REE in general, however, occurred in a phosphorite, sample JC2T02T, section T.)

The element Nb increases southeastward, and possibly represents a distinctive mineral occurrence in the Spokane Formation (fig. 4E). The highest concentration of Nb, however, was an unexceptional 19 ppm in sample JC1P08R (argillite) from section P.

The element Yb is highest in area 1 (fig. 4E). The high Yb, like the high Nb, perhaps reflects the presence of a distinctive heavy mineral suite in the Spokane Formation; if so, such a suite supports the contention of an independent sediment source (Dillon Block?) for the Spokane.

Local geographic variation

Geochemical variation at local geographic scales, although generally low in percentage terms, is significant for many constituents. Variation at level V(B), 10-50 km, is judged to be significant for eight constituents: CaO, Co, $FeTO_3$, MgO, Mn, Na_2O, SiO_2, and Sr. Again, much of this variation results from the unique nature of the Grinnell Formation.

Section P is, at an average 59 percent quartzite, the sandiest section in the sequence, presumably because of its position near the apex of the Grinnell fan (fig. 2). The geochemical contrast between this section and the less sandy sections E and M, with which P was mated at the V(B) level of the design, causes the significance for Co, $FeTO_3$, Mn, Na_2O (low in section P, high in E and M), and SiO_2 (high in P, low in E and M). Exclusion of section P from the design results in non-significance at level V(B) for these five constituents.

Variation in CaO, MgO, and Sr remains significant at level V(B) even if section P is excluded. Mapping of this variation would require a spacing of stratigraphic sections as tight as 10 km over the basin, a clear impossibility. Whatever those patterns might look like, however, the significance of V(B) for these constituents indicates that they are erratic in their geographic distribution, changing in average concentration rather

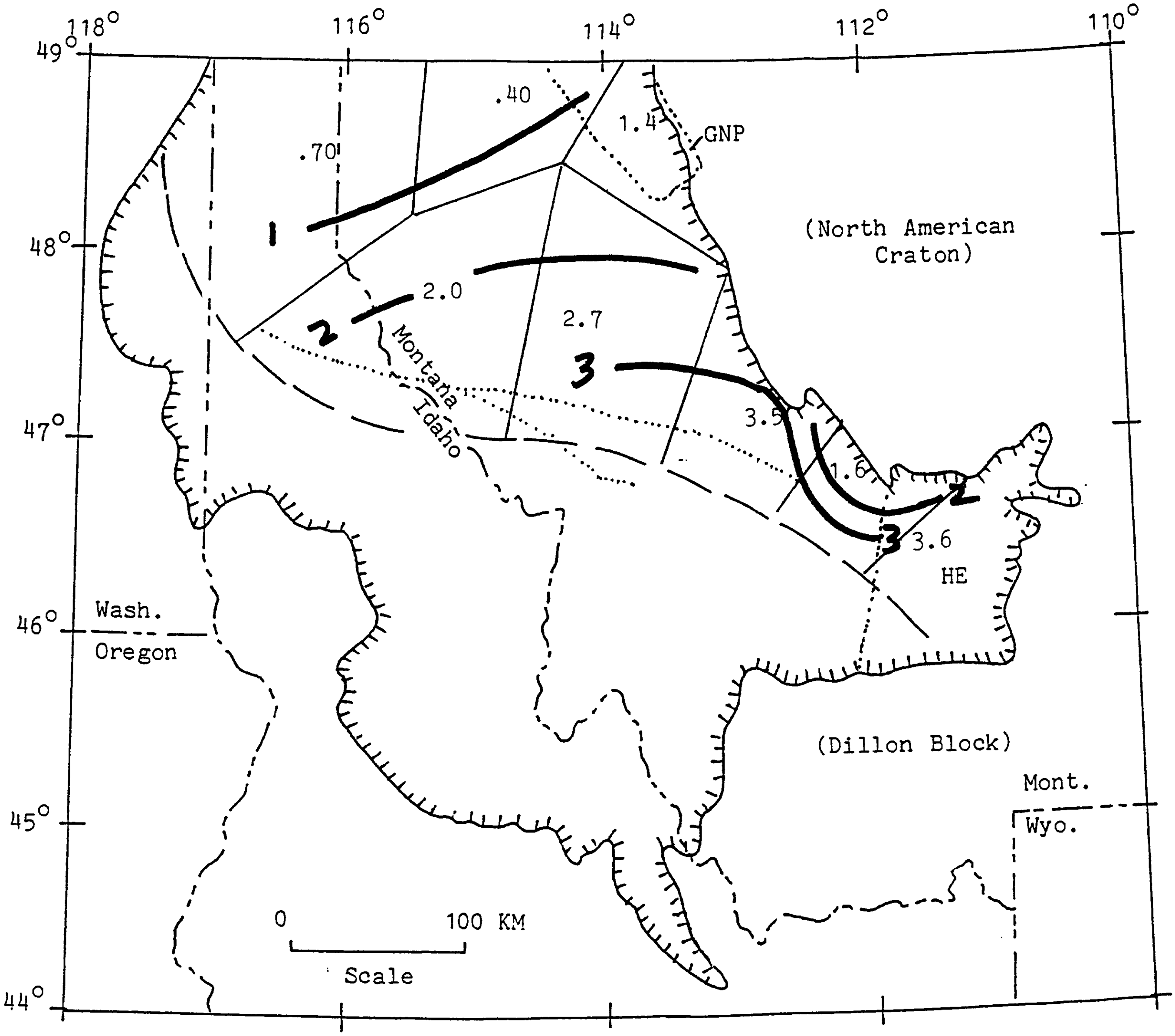


Figure 4A. Regional distribution of As. Contours (heavy lines) in ppm Dotted lines indicate Lewis and Clark line.

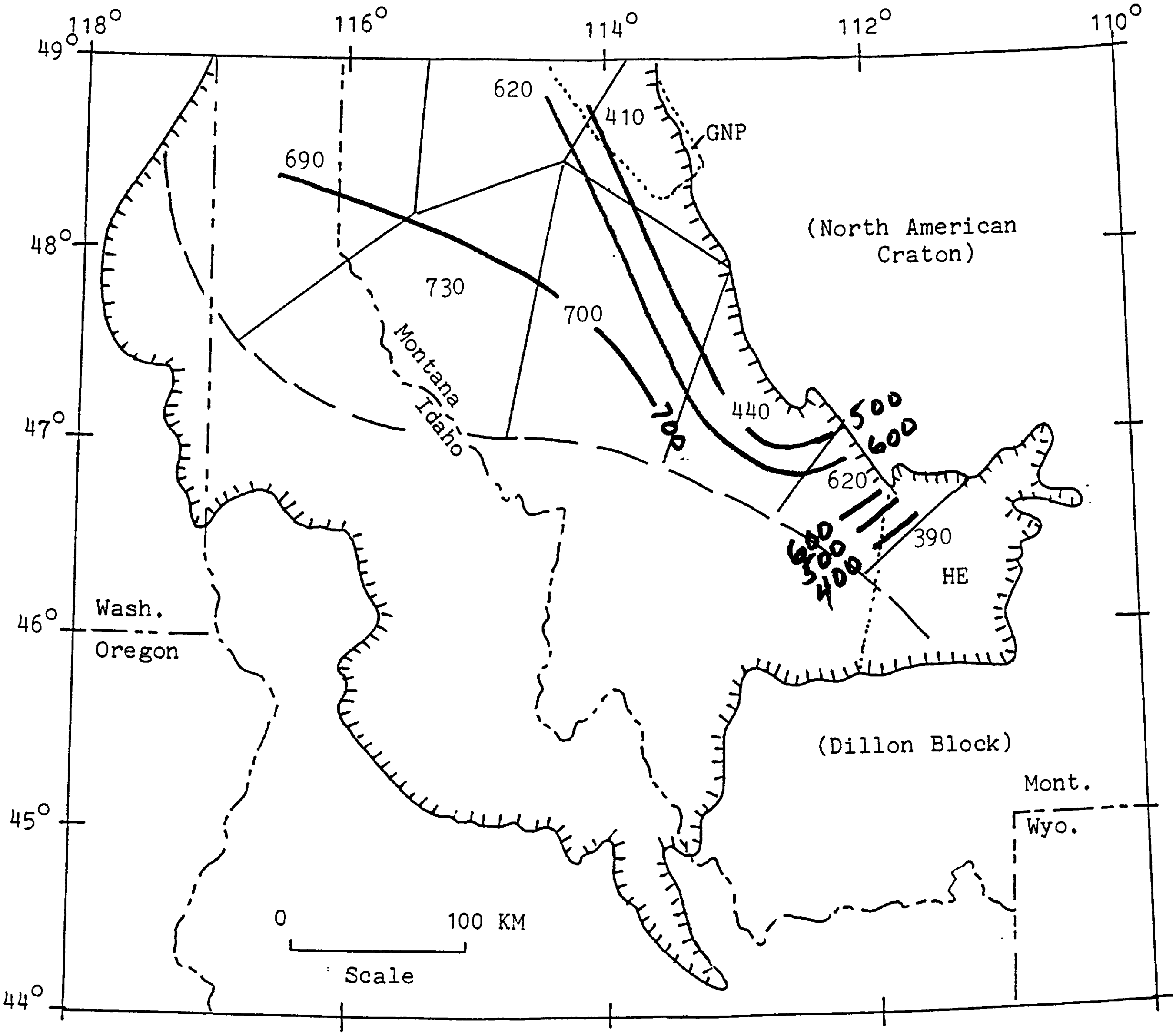


Figure 4B. Regional distribution of Ba. Contours (heavy lines) in ppm.

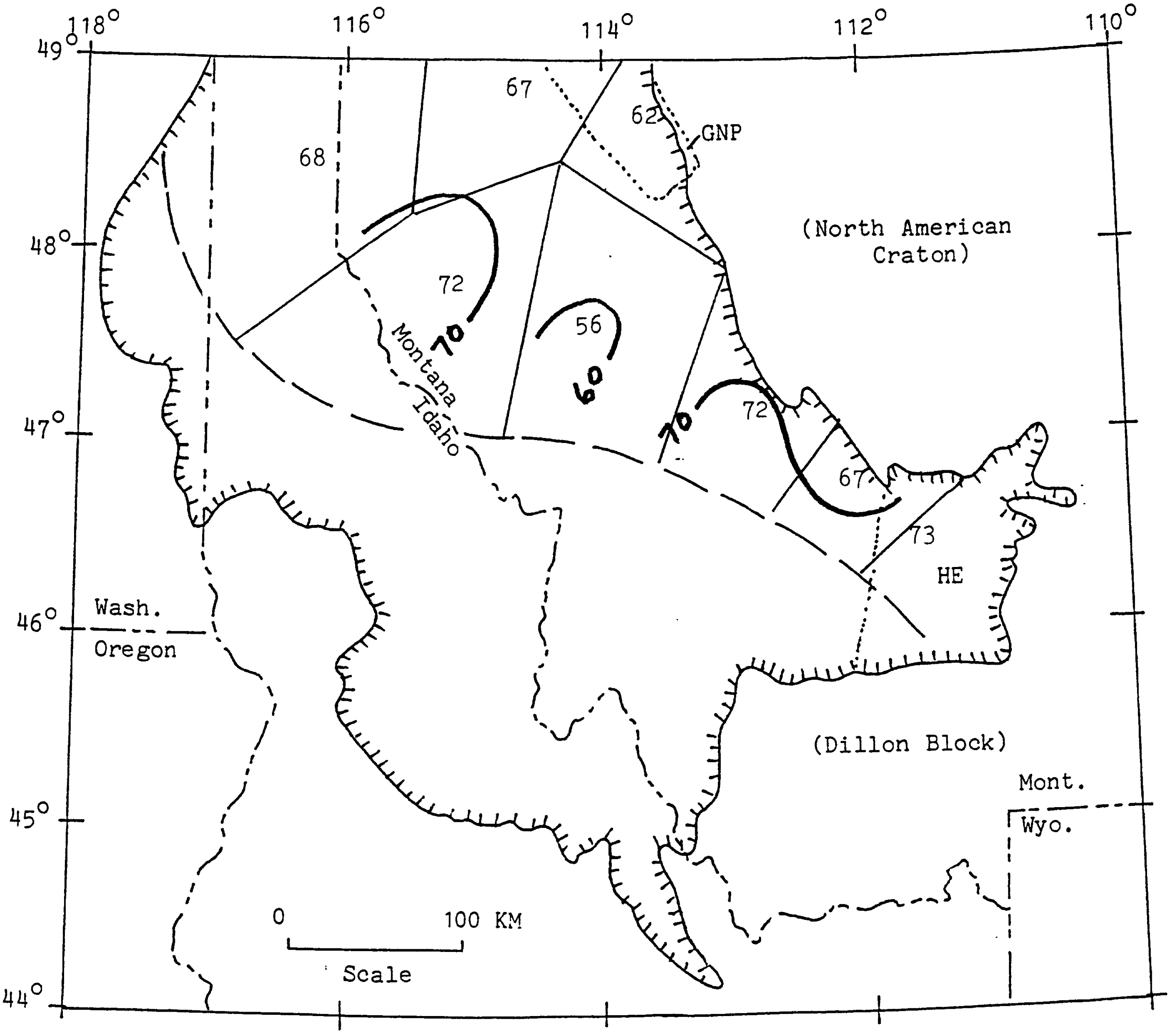


Figure 4C. Regional distribution of Ce. Contours (heavy lines) in ppm.

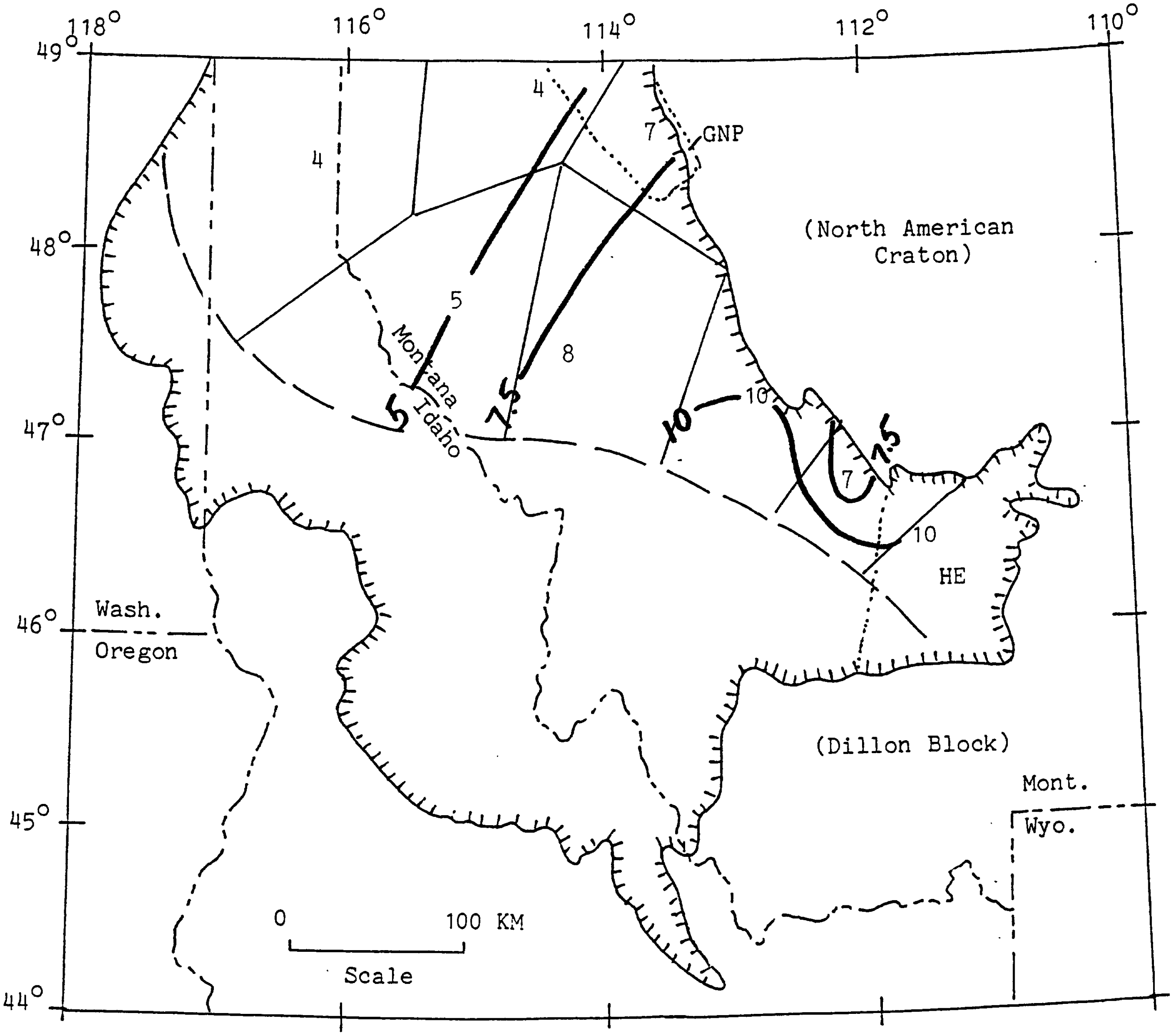


Figure 4D. Regional distribution of Nb. Contours (heavy lines) in ppm.

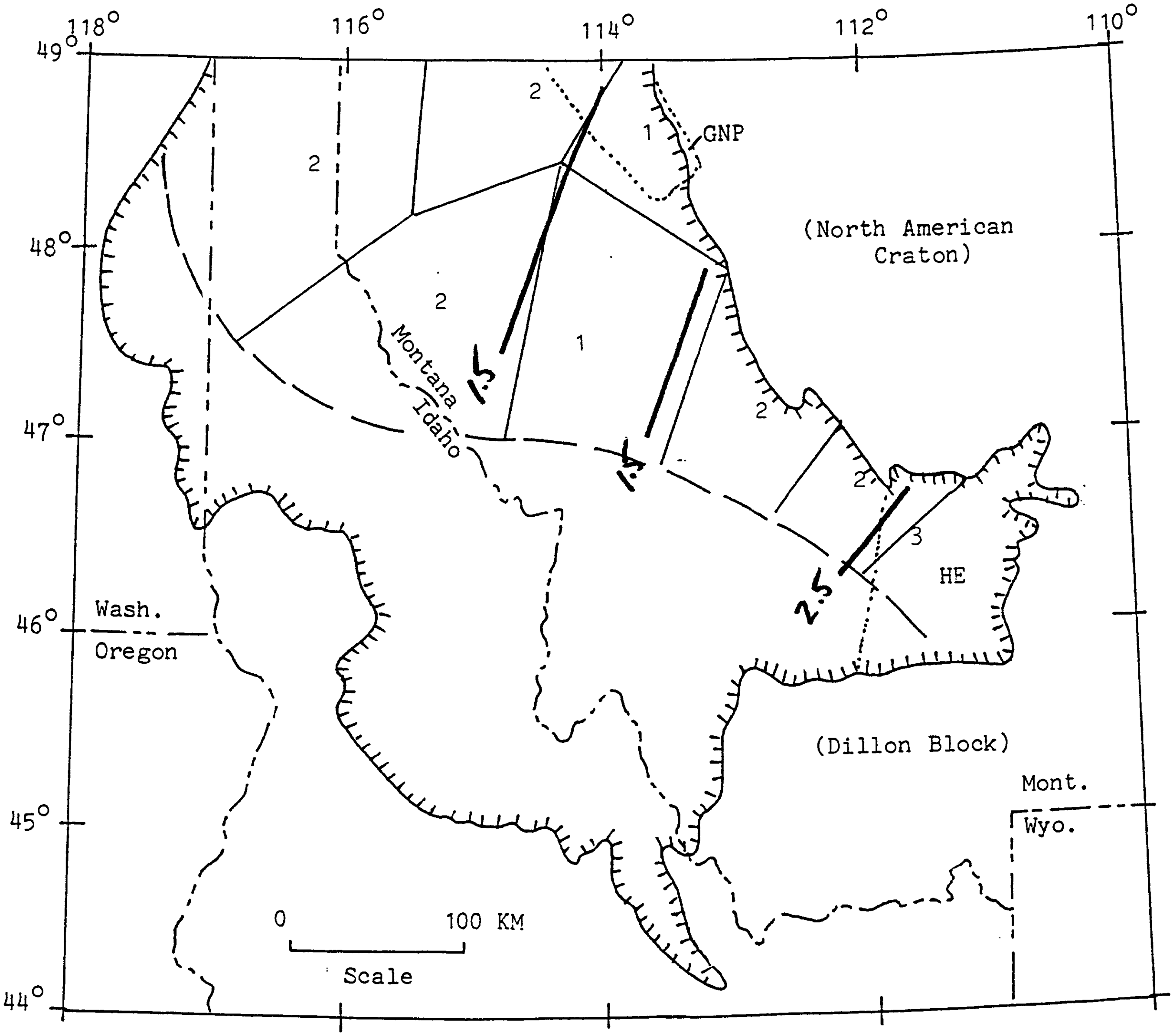


Figure 4E. Regional distribution of Yb. Contours (heavy lines) in ppm.

rapidly with distance. Much of the variation in CaO reflects a spotty distribution of limestone in the Helena Embayment. The distribution of MgO reflects, in part, a spotty distribution of dolomite cement.

MgO also occurs in chlorite, an ubiquitous constituent of the sequence. And such MgO (that is, MgO in excess of that required for dolomite) ranges as high as 4.9 percent (table 6). If this MgO resided in the original mud, and if this mud comprised about half of the original sediment (as suggested by the Al_2O_3 levels, table 6), then that mud contained as much as 9.8 percent MgO, exceptionally high for smectite (Grim, 1968, p. 578-580 gives an average MgO content of 3-4 percent for such clay). The reason for such high levels of MgO in the original sediment is unknown; perhaps it reflects a volcanogenic input. But the samples in table 6 contain no vestige of volcanic detritus. The Mg anomaly in these rocks, if such it be, is possibly diagenetic and perhaps represents the passage of Mg-rich (briney?) fluids.

The element Sr is only weakly correlated with calcite and dolomite and reasons for its spotty distribution are obscure. Like As , Sr exhibits an exceptionally low concentration (44 ppm average, table 3) compared to muddy rocks in general. This paucity may reflect some kind of widespread loss as Sr is one of the more soluble divalent cations. Perhaps severe post-depositional Sr loss in such ancient rocks is to be expected.

Variation at level V(C), 0-10 km, was significant for seven constituents: K_2O, La, Pb, Th, U, Y, and Yb. And once again, most of this significance can be accounted for by a single geochemically peculiar section. The St. Regis Formation in Section T is noticeably low in K_2O, La, Th, U, Y, and Yb when contrasted with its pair mate (section S). If section T is excluded from the Figures 4A-F. Regional distribution of __. [Medians in each area given in parts per million; contours drawn on medians] analysis, these constituents lose their significance at level V(C).

Why section T should be low in these elements is puzzling; the section is not sufficiently high in ordinary rock-forming minerals (such as quartz) to force a significant dilution in clay content (where most of the K_2O resides). By an odd coincidence(?), section T also contains phosphorite; 13.8 percent P_2O_5 in sample JC2T02T, equivalent to about 36 percent fluorapatite. The geochemical uniqueness of section T remains unexplained.

The element Pb is high in section F compared to its pair mate, section L, in the Rogers Pass area and Connor and McNeal (1988) concluded that Pb has been hydrothermally enriched in these rocks. The highest Pb measured in this work, however, was 160 ppm in sample JC1N04R from section N. Minor accumulations of stratabound Pb (or Pb-Zn) are common in Belt rocks (see, for example, Earhart and others, 1981), and the anomalous Pb in section N likely represents such an occurrence.

Stratigraphic and analytical variation

Geochemical variation across layering (stratigraphic variation, V(D)), accounts for the lion's share of the geochemical variability in the sequence. By definition, high geochemical variability is to be expected across

Table 6.--Some Mg-anomalous samples.

[All data given as percent (%)]

Sample No.	Section	Al_2O_3	CaO	MgO	MgO*
JC9D06R	Avalanche Creek	12.3	0.18	5.01	4.9
JC1M01R	Mt. Grinnell	15.4	1.23	5.49	4.6
JC2R10R	Lamoose Creek	12.7	1.28	5.14	4.2
JC9A07R	Newlan Creek	10.8	6.42	8.66	4.0
JC1N10R	Coak Creek Canyon	12.8	.57	4.32	3.9

* MgO in excess of that required for dolomite

compositionally stratified rocks. For most elements in table 4, more than half of the geochemical variation in the sequence occurs at level V(D). The impact of this (generally large) variation on attempts to make regional (basinwide) element distribution maps is examined in the appendix.

Analytical error, V(E), commonly constitutes an acceptably low 20 percent or less of the total geochemical variability in the sequence (table 4). Where V(E) is large (40 percent or more?), more precise instrumentation may be desirable if future geochemical work in these rocks is contemplated. Analytical imprecision in absolute terms is listed in table 1. The error variance (table 1) is required to estimate V(E), and the geometric error suggests the range in reproducibility of each analysis. For example, a GE of 1.5 indicates (roughly) that repeated analysis should give values ranging from 0.7 to 1.5 times the actual concentration in the sample. A GE below 1.5 indicates a more precise analysis; a GE above 1.5 indicates a less precise analysis.

The special case of copper

Cu, as all Belt workers know, is a special element in the sequence and its distribution is unique. Variation of Cu in the sequence is enormous; in this work observed Cu concentrations ranged from <1 - 6700 ppm (see tables in Connor, 1991). Regionally, Cu is high in the east, particularly in the Helena Embayment (area 1), and low in the west (fig. 5). At an overall average of 4 ppm (table 3), however, Cu (like As and Sr) seems to be exceptionally low for shale. The most Cu-rich sample in the study (6700 ppm) was JC9B12T, a limestone, from section B.

Cu occurs in several statistical populations in the sequence, reflecting in part multiple mineral residence. The primary mode for Cu (5 ppm, fig. 5) lies close to the sequence median (4 ppm, table 3). The drawn-out right-hand tail in figure 5 demonstrates the presence of at least one additional population, probably centered on or about 100 ppm; and the single value at 1500 ppm could represent a third population.

Connor and others (1981), in a study of Cu in the Blacktail Mountain deposit, postulated a minimum of four such populations there; a dominant population at about 3 ppm, and three lesser populations at 22, 100, and 1500 ppm, respectively. The 3 and 100 ppm populations of Blacktail Mountain are clearly present in this work as the 5 and 100 ppm populations, respectively. The 22 and 1500 ppm populations of Blacktail Mountain, if present here, are vanishingly small.

Connor and others (1981) also argued that the 22 ppm population in Blacktail Mountain represented the original average concentration of the host rocks in the deposit, and that the 3 ppm population represented leached or otherwise Cu-depleted rock. If such a conjecture holds for the sequence overall, then the apparent lack of the 22 ppm population in figure 5 indicates that the entire sequence is strongly Cu-depleted.

Copper-rich rocks.--Cu-anomalous samples, defined as containing more than 62 ppm (97.5th percentile, table 3) (fig. 6), were observed in all parts

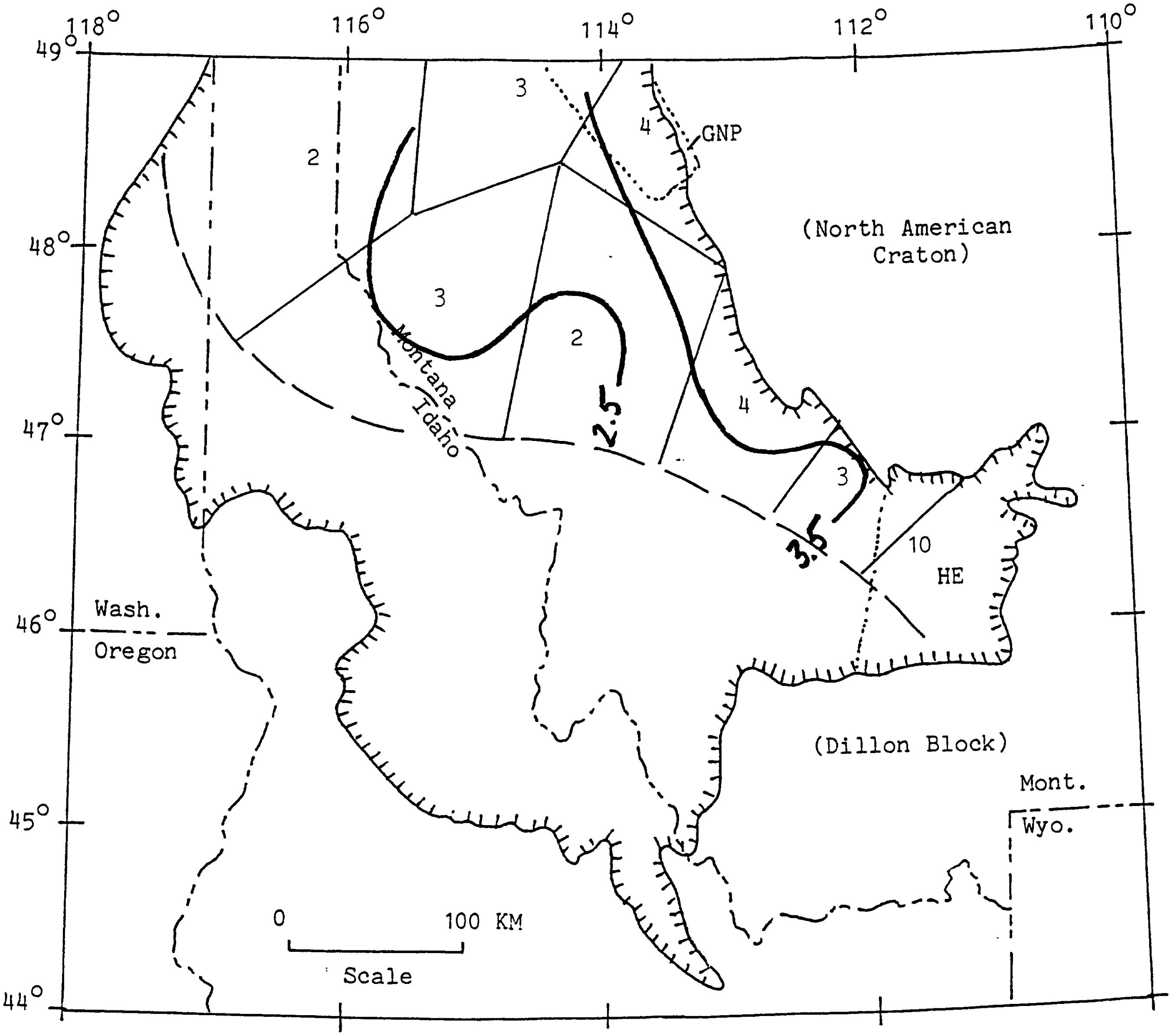


Figure 5. Regional distribution of Cu. Contours (heavy lines) in ppm.

of the local stratigraphy and in most parts of the study area. Of 35 stratigraphic sections examined in whole or in part during this work, I saw visible Cu, mostly malachite, at one or more places in 17 (almost half). Of the 173 random samples used in this study 5, or 2.9 percent, were anomalous in Cu. This demonstrates that about three percent of the volume of the sequence contains anomalously high Cu.

Throughout the Belt Supergroup, rocks showing anomalously high Cu generally contain anomalously high Ag and Hg as well (Harrison, 1972, p. 1232). The data on Ag are severely limited in this study, but two of three samples with detectable Ag were also Cu-anomalous (footnote 3, table 7). The third Ag-anomalous sample was a phosphorite (JC2T02T, section T). The element Hg, on the other hand, is not discernibly enriched in the Cu-anomalous rocks of this study.

A comparison of median element content between Cu-rich and Cu-poor rocks is given in table 7. All samples in this comparison were collected from outcrop and, hence, all are weathered to a greater or lesser degree. Because weathering tends to both decrease and disperse accumulated Cu, the comparisons in table 7 may be misleading. Ferrous Fe (FeO) appears to be weakly enriched in the Cu-rich rocks. This enrichment cannot be accounted for in Fe-bearing Cu sulfide. The bornite needed to account for the extra 0.98 percent of FeO (table 7) over that in the Cu-poor rocks would require Cu levels of over 50,000 ppm, a content not seen in this study. The excess Fe, if a true enrichment, may have been internally rearranged as part of the Cu-mineralizing process. Alternatively, the excess Fe could represent the residue of pre-existing pyrite, replaced during Cu deposition.

Enrichment factors for constituents other than Cu are not compelling and, except for FeO, do not in fact reflect enrichment. For example, the factors for Yb, Y, CaO, and Nd, result not from higher concentrations in Cu-rich rocks but, rather, from lower concentrations in Cu-poor rocks.

Only two additional elements in this study can even be remotely considered as potential candidates for enrichment: Mo and Sn (footnotes 4 and 5, table 7). For these elements the high-Cu assemblage contained samples with detectable levels whereas the low-Cu assemblage contained no samples with detectable levels. The most Mo-rich sample, at 8 ppm, was sample JC9B12T (Section B), which was also the most Cu-rich sample collected. The highest Sn, at 11 ppm, however, was not in a high-Cu rock, but in sample JC9E06R (section E).

Copper-poor rocks.--Perhaps the most startling geochemical feature in this study is the enormously large surfeit of low Cu values (fig. 6. Connor and others (1981) suggested that a similarly low average in the Blacktail Mountain deposit was caused by severe post-depositional Cu-depletion (leaching).

Regionally, Cu in the sequence is lower in the western part of the area than in the eastern part (fig. 5). Only 13 percent of the random samples in areas 1, 2, and 3 contain <4 ppm Cu, but 64 percent of the samples in areas 7 and 8 contain <4 ppm. If this low Cu in fact reflects post-depositional leaching, the leaching was apparently more intense to the west.

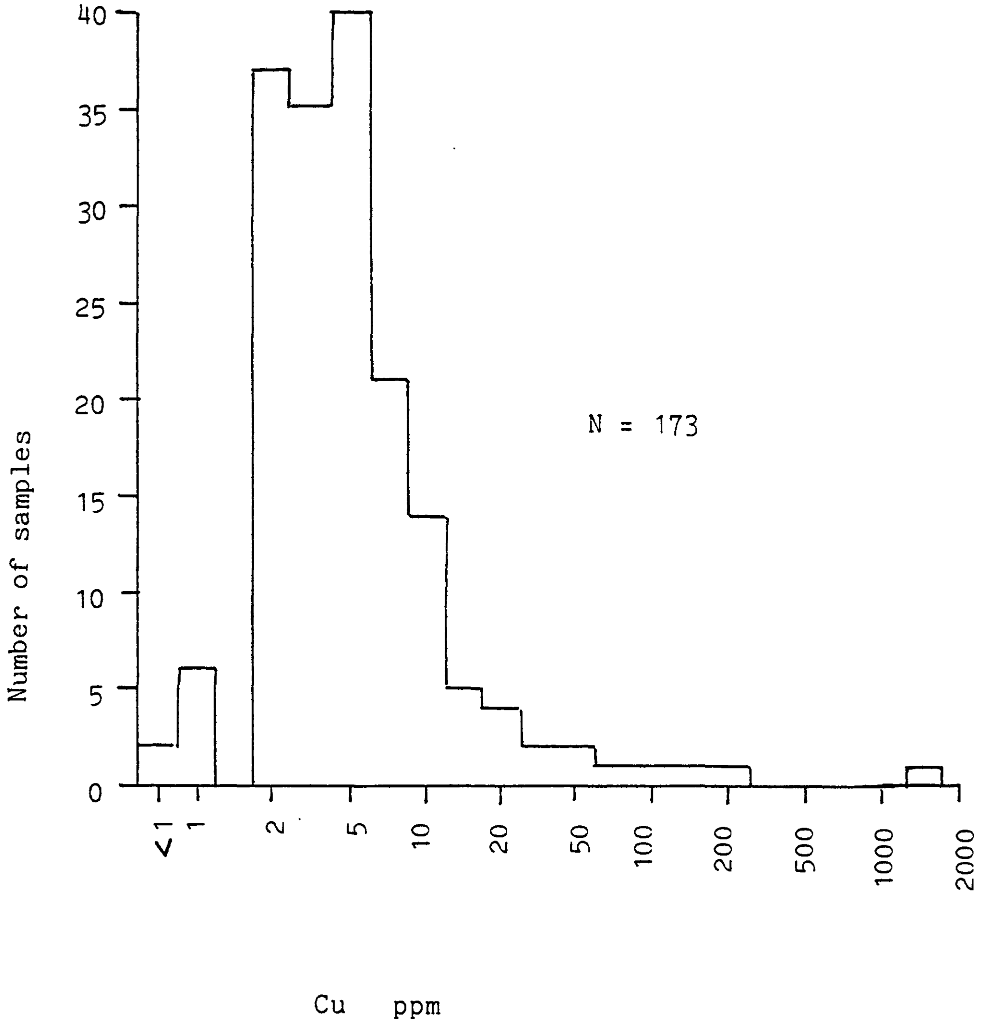


Figure 6. Cu histogram.

Table 7.--Comparison of Cu-poor to Cu-rich rocks.

[All data given as medians in parts per million, except where noted as percent (%); N, number of samples]

	Cu content		
	<1.7 ppm	>25 ppm	
Element or oxide	(N=13)	(N=23)	Enrichment factor
Cu	1.0	76	76.0
FeO %(1)	.52	1.5	2.9
Yb	1.0	2.0	2.0
Y	7.5	14	1.9
CaO %	.28	.50	1.8
Nd	21	35	1.7
P_2O_5 %	.075	.11	1.5
Pb	6.0	9.0	1.5
Mn	270	370	1.4
Ga	12	15	1.3
Sc	8.0	10	1.3
Th	5.5	7.0	1.3
U(2)	2.5	3.2	1.3
Zn	60	80	1.3
Ce	52	61	1.2
La	24	29	1.2
Li	30	35	1.2
Sr	45	52	1.2
Al_2O_3 %	12	13	1.1
Cr	29	33	1.1
MgO %	2.2	2.3	1.1
Na_2O %	1.5	1.7	1.1
TiO_2 %	.44	.49	1.1
V	37	42	1.1
Nb	<4.0	4.0	>1.0
Ag	<2.0	<2.0	?(3)
Mo	<2.0	<2.0	?(4)
Sn	<4.0	<4.0	?(5)
As(1)	1.4	1.4	1.0
Be	2.0	2.0	1.0
Hg(1)	.010	.010	1.0
$FeTO_3$ %(2)	3.2	3.1	1.0
SiO_2 %	72	69	1.0
Ba	630	560	.9
K_2O %	3.0	2.8	.9
Ni	14	13	.9
Co	13	9.0	.7
Sb(1)	1.1	.60	.5
Sm	20	<10	<.5

Table 7.--Cont.

(1) N = 3 and 11, respectively, for these elements
(2) Total Fe as Fe_2O_3
(3) Two samples in the high-Cu group have Ag >2 ppm; no sample in the low-Cu group has Ag >2 ppm
(4) Three samples in the high-Cu group have Mo >2 ppm; no sample in the low-Cu group has Mo >2 ppm
(5) Three samples in the high-Cu group have Sn >4 ppm; no sample in the low-Cu group has Sn >4 ppm

If the Cu-poor rocks have been leached, the process appears to have been about 80 percent effective, lowering a probable original 22 ppm concentration to an average 4 (table 3) or 5 ppm (fig. 6). The amount of Cu so removed would be enormous. Consider the area west of the Rocky Mountain Trench, where the greatest apparent depletion occurs. The sequence here is about a third of kilometer thick over an area of about 100 km on a side; that constitutes a block of rock of about 3300 cubic km. If a specific gravity of 2.7 is assumed for the block, 3300 cubic km weighs just under 9,000,000 T (teragrams; tera is 1 followed by 12 zeros) and would contain, at 22 ppm, about 200 T of Cu. An 80 percent depletion in this block would then free about 160 T or approximately 160,000,000 metric tons (t) Cu. For comparative purposes, the Spar Lake deposit, which lies a few hundred meters below the St. Regis in the western part of this block, had pre-mining reserves of about 500,000 t Cu (Hayes and Balla, 1986, p. 54).

I stated above about 3 percent of the sequence overall contained anomalously high Cu. If the sequence as a whole contains 30,000 cubic km (in a volume 400 km long, 100 km wide, and .75 km thick), and 3 percent of that has been enriched from 22 to 62 ppm Cu, an analysis similar to the one in the last paragraph suggests that about 100 T Cu is required for the enrichment; this is about 7 percent of the 1400 T estimated to be released from the remaining 97 percent of the sequence, if Cu there drops from 22 to 4 ppm. Raising 3 percent of the sequence to 100-200 ppm Cu requires about 200-450 T, still less than one third of the available 1400 T. Mass balance considerations, then, are consistent with the notion of internally rearranging the Cu during diagenesis.

Copper mineralization--Speculation on Cu sources for redbed stratabound deposits, like those in this sequence, include both intrabasinal and extrabasinal sites. Views espousing intrabasinal sources are favored, the most favorite being a large volcanic pile in the local succession (Gustafson and Williams, 1981, p. 170). There is, however, no large volcanic pile known to exist below (or within) the sequence of this study and I propose that the source of the Cu in this sequence is the host rock itself. The strongest evidence for this lies in the inordinately low overall Cu content of the sequence.

Walker (1989), among others, has invoked reddening of sediments by intrastratal oxidation as a means of "freeing up" trace elements for later transport. As a redbed sequence, the strata in this study presumably experienced such oxidation and consequent production of potentially soluble Cu.

Speculation on ore solutions in these kinds of deposits generally involves a briney fluid carrying metal-chloride complexes (Rose, 1989). The data of this work sheds little light on such ruminations and about all that can be said here is that passage of such solutions is possible. Locally anomalous amounts of MgO, noted above, could reflect the passage of brines. Also, red strata enclosing Grinnell-type quartzite layers are locally bleached for a distance of centimeters from the quartzite. This bleaching attests to the passage of reducing solutions of some kind, the implication being that such quartzite layers have acted as conduits for mineralizing solutions.

Speculation on redbed Cu deposition revolves about the necessary presence of reduced S (Gustafson and Williams, 1981, p. 171), such as pyrite. The only (weak) evidence of a pyrite precursor in the Cu deposits of this sequence is the presence of slightly elevated ferrous Fe in the Cu-rich rocks. Such Fe is now presumably in chlorite (there is too much to be carried in Cu-sulfide), but it may have originally resided in pyrite.

Trapping mechanisms responsible for the metals in these deposits may have been rather selective, involving mostly Cu, Ag, and Hg. In dilute aqueous solutions under standard conditions, the sulfides of these metals are most sparingly soluble, with solubility constants near 10 to the -50. Sulfide reduction of these three metals from extremely dilute, low-temperature, through-passing solutions is conceivable, if simplistic. For example, sulfide deposition would be expected at metal solution levels in the parts per trillion range (nanomoles/l), if the local sulfide or bisulfide ion activity exceeds even the minutest levels, say 10^{-35} moles/l.

Geochemical stratigraphy

As is expected in muddy rocks, the distribution of many elements mimics the distribution of original mud in the sequence. In particular, samples from area 4 figure prominently in the control on regional distributions because the rocks there (Grinnell Formation), are distinctly less muddy than rocks from other areas. The controlling role of the Grinnell in these patterns raises the possibility of similar control on element variation by the other two formations (Spokane and St. Regis).

To examine this possibility, data collected from in or near the type areas of the Spokane, Grinnell, and St. Regis Formations were subjected to multiple-group, multi-element discriminant function analysis (Dixon, 1968). Partial, and promising, results of this evaluation were presented earlier (Connor, 1984), where it was concluded that the lower part of the Spokane Formation in and near the Rocky Mountain Trench resembled much more the St. Regis Formation in its composition than the Spokane Formation.

For this evaluation, the 173 random samples were divided into four groups; 26 samples from sections A, B, and D were used to define the geochemical character of the Spokane Formation, 30 samples (sections P, E, and M) were used to define the character of the Grinnell, and 30 samples (sections S, T, and U) were used to define the St. Regis. These 86 samples constituted the training set (the "knowns") with which geochemical indices (canonical variates) based on formation differences were computed. The remaining 87 random samples were treated as stratigraphically "unknown" and, based on the geochemical indices, each was subsequently assigned to that formation to which it was most geochemically similar.

Indices were defined as weighted sums of selected geochemical constituents deemed to be statistically important in defining differences among the formations. Two such indices served to adequately define these differences. They are:

$$Z(1) = -53.97+20.02(\mathrm{Log}(\mathrm{SiO_2\%}))-2.029(\mathrm{Log}(\mathrm{CaO\%}))-2.131(\mathrm{Log}(\mathrm{Na_2O\%}))$$

$$+4.594(\mathrm{Log}(\mathrm{Mnppm}))+5.969(\mathrm{Log\ Lappm}))-3.195(\mathrm{Log}(\mathrm{Yppm})) \qquad (4)$$

$$Z(2) = 10.41-5.565(\mathrm{Log}(\mathrm{SiO_2\%}))+0.0083(\mathrm{Log}(\mathrm{CaO\%}))-3.204(\mathrm{Log}(\mathrm{Na_2O\%})) -0.0222(\mathrm{Log}(\mathrm{Mnppm}))-0.8826(\mathrm{Log}(\mathrm{Lappm}))+0.7082(\mathrm{Log}(\mathrm{Yppm})) \qquad (5)$$

Values of Z(1) and Z(2) were computed for each of the 86 "known" samples, and the samples plotted on figure 7. Separation of the three formations based on these indices is reasonably good; 77 of 86, or 90 percent, of these samples were classified correctly using the indices. The utility of the X-Y plot in figure 6 as an assignment device is apparent; by plotting an "unknown", it may then be assigned to that group to which it lies closest, where closest is defined as the nearest group centroid.

A more formal, and more technically correct, method of assignment is based on Mahalanobis' D-squared (Dixon, 1968) which was used to assign both knowns and unknowns to one of the three formations. The results of such assignment are shown in figure 8. Here, sample assignments are displayed on two cross-sections of the sequence.

The virtual lack of Grinnell assignments west of the eastern edge of Glacier National Park reinforces the conclusions given above concerning the geochemical uniqueness of that area of the formation. Only 4 of 87 unknowns were assigned to the Grinnell using the indices (equations (4) and (5)). By this evaluation then, typical Grinnell is reduced to the role of a geographically restricted geochemical variant in the sequence.

An additional surprise from this evaluation is a somewhat similar geographic restriction on Spokane geochemistry. Although the upper parts of sections R and Q, in or near the Rocky Mountain Trench, show a strong Spokane affinity, the lower parts of those sections and nearly all samples from the sections I, F, and L (the Rogers Pass area) show a strong St. Regis affinity. This confines the bulk of Spokane assignments to the Helena Embayment.

Geochemically, the sequence as a whole is clearly dominated by St. Regis-type rocks with typical Spokane- and Grinnell-type rocks pretty much confined to the eastern parts of the outcrop area. If these compositionally-determined distributions on rock type represent sediment source, the bulk of the sequence was apparently derived from the southwest, the direction to source of the St. Regis. In other words, the Spokane and Grinnell Formations represent localized eastern variants (with eastern sources) in a much larger area of St. Regis deposition.

CONCLUSIONS

1. Geochemical variation in a muddy Cu-bearing redbed sequence in the Middle Proterozoic Ravalli Group (Belt Supergroup) of northwest Montana and northern Idaho was examined using hierarchical analysis of variance and Figure 7. Geochemical discrimination of samples collected in or near the type areas of the Spokane, Grinnell, and St. Regis Formations. [Group averages noted by inscribed letters: S, Spokane average; G, Grinnell average; R, St. Regis average] Figure 8. Geochemical affinity of 173 random samples. [RP, Rogers Pass area; HE, Helena Embayment; GNP, Glacier National Park] discriminant function analysis techniques. The sequence included the Spokane, Grinnell, and St. Regis Formations and their probable lithostratigraphic correlatives. These rocks collectively represent a major regressive redbed event in the Belt Supergroup prior to the deposition of the middle Belt carbonate.

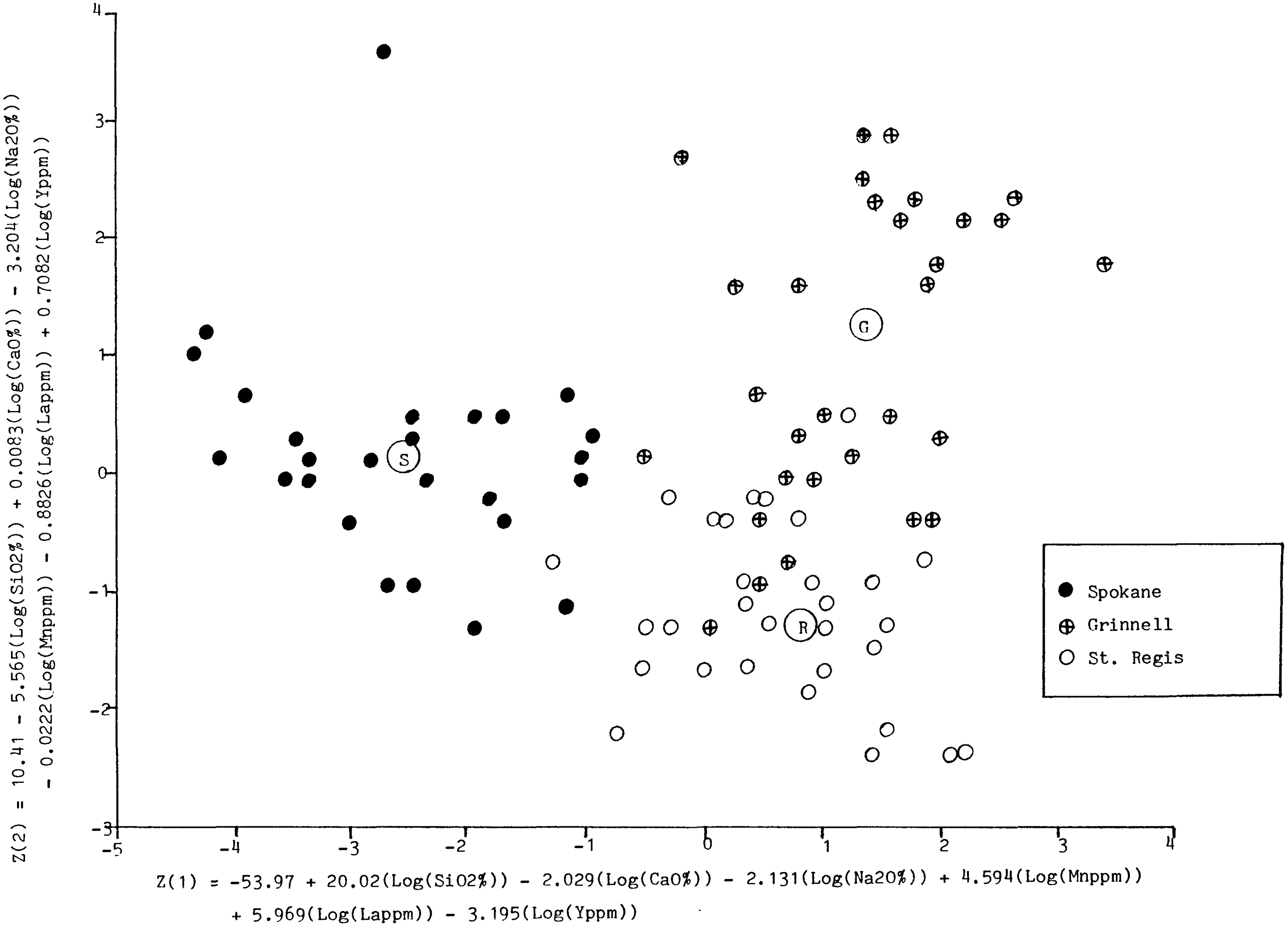


Figure 7. Geochemical discrimination of samples collected in or near the type areas of the Spokane (o), Grinnell (o), and St. Regis (o) Formations. (Group centroids noted by circled letters: S, Spokane average; G, Grinnell average: R, St. Regis average).

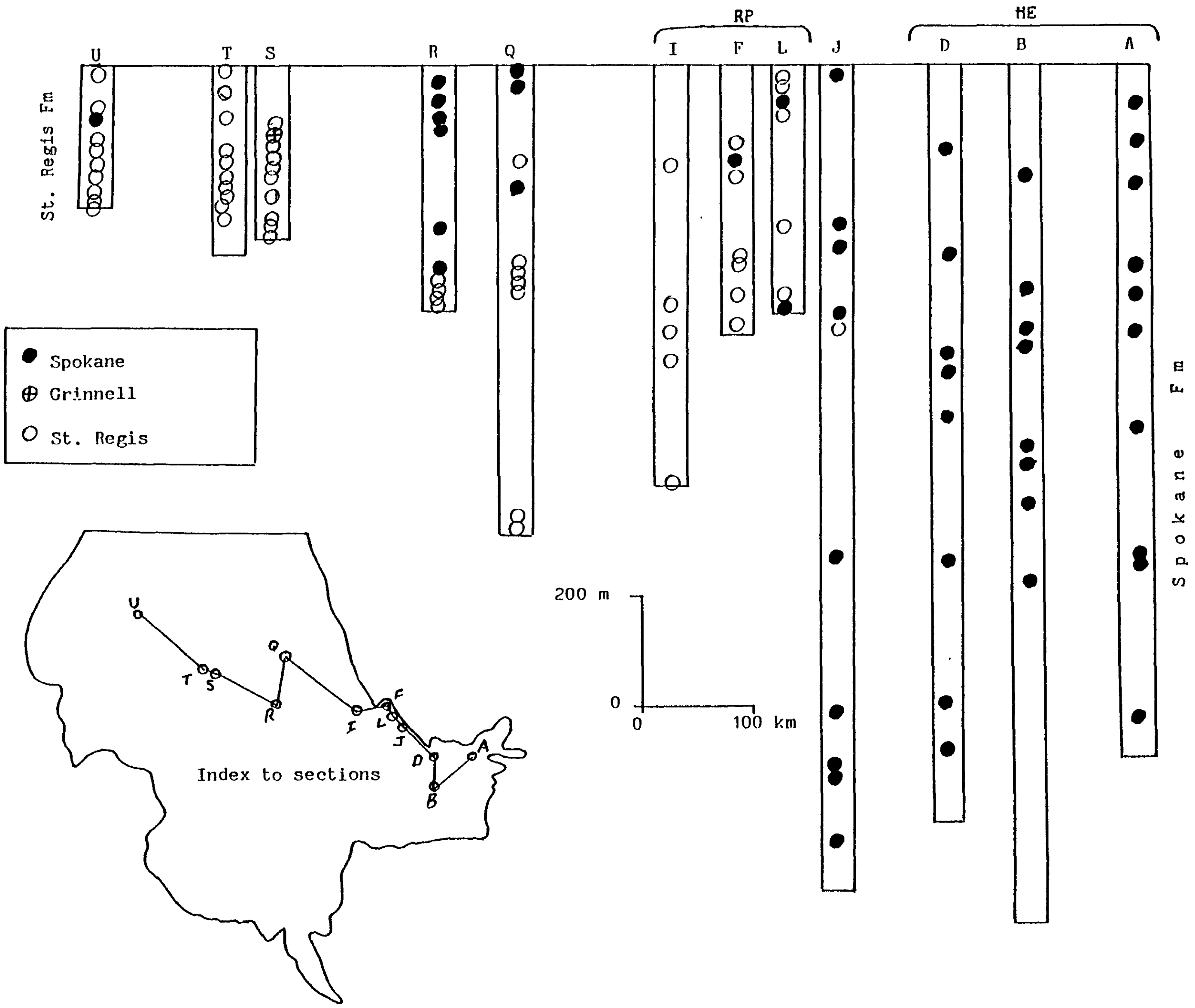


Figure 8. Geochemical affinity of 173 random samples collected from the Spokane, Grinnell, and St. Regis Formations and their probable lithostratigraphics equivalents.
A. RP, Rogers Pass area; HE, Helena Emplacement (lettered sections are named on figure 2).

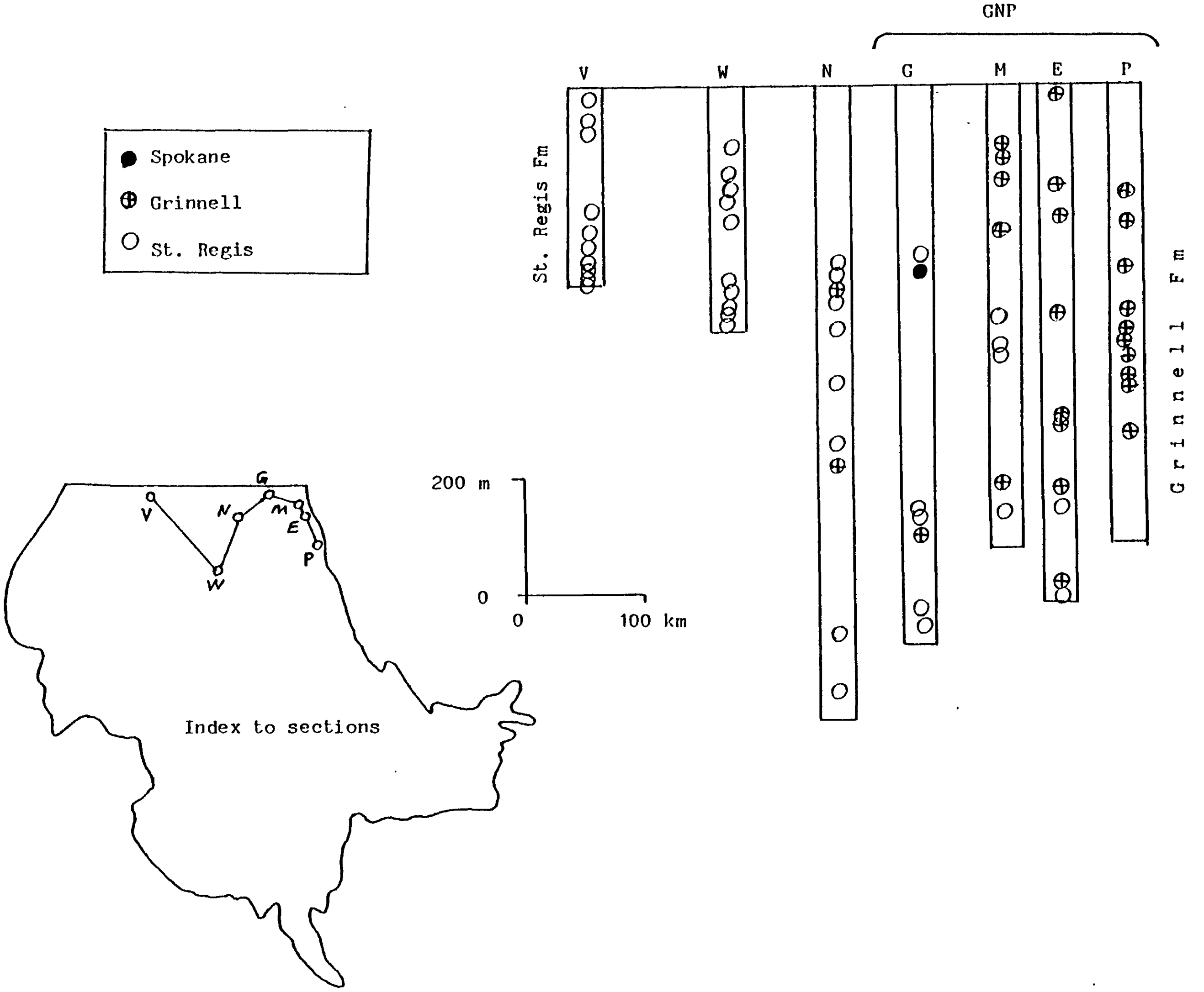


Figure 8. Geochemical affinity of 173 random samples collected from the Spokane, Grinnell and St. Regis Formations and their probable lithostratigraphic equivalents.
B. GNP, Glacier National Park (lettered sections are named on figure 2).

2. Each formation in and near its type area contains a distinctive type of quartzite which decreases away from the type area, suggesting multiple sources for these rocks. A prominent Grinnell sediment source is located to the northeast; the St. Regis sediment source apparently lay to the southwest; sources for the Spokane are presumably cratonic but apparently different from those of the Grinnell. Y/Yb ratios suggest that all source provenances were continental.

3. A large number of elements in the sequence display weak regional patterns. Because many elements in muddy rocks tend to reside largely in the micas, many of these patterns mimic the distribution of original mud in the rocks. Elements not following this pattern include Cu (probably because of widespread post-depositional rearrangement), Nb and Yb (high in the Helena embayment, perhaps contained in a distinctive heavy mineral suite there), Pb (high in the Rogers Pass area, an area of known hydrothermal activity), As (high near the Lewis and Clark line, for unknown reasons), and Hg (high in east-central Glacier National Park, also for unknown reasons). Additional geochemical oddities in the sequence include local presence of phosphorite, and perhaps exceptionally low concentrations overall of As and Sr.

4. Some samples collected from outcrops east of the Rocky Mountain trench contain MgO in substantial excess of that required for dolomite, suggesting that the original mud in some of these rocks may have contained an exceptionally high 8-10 percent MgO. The source of this putative Mg-rich mud is unknown.

5. The most probable source of the Cu in the deposits contained in this redbed sequence is the sequence itself. The Cu content overall is quite low, about 4 ppm. The expected concentration west of the Rocky Mountain Trench is even lower. The presumption is that the rocks of this study have been widely depleted (leached) of Cu. Such depletion is here viewed as part of the same process that formed the Cu-enriched deposits.

6. Random sampling of the sequence indicated that about 3 percent of the total volume of the sequence contains anomalously high Cu (>62 ppm). If the volume of rock in the study area is 30,000 cubic km, simple arithmetic suggests that raising the average Cu concentration from (a presumed original level of) 22 to 200 ppm in 3 percent of that volume would require about 450 teragrams (T) Cu, but depleting the average Cu concentration from 22 to 4 ppm in the remaining 97 percent of that volume would free up about 1400 T Cu. In terms of mass balance, lateral rearrangement of Cu in these rocks is clearly a feasible hypothesis.

7. Cu is the major element of mineralization, but Ag and Hg are also enriched in these deposits. Other elements possibly enriched in the Cu-anomalous rocks of this study include ferrous Fe, Mo, and Sn.

8. Geochemical discriminant function analysis demonstrates that most of the rocks in the sequence display a much greater geochemical resemblance to the St. Regis Formation than they do to either the Spokane or the Grinnell Formations; these latter two formations apparently represent eastern variants in a much larger area of St. Regis-type deposition.

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APPENDIX: Hierarchical designs and sampling efficiency

Efficient geochemical sampling results in maximum geochemical information at minimum sampling cost, where cost is measured in either time or money. Inefficient sampling produces waste; too many samples result in excess cost, too few result in unstable (unusable) results. For example, a goal of this work was the production of the maps in figures 4 and 5; 211 analyses (173 samples plus 38 analytical replicates) were used to produce these maps. Is 211 an efficient number? That is, is it too many (perhaps the same maps could have been produced with fewer analyses) or too few (perhaps the map region is so underanalyzed that the resulting patterns are largely noise). Or perhaps 211 is indeed efficient, being the minimum number of analyses required to produce a reasonably stable map. The question may be answered in terms of the results of the hierarchical analysis of variance in table 4.

The map patterns in figures 4 and 5 represent differences among means in eight areas of the map. If these differences are large compared to the imprecision attaching to the area means, the map patterns will be stable. Pattern stability is thus measured as a ratio: variation-among-map-areas divided by imprecision-of-area-means. For the patterns in figures 4 and 5, the variation among areas is estimated by variance component V(A); that is, variation occurring at scales greater than about 50 km.

Estimating the imprecision of the means is a trickier process. For example if, in a single area, many means were to be computed, each based on newly collected data, the variation from mean to mean would reflect the imprecision attaching to the mean of that area. It turns out that this imprecision may be approximated as a function of variance components V(B), V(C), V(D), and V(E); as follows:

$$I = \frac{\dfrac{\dfrac{\dfrac{V(E)}{N(e)} + V(D)}{N(d)} + V(C)}{N(c)} + V(B)}{N(b)} \qquad (1)$$

where I is the imprecision, and the N's are the number of sampling units at each level of the sampling design. That is, N(e) is the number of analyses per sample, N(d) is the number of samples per stratigraphic section, N(c) is the number of sections per locality, and N(b) is the number of localities per area.

In this work, unfortunately, three of the N's in equation (5) vary from place to place in the sampling design (see section on Variance components). Thirty-eight of 173 samples were analyzed twice; thus, N(e) is more than 1 but much less than 2. Similarly, N(d) in most sections is 10 but less than that in other sections. N(c) equals 2 in three localities but equals 1 in the remaining localities. N(b), however, is equal to exactly 2 because each of the eight areas contained two localities. Thus, only N(b) is known with confidence. For purposes of this exercise, however, I assign average (fractional) values to N(e), N(d), and N(c) of 1.2, 9, and 1.2, respectively; that is, the average number of analyses per sample is taken as 211/173; the average number of samples per section as 173/19, and the average number of sections per locality as 19/16. These fractional N's are arbitrary and their use is justified only in that they seem intuitively reasonable.

Miesch (1976, p. 101) defined the ratio of variation-among-areas to imprecision-within-areas as the variance mean ratio, v(m). Here, that ratio is computed as:

$$v(m) = \frac{V(A)}{I} \qquad (2)$$

For example, V(A) for Log Cu (table 4) equals 26; I (from equation (1)) for Log Cu equals 5.35; consequently, v(m) for the Cu map in figure 4 becomes 4.9. Values of v(m) for this and other geochemical maps are listed in table 4.

It is not exactly known how large v(m) must be to insure stability in a map pattern, but Miesch (1976, p. 102-3) suggests that values below 1.0 indicate serious instability and values above 3.0 indicate high stability. Such a judgment suggests that the Cu map is highly stable, so stable in fact that sampling may have been excessive (and, hence, inefficient). The map of Ce, where v(m) is less than 1, is excessively noisy; sampling here was clearly inefficient and the sampling effort wasted, at least for purposes of making that map. The remaining maps are reasonably stable (v(m) lies around 2 or 3) and represent efficient sampling. These latter patterns (plus the Cu pattern) are potentially useful in geologic interpretation and prediction. The interested reader is referred to Miesch (1976, p. 90-106) for a detailed discussion of hierarchical designs and efficient geochemical sampling.

The variance components in table 4 describe real and permanent features of the geochemical variation in the redbed sequence of this study. In terms of future, efficient (cost-effective) sampling, they indicate to the sampler where, in the hierarchical scheme, sampling should be concentrated. Design levels with large components require a greater sampling effort than levels with small components, if imprecision in mean values is to be efficiently reduced.

For example, the components (as percentages) for Log Cu (table 4) are:

V(A) = 26%
V(B) = 5
V(C) = <1
V(D) = 25
V(E) = 44

Sampling multiple localities within areas, to reduce the effects of V(B), or multiple sections within localities, to reduce the effects of V(C), would be wasteful. Rather, sampling needs to be concentrated within sections, in order to reduce the large effects of V(D), as follows:

N(b)	N(c)	N(d)	N(e)	I	v(m)
1	1	10	1	11.9	2.2
1	1	9	1	12.7	2.1
1	1	8	1	13.6	1.9
1	1	7	1	14.9	1.8
1	1	6	1	16.5	1.6
1	1	5	1	18.8	1.4

Thus, absent multiple sampling at other levels, it appears that a minimum of 9 samples per section is needed to produce a stable map of Cu.

The relatively large error in the analysis (V(E) = 44 percent) suggests that multiple analyses of each sample are in order. Note, however, that increasing the samples per section reduces the effect of both V(D) and V(E) simultaneously, because of the structure of equation (1).

In general, v(m) increases as the N's increase and efficient sampling is a matter of efficient allocation of the sampling load among the N's. Thus, if a basinwide map of Ce, say, is of importance, the sampling design must include values of the N's that will produce a suitably large v(m). The components for Log Ce are:

V(A) = 5%
V(B) = <1
V(C) = 11
V(D) = 76
V(E) = 8

The proportion of variation to be mapped, V(A), is only 5 percent of the total. As is customary in sedimentary rocks, most of the variation is across stratification, so N(d) must be large. But, in addition, N(c) must be more than 1, as the following listing shows:

N(b)	N(c)	N(d)	N(e)	I	v(m)
1	1	10	1	19.4	0.3
1	1	100	1	11.8	.4
1	1	infinity	1	11.0	.5
1	5	10	1	3.88	1.3
1	5	30	1	2.76	1.8
1	5	100	1	2.37	2.1
1	10	10	1	1.94	2.6

To attain a value of v(m) above 2 is clearly going to be costly. Multiple samples per section (N(d)) and multiple sections per locality (N(c)) will be required; one locality per area (N(b)) is sufficient, however. A v(m) of 2.1 is expected if the design contains 100 samples per section and 5 sections per locality, for a total of 500 samples per locality. Alternatively, an equally good value of 2.6 is expected with 10 samples per section and 10 sections per locality, for a total of 100 samples per locality. A drastic reduction in total sample load (500 vs. 100) is possible with a doubling of sampled sections (5 vs. 10). Cost efficiency here depends largely on the relative cost of field and laboratory work; that is, which is cheaper, sampling five more sections per locality or analyzing 400 more samples per locality?

In actuality, outcrop limitations in this work would preclude sampling in 10 (or even two) sections per locality. Thus, a stable basinwide map of Ce is simply not practical. A similar conclusions can be drawn for any element where V(A) is judged significant but V(B)+V(C) equals or exceeds V(A).

For the remaining elements a sense of efficient sampling costs is indicated by values for N(d) in table 4. N(d) estimates the minimum number of samples to be collected across each section if N(b) is set equal to 2 and N(c) is set equal to 1; the total sample load within each sampled area then becomes N(b) x N(d). This load ranges from 4 (Cu) to 90 (Hg), a load easily attainable in terms of time or money.