

# Shorter Contributions to Geochemistry, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-A-I



# Shorter Contributions to Geochemistry, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-A-I



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## CONVERSION FACTORS

Metric unit	Inch-Pound equivalent	Metric unit	Inch-Pound equivalent
<b>Length</b>		<b>Specific combinations—Continued</b>	
millimeter (mm)	= 0.03937 inch (in)	liter per second (L/s)	= .0353 cubic foot per second
meter (m)	= 3.28 feet (ft)	cubic meter per second per square kilometer [(m <sup>3</sup> /s)/km <sup>2</sup> ]	= 91.47 cubic feet per second per square mile [(ft <sup>3</sup> /s)/mi <sup>2</sup> ]
kilometer (km)	= .62 mile (mi)	meter per day (m/d)	= 3.28 feet per day (hydraulic conductivity) (ft/d)
<b>Area</b>		meter per kilometer (m/km)	= 5.28 feet per mile (ft/mi)
square meter (m <sup>2</sup> )	= 10.76 square feet (ft <sup>2</sup> )	kilometer per hour (km/h)	= .9113 foot per second (ft/s)
square kilometer (km <sup>2</sup> )	= .386 square mile (mi <sup>2</sup> )	meter per second (m/s)	= 3.28 feet per second
hectare (ha)	= 2.47 acres	meter squared per day (m <sup>2</sup> /d)	= 10.764 feet squared per day (ft <sup>2</sup> /d) (transmissivity)
<b>Volume</b>		cubic meter per second (m <sup>3</sup> /s)	= 22.826 million gallons per day (Mgal/d)
cubic centimeter (cm <sup>3</sup> )	= 0.061 cubic inch (in <sup>3</sup> )	cubic meter per minute (m <sup>3</sup> /min)	= 264.2 gallons per minute (gal/min)
liter (L)	= 61.03 cubic inches	liter per second (L/s)	= 15.85 gallons per minute
cubic meter (m <sup>3</sup> )	= 35.31 cubic feet (ft <sup>3</sup> )	liter per second per meter [(L/s)/m]	= 4.83 gallons per minute per foot [(gal/min)/ft]
cubic meter	= .00081 acre-foot (acre-ft)	kilometer per hour (km/h)	= .62 mile per hour (mi/h)
cubic hectometer (hm <sup>3</sup> )	= 810.7 acre-feet	meter per second (m/s)	= 2.237 miles per hour
liter	= 2.113 pints (pt)	gram per cubic centimeter (g/cm <sup>3</sup> )	= 62.43 pounds per cubic foot (lb/ft <sup>3</sup> )
liter	= 1.06 quarts (qt)	gram per square centimeter (g/cm <sup>2</sup> )	= 2.048 pounds per square foot (lb/ft <sup>2</sup> )
liter	= .26 gallon (gal)	gram per square centimeter	= .0142 pound per square inch (lb/in <sup>2</sup> )
cubic meter	= .00026 million gallons (Mgal or 10 <sup>6</sup> gal)	<b>Temperature</b>	
cubic meter	= 6.290 barrels (bbl) (1 bbl=42 gal)	degree Celsius (°C)	= 1.8 degrees Fahrenheit (°F)
<b>Weight</b>		degrees Celsius (temperature)	= [(1.8 × °C) + 32] degrees Fahrenheit
gram (g)	= 0.035 ounce, avoirdupois (oz avdp)		
gram	= .0022 pound, avoirdupois (lb avdp)		
metric tons (t)	= 1.102 tons, short (2,000 lb)		
metric tons	= 0.9842 ton, long (2,240 lb)		
<b>Specific combinations</b>			
kilogram per square centimeter (kg/cm <sup>2</sup> )	= 0.96 atmosphere (atm)		
kilogram per square centimeter	= .98 bar (0.9869 atm)		
cubic meter per second (m <sup>3</sup> /s)	= 35.3 cubic feet per second (ft <sup>3</sup> /s)		

# A Computerized Multichannel Data Acquisition and Control System for High-Precision Mass Spectrometry

*By* NATHANIEL D. SHERRILL *and* G. BRENT DALRYMPLE

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-A





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## A COMPUTERIZED MULTICHANNEL DATA ACQUISITION AND CONTROL SYSTEM FOR HIGH-PRECISION MASS SPECTROMETRY

By NATHANIEL D. SHERRILL and G. BRENT DALRYMPLE

### ABSTRACT

The hardware and assembly language software for a simple multichannel digital data system has been built around a 12-bit minicomputer. The system is capable of controlling an external device and taking data simultaneously from as many as five data channels and an elapsed-time counter. Input of 0 to 10 volts to the data channels provides six significant decimal digits for computation. Although the system was designed for use with mass spectrometers, it could easily be adapted, with little or no change in either the hardware or software, to a variety of analytical instruments; it could also be easily expanded to include additional channels.

### INTRODUCTION

Mass spectrometry, for geochronological and isotopic tracer studies requires data of high precision over a dynamic signal range of more than  $10^5$ . As examples,  $^{40}\text{Ar}/^{36}\text{Ar}$  isotope ratios for potassium-argon dating are frequently more than  $10^4$ , and the precision required for  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are typically better than 1 part in 7000. Input signals to the data system may range from less than 0.1 millivolt to 10 volts dc. We have designed and constructed a relatively simple and versatile computerized control and data acquisition system that not only meets these requirements of precision and dynamic range, but also is capable of acquiring data simultaneously from as many as five data channels and keeping track of elapsed time during an analysis.

The system is designed around a dedicated Digital Equipment Corporation<sup>1</sup> (DEC) PDP8/E 12-bit minicomputer and uses DEC logic hardware and programming languages. Both control and data acquisition are by programmed input/output via three PAL8 assembly language functions that are called

<sup>1</sup> Any use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

directly from OS/8 BASIC, which makes programming the system very easy for the user. The software does not expect the external devices to set device-ready flags, which simplifies the necessary hardware and the interfacing of the external devices to the computer system. Data from the system are input with a 23-bit mantissa giving six significant decimal digits for computation. The elapsed-time counter can be reset and will record intervals of from 0.02 s to more than 46 h; integration times are precise to better than 0.0002 s. The dynamic range of the system permits integration times as long as 8 s at 10 V signal input without overflowing the digital data counters.

Although the system was designed for use with mass spectrometers, it could easily be adapted, with little or no change in either the hardware or software, to a variety of analytical instruments; it could also be easily expanded to include additional channels. The assembly language routines could also be rewritten in the assembly languages RALF or SABR for use with FORTRAN IV or II, respectively, with no changes in hardware configuration, and most if not all of the system concept could be adapted to other minicomputer or microcomputer systems.

### HARDWARE CONFIGURATION

For single-channel operation, the system can be configured as in figure 1. Our system has four additional but identical data channels. Input signals of 0 to 10 V dc are fed to a Teledyne Philbrick model 470501 voltage to frequency converter (V/F), which has a transfer characteristic of 1-MHz (megahertz) output for a 10 V dc input and a linearity of 0.05 percent or better over its entire range. The output

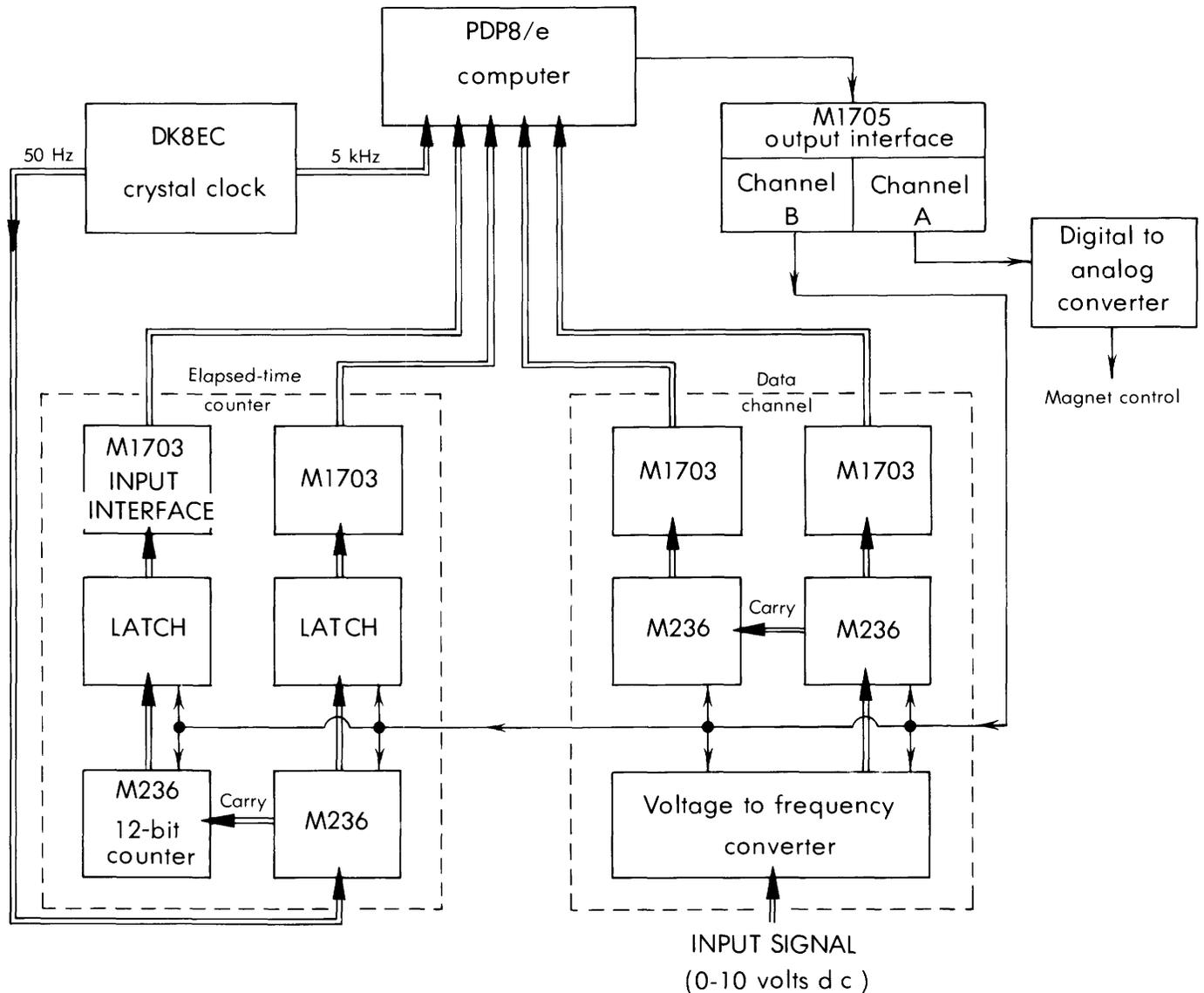


FIGURE 1.—Block diagram of multichannel data system with elapsed-time counter. Only one of the five data channels is shown. Control paths (output from the computer bus) are shown as single lines; data paths (input to the computer bus), as double lines.

of the V/F is fed to two DEC M236 12-bit counters that are cascaded so that the carry-out signal of the low-order counter is a count input to the high-order counter. Each counter is read independently by the computer through its own DEC M1703 input interface and the low-order and high-order 12-bit words combined internally by the software into a standard PDP8 23-bit floating-point number. Counting control is via one channel of a DEC M1705 dual channel 12-bit output interface. One bit per data channel is used to set counter outputs to zero via the counter LOAD DATA connection. Because all counter DATA INPUTS are permanently grounded, receipt

of a LOAD DATA command (LOGIC LOW) from the output interface causes all zeros to appear on the counter outputs. When LOAD DATA is released, the counters will respond to any pulse that are present at the COUNT IN terminal.

A design restriction of the counters prohibits changing the state of the ENABLE input, which starts and stops the counter, except when the count in pulse is in the high state. The 350-nanosecond width of the input pulses would require extensive gating in order to use the ENABLE input, and so it was decided to gate the output of the V/F with a high-speed optical isolator and leave the counters

permanently enabled. The choice of an optical isolator (Litronix model IL-100), in addition to providing control of the V/F signal to the counters, offers the opportunity to isolate the analog and digital grounds, thereby reducing system noise.

The second channel of the output interface is used to control the beam deflection magnet field strength via a 12-bit digital to analog converter (DAC), which produces an output voltage proportional to the digital input code. This voltage is compared to the output of a gaussmeter by an operational amplifier that drives the magnet power supply to produce the field value represented by the digital code.

Timing is provided by a nonprogramable DK8EC quartz crystal clock. The 5-kHz output from the clock is fed directly to the computer bus where it is available to the software for timing of integration times and program delays. The 50-Hz output is fed to the two cascaded 12-bit counters in the elapsed-time (E-T) counter. The output from each counter drives a 12-bit latch that can be latched on command via the M1705 output interface. This latch allows the count to be read via the two M1703 input interfaces without interrupting the elapsed-time counters, which continue to operate. On command to unlatch, the latches assume the current counter output states. To reset the elapsed-time counter, the counters are zeroed, but, like the data counters, they are always left enabled.

### SOFTWARE

The software for the system consists of three assembly language functions, CKW(N), CTL(M,N), and RDA(N), that are written in PAL8 and called as user-defined functions from OS/8 BASIC (BASIC ver. 5A, OS/8 ver. 3D). An annotated list of these functions is given at the end of this report. Details about PAL8, OS/8 BASIC, and instructions for interfacing the functions to the BASIC Run-Time System (BRTS) are given in the Digital Equipment Corporation OS/8 Handbook (Maynard, Mass., Digital Equipment Corp.).

#### CLOCK WAIT FUNCTION—CKW(N)

The clock wait function causes a simple delay in the execution of a BASIC program and is called as a statement of the form

$$Y = \text{CKW}(N),$$

where Y is a dummy variable and N specifies the decimal number of clock pulses before the function returns to the main program. For mass spectrometry, the function is used to time integration inter-

vals and to delay the program in order to allow the magnetic field to settle after the DAC has been switched to a new value.

Because the argument N is passed to the software counter as a 12-bit word, its value is restricted to the range  $0 \leq N \leq 4095$ . The frequency of the crystal clock output is 5 kHz, but in order to increase the precision of the function without severely limiting the maximum interval length, the software counters within CKW(N) make it appear to the user as if the clock is running at 50 Hz. This arrangement results in a clock resolution of 0.02 percent for a 1-s delay ( $\pm 1$  count at 5 kHz), a minimum specifiable delay interval of 0.02 s ( $N=1$ ), and a maximum delay interval of 81.9 s ( $N=4095$ ). Note that the program delays caused by the function, although precise, are actually a little longer than specified (that is, a 50-count delay will be slightly longer than 1 s) because of the execution time of the function software. The error, however, is less than 1 millisecond and is negligible for most applications, particularly when a constant integration time is used throughout a single program. If the CKW(N) function is to be used for precise timing, for example, integration times, the user functions must be in core before the first data are taken or significant timing errors will occur while BRTS executes the overlay.

#### CONTROL FUNCTION—CTL(M,N)

The control function is used to pass a bit pattern to an external device by setting the bits of either of the two digital output registers of the M1705 output interface. The function is called with a dummy vari-

$$Y = \text{CTL}(M,N)$$

able and uses two decimal arguments,  $0 \leq N \leq 1$  where 0=channel A and 1=channel B, and  $0 \leq M \leq 4095$  is the bit pattern to be passed. For our application, channel A is used to control the magnet by passing a bit pattern, which specifies the field strength, to the magnet control system.

Channel B is used to control the data system and the elapsed-time (E-T) counter. Each channel, including the E-T counter, requires only two bits for complete control so all six channels can be controlled independently with a single command by passing the proper bit pattern to channel B of the output interface. The bit assignments for the argument M are shown in figure 2. As an example of the flexibility of this system, the decimal argument 2298 (100 011 111 010 binary or 4372 octal) would latch the E-T counter outputs, reset the data counters for channel 5 to zero, gate on the V/Fs for channels 3

and 4, and gate off the V/Fs for channels 1 and 2. In practice, however, only a few arguments are necessary because, for most applications, the five data channels are controlled simultaneously.

- M=1024=E-T counter reset to zero, data counters reset to zero
- M=3072=E-T counter outputs unlatched, data counters reset to zero
- M=4095=E-T counter outputs unlatched, V/F gated on
- M=2730=E-T counter outputs latched, VF gated off

Note that these same arguments work equally well with a system of less than five data channels because the commands for the missing channels are simply ignored.

READ DATA FUNCTION—RDA(N)

The read data function is used to read the five data channels and the E-T counter. It is called from BASIC in the form

$$Y = RDA(N),$$

where  $0 \leq N \leq 5$  specifies the channel to be read according to the channel assignments in figure 2. The function returns with the value (either data or E-T count) in the mantissa of the 23-bit floating point accumulator, and that value is assigned to the variable Y, which may be treated as any other decimal variable.

SAMPLE PROGRAM

An example of the use of these functions for mass spectrometer control and data acquisition is illustrated in the following annotated BASIC program segment.

```

220 Y=CTL(2241,0) /switch magnet to new field strength
230 Y=CKW(200) /wait 4 s for field to settle
240 Y=CTL(1024,1) /reset E-T and data counters to zero
250 Y=CTL(4095,1) /gate V/Fs on
260 Y=CKW(150) /integrate 3s
270 Y=CTL(2730,1) /gate V/Fs off, latch E-T counter outputs
280 T=50*RDA(0) /read elapsed time in seconds, assign value to variable T
290 X1=RDA(1) /read data channel 1, assign to variable X1
300 X2=RDA(2) /read data channel 2, assign to variable X2
    
```

List of functions

/CKW----CLOCK WAIT  
/BASIC FUNCTION THAT CAUSES A DELAY IN PROGRAM EXECUTION USING THE DK8-EC  
/REAL-TIME CLOCK. FUNCTION USES ONE ARGUMENT  $0 \leq N \leq 4095$  TO SPECIFY THE NUMBER OF CLOCK COUNTS BEFORE RETURNING TO THE MAIN BASIC PROGRAM. CHANGE DELAY FOR CLOCK FREQUENCIES AS FOLLOWS:  
/50HZ=777, 500HZ=7770, 5KHZ=7634.  
/2-19-76 G. BRENT DALRYMPLE, U.S.G.S.

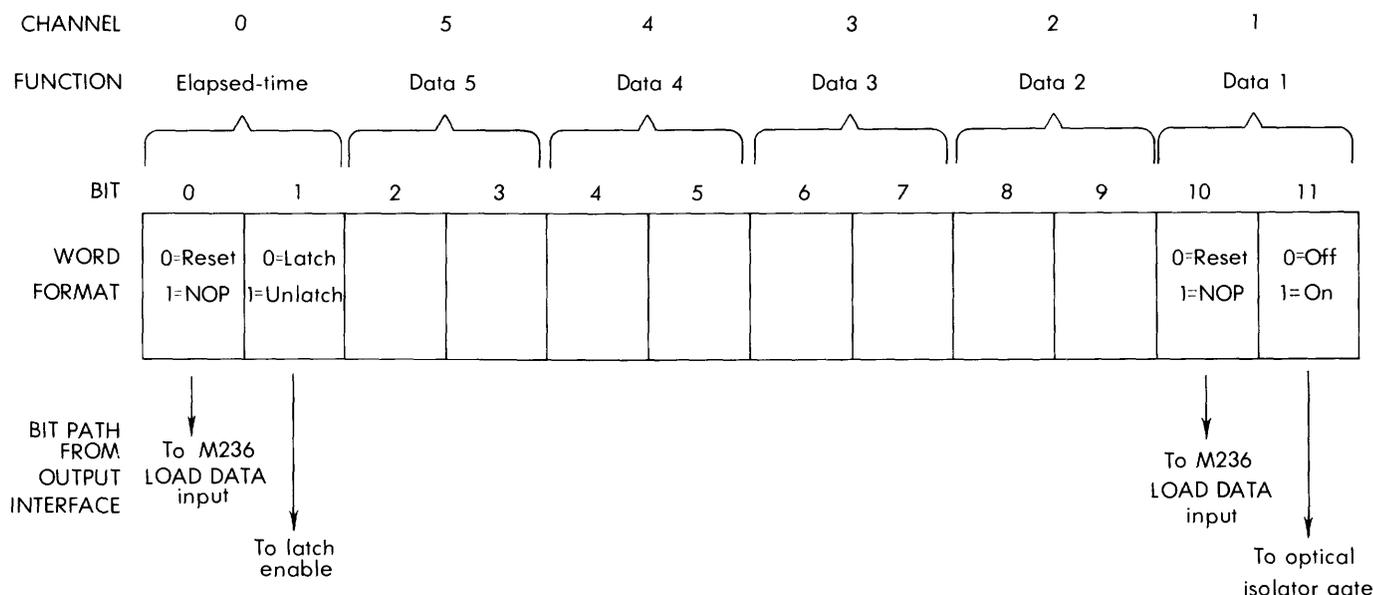


FIGURE 2.—Bit assignment and word format for the argument M in the control function CTL(M,N). The bit assignments data channel 1 and the E-T counter are shown; all five data channels are identical.

```

INTL=156      /BRTS POINTER TO
               UNSFIX
CLKS=6133     /CLOCK SKIP ON FLAG
               IOT
FIELD 0
*3400
CKW, 0        /ENTRY POINT
CLA
JMS I INTL    /FIX ARG TO INTEGER
               IN AC
CIA          /NEGATE INTEGER
DCA COUNTR   /STORE AS COUNTER
AGAIN, TAD DELAY /SET DELAY COUNTER
DCA DCOUNT
WAIT, CLSK    /WAIT FOR CLOCK FLAG
JMP .-1
ISZ DCOUNT  /DONE COUNTING?
JMP WAIT     /NO. WAIT FOR
               ANOTHER FLAG
ISZ COUNTR   /DONE COUNTING?
JMP AGAIN    /NO
JMP I CKW    /YES. RETURN TO BASIC
COUNTR, 0
DELAY, 7634  /-100(10) FOR 5KHZ
               CLOCK
DCOUNT, 0
/CTL ---- CONTROL
/BASIC FUNCTION TO SET THE BITS OF THE
/DIGITAL OUTPUT REGISTERS OF A M1705
/OUTPUT INTERFACE, FUNCTION USES TWO
/ARGUMENTS (M,N). 0<=N<=1 WHERE 0=
CHANNEL A
/AND 1=CHANNEL B. 0<=M<=4095(10)
/SPECIFIES THE BIT PATTERN TO BE PASSED
/10-18-74. G. BRENT DALRYMPLE, U.S.G.S.
INTL=156      /BRTS POINTER TO
               UNSFIX
IA=1465       /BRTS ILLEG ARG ERROR
               MESSAGE
FGETL=157     /BRTS POINTER TO
               FFGET
ARGPRE=311    /BRTS SUB TO LOCATE
               SCALAR VAR
INSAV=56      /SCALAR LOC USED BY
               ARGPRE
*3450
CTL, 0        /ENTRY POINT
CLA
JMS I INTL    /FIX ARG M TO INTEGER
               IN AC
DCA VALUE     /SAVE M
JMS GETARG    /PUT N INTO FAC
JMS I INTL    /FIX ARG N TO INTEGER
               IN AC
CIA          /NEGATE N
IAC          /IS N<=1?
SPA
JMP IA        /NO. FATAL ERROR
               MESSAGE
CIA          /YES
IAC          /RECOVER N
    
```

```

RTL          /ROTATE
RAL          /THREE LEFT
TAD WRCHA    /MAKE M1705 WRITE IOT
DCA WRITE    /DCA IOT
TAD WRITE    /RECOVER WRITE IOT
TAD K0001    /MAKE STROBE IOT
DCA STROBE   /DCA STROBE IOT
TAD VALUE    /RECALL M
WRITE, 0      /OUTPUT DIGITAL
               VALUE
NOP          /ALLOW DATA TO
               SETTLE
STROBE, 0    /STROBE DATA TO
               DEVICE
CLA
JMP I CTL    /RETURN TO BASIC
/SUBROUTINE BORROWED FROM DEC UF.8E
/ENTER WITH SCALAR (0=ARG2, 1=ARG3, 2=ARG4)
/IN AC: RETURN WITH ARG IN FAC
GETARG, 0
DCA INSAV    /USED BY ARGPRE
JMS I KARG    /GET ADR OF ARG
JMS I FGETL   /PUT ARG IN FAC
KARG, ARGPRE /THIS LOC SKIPPED BY
               FFGET
CDF          /RESET DATA FIELD
JMP I GETARG /RETURN
VALUE, 0     /M STORAGE
WRCHA, 6153  /M1705 WRITE IOT, CHAN
               A
K0001, 1
/RDA ---- READ DATA
/BASIC FUNCTION TO READ UP TO N 23-BIT DATA
/CHANNELS USING TWO M236 12-BIT COUNTERS
/IN SERIES AND TWO M1703 INPUT INTERFACES
/PER CHANNEL. 0<=N<=5. FUNCTION RETURNS TO
/BASIC WITH DATA IN FAC.
/REVISED 5-17-76. G. BRENT DALRYMPLE, U.S.G.S.
EXP=44       /FAC LOCATIONS
HORD=45
LORD=46
INTL=156     /BRTS POINTER TO
               UNSFIX
FNORL=124    /BRTS POINTER TO
               FFNOR
IA=1465      /BRTS ILLEG ARG ERROR
               MESSAGE
K0010=177    /CONSTANT 10 (BRTS
               LOC)
*3520
RDA, 0       /ENTRY POINT
CLA
JMS I INTL    /FIX ARG TO INTEGER
               IN AC
CIA          /NEGATE ARG
TAD K0005
SPA          /IS N<=5?
JMP IA        /NO. FATAL ERROR
               MESSAGE
CIA          /YES
TAD K0005    /RECOVER N
RTL          /MULT N X 2 AND
    
```

	RTL	/ROTATE 3 LEFT	RDDAH,	0	/READ HI ORDER BITS
	TAD RDDAO	/MAKE LO ORD READ		DCA HORD	/DEPOSIT IN FAC
		IOT		TAD K0027	/PUT 23(10) INTO EXP
	DCA RDDAL	/DEPOSIT IOT		DCA EXP	
RDDAL,	0	/READ LO ORDER BITS		JMS I FNORL	/NORMALIZE FAC
	DCA LORD	/DEPOSIT IN FAC		JMP I RDA	/RETURN TO BASIC
	TAD RDDAL	/RECOVER IOT	RDDAO,	6424	/M1703 READ IOT, LO
	TAD K0010	/MAKE HI ORDER READ			ORD, CH O
		IOT			/23(10)
	DCA RDDAH	/DEPOSIT IOT	K0027,	27	
			K0005,	5	

Contributions of Major and Minor Elements  
to Soils and Vegetation by  
the Coal-Fired Four Corners Power Plant,  
San Juan County, New Mexico

By HELEN L. CANNON *and* VERNON E. SWANSON

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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**CONTRIBUTIONS OF MAJOR AND MINOR ELEMENTS TO  
SOILS AND VEGETATION BY THE COAL-FIRED  
FOUR CORNERS POWER PLANT, SAN JUAN COUNTY, NEW MEXICO**

By HELEN L. CANNON and VERNON E. SWANSON

ABSTRACT

The major chemical components in the ash from the Four Corners coal-fired power plant in San Juan County, N. Mex., are  $Al_2O_3$ ,  $SiO_2$ ,  $K_2O$ ,  $CaO$ ,  $MgO$ ,  $Na_2O$ , and  $Fe_2O_3$ . Many minor elements, including Sb, As, F, Hg, Se, Te, U, and Zn are enriched in the fly ash relative to the bottom ash or coal. Except for F and Hg, particulate effluvium collected from the crowns of shrubs near the power plant has lower concentrations of the enumerated minor elements than does the fly ash collected within the generating station; F and Hg show a relative enrichment in the effluent. In the vicinity of the power plant, the fly ash is currently contributing major and minor elements that are essential to vegetative growth to otherwise deficient soils. The concentrations of potentially harmful minor elements, such as Hg, As, Cd, and Pb, that originate at the power plant drop off rapidly with distance from the stacks and, at distances greater than 3 km, are lower than the average contents in United States soils. Pb concentrations in samples collected near highways and Hg in samples taken near gas-well fittings are higher than the concentrations in samples collected near the power plant. Vegetation even within 3 kilometers of the Four Corners Power Plant contains only normal concentrations of those elements considered to be hazardous to livestock or to man.

INTRODUCTION

By 1971, the people of Farmington and Shiprock, the Navajo tribe, and State officials in New Mexico had become concerned about the large quantities of smoke issuing from the stacks of the Four Corners Power Plant built near Fruitland, in San Juan County (fig. 1). A few people expressed concern about possible widespread destruction and contamination of large areas of the Southwest by the strip mines and power plants slated to be opened in the near future. To address these concerns and to provide facts on which thoughtful decisions could be based, and because most of the coal to be used as

fuel for these plants would be mined on Federal lands, the U.S. Department of the Interior initiated a multiagency project called the Southwest Energy Study. Three parts of this study were principally the responsibility of the U.S. Geological Survey: (1) to estimate and evaluate the coal resources in southwest United States (Averitt and others, 1972), (2) to determine the composition of the coal to be mined for use in the 10 power plants either anticipated or already in production (Swanson, 1972), and (3) to determine the effects of the effluent from the Four Corners Power Plant on the composition of soils and vegetation in the surrounding area (Cannon and Anderson, 1972) (fig. 2). The latter task was also a responsibility of EPA (U.S. Environmental Protection Agency).

The 2,170-megawatt Four Corners Power Plant was built by the Arizona Public Service Co. as operator for a combine of several power companies. It is located on a semiarid mesa south of the San Juan River on a relatively unpopulated part of the Navajo Indian Reservation. The mesa, which is capped by the Pictured Cliffs Sandstone of Cretaceous age (Fassett and Hinds, 1971), supports a sparse 10-percent cover of low xerophytic shrubs and grasses growing under semiarid conditions. The dry unproductive land near the power station has attracted few inhabitants and has been used by the Navajos only for sheep grazing. The artificial Lake Morgan, which supplies cooling water for the power station, has changed the appearance of the area and is stocked with fish. However, blue-green algae are now growing in the lake and are potentially toxic to fish (EPA, written commun., 1975). The Quaternary terrace alluvium along the nearby San Juan

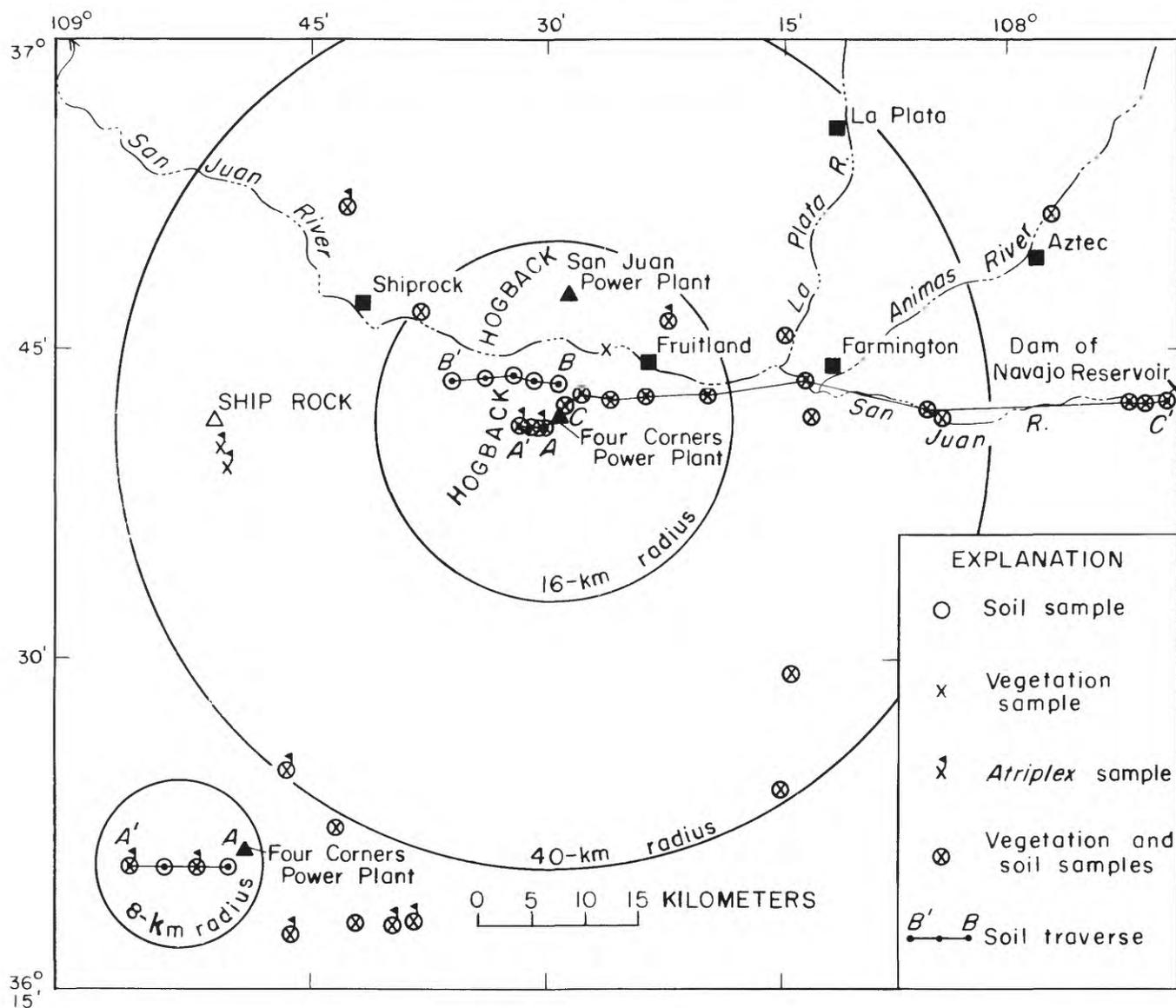


FIGURE 1.—Map showing sample localities in relation to the Four Corners Power Plant, northwestern New Mexico.



FIGURE 2.—View of the Four Corners Power Plant, looking west from the east side of Lake Morgan.

River is irrigated and cultivated for garden vegetables, fruit, alfalfa, and field corn. The towns of Shiprock, Fruitland, and Farmington are within 32 km of the plant. At the time of our study in 1971, the plant was releasing 300,000 kg of particulate matter per day to the atmosphere when all four units were operating; corrective measures since taken at considerable expense have substantially reduced that amount.

The annual precipitation at Fruitland is 177 mm a year, the amount of rainfall being greatest in late summer and early fall. The presence of "black alkali" prevents infiltration to the ground-water table, as does the commonly torrential nature of the

rains, which results in rapid runoff rather than penetration to the water table. Predominant wind directions, influenced by the orientation of the valley of the San Juan River, are from both east and west; the wind commonly blows from the east in the morning as cold air drains from the San Juan Mountains and reverses directions in the warm afternoons. Plume release from the power plant is at 91.4 m.

### SAMPLING PLAN

The objectives of the ecologic impact study were (1) to study the products of combustion and the composition of coal used in the power plant, (2) to collect and analyze samples of soils and vegetation from the San Juan County stations that had been studied in 1961–62 before the power plant was constructed, and (3) to reanalyze the older samples for comparison with the present collection.

Only 11 of the original stations were within 24 km of the power plant, and therefore additional soil and plant samples were collected along several new traverses both east and west from the plant for distances sufficient to obtain background samples. Plants collected along traverses A–A' and B–B' (fig. 1) were restricted to xerophytic species of *Atriplex* (*A. confertifolia*, *A. nuttali*, *A. powelli*, and *A. corrugata*) having similar habits of ion uptake. The eastern traverse, C–C', was extended for a distance of about 80 km. Species of grass and sage were collected on traverse C–C' along the San Juan River. These included *Oryzopsis hymenoides*, *Sporobolus airoides*, *Calamagrostis inexpansa*, and *Artemisia tridentata*. The samples most contaminated were collected 3.2 km directly west of the power plant in an ash-slurry disposal area, which is ditched to ponds at the end of traverse A–A' (fig. 3). The east



FIGURE 3.—View to the west from the Four Corners Power Plant along traverse A–A' toward the ash-disposal ponds.



FIGURE 4.—View looking west at the Navajo mine spoil piles from a station on traverse C–C'.

traverse, C–C', crossed the spoil piles of the Navajo mine and continued east to Navajo Lake (fig. 4).

The analyses showed that the earlier soil samples, from which ground splits had been saved, contained more metal than did later samples, because of improvements made in grinding equipment since the earlier samples had been ground. The two sets of soil samples, therefore, could not be compared for the purposes of this study. Both sets of vegetation samples, however, were ground in the same mill, were not washed, and therefore could be compared.

### SAMPLING AND ANALYTICAL TECHNIQUES

One composite vegetation sample and four soil samples—two from the top 0–13 mm of soil and two within a depth of 25–152 mm—were collected at most traverse stations. Soil samples were collected within a depth interval of 0–152 mm at stations where similar samples had been collected in 1961. The soil samples were put into paper envelopes designed for soil samples, and the plants were placed in #10 paper bags, which were sealed with tape. This procedure allowed the samples to be placed directly into the laboratory drier without transfer or additional handling. The samples were dried at 30° C and ground to –80 mesh. The results are reported for air-dried samples.

End branches, including twigs and leaves, were collected from shrubs; herbs and grasses were cut off 50 mm above the ground, to avoid soil contamination. The plant samples were not washed, because their metal concentrations were compared with those of unwashed samples collected previously. Furthermore, the samples were of forage plants consumed by grazing animals rather than of corn, which is husked and shelled by man before being consumed. Plant samples collected by the EPA and

the Arizona Public Service Co. were also unwashed (EPA, written commun., 1975).

Two types of coal samples were collected: channel samples of the coal beds and plant-feed samples from the blend piles. Samples of bottom ash and fly ash were also obtained (collected by J. F. Fassett, U.S. Geological Survey). The coal and soil samples were dried, ground, and analyzed by several methods, including emission spectrographic, X-ray fluorescence, neutron activation, atomic absorption, and wet chemical. The coal samples were analyzed for trace elements, following procedures outlined by Swanson (1972, p. 9-19), and forms-of-sulfur determinations on the coal were made by the U.S. Bureau of Mines (Staff office of the Director of Coal Research, 1967). Analyses of the soil and plant samples were made following the procedures of Ward and others (1963; 1969). B, Ba, Be, Co, Cu, Mn, Ni, Pb, Sr, and V were determined by the six-step emission-spectrographic method (Myers and others, 1961; Myers and Havens, 1970). By this method, the results are reported as the midpoints (1, 1.5, 2, 3, 5, 7) of geometric brackets within each order of magnitude. The precision of a reported

value is  $\pm 1$  bracket at the 68-percent confidence level or  $\pm 2$  brackets at the 95-percent confidence level. The reported midpoints are used in the tables and graphs.

A list of the analytical methods used and the limits of detection for each element are given in table 1. The analytical work was done in the laboratories of the U.S. Geological Survey under the direction of Claude Huffman, Jr., and Frederick N. Ward. The authors are grateful to them and to the chemists under their direction for providing the analyses used for the preparation of this report.

#### COAL AND COAL-COMBUSTION PRODUCTS

Upper Cretaceous coal, estimated at 720 or more billion metric tons, is widely distributed throughout the Southwest. The coal ranges in rank from sub-bituminous C to high-volatile C bituminous; it is low in sulfur, averaging about 0.6 percent S. The Four Corners Power Plant is using coal strip mined from six to eight beds in the Fruitland Formation of Cretaceous age (Fassett and Hinds, 1971) at the nearby Navajo mine. The major constituents of the ash of the coal used at the Four Corners Power

TABLE 1.—Analytical methods used and lower limits of detection shown for selected elements, in parts per million  
[Coal and plant samples reported in ash unless otherwise indicated. Leaders (---) indicate method not used for this material]

Element	Method	Lower limits of detection		
		Coal	Soil	Plant
Al	Emission spectrograph	20	10	20
As	Spectrophotometry	<sup>1</sup> 1.0	10	<sup>1</sup> .25
Be	Emission spectrograph	2	1	2
B	do	50	20	50
Ba	do	3	1.5	3
Ca	Atomic absorption	<sup>1</sup> 100	20	50
Cd	do	<sup>1</sup> .5	.2	.3
Co	Emission spectrograph	7	3	7
Cr	do	2	1	2
Cu	Atomic absorption	5	---	---
	Emission spectrograph	---	1	2
F	Specific ion electrode	<sup>1</sup> 50	---	<sup>1</sup> .6
Hg	Atomic absorption	.01	.001	<sup>1</sup> .025
Li	Atomic absorption	5	---	---
	Emission spectrograph	---	50	100
Fe	Emission spectrograph	20	10	20
Mg	Atomic absorption	100	20	50
Mo	Emission spectrograph	7	3	7
Mn	do	2	2	2
Na	Flame photometer	100	---	---
	Emission spectrograph	---	500	---
Ni	Emission spectrograph	10	5	10
Pb	do	20	10	20
Sb	Spectrophotometer	<sup>1</sup> .05	1	1
Se	X-ray fluorescence	<sup>1</sup> .1	.1	<sup>1</sup> .1
Sr	Emission spectrograph	10	5	10
U	Neutron activation	<sup>1</sup> .1	---	---
V	Emission spectrograph	15	7	15
Zn	Atomic absorption	10	.5	.5

<sup>1</sup> Dry weight.

TABLE 2.—Average major-oxide composition, in percent, of ash of coal used at Four Corners Power Plant (21 samples) and of coal used in the entire southwestern United States (71 samples)

[Data from Swanson (1972)]

Oxide	Four Corners Power Plant	Southwestern United States
SiO <sub>2</sub> -----	54.1	46.0
Al <sub>2</sub> O <sub>3</sub> -----	25.0	21.0
Na <sub>2</sub> O -----	1.5	1.4
K <sub>2</sub> O -----	.7	.5
CaO -----	3.8	8.5
MgO -----	.8	1.7
P <sub>2</sub> O <sub>5</sub> -----	.2	.4
Fe <sub>2</sub> O <sub>3</sub> -----	3.1	4.8
SO <sub>2</sub> -----	3.3	7.7
Other -----	7.5	8.0
Total -----	100.0	100.0

Plant are reported in table 2 as oxides. The compositions of all the southwest coals are remarkably similar, except for variations in the percent of ash (Swanson, 1972). The Four Corners Power Plant uses a blend of coal from two or more beds to maintain an average heat value of 5,000 kcal/kg and an average ash content of 21 percent.

The minor-element content of air-dried coal is compared with that of bottom ash, fly ash, and effluent in figure 5. Most heavy or inert elements are enriched in the bottom ash, as compared with the original coal, by the loss of combustible material. Considerable but unknown amounts of the volatile elements F, As, Se, and Hg are probably vaporized during combustion. The minor-element content of fly ash collected in the stack by the scrubbers and precipitators is also compared with the emitted particulate fraction being deposited on the soil and vegetation 1.6 km west of the plant. The latter material is more than 13 mm thick in the crowns of some of the shrubs. Although a certain amount of dilution by windblown silt has occurred, the volatile elements Hg and F are considerably more abundant in the windblown material than in the fly ash taken from the stack. The windborne material may be similarly enriched in As and Se, but no analytical data are available to verify this.

#### SOILS

Log-log graphs of the concentrations of Ba, B, Be, Ca, Pb, Ni, Mn, Cu, Hg, Se, Sr, V, Zn, and As in the top 12 mm of soils collected along three traverses from the power plant west (A-A'), northwest (B-B'), and east (C-C') are shown in figure 6. Two soil samples were collected at each station (fig. 1). Traverses A-A' and B-B' were across soils classified as badlands. Traverse C-C' was almost en-

tirely across soils of the Werlow-Fruitland-Turley association, consisting of stratified alluvium of the San Juan River (Maker and others, 1973).

Contents of Ba, B, Be, Cu, Se, Sr, and As were uncommonly great in the area of ash disposal on traverse A-A' compared with their contents in average soils (Shacklette and others, 1971). As, Ca, Zn, and Cu were above average in soils along traverse A-A' only; Sr, B, and Se are above average for 3.2-4.8 km on the A-A' and B-B' traverses; V, Ni, and Mn in all traverse samples, regardless of the rocks from which they are derived, are below the national average for soils (Shacklette and others, 1971). At places on all three traverses, Be, B, Pb, and Hg appear to be more abundant than is normal, but sources of contamination other than the power plant are indicated for Pb and Hg. Lead contents are greater than normal in samples collected near highways. Although traverse A-A' paralleled only a dirt track, the track had heavy truck travel related to construction of new ash-pond facilities during the period of sampling.

Soils were collected in 1971 at 27 of the same sites sampled in 1961-62. Previously ground splits of the 1961-62 samples and newly ground 1971 samples were randomized and analyzed at the same time. The samples collected in 1961-62 contained slightly larger amounts of metal than those collected from the same sites in 1971. Experiments to determine the cause of this discrepancy show that the lower contents in the later samples are due to improved grinding practices. A comparison of samples collected at two sites from soil depths of 0-12 mm and 0-150 mm is given in table 3. No significant difference between samples collected at 0-150 mm and those collected from the top 12 mm can be discerned, except for a possible 1-step increase in lead in the top 12 mm.

#### VEGETATION

Splits of the early samples of vegetation were arranged in random sequence with samples from the later collection, and the entire lot of samples was analyzed as a group. The average quantities of elements in the 1971 samples are compared (fig. 7) with average quantities in 1961 samples. Certain minor elements in the vegetation are slightly more abundant in the 1971 samples than in the 1961 samples of the same species, which were collected at the same stations before construction of the power plant. An expectable decrease also occurs with increasing distance from the stacks.

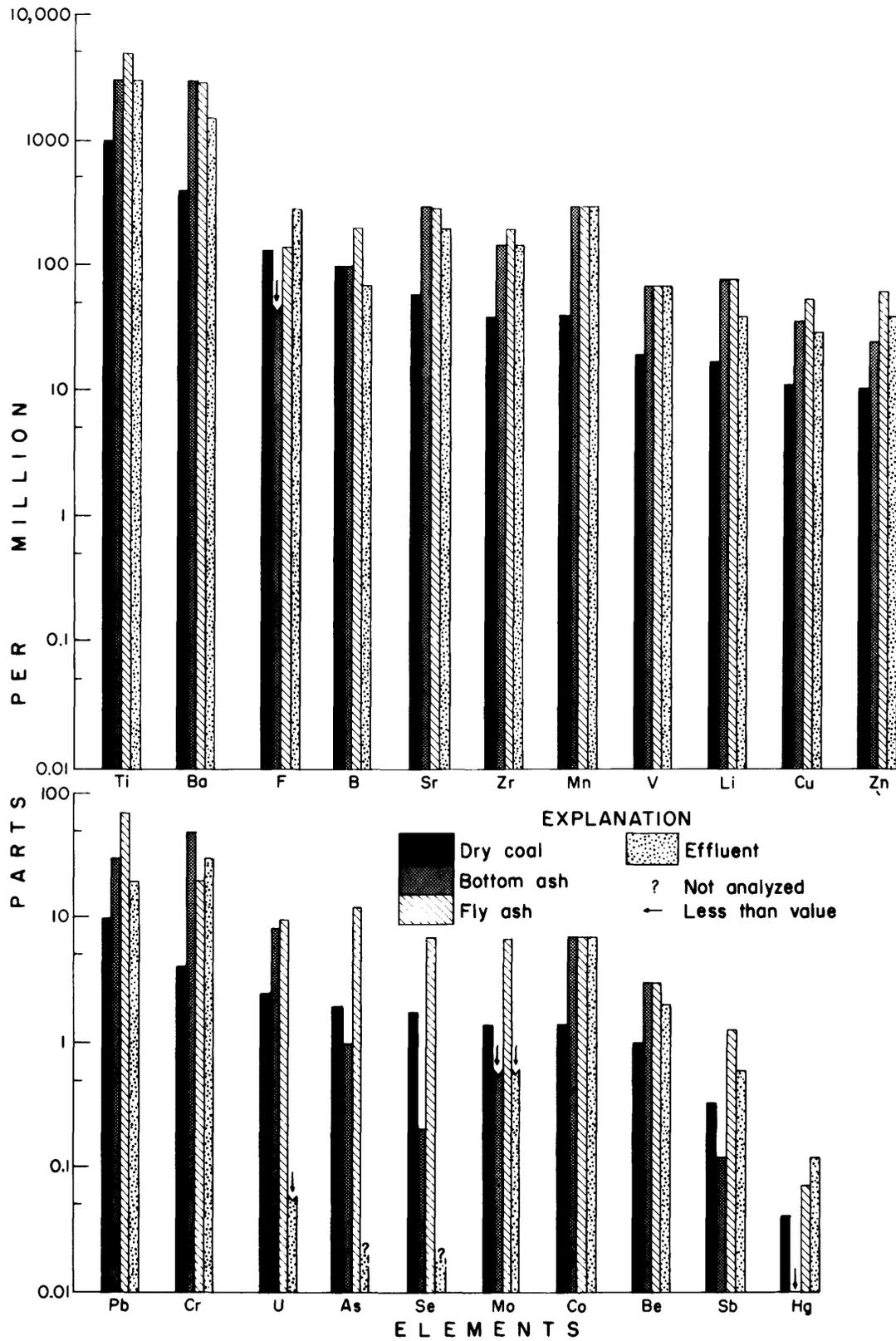


FIGURE 5.—Graph showing elemental components of coal and stack products of the Four Corners Power Plant.

TABLE 3.—Inorganic composition of soils collected from two stations

[Analyses by L. A. Bradley, H. G. Nieman, R. J. Turner, E. J. Fennelly, and J. A. Thomas, U.S. Geological Survey. N, not detected; L, below limit of detection. Leaders (---) indicate not analyzed for those elements]

Element	Station 21, 5.4 km NE.			Station 25, 9 km E.		
	1961	1971	1971	1961	1971	1971
	0-150 mm	0-150 mm	top 12 mm	0-150 mm	0-150 mm	top 12 mm
<b>Percent</b>						
Al	7	10	7	10	5	5
Mg	.7	.5	.5	.5	2	.1
Fe	2	2	2	3	1	1.5
Ca	7	3	2	1	.15	.15
Ti	.30	.20	.15	.20	.10	.1
K	2	2	3	5	3	3
Na	2	3	2	1	.7	1
<b>Parts per million</b>						
Ba	1000	2000	1000	700	1000	1000
Mn	300	300	300	300	200	200
B	30	L	L	70	50	20
Be	1	1.5	1.5	2	1	N
Co	5	10	10	7	5	7
Cr	20	15	15	50	7	7
Cu	30	20	20	20	5	7
La	30	30	50	70	30	30
Mo	N	N	30	5	N	50
Ni	5	7	7	15	L	L
Pb	20	20	30	20	20	30
Sr	2000	1000	700	200	100	100
V	70	70	70	100	20	20
Y	15	30	30	30	10	15
Zr	300	200	150	200	100	100
Ga	20	30	20	20	15	15
Yb	2	3	3	5	1.5	1.5
Hg	---	.02	.02	---	<.01	L
As	---	4	5	---	3	3
Zn	---	51	53	---	20	17

Mercury contents of the early samples averaged 0.41 ppm and those of the 1971 samples, only <0.025 ppm. It can only be concluded that the early samples were highly contaminated with mercury during the 10-year period of storage in a bunker formerly used for munitions storage at the Denver Federal Center. Although the percentage of mercury is slightly higher in the effluent than in the fly ash collected from the stacks of the Four Corners Power Plant (fig. 5), no mercury values greater than 0.025 ppm in dry weight were reported in the vegetation samples collected in 1971.

A later study of mercury in soils, vegetation, and water in the San Juan drainage basin was made to determine whether the power plant could be the source of mercury that had been detected in fish in Navajo Reservoir, 72.5 km northeast of the plant (Cannon and Swanson, unpub. data, 1972). The mercury in fish averaged slightly less than 0.5 ppm but was reported to be as high as 8.9 ppm in one chub (U.S. EPA, 1971). No evidence was found of a definable concentration of mercury in the environment that could be related to the power plant. Uncontaminated soils, in general, contained 0.05 ppm,

or less, all vegetation contained less than 0.025 ppm, and all water samples contained less than 0.5 µg/L of Hg.

Our mercury study included an 80-km traverse from the power plant to the lake. The traverse was run along the alluvium of the San Juan River in order to avoid chemical variations in soils related to different geologic origins. Samples of sediments and plants were also collected from all drainages entering the lake. We expected to find mercury coming into the lake from the watershed to the north, where rocks of the San Juan Mountains might be a contributor of as much as 11.8 metric tons Hg per year, according to EPA estimates (1971). However, no increases attributable to this source were observed. Mercury contamination from gas pressure valves 54.7 km east of the power plant was considerably greater than that near the power plant itself. Because of this apparent association, additional samples were collected near gas wells, gas separators, gas pressure valves, and storage tanks; erratic mercury contamination in soils and plants of as much as 0.24 ppm in soils and 0.05 ppm in *Artemisia tridentata* (sage) was shown.

The elements that appear to have increased in concentration in the vegetation since the power plant was built are Cd, Ba, Cu, Pb, Sr, Fe, Mg, and Ti (fig. 7). The analyses, plant identifications, and distance and direction from power plant are given in table 4. However, no significant difference exists between the means of samples collected 0.6-1.7 km and 42-84 km from the power plant, for any element, determined on the basis of either a significance level of 0.01 or the application of the *t* test given by Natrella (1963). The lead concentration at station 186 is believed to be caused by highway pollution, because this station is adjacent to U.S. Highway 666. Mercury was not plotted, because it was generally below the limit of detection (0.025 ppm).

Because there was no record in the literature of fluorine concentrations in vegetation growing near power stations, 5 plants and 13 soils were analyzed for fluorine (table 5). In general, the top 13 mm of soil contained less fluorine than the soil at a depth of 25-152 mm. The highest fluorine concentrations occurred in alfalfa and grass growing on the alluvial flat of the San Juan River. No consistent relationship exists between the fluorine contents of soils and plants and their distance from the power plant. The higher concentrations of fluorine in the plants growing on alluvium reflect availability and may be related to the lower concentrations of calcium and

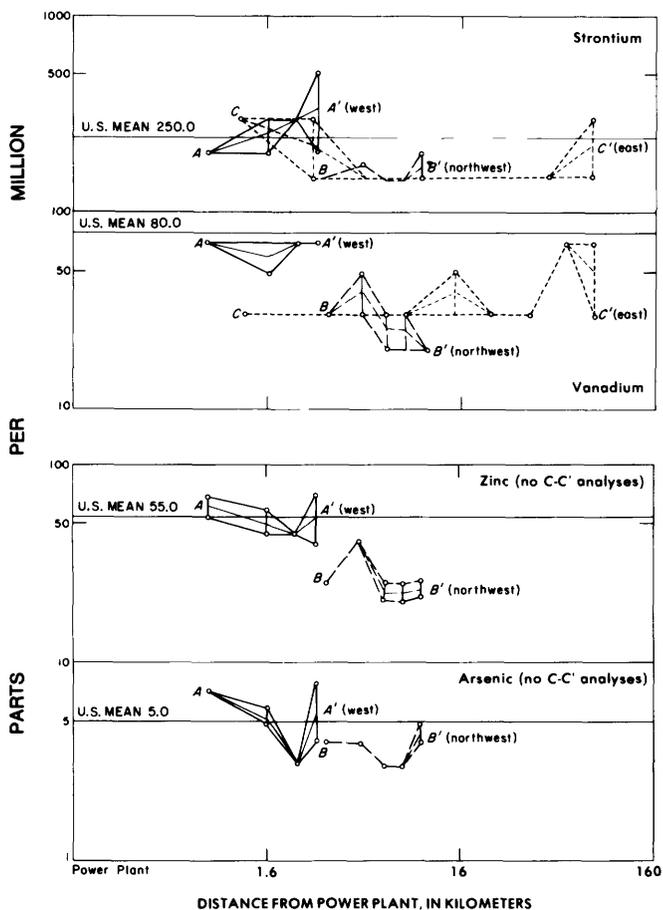


FIGURE 6.—Graphs of elemental concentration in top 12 mm of soils determined from sample pairs collected at stations along three traverses away from the Four Corners Power Plant.

phosphorus. These fluorine values may be compared with those in plants collected by the senior author from anomalous areas: for example, plants from the Gila Indian Reservation, Ariz., where the water is high in fluorine, contained 0.6–3.0 ppm F; plants from closed basins in Nevada and California contained 6–20 ppm; and plants growing on tailings of the Augusta gold mine, Colorado (5.7 percent F), contained 220–1,500 ppm. Fluorine accumulators, such as camellia, have been reported to contain as much as 3,060 ppm (Fleischer and Robinson, 1963).

SUMMARY AND CONCLUSIONS

Several conclusions can be drawn from this study. First, extra care must be taken to store and preserve unground splits of samples collected from uncontaminated areas in inert containers that cannot absorb volatile elements. These precautions are nec-

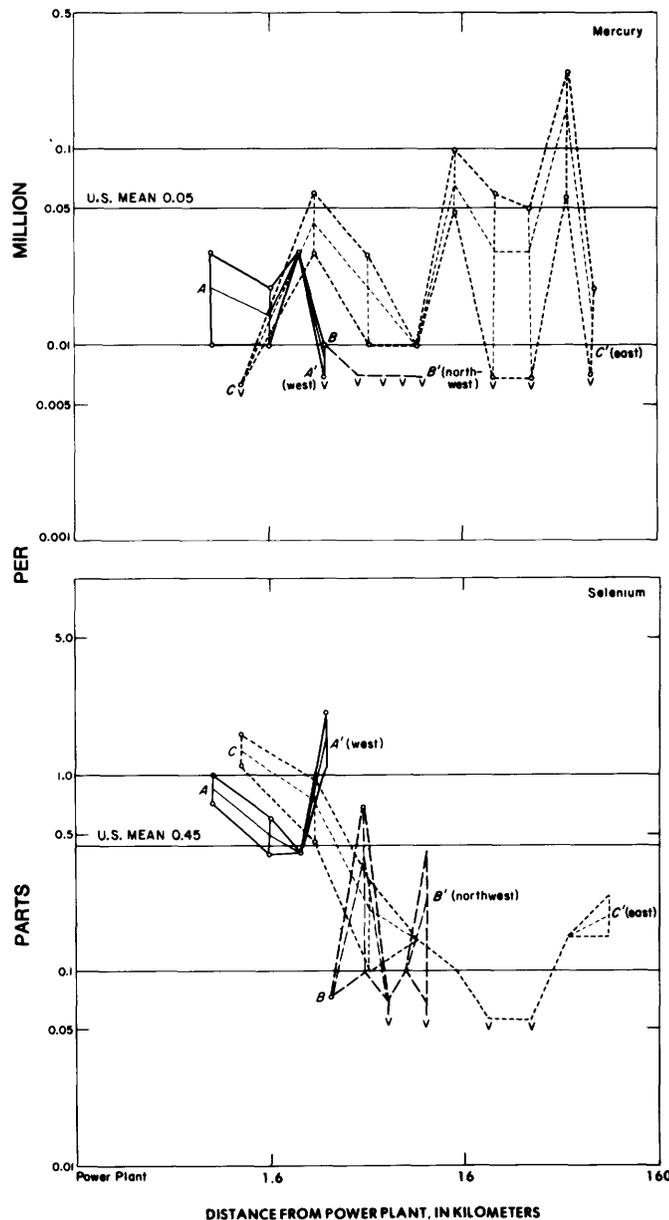


FIGURE 6.—Continued.

essary because older samples will become increasingly important to studies of long-term changes in the environment.

Second, the present control of fly-ash emissions in the Four Corners plant reduces the contents of harmful metals in the effluent, except for fluorine and mercury, which are increased in the soil and vegetation near the plant. The levels of other elements present in the effluent drop off rapidly within a distance of a few kilometers; barium, strontium, beryllium, and lead are typical elements in this category. Both soils and vegetation in San Juan

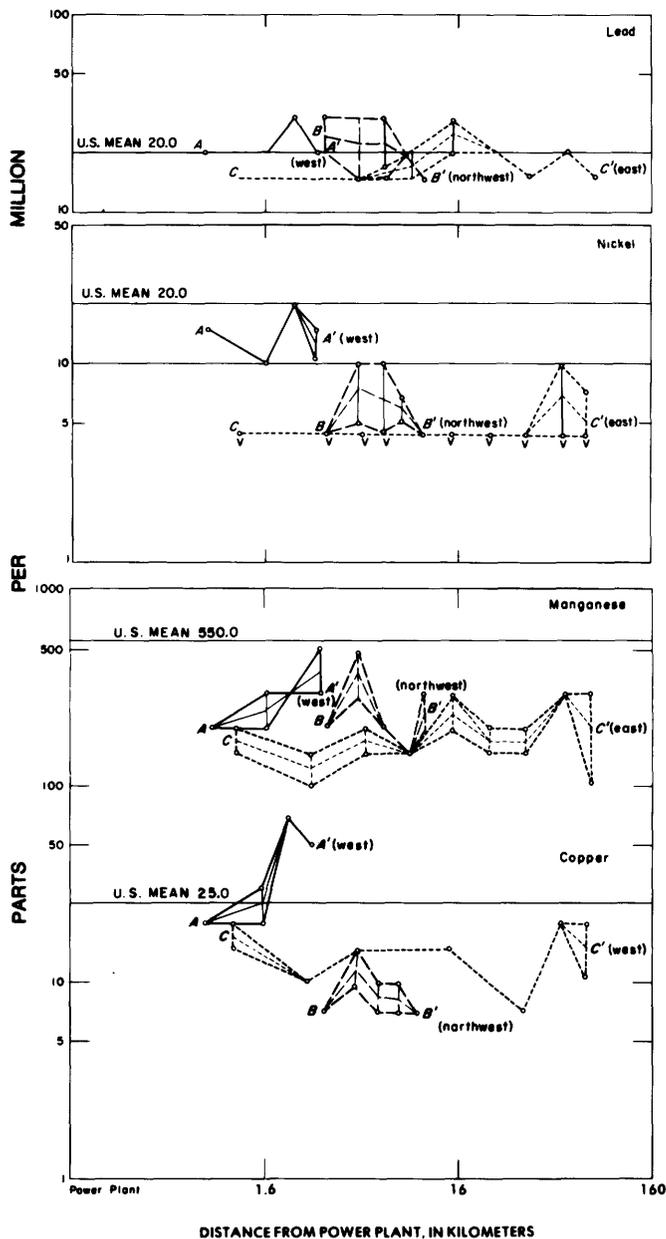


FIGURE 6.—Continued.

County are very deficient in these and most other essential elements. In an area of such deficiency, the addition of some elements from the effluent may actually be beneficial; plants do not require the elements most harmful to man and are therefore not concentrating them in greater quantities than occur in the soil. Levels of harmful metals in vegetation are very low or even below the limits of detection, except for lead, which appears to have increased throughout the area since 1961 and is highest near highways.

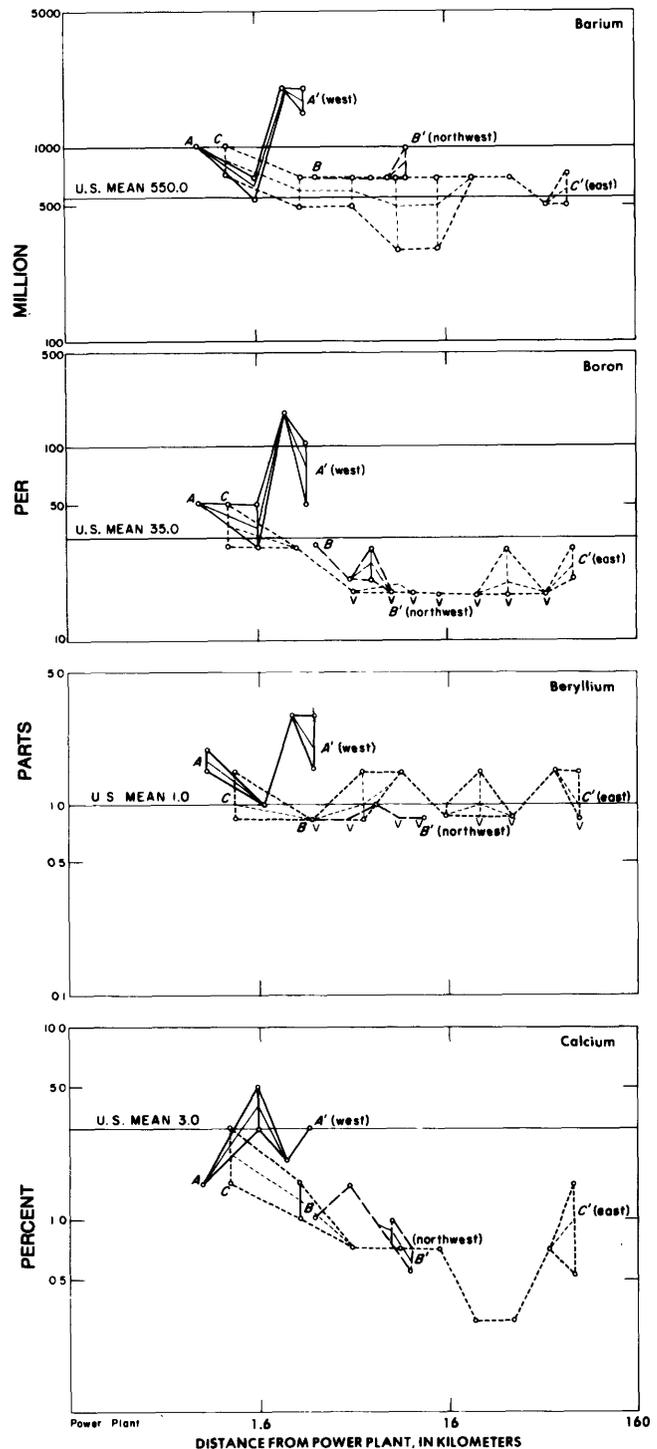


FIGURE 6.—Continued.

Third, there is no evidence that mercury, which had been detected in Navajo Lake, is coming from the power plant or from geologic sources in the watershed; the nearby gas field is a more likely source.

TABLE 4.—Composition of vegetation collected at various  
[Analyses by T. F. Harms, C. S. E. Papp, and L. D. Forshey, U.S. Geological  
leaders (---) indicate no sample available; ≈, approximately equal to. Means

Distance (km) and direction from power plant	Species	Sta- tion	Lab No. <sup>1</sup>	Chemical analyses, in parts per million										Spectro- graphic analysis, in parts per million				
				Ash, in percent		As		Hg		Cd		Zn		Se		Mn		
				1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	
1.2	N		<i>Tamarix gallica</i> -----	411	415911	---	11	---	---	---	<.025	---	---	---	---	---	---	16
1.7	W		<i>Atriplex corrugata</i> -----	303	415658	---	33	---	.5	---	<.025	---	.13	---	26	---	.2	100
2.9	ENE		<i>Oryzopsis hymenoides</i> -----	412B	415915	---	8.9	---	---	---	<.025	---	---	---	---	---	---	27
2.9	ENE		<i>Juncus balticus</i> -----	412A	415908	---	11	---	---	---	<.025	---	---	---	---	---	---	350
3.2	W		<i>Atriplex powelli</i> -----	305A	415665	---	30	---	<.25	---	<.025	---	.10	---	22	---	1.5	60
3.2	W		<i>Atriplex nuttali</i> -----	305B	415653	---	29	---	<.25	---	<.025	---	.09	---	22	---	1.5	58
5.1	E		<i>Sporobolus airoides</i> -----	413	415914	---	8.9	---	---	---	<.025	---	---	---	---	---	---	28
9.7	NW		Corn -----	70	415738	---	2.9	---	<.25	---	<.025	---	.01	---	38	---	.05	9
9.7	NE		<i>Sporobolus airoides</i> -----	414	415912	---	9.9	---	---	---	<.025	---	---	---	25	---	.3	30
14.5	NE		<i>Atriplex nuttali</i> -----	21	415654	---	26	---	.5	---	<.025	---	.08	---	---	---	---	78
14.5	NE		<i>Calamagrostis inexpansa</i> -----	415	415916	---	10	---	---	---	<.025	---	---	---	---	---	---	70
16.1	NW		Alfalfa -----	182	415725	12	9.2	<.25	<.25	0.4	<.025	.048	.04	27	18	.7	.1	19 28
Mean 1-20 km						16		<.25		<.025		0.07		25		0.6		88
23	ENE		<i>Artemisia tridentata</i> -----	416	415919	---	9.2	---	---	---	<.025	---	---	---	---	---	---	28
22.5	NE		<i>Gutierrezia lucida</i> -----	22	415729}	6	7.2	<.25	.25	.2	<.025	.13	.11	40	14	.3	.3	30 36
			<i>Gutierrezia lucida</i> -----	22	415735{													
24.1	E		<i>Chrysothamnus nauseosus</i> -----	25	415726}	8.2	7.1	<.25	<.25	.3	<.025	.082	.71	57	78	.2	.1	80 22
			<i>Chrysothamnus nauseosus</i> -----	25	415734{													
27.4	NW		<i>Atriplex corrugata</i> -----	186	415662}	29	27	<.25	.5	<.025	<.025	.2	.19	20	13	5.04	.5	58 80
			<i>Atriplex corrugata</i> -----	186	415659{													
31.5	SE		<i>Ephedra torreyana</i> -----	65	415731}	13	12	<.25	<.25	.3	.025	.065	.08	17	9	.3	.1	65 36
			<i>Ephedra torreyana</i> -----	65	415736{													
31.5	W		<i>Atriplex confertifolia</i> -----	56	415657}	30	17	<.25	.25	.8	<.025	.09	.08	9	8	.4	.7	30 34
			<i>Atriplex confertifolia</i> -----	56	415666{													
32.1	W		<i>Atriplex confertifolia</i> -----	57	415667}	37	20	.25	<.25	.7	<.025	.11	.12	11	8	.1	.4	74 40
			<i>Atriplex confertifolia</i> -----	57	415661{													
35.4	E		<i>Artemisia tridentata</i> -----	67	415733}	6.8	5.5	<.25	<.25	.4	<.025	.136	.14	46	31	.1	.075	48 28
			<i>Artemisia tridentata</i> -----	67	415739{													
35.9	ENE		<i>Artemisia tridentata</i> -----	417	415917	---	9.1	---	---	---	<.025	---	---	---	---	---	---	26
38.6	SE		<i>Eriogonum leptophyllum</i> -----	62	415732	---	6.5	---	<.25	---	<.025	---	.08	---	21	---	1.5	20
40.2	SE		<i>Atriplex powelli</i> -----	16	415660}	26	28	.25	<.25	<.025	<.025	.08	.08	29	29	.2	5.	40 8.4
			<i>Atriplex powelli</i> -----	16	415665{													
Mean 21-40 km						19	14	<.25	<.25	0.44	<.025	0.11	0.18	29	23	0.8	1.0	53 33
44.1	SSE		<i>Betula erecta</i> -----	11	415740}	26	24	<.25	<.25	<.025	<.025	0.1	0.17	21	48	0.05	0.075	78 73
			<i>Betula erecta</i> -----	11	415730{													
46.8	SW		<i>Atriplex confertifolia</i> -----	44	415664}	36	13	.25	<.25	.3	<.025	<.1	.08	13	10	.1	.2	54 65
			<i>Atriplex confertifolia</i> -----	44	415652{													
48.3	SW		<i>Atriplex confertifolia</i> -----	43	415656}	23	16	<.25	<.25	1	<.025	.6	.18	42	13	.075	.1	115 80
			<i>Atriplex confertifolia</i> -----	43	415669{													
49.9	ENE		<i>Artemisia tridentata</i> -----	28	415728	---	4.7	---	<.25	---	<.025	---	.30	---	38	---	.075	14
53.1	SW		<i>Atriplex confertifolia</i> -----	47	415668}	28	6	<.25	<.25	.7	<.025	.25	.56	20	110	.6	.4	84 200
			<i>Atriplex confertifolia</i> -----	47	415663{													
54.7	E		Alfalfa -----	74	415737}	15	7.4	.25	.25	.3	.025	.06	.03	15	15	.3	.075	30 22
			do -----	74	415727{													
55.1	ENE		<i>Artemisia tridentata</i> -----	418	415910	---	9.1	---	---	---	<.025	---	---	---	---	---	---	27
78.9	ENE		<i>Artemisia tridentata</i> -----	419	415918	---	9.2	---	---	---	<.025	---	---	---	---	---	---	64
Mean 41-80 km						26	11	<.25	<.25	0.46	<.025	0.41	0.22	23	39	0.22	0.15	72 68

<sup>1</sup> Where two laboratory numbers are given, top is 1961, bottom is 1971.

*distances from the Four Corners Power Plant, shown in dry weight*

Survey. >, greater than value given; <, less than detection limit; N, not detected; computed using 0.5 of the less-than values and two times greater-than values]

Spectrographic analysis, in parts per million—Continued

Spectrographic analysis, in percent

B		Ba		Cr		Cu		Mo		Pb		Sr		V		Fe		Mg		K		P		
1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	1961	1971	
--	16	---	33	< 1.1	0.55	---	7.7	---	< 0.8	< 2	< 2	---	77	---	< 1.6	---	0.02	---	0.33	---	0.77	---	0.11	
--	50	---	500	N	6.5	---	10	---	< 2.3	---	6.5	---	100	---	10.	---	.60	---	1.0	---	2.3	---	< .23	
--	13	---	27	---	.62	---	4.5	---	.62	---	6.2	---	27	---	1.3	---	.045	---	.09	---	> .89	---	.06	
--	17	---	16	---	< .2	---	5.5	---	1.1	---	2.5	---	77	---	< 1.6	---	.0077	---	.08	---	> 1.1	---	.055	
--	45	---	150	---	2.1	---	9.	---	.9	---	< 6.	---	150	---	4.5	---	.15	---	.45	---	3.3	---	< .21	
--	44	---	200	---	2.0	---	8.7	---	< 2.	---	< 6.	---	145	---	8.7	---	.20	---	.43	---	2.0	---	< .21	
--	13	---	27	---	.89	---	6.2	---	.62	---	2.7	---	27	---	1.8	---	.045	---	.09	---	> .89	---	.06	
--	2.0	---	.87	---	.03	---	5.8	---	.58	---	< .6	---	5.8	---	< .45	---	.004	---	.145	---	> .29	---	.3	
--	15	---	30	---	1.5	---	6.9	---	.69	---	3.0	---	30	---	2.0	---	.069	---	.1	---	> 1.0	---	< .05	
--	25	---	182	---	3.9	---	13	---	< 1.6	---	5.	---	250	---	13	---	.4	---	.52	---	1.8	---	< .18	
--	14	---	7	---	.2	---	7.0	---	.7	---	< 2.0	---	30	---	< 1.5	---	.007	---	.1	---	> 1.0	---	.07	
84	65	12	28	---	.64	8.4	9.2	6.4	14	3.6	1.84	360	180	---	< 1.4	0.024	.018	---	.27	---	> .92	.12	.09	
	27		100		1.6		7.8		≅1.8		≅3.		92		≅3.7		0.13		0.30		≅1.1		≅0.10	
--	14	---	28	---	1.4	---	14	---	0.65	---	6.4	---	140	---	4.6	---	0.09	---	0.14	---	> 0.9	---	0.09	
30	36	42	100	---	.6	1.4	9	11	.9	.72	3	11	120	140	1.2	5.0	.006	.14	.18	.14	> .6	.5	.12	.07
40	35	12	21	---	1.2	1.0	16	35	1.6	1.0	2.5	7	410	355	1.2	1.4	.04	.07	.25	.14	> .8	> .7	.08	.07
	9	27	29	81	5.8	5.4	5.8	5.4	< 2.	< 1.9	8.7	13	145	400	8.7	5.4	.14	.135	.87	.54	.17	1.9	< .2	< .2
13	12	130	120	---	2.	1.2	4	3.6	< .9	< .8	2.6	3.6	910	600	4.	2.4	.13	.08	.26	.18	.9	.84	.09	< .02
21	17	45	25	---	9.	1.7	6	6	< 2	< .9	< 6	< 1.2	450	250	< 4.5	< 2.5	.09	.05	.9	.5	3.	1.7	< .2	< .12
55	30	74	60	---	11	2	5.7	6	< 2.5	< 1.4	< 7	4.	370	300	5.5	< 3.	.18	.06	1.8	.6	2.6	> 2.	< .26	< .14
48	16	14	48	---	68	1.1	20	16	1.4	.82	2	3.8	340	165	1.4	2.7	.05	.04	.2	.16	> .68	> .55	.2	.11
--	13	---	26	---	1.3	---	8.6	---	< .6	---	6.0	---	130	---	5.1	---	.06	---	.14	---	> .9	---	.06	
--	45	---	65	---	1.0	---	4.5	---	1.0	---	3.2	---	320	---	3.2	---	.06	---	.45	---	> .0	---	.06	
18	28	78	55	---	13	5.6	7.8	8.4	.78	< 2	< 5	5.6	130	130	7.8	7.8	.26	.28	.39	.42	> 2.6	2.8	< .18	< .2
32	25	53	53	---	5.4	2.1	9.3	10.7	≅1.	≅0.68	≅3.5	5.8	360	280	≅4.	≅3.7	0.11	0.10	0.6	0.32	≅2.0	≅1.7	≅0.11	≅0.16
39	36	260	120	---	7.8	2.4	5.2	12	< 2	< 1.7	< 5	< 4.8	1300	720	5.2	< 3.6	0.13	0.17	0.26	0.36	> 2.6	2.6	< 0.16	0.26
36	20	108	65	---	7.2	.65	3.6	3.9	< 2.6	< 1.3	< 7	< 2.6	100	90	< 5.4	1.9	.18	.04	.54	.26	2.5	1.3	< 25	.007
70	24	35	48	---	3.5	2.4	4.6	4.8	< 1.6	< 1.2	< 5	4.6	115	460	< 3.5	< 2.4	.11	.08	.35	.32	.8	.8	< .16	< .11
--	14	---	.7	---	.47	---	14	---	.33	---	1.4	---	140	---	.7	---	.02	---	.33	---	> .47	---	.09	
84	42	140	420	---	4.2	4.2	56	4.2	2.8	< .4	8.4	< 1.2	840	420	5.6	4.2	.28	.20	.42	.56	> 2.8	1.4	.23	< .04
45	52	150	22	---	2.2	.37	22	7.4	< 1.	.74	< 3.	2.2	225	520	4.5	< 1.1	.10	.04	.15	.11	1.5	> .74	.1	.15
--	14	---	14	---	1.4	---	14	---	.91	---	14	---	64	---	1.8	---	.23	---	.09	---	> .91	---	.14	
--	18	---	4.6	---	2.8	---	6.4	---	.64	---	6.4	---	92	---	6.4	---	.09	---	.14	---	> .92	---	.06	
55	28	138	92	---	5	1.8	18	8.3	≅1.3	≅0.6	≅3.7	≅4.1	515	310	≅3.8	2.3	0.16	0.11	0.34	0.26	≅3.1	≅1.5	≅0.16	≅0.13

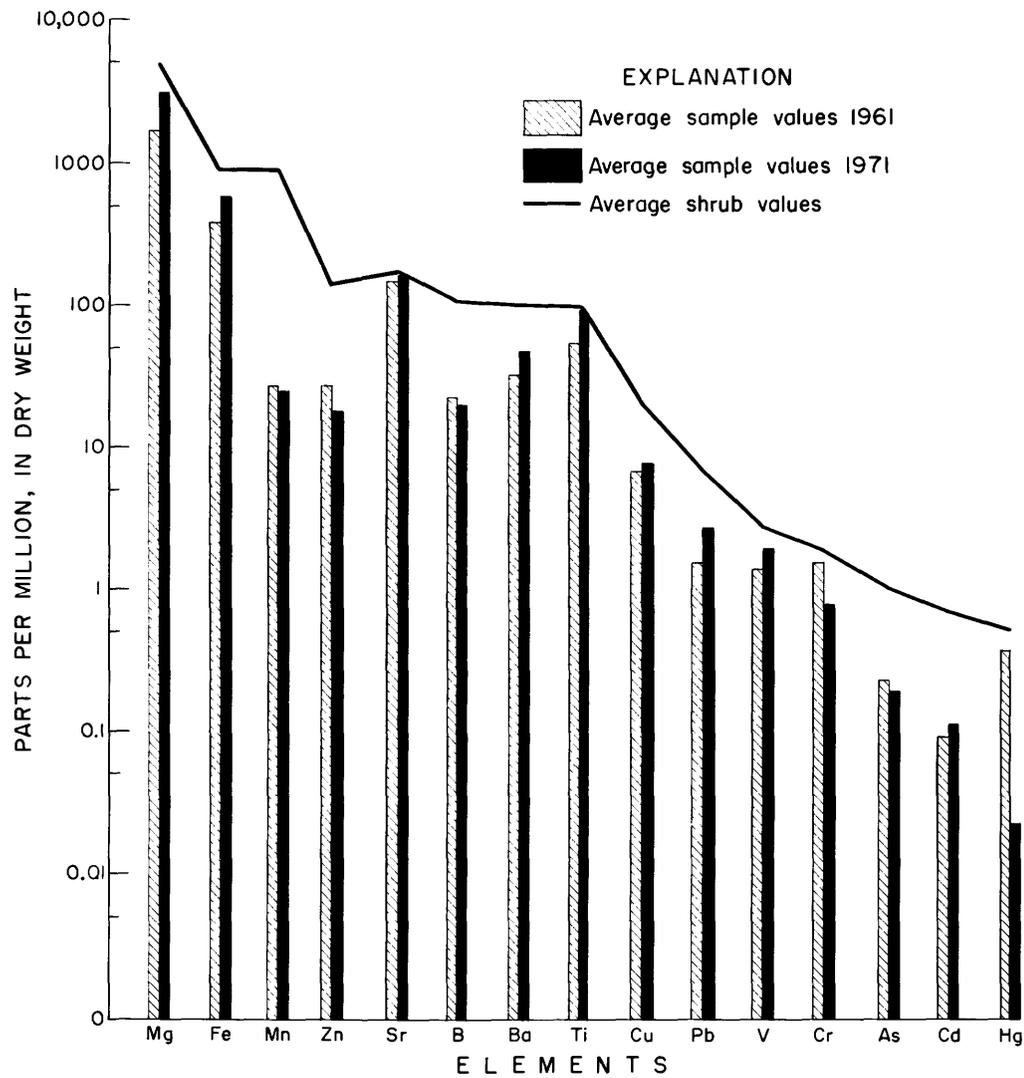


FIGURE 7.—Graph showing concentrations of some elements in San Juan County vegetation collected in 1961 and 1971 compared with concentrations in the average shrub.

TABLE 5.—Fluorine analyses of soils and vegetation in relationship to the Four Corners Power Plant, shown in parts per million

[Analysis by T. F. Harms and F. N. Ward. Leaders (---) indicate no sample]

Distance (km) and direction from plant	Plant			Soil		
	Genus and species (common name)	Lab. No.	F, in dry weight	Lab. No.	F, in dry weight	Depth (millimeters)
0.8 W. -----	-----	---	---	153500	390	15
1.6 W. -----	<i>Atriplex corrugata</i> (saltbush) -----	415658	3.0	153493	300	15
3.2 NW. -----	<i>Atriplex nuttali</i> (saltbush) -----	415653	7.0	153496	340	15
6.4 NW. -----	-----	---	---	154644	90	15
8.9 E. <sup>1</sup> -----	<i>Sporobolus airoides</i> (alkali sacaton) --	414912	25.0	415966	280	15
				415969	270	25-150
				415972	290	15
				415967	340	25-150
14.5 E. <sup>1</sup> -----	<i>Calamagrostis inexpansa</i> (reedgrass) --	415916	7.0	415971	300	15
				415974	330	25-150
				415977	290	15
				415981	340	25-150
16.1 NW. <sup>1</sup> -----	<i>Medicago sativa</i> (alfalfa) -----	415741	20.0	153479	510	15

<sup>1</sup> Plant growing in alluvium along San Juan River; both plant and alluvium sampled.

With the installation of equipment for further treatment of the fly ash, much of which had already been installed (as of 1972), the Four Corners Power Plant effluent may be considered as not detrimental, except for (1) a decrease in visibility and, possibly, (2) the effects of SO<sub>2</sub>, which were not investigated in this study. However, in areas where prior high levels of metals occur in the geologic substrate and related biosphere, increments from industrial plants should be carefully monitored.

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# Radioelement Concentrations and Preliminary Radiometric Ages of Rocks of the Kigluaik Mountains, Seward Peninsula, Alaska

By CARL M. BUNKER, CARL E. HEDGE, and C. L. SAINSBURY

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-C

*A long-lived thorium-rich province indicated by isotopic analyses*





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## RADIOELEMENT CONCENTRATIONS AND PRELIMINARY RADIOMETRIC AGES OF ROCKS OF THE KIGLUAIK MOUNTAINS, SEWARD PENINSULA, ALASKA

By CARL M. BUNKER, CARL E. HEDGE, and C. L. SAINSBURY<sup>1</sup>

### ABSTRACT

A sequence of old metamorphic rocks including the Kigluaik and Nome Groups is exposed in the Kigluaik Mountains of the Seward Peninsula. The high-grade metasedimentary rocks give a whole-rock Rb-Sr age of 735 million years. This late Precambrian age is believed to be the time of metamorphism. Orthogneisses, intrusive into the metasedimentary rocks, are probably also Precambrian in age, but many samples have had the evidence for their ages disturbed by Cretaceous intrusions and thrusting.

Samples of Precambrian metagabbro are low in radioelements (U, Th, and K) typical of basaltic rocks. The Precambrian metasedimentary rocks have normal radioelement concentrations, but both the Precambrian orthogneisses and the Cretaceous granitic rocks are uncommonly rich in thorium.

### INTRODUCTION

The existence of rocks of Precambrian age on the Seward Peninsula, Alaska, has been a matter of lively argument. The rocks discussed herein were suspected by Moffit (1913) to be of Precambrian (?) age but were subsequently shown on later maps to be of Paleozoic (?) age (Hummel, 1962; Patton, 1967). After several years of mapping on the Seward Peninsula, Sainsbury (1969a) demonstrated that fossiliferous limestones of Early Ordovician age on the western Seward Peninsula were underlain by an older, unfossiliferous limestone that graded downward into slates and phyllites of possible Precambrian age but that, on the basis of stratigraphic evidence, could be proved only to be pre-Ordovician. As mapping progressed eastward into the area discussed in this report, the determination that the age of the rocks is Precambrian seemed almost certain. However, the widespread thrusting,

with both regional dynamic metamorphism and younger thermal metamorphism impressed upon the thrust plates, made dating of the rocks of the Seward Peninsula by stratigraphic position and metamorphic rank impossible. Nevertheless, the stratigraphic evidence gathered in the western Seward Peninsula was sufficient to warrant an assignment of Precambrian age to most of the rocks older than the Lower Ordovician limestones.

This study was initiated in an attempt to verify the assignment of a Precambrian age to certain units and to determine the radioelement characteristics of various suites of metamorphosed rocks. Results of the study are that a Precambrian age has been verified for gneisses in the Kigluaik Mountains and that certain units have radioelement "signatures," which can be used for making correlations.

Although the preliminary work was published several years ago (Sainsbury, Coleman, and Kachadoorian, 1970; Sainsbury, Hedge, and Bunker, 1970), recent maps of the Seward Peninsula still show the bulk of the rocks to be of Paleozoic age (Clark and others, 1972). Since the initial work, more collections of rocks have been dated and analyzed for radioelement content. Because such data have not been published for Alaskan rocks, it was considered important to present the data that have been collected so that other workers will have a basis for comparing Alaskan rocks with those studied elsewhere.

The Kigluaik Mountains were chosen for this study for the following reasons: (1) A large variety of rock types ranging in age from Precambrian to Cretaceous are well exposed in a relatively small area; elsewhere in the Seward Peninsula, much of the land surface is covered by tundra, outcrops of

<sup>1</sup> AirSamplex Corporation, Indian Hills, Colo.

similar rocks are isolated, and stratigraphic relationships are less evident. (2) Rocks exposed in the Kigluaik Mountains are less weathered than are other rocks that crop out in much of the Seward Peninsula; thin layers of visible alteration on the samples were common, but these were removed prior to analyses.

The Kigluaik Mountains are about 24 km wide (north to south) and about 72 km long within the area of 64°45' to 65°05' N. latitude and 164°45' to 166°15' W. longitude (fig. 1). The center of the mountain range is about 48 km north of Nome. Much of the northern part of the range is delineated by an escarpment along the Kigluaik fault; part of the southern boundary generally coincides with a group of lesser faults. This area is included in parts of the Nome and Teller 1:250,000 Alaska Topographic Series maps.

#### ACKNOWLEDGMENTS

The geologic mapping of the region under study was the responsibility of Sainsbury, who was assisted ably by Travis Hudson, Reuben Kacha-

doorian, T. W. Smith, Thomas R. Richards, Rodney Ewing, and William R. Marsh at various times. Assignment of units and ages is the responsibility of Sainsbury. The rocks discussed herein were analyzed for radioelements by Bunker, who has guided the writing of the report; Charles A. Bush assisted with the analytical work. The age dating of the rocks by rubidium-strontium methods was done by Hedge, assisted by William T. Henderson, Robert A. Hildreth, and Willis P. Doering. Each of the authors of this report thereby assumes responsibility for his part of the report.

#### GENERAL GEOLOGY

The general geology for that part of the area within the Teller 1:250,000 quadrangle has been described by Sainsbury (1972). For the general area of the Seward Peninsula, the geology was summarized by Sainsbury (1975) and by Sainsbury, Coleman, and Kachadoorian (1970), in a report in which arguments for the Precambrian age of the rocks were presented. Short texts in which the rock units are described in some detail were prepared by Sainsbury and his coworkers to accompany numerous published geologic maps (Sainsbury, 1969a, 1969b; Sainsbury, Kachadoorian, Hudson, and others, 1969; Sainsbury, Kachadoorian, and Smith, 1970; Sainsbury, 1972; Sainsbury, Hummel, and Hudson, 1972; Sainsbury, Smith, and Kachadoorian, 1972; and Sainsbury, 1974).

Briefly stated, the Seward Peninsula consists of a great number of thrust plates of Paleozoic carbonate rocks intimately intermixed tectonically with Precambrian rocks. Present are argillaceous and dolomitic limestone, the slate of the York region, and several types of chloritic schists, feldspathic-chloritic schists, and high-rank gneisses and schists predominantly of leucocratic composition. Whether the chloritic schists are all old volcanic rocks that were intercalated in the slate of the York region or whether some are younger mafic rocks possibly intruded during the thrusting is as yet unsettled. All of the Paleozoic rocks on the western part of the Seward Peninsula that have been dated by fossils are carbonate rocks of Ordovician, Silurian, Devonian, and Mississippian(?) ages. Unfossiliferous rocks of noncarbonate composition cannot be assigned to the Paleozoic, and furthermore, whenever the slate of the York region is overlain by massive carbonate rocks without the intervening argillaceous and dolomitic limestone, the two units are separated by either a thrust fault or an unconformity.

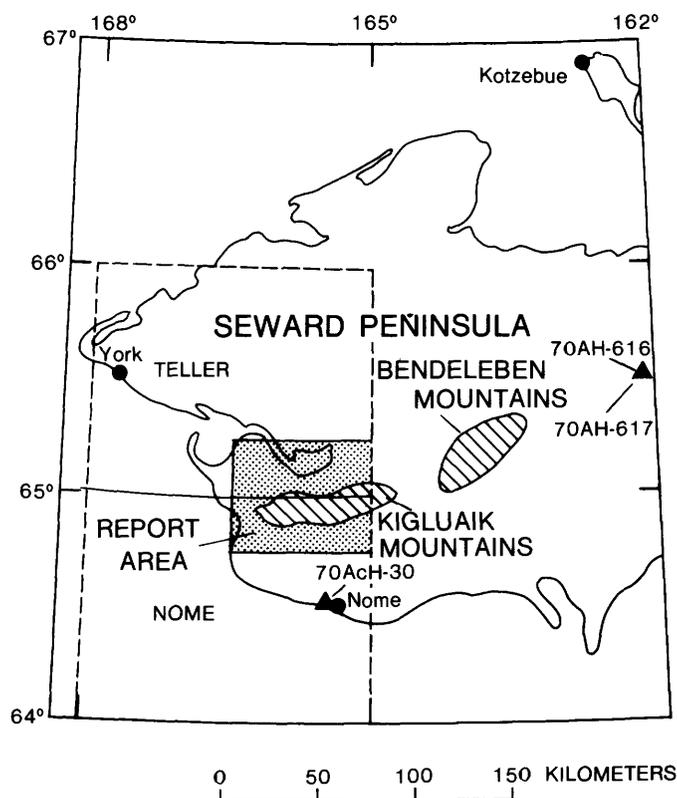


FIGURE 1.—Index map of Seward Peninsula, Alaska, showing area of detailed study and sample localities outside the study area.

Along the axes of the Kigluaik and Bendeleben Mountains, which trend eastward across the Seward Peninsula, high-rank gneisses, semigneisses, and schists are exposed, and these are intruded by numerous granitic intrusive rocks mostly of Cretaceous age. However, some gneissic intrusives of granitic composition have been mapped, and these may be of Precambrian age. Because the gneisses and intrusive rocks of the Kigluaik Mountains have been studied more extensively, the initial work of age dating and determining radioelement contents has been concentrated in this area, but data from elsewhere on the Seward Peninsula are included.

The complications introduced as a consequence of the intense tectonic deformation of the thrust belt covering the Seward Peninsula, named the A. J. Collier thrust belt to honor a pioneer worker of the Seward Peninsula (Sainsbury, 1969b), are immense. Large-scale migration of material took place during thrusting, and the thermal metamorphism imprinted upon the dynamically metamorphosed rocks has been widespread. Nevertheless, the data that have been gathered substantially support the geologic interpretations made over the years. More importantly, the Precambrian age of most of the metamorphic rocks of noncarbonate composition is clearly established. Only by application of whole-rock Rb-Sr age dating was the correct age established, because dating of the high-rank schist by K-Ar methods yielded Cretaceous dates similar to the ages of the intrusive rocks.

The geology of the Kigluaik Mountains and the location of samples analyzed in this study are shown in figure 2. Three samples of orthogneiss, which were included in the Rb-Sr dating, are outside of this map area and are shown in figure 1.

The oldest rocks are the paragneisses of the Kigluaik Group. These rocks are well exposed in the Kigluaik Mountains. The dominant lithologies of the Kigluaik Group are plagioclase-orthoclase-biotite-hornblende gneiss and gneissic marble. These paragneisses are intruded by orthogneisses ranging in composition from granite to quartz monzonite.

Two major lithologic units, which either may be the unmetamorphosed equivalents of part of the paragneisses herein discussed or may be somewhat younger in age, are found in the Kigluaik Mountains and nearby areas discussed in this report. These were named the Nome Group and the Kuzitrin Series by Moffit (1913) and by Brooks, Richardson, and Collier (1901), respectively. In his latest publication, written after a detailed study of the metamorphic rocks in the Kigluaik Mountains

and elsewhere on the Seward Peninsula, Sainsbury (1975, p. 8-19) presented evidence that the high-rank gneisses of the Kigluaik Mountains are transitional, at least in part, into graphitic slates and siltites of the Kuzitrin Series, which he includes with the slate of the York region. He further concluded that the rocks of the Nome Group as originally defined by Brooks, Richardson, and Collier (1901) included chloritic schists, probably derived from volcanic material originally included in the slate of the York region, as well as thrust slices of Paleozoic carbonate rocks and younger metagabbroic rocks of uncertain age. Thus, the Nome Group rocks may be a subunit within the slate of the York region, but only detailed study will solve the problem.

No rocks of proved Paleozoic age are found in the Kigluaik Mountains, but thick carbonates containing relict fossils occur immediately south and west of the range. These were grouped by earlier workers as part of the Nome Group, but the known existence of relict fossils and the lithologic resemblance to other carbonate rocks of Paleozoic age that occur nearby are considered by Sainsbury to be sufficient evidence to assign these carbonate rocks to the Paleozoic.

The rocks forming the core of the Kigluaik Mountains are intruded by stocks, bosses, and batholiths of probable Cretaceous age. In broad outline, the high-rank gneisses herein discussed tend to form mantles around these intrusives, as they do elsewhere on the Seward Peninsula (Sainsbury, 1974, 1975).

#### METHOD OF ANALYSIS

Rubidium and strontium concentrations were determined either by X-ray fluorescence or by isotope dilution techniques. Concentrations in all of the samples with extreme Rb-Sr ratios were measured by isotope dilution. The Rb-Sr ratios have a precision of  $\pm 3$  percent.  $\text{Sr}^{87}/\text{Sr}^{86}$  were measured on a separate unspiked run; they were normalized to correspond to an  $\text{Sr}^{86}/\text{Sr}^{88}$  of 0.1194 and have a precision of  $\pm 0.0005$ .

Radioelement (K, Ra, U (radium-equivalent uranium) and Th) contents of the samples were measured by gamma-ray spectrometry. Basic operational procedures, calibration techniques, and sample preparation were described by Bunker and Bush (1966, 1967). Approximately 600 g of the material were sealed in plastic containers 15 cm in diameter. The containers were placed on a sodium iodide crystal, 12.5 cm in diameter and 10 cm thick. The

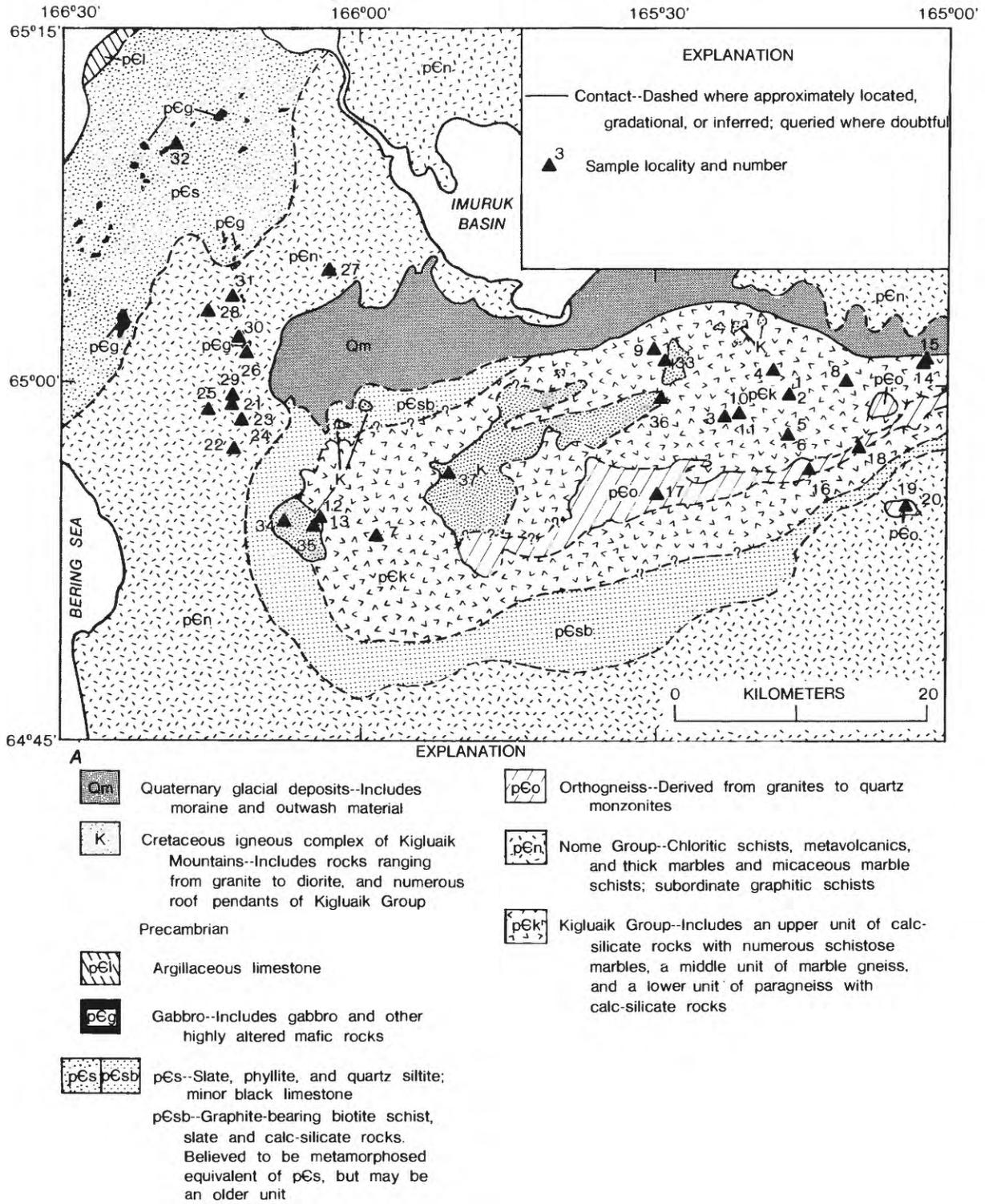


FIGURE 2.—A, Generalized geologic map showing sample localities, Kigluaik Mountains area, Alaska.

gamma radiation penetrating the crystal was sorted according to energy by the associated electronic devices, and the resulting spectra were stored in a 100-channel memory. The spectra were interpreted with the aid of a linear-least-squares computer

method that matches the spectrum from a sample to a library of radioelement standards; the computer method for determining concentrations is a modification of a program written by Schonfeld (1966). Standards used to reduce the data include

Sample locality	Field number	Sample locality	Field number
1	70AcH-17	21	67ATS-159
2	70AcH-18	22	67ATS-80
3	70AcH-21	23	67ATS-156
4	70AcH-26	24	67ATS-156A
5	70AcH-15	25	67ATS-163
6	70AcH-16	26	67ATS-195
7	67ATS-132	27	67ATS-223
8	70AcH-27	28	67AKd-190
9	70AcH-24	29	67ATS-161
10	68ASn-282	30	67ATS-197A
11	68ASn-282A	31	67ATS-222
12	67ATS-184-1	32	67AKd-212
13	67ATS-184-2	33	70AcH-23
14	68ASn-301B	34	67ASn-31A
15	70AcH-28	35	67ATS-184A
16	70AcH-14	36	68ASn-280
17	70AcH-20	37	67ASn-124
18	70AcH-19		
19	70AcH-1		
20	70AcH-2		

**B**

FIGURE 2.—B, List of sample localities shown on A and their field numbers.

the USGS standard rocks, New Brunswick Laboratories standards, and several samples for which uranium and thorium concentrations had been determined by isotope dilution and mass or alpha spectrometry.

Uranium contents were measured indirectly by measuring the Ra<sup>226</sup> daughters (Bi<sup>211</sup> and Pb<sup>211</sup>) to obtain RaeU values. Isotopic equilibrium between these daughters and Ra<sup>226</sup> was reached by allowing the sealed sample containers to sit for at least 21 days prior to the analyses. (Radium-equivalent uranium is the amount of uranium required for secular isotopic equilibrium with the Ra<sup>226</sup> and its daughters measured in a sample. Unless otherwise stated, all uranium concentrations referred to in this paper are radium-equivalent values.)

Although thorium is also measured from daughter products (Bi<sup>212</sup>, Pb<sup>212</sup>, and Tl<sup>208</sup>), isotopic disequilibrium is improbable because of the short half-lives of the daughter products of Th<sup>232</sup>. Therefore, the daughter products measured are considered to be a direct measurement of thorium. Potassium is determined from the K<sup>40</sup> constituent, which is radioactive and directly proportional to the total potassium.

All the radioelement data reported in this paper are based on replicate analyses. The coefficient of

variation for the accuracy of these data, when compared to isotope-dilution and flame-photometry analyses, is about ±2 percent for RaeU and Th and about ±1 percent for K. These percentages are in addition to minimum standard deviations of about 0.06 ppm for RaeU and Th and 0.03 for K.

**RADIOMETRIC AGES**

Seven whole-rock samples of paragneiss from the Kigluaik Group were dated by the Rb-Sr method. Samples were obtained from both the uppermost and lowermost accessible portions of the unit. Analytical data for the paragneiss samples are given in table 1 and are plotted on an isochron diagram in figure 3. Also dated from the Kigluaik Group were one sample of biotite separated from the paragneiss and a whole-rock sample of a conformable pegmatite.

The scatter in apparent ages is very large (table 1). Five of the seven paragneiss samples do fit a single line on the isochron diagram (fig. 3), however, and this line corresponds to an age of 735

TABLE 1.—Rb-Sr analytical data

Sample No.	Rb (ppm)	Sr (ppm)	Rb <sup>87</sup> /Sr <sup>86</sup>	Sr <sup>87</sup> /Sr <sup>86</sup>	Apparent age <sup>1</sup> (m.y.)
<b>Whole-rock paragneiss (Kigluaik Group) samples</b>					
70AcH-15	87.2	130	1.949	0.7247	750
70AcH-16	101	199	1.467	.7193	732
70AcH-17	214	51.3	12.20	.8292	733
70AcH-21	193	85.5	6.579	.7744	763
70AcH-26	75.3	121	1.806	.7296	985
70AcH-27	150	283	1.536	.7180	639
68ASn-282	137	79.2	5.024	.7293	357
<b>Biotite from paragneiss (Kigluaik Group)</b>					
68ASn-282	340	15.9	62.04	0.7920	102
<b>Whole-rock segregation pegmatite</b>					
70AcH-18	209	307	1.975	0.7257	775
<b>Whole-rock orthogneiss samples</b>					
70AcH-1	29.7	58.3	1.490	0.7316	1306
70AcH-2	15.9	44.6	1.033	.7243	1380
70AcH-14	228	25.8	26.07	.8821	489
70AcH-19	564	37.4	43.91	.7600	91
70AcH-20	359	40.9	25.74	.8393	376
70AcH-28	332	91.7	10.65	.7713	451
70AcH-30	189	90.5	6.086	.7653	717
70AH-616	55.8	115	1.406	.7157	581
70AH-617	70.7	144	1.423	.7165	614
68ASn-300	109	116	2.736	.7136	714
68ASn-282a	234	469	1.448	.7191	732
68ASn-301B	516	77.9	19.34	.8051	374
<b>K-feldspar from orthogneiss</b>					
68ASn-282a	321	219	4.251	0.7292	420

<sup>1</sup> Assuming an initial Sr<sup>87</sup>/Sr<sup>86</sup> of 0.7043.

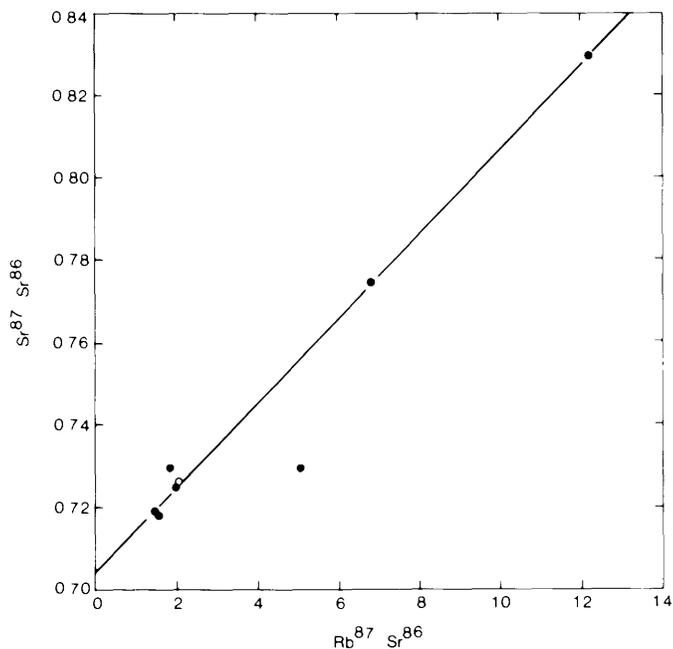


FIGURE 3.—Isochron diagram of Rb-Sr data for whole-rock paragneiss (Kigluaik Group) samples. Open circle is the segregation pegmatite sample 70AcH-18. Original  $Sr^{87}/Sr^{86}=0.7043$ ;  $T=735$  m.y.

m.y. (million years). Experience from other areas indicates that such whole-rock isochrons, for high-rank metamorphic rocks, are commonly dating the time of metamorphism, and this is the interpretation that we make from these data. If this interpretation is correct, then the gneisses, which tend to occur as mantles around the Cretaceous intrusives, were metamorphosed much prior to the Cretaceous intrusion. The alternative explanation must be considered: The evidence for the original age of the slate of the York region and (or) other rocks that were metamorphosed to the dated gneisses was not seriously disturbed during the intrusion of the Cretaceous intrusives.

That the 735-m.y. age probably represents the time of metamorphism and not the age of the sedimentation or the age of the source terrane of the sediments is confirmed by sample 70AcH-18. This sample is from a conformable pegmatite. The pegmatite is entirely enclosed in paragneiss, and the field evidence indicates that it formed by segregation from the gneiss during metamorphism. Sample 70AcH-17 is from the gneiss immediately adjacent to the pegmatite. A line connecting the two points places the time at which the samples were in equilibrium, in terms of strontium isotopic composition, at 725 m.y. ago, an age not significantly different

analytically from that obtained from the paragneiss samples. If our interpretation—that the pegmatite is a segregation—is incorrect and the pegmatite is actually of igneous origin, its age would still provide a minimum for the paragneiss unit.

Two of the Kigluaik Group paragneiss samples do not lie on the 735-m.y. isochron defined by the other samples. The sample that plots to the left of the line (70AcH-26) also has a peculiar Th/U. There is no obvious reason why 68ASn-282 plots to the right of the line and appears to give a young age. Biotite was separated from 68ASn-282 and analyzed for Rb, Sr, and  $Sr^{87}/Sr^{86}$ . The apparent age of the biotite is 103 m.y. if we assume the initial  $Sr^{87}/Sr^{86}$  of the paragneiss suite (0.7043 from fig. 3), or it is 80 m.y. if we assume that the biotite came into isotopic equilibrium with the whole-rock sample. In either assumption, the biotite age has been reset during Cretaceous time.

The Precambrian paragneisses of the Kigluaik Group are intruded by bodies of gneissic granite. The foliation of these orthogneisses tends to be parallel to that of the surrounding paragneisses. If this foliation was produced 735 m.y. ago, then the orthogneisses must also be of Precambrian age. Unfortunately, the Rb-Sr data for the orthogneiss samples do not define a single line (fig. 4; data given in table 1). The sample from near Nome (70AcH-30), the two samples from Kawalik Mountain (70AH-616 and 70AH-617, fig. 1), and one sample from the Kigluaik Mountains (68ASn-282a) plot near the same isochron (solid line, fig. 4) as the paragneisses. The other samples from the Kigluaik Mountains give apparent ages both younger and older than 735 m.y. Five of these samples define a crude isochron of about 335 m.y. (dashed line, fig. 4). One orthogneiss (70AcH-14) gives an apparent age of about 490 m.y., and another (70AcH-19), about 90 m.y. This scatter in the orthogneiss data can be interpreted in several ways, and no unique interpretation can be made at this time. Our preferred interpretation is that the orthogneisses are all of Precambrian age and that those in the Kigluaik Mountains have been more or less reset by the Cretaceous plutonism and tectonism. Thus, the crude alignment of the five samples along a 335-m.y. isochron is fortuitous.

Sainsbury revisited the Kigluaik Mountains area in 1972 and 1973. He believes that these rocks (70AH-616 and 70AH-617) may be hybrid rocks formed by K-metasomatism of Precambrian rocks, the potash being derived from a granitic intrusive of Cretaceous age. If so, the anomalous ages de-

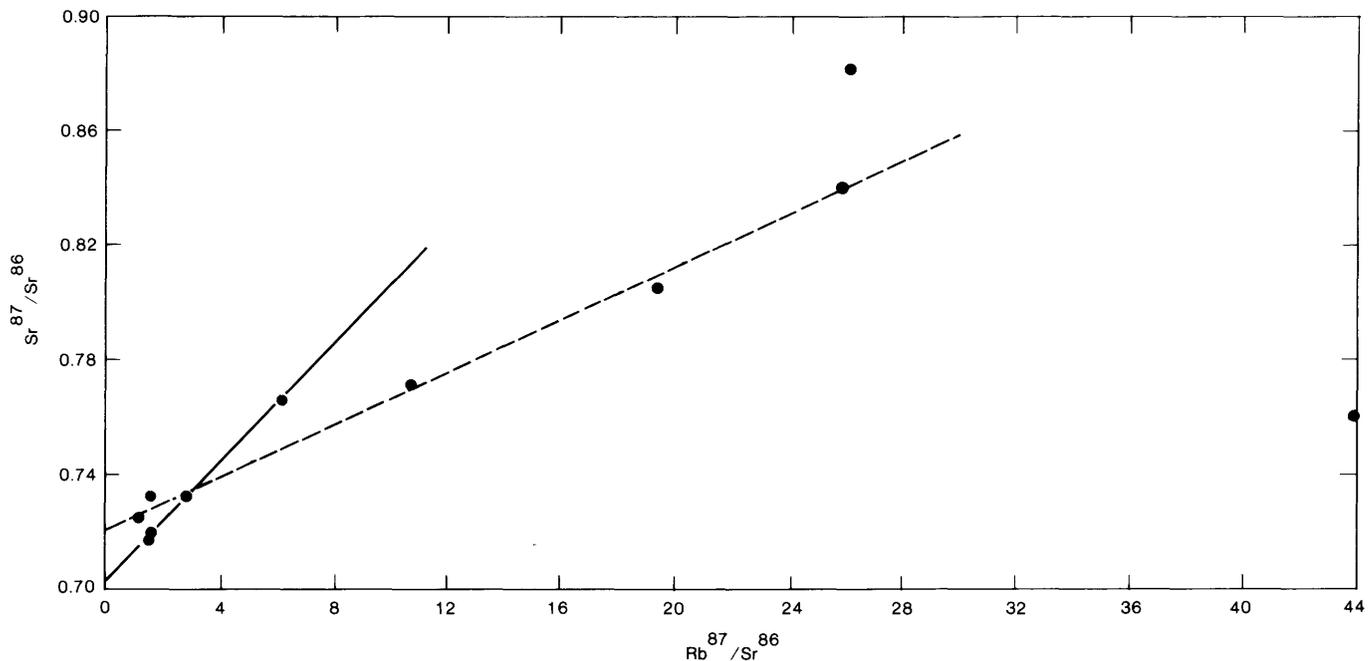


FIGURE 4.—Isochron diagram of Rb-Sr data for whole-rock orthogneiss samples. Solid line,  $T=735$  m.y.; dashed line,  $T=335$  m.y.

rived for these rocks are explained on the basis of isotopic mixing.

To give credence to the 335-m.y. age would require that the orthogneisses of the Kigluaik Mountains formed by anatexis of a preexisting crustal rock 335 m.y. ago. This conclusion is based on the high initial  $Sr^{87}/Sr^{86}$  (0.720) of the 335-m.y. isochron. Such crustal anatexis would require an uncommon geothermal gradient, and presumably such an event would be manifest in other ways. No known evidence in the geologic record supports such an interpretation.

Inspection of figure 4 might also suggest that the 335-m.y. isochron is a metamorphic isochron (that is, an older rock was metamorphosed at 335 m.y. causing the strontium isotopes to equilibrate between samples). The samples are too widely spaced, however, for such an interpretation to be plausible.

#### RADIOELEMENT DISTRIBUTION

The radioelement (RaeU, Th, and K) contents of all the major geologic units of the Kigluaik Mountains except an unnamed slate-phyllite-schist unit were determined. The purposes of this analysis were to confirm the presence of the regional high thorium contents found in a few early reconnaissance samples and to ascertain whether the various geologic units might have characteristic radioelement con-

tents and ratios that could be used in reconnaissance mapping.

The radioelement contents of the samples collected near the Kigluaik Mountains are given in table 2 and are shown in relation to the geologic units in figure 5. Averages of radioelement contents and ratios in the rocks are given in table 3; values given in the literature for average radioelement contents in major categories of igneous rocks are included for comparison. The relation between Th and RaeU contents in the rocks of the Kigluaik Mountains is shown in figure 6A; similar data for RaeU and K contents are shown in figure 6B.

The radioelement contents in the paragneiss samples of the Kigluaik Group are near the averages for intermediate igneous rocks (table 3). The RaeU content in the paragneiss is slightly lower than the average, and the high Th/RaeU and low RaeU/K indicate that the paragneiss may be depleted in RaeU. The depletion may be a near-surface effect of weathering and surface-water movement that has removed soluble  $Ra^{226}$  from the rock. The Th/K is close to the average for most igneous rocks, which indicates that the process causing the RaeU depletion had little effect on the other radioelements.

The orthogneiss samples appear to form two groups distinguished by the RaeU and K contents; the average Th content is nearly the same in both

TABLE 2.—Concentrations and ratios of radioelements, Kigluaik Mountains, Alaska

Sample No.	RaeU (ppm)	Th (ppm)	K (percent)	Th RaeU	RaeU K × 10 <sup>-4</sup>	Th K × 10 <sup>-4</sup>
<b>Paragneisses of Kigluaik Group</b>						
70AcH-17	0.37	1.10	4.13	2.8	0.09	0.27
70AcH-21	1.07	7.48	4.77	7.0	.22	1.6
70AcH-26	.77	9.44	1.93	12.3	.40	4.9
70AcH-15	1.82	9.91	1.90	5.4	.96	5.2
67ATs-132	2.29	10.77	2.61	4.7	.88	4.1
70AcH-16	1.98	11.05	2.31	5.6	.86	4.8
70AcH-27	1.52	11.49	3.51	7.6	.43	3.3
70AcH-24	2.22	15.21	3.02	6.9	.74	5.0
68ASn-282	1.69	8.45	2.58	5.0	.66	3.3
68ATs-184-1	2.01	19.31	3.88	9.6	.52	5.0
68ATs-184-2	1.86	10.28	2.21	5.5	.84	4.6
<b>Orthogneisses</b>						
68ASn-282A	9.76	39.48	4.79	4.0	2.0	8.2
68ASn-301B	12.66	41.46	4.67	3.3	2.7	8.9
70AcH-28	6.30	42.25	4.20	6.7	1.5	10.1
70AcH-14	7.60	33.79	4.56	4.4	1.7	7.4
70AcH-20	15.21	39.87	4.04	2.6	3.8	9.9
70AcH-19	11.93	51.91	4.20	4.4	2.8	12.4
70AcH-30	3.28	25.95	2.38	7.9	1.4	10.9
70AcH-1	3.60	45.99	.34	12.8	10.6	135
70AcH-2	1.82	52.35	.26	28.8	7.0	202
70AH-616	3.17	28.34	1.20	8.9	2.6	23.6
70AH-617	3.69	27.81	1.46	7.5	2.5	19.0
<b>Schists of the Nome Group</b>						
67ATs-159	0.25	1.25	0.33	5.0	0.76	3.8
67ATs-80	1.95	8.06	.98	4.1	2.0	8.2
67ATs-156	1.69	8.55	1.61	5.1	1.0	5.3
67ATs-163	2.01	8.18	.85	4.1	2.4	9.6
67ATs-195	2.01	8.54	1.96	4.2	1.0	4.4
67ATs-223	1.72	7.98	1.95	4.6	.88	4.1
67AKd-190	1.60	7.16	.39	4.5	4.1	18.4
<b>Metagabbro</b>						
67ATs-156A	0.39	0.51	0.01	1.3	39.0	51.0
67ATs-161	.41	.40	.08	1.0	5.1	5.0
67ATs-197A	.35	1.21	.25	3.5	1.4	4.8
67ATs-222	.54	1.63	.62	3.1	.87	2.6
67AKd-212	.91	1.94	.12	2.1	7.6	16.2
<b>Cretaceous granitic rocks</b>						
70AcH-23	3.44	26.99	4.15	7.9	0.83	6.5
67ASn-31A	3.97	41.39	5.15	10.4	.77	8.0
67ATs-184A	4.52	27.85	4.60	6.2	.98	6.1
68ASn-280	6.17	48.48	4.49	7.9	1.4	10.8
67ASn-124	8.25	57.39	4.52	7.0	1.8	12.7

groups. The samples in one group contain more than 6 ppm RaeU and more than 4 percent K; samples in the other group contain less than 4 ppm RaeU and less than 3 percent K (table 3). The group with the higher RaeU and K contents has radioelement contents and ratios similar to those in typical alkali granites. The near-normal ratios in the samples indicate little disturbance or migration of the radioelements in the rock during metamorphism. The group containing lower amounts of RaeU and K appears to be either depleted in both of those radioelements or enriched in Th, and the

radioelement ratios are abnormal. The data indicate that the radioelement contents in the groups containing the lower RaeU and K have been altered greatly and that the two distinctively different types of rocks constituting the orthogneiss were either of different materials initially or were subjected to different conditions during metamorphism.

Most of the samples of schists of the Nome Group have radioelement contents similar to the averages for intermediate igneous rocks (table 3). The normal ratios of the radioelements (fig. 6) in most of the samples indicate that neither metamorphism nor

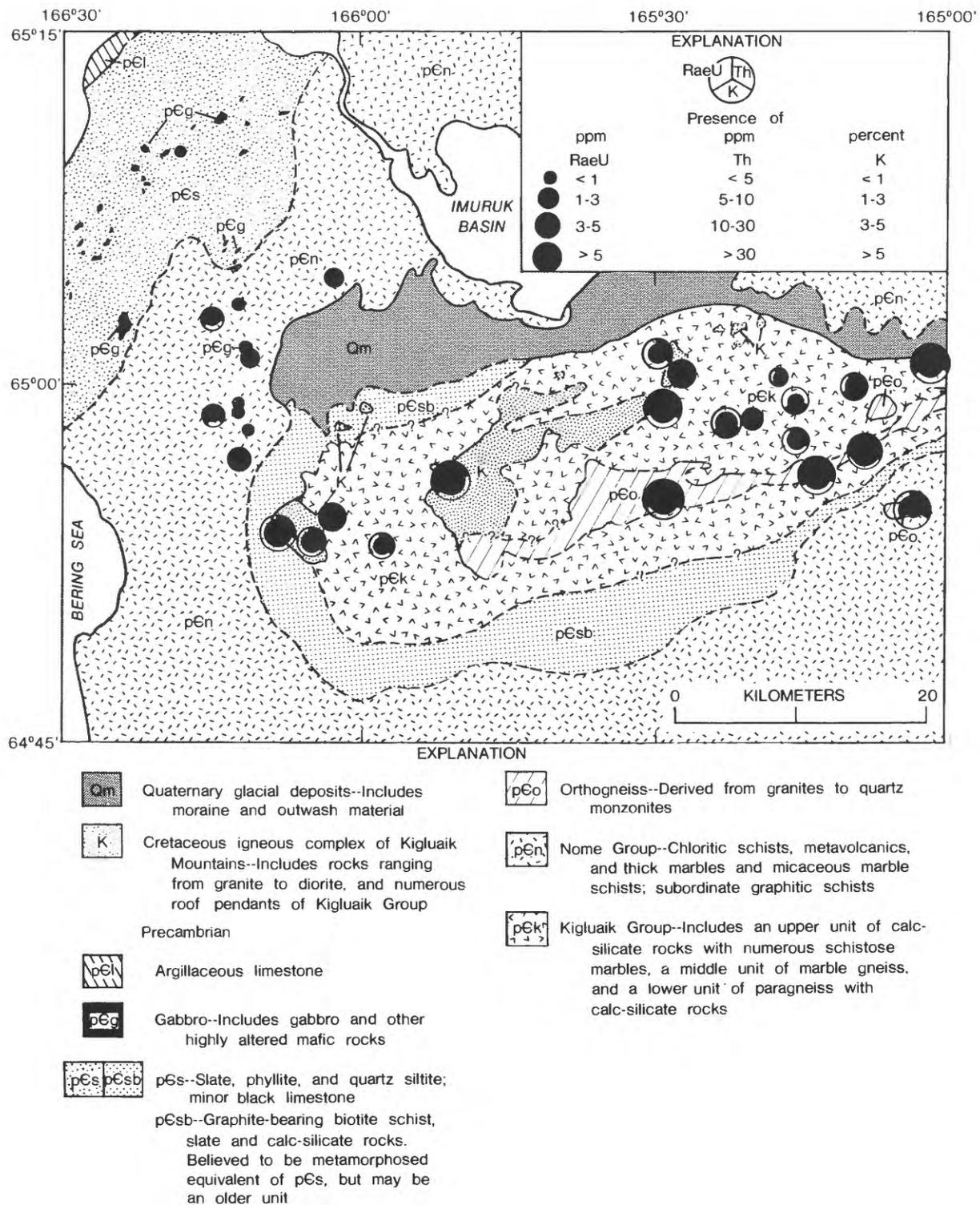


FIGURE 5.—Radioelement concentrations related to geology, Kigluaik Mountains area, Alaska.

recent weathering has preferentially mobilized the radioelements. The RaeU and Th contents of the schists of the Nome Group and the paragneiss of the Kigluaik Group are very similar, but the K contents are significantly different.

The lowest radioelement contents occur in gabbro and metagabbro, which intrude slate and chloritic schists. The gabbros occur as a series of small intrusives that trend northward in the western part of the Kigluaiks. The radioelement contents in the

TABLE 3.—Averages of radioelement contents and ratios in rocks of the Kigluaik Mountains, Alaska, and summary of published averages for igneous rocks

Rock type	RaeU (ppm)	Th (ppm)	K (percent)	Th/RaeU	RaeU/K × 10 <sup>-4</sup>	Th/K × 10 <sup>-4</sup>
Paragneiss of Kigluaik Group - Orthogneiss:	1.60	10.4	2.98	6.6	0.60	3.8
All samples -----	7.18	39.0	2.92	8.3	3.5	41
>6 ppm RaeU, >4 percent K -----	10.6	41.5	4.41	4.2	2.4	9.1
<4 ppm RaeU, <3 percent K -----	3.11	36.1	1.12	13	4.8	78
Schists of Nome Group -----	1.61	7.10	1.15	4.5	1.7	7.7
Metagabbro -----	.50	1.13	.21	2.2	10.8	16
Cretaceous granitic rocks -----	5.27	40.4	4.58	7.9	1.2	8.8
Averages in igneous rocks						
Continental crust -----	<sup>1,2</sup> 2.8	<sup>6</sup> 10-10	<sup>4</sup> 1.6-2.6	<sup>3</sup> 3.5-4	<sup>1</sup>	<sup>3</sup> 3.3
Mafic -----	0.9	2.7	<sup>1</sup> 0.6-0.75	<sup>3</sup> <3	<sup>2</sup> 0.6	<sup>2</sup> 2.8
Intermediate -----	<sup>5</sup> 2.0-2.6	<sup>5</sup> 8.5-9.3	<sup>1</sup> 2.7-3.0	<sup>2</sup> 4.8	<sup>7</sup> 0.7-1	<sup>7</sup> 2.8-3.4
Silicic -----	<sup>5</sup> 4.7	<sup>1</sup> 20	<sup>1</sup> 3.6	<sup>6</sup> 4.5	<sup>2</sup> 1.29	<sup>5</sup> 5.0
	<sup>3</sup> 4	<sup>1</sup> 18	<sup>2</sup> 3.79	<sup>5</sup> 4.0	<sup>2</sup> 1.3	<sup>3</sup> 4.9
	<sup>2</sup> 4.75					

<sup>1</sup> Rogers and Adams (1969b).  
<sup>2</sup> Heier and Rogers (1963).  
<sup>3</sup> Rogers and Adams (1969a).  
<sup>4</sup> Cocco and others (1970).

<sup>5</sup> Clark and others (1966).  
<sup>6</sup> Z. E. Peterman (written commun., 1963).  
<sup>7</sup> Calculated from published values.

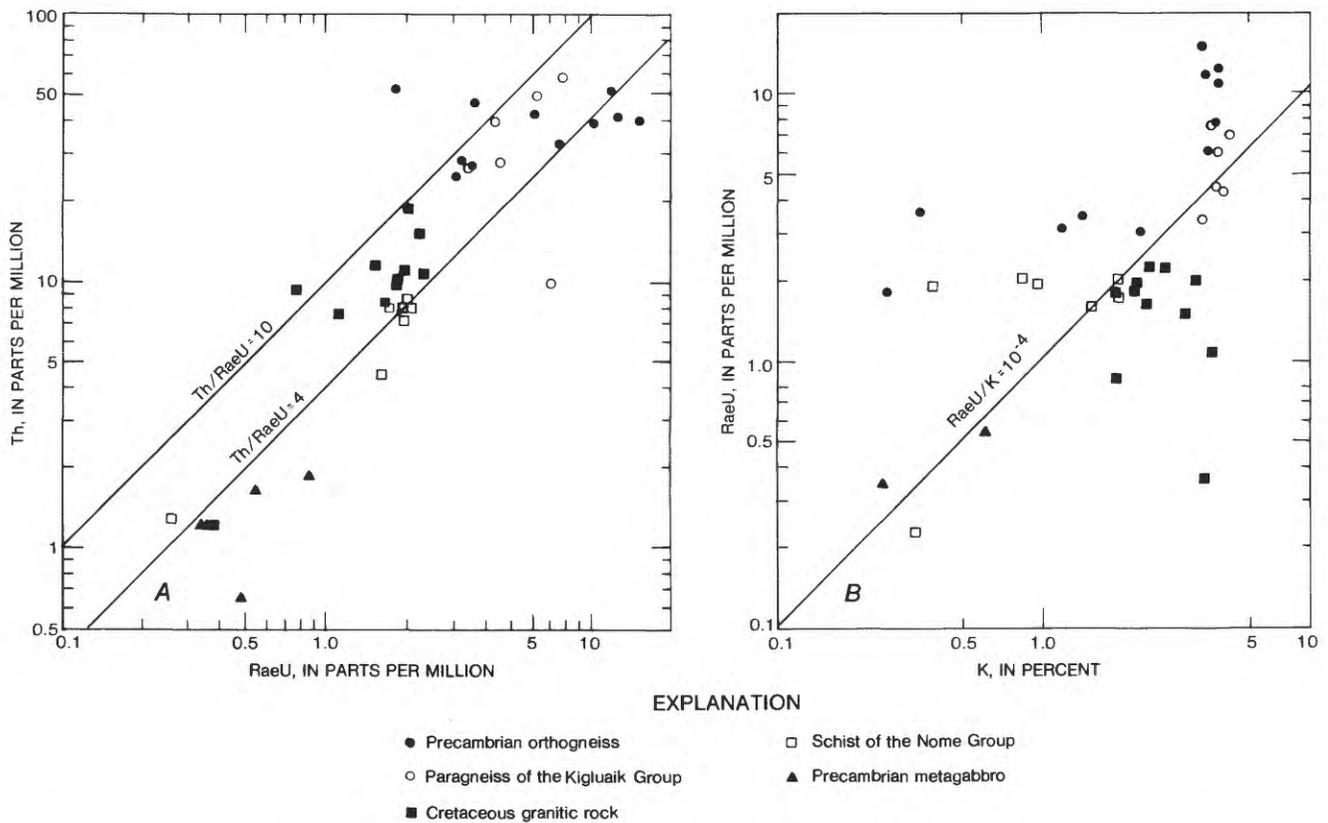


FIGURE 6.—Log-log plots of concentrations of radioelements in rocks of the Kigluaik Mountains, Alaska. A, Thorium (Th) versus uranium (RaeU). B, Uranium versus potassium (K).

metagabbro are less than 0.9 ppm RaeU, less than 2.0 ppm Th, and less than 0.7 percent K. Radioelement contents such as these are typical for basalts and gabbros.

The average Th and K contents of the Cretaceous granitic rocks and the Precambrian orthogneisses containing the greater abundances of RaeU and K are very similar (table 3). The characteristic that distinguishes the granitic rocks from the orthogneisses is the greater RaeU abundance in the orthogneiss. The Th content in both groups is about twice the average of that for silicic igneous rocks. The above-average thorium content in the Kigluaik Mountains samples is not unique. Similar Th contents have been reported (Rogers and Adams, 1969a, p. 90-E-1) for Precambrian mica granites in the Ukrainian shield (33 ppm average), second intrusive-phase alkalic granodiorites to alkalic granites in Tertiary Megrinsk intrusives of Armenia (32 ppm average), and the Mesozoic Conway Granite, an alkalic granite of New Hampshire (56 ppm average).

The radioelement analysis of the samples from the Kigluaik Mountains show that uncommonly high thorium contents measured in a few reconnaissance samples were representative and confirm the presence of regional high thorium contents. In this area, Th contents of about 25-55 ppm are common; a long-lived thorium-rich province is indicated by the similarity in the Th contents in the rocks of a wide range of geologic age. The data also show that most rocks in the major geologic units can be identified from the radioelement content and ratios.

Sainsbury reports that exploration for radioactive minerals during the years 1972-74 by AirSamplex Corp., under contract to Wyoming Minerals Corp., led to the discovery of highly radioactive deposits containing ore-grade concentrations of uranium and thorium along the eastward continuation of the Kigluaik and Bendeleben Mountains. Descriptions of these deposits have not yet been published.

We can conclude that the results of the work reported herein, which demonstrate the uncommonly high thorium content of many rocks in the Kigluaik Mountains, may be expected to delineate other belts of rocks favorable for the occurrence of primary deposits of uranium and thorium if applied elsewhere in Alaska. We hope that the data presented in this report will enable the researcher to recognize what must be considered abnormal variations and concentrations of uranium and thorium in rocks similar to those studied in the Kigluaik Mountains.

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Chemical Variability of a Metavolcanic Rock Unit in the  
Tracy Arm-Fords Terror Wilderness Study Area, Alaska, and  
the Definition of Background Values for Geochemical Purposes

By J. D. HOFFMAN, D. A. BREW, C. L. FORN, *and* B. R. JOHNSON

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-D





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**CHEMICAL VARIABILITY OF A METAVOLCANIC ROCK UNIT IN THE TRACY ARM-FORDS TERROR WILDERNESS STUDY AREA, ALASKA, AND THE DEFINITION OF BACKGROUND VALUES FOR GEOCHEMICAL PURPOSES**

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By J. D. HOFFMAN, D. A. BREW, C. L. FORN, and B. R. JOHNSON

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**ABSTRACT**

Approximately 150 samples from a metavolcanic rock unit in the Tracy Arm-Fords Terror Wilderness study area, southeastern Alaska, were analyzed by routine U.S. Geological Survey semiquantitative spectrographic and analytical chemistry procedures. Of the 35 determinations performed on each sample, 18 were kept in the data set, and the resulting data were statistically analyzed to estimate (1) the distribution of each element about its mean concentration, (2) four components of chemical variability (using a hierarchical analysis of variance model), and (3) correlations between these elements. Over 75 percent of the total variance occurs at the lowest hierarchical level (between samples within sites) for Fe, Mn, Ba, Sc, V, and Y; thus, for these elements, so little geochemical variation is expected at map scales greater than a few meters that an enormous sampling effort would be required to define it. The sampled rock unit is geochemically homogeneous in these elements, at least in terms of mineral exploration surveys. Because of this, intense sampling is not necessary for further characterization of the distribution of these elements in the rock unit. On the other hand, Ca, Co, Cr, Cu, Ni, Ti, Mg, Sr, Zr, Pb, and Zn are not homogeneously distributed, and further sampling would be justified if map patterns for these elements are of interest.

**INTRODUCTION**

The wilderness study program of the U.S. Geological Survey and the U.S. Bureau of Mines consists of mineral-resource appraisal of generally large remote areas. The program relies heavily on geochemical studies to provide information on background abundance of certain elements in bedrock and stream sediments and on the abundance of metallic elements in mineralized rocks or areas. Most of the wilderness studies have used a tightly adjusted grid or other regular close-spacing procedure to select sample sites for background abundance information.

Recent (1973-1976) studies in the Tracy Arm-Fords Terror Wilderness study area, Alaska, provided the opportunity to test, by carefully designed sampling and analysis, the efficiency and the effectiveness of the close- and regular-spacing approach within an areally extensive metavolcanic rock unit. The ultimate purposes of the experiment were (1) to establish what kind of sampling and chemical analysis program is needed to adequately characterize the bedrock geochemistry for the determination of background abundance and for the recognition of any anomalously high values and (2) to provide this information for the guidance of others involved with wilderness-type studies.

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**GEOLOGIC SETTING**

The metavolcanic rock unit sampled is the most widespread in the western metamorphic belt adjacent to the Coast Range batholith complex in this part of southeastern Alaska (Brew and others, 1977). The whole Tracy Arm-Fords Terror study area cuts across most of the batholithic complex and the rocks of the western metamorphic belt adjacent to it on the southwest (fig. 1). The batholithic complex consists of a remarkably long, foliated tonalite sill adjacent to a broad terrane of complexly deformed amphibolite-facies gneiss, marble, and some

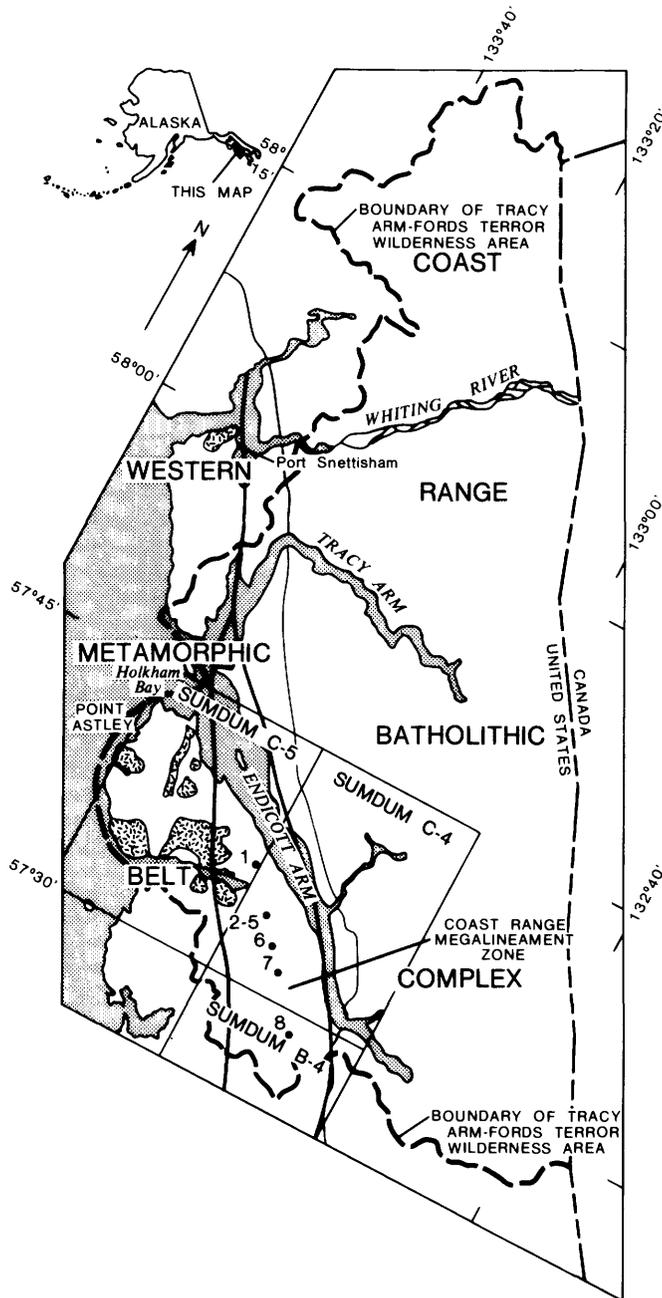


FIGURE 1.—Tracy Arm-Fords Terror Wilderness study area and vicinity. Coast Range batholithic complex, western metamorphic belt and intrusions (pattered) within it, and locations of three quadrangles and eight traverses (including subtraverses 2-5) discussed in this report are shown.

schist in the northeast. Near the Canadian border, this terrane is intruded by a series of generally unfoliated granodiorite bodies of mid-Tertiary age, which are locally associated with migmatite zones.

The western metamorphic-belt rocks immediately adjacent to the complex are high-grade, highly de-

formed gneiss, schist, quartzite, and calc-silicate rock. To the southwest, the metamorphic grade diminishes abruptly, and complexly deformed greenschist-facies phyllite, slate, greenschist, and some limestone and quartzite are exposed over most of the area. The granitic rocks that locally intrude these low-grade metamorphic rocks with local contact-metamorphic effects are diorite, diorite porphyry, granodiorite, and hornblendite of inferred Cretaceous age.

The specific metavolcanic unit described crops out as a 61-km-long, 8-km-wide, irregularly shaped, northwest-trending belt. Although much of the unit contains appreciable quartzite, phyllite, semischist, and marble, the present study included only the dominant greenstone, greenschist, hornblende schist, and amphibolite. The unit is dominantly a greenschist metamorphic facies, but the metamorphic grade increases to the east-southeast; the unit there consists of hornblende schist, hornblende gneiss, and amphibolite. This increase in metamorphic grade is apparently regional and does not reflect any local intrusions.

The unit is probably metamorphosed volcanic rocks, carbonaceous shale, limestone, and chert. The nature and composition of the metavolcanics are uncertain: some of the greenstones and semischists probably were diabase intrusions; some may have been massive flows. At a few localities, the massive greenstones and greenschists contain relict pyroxene phenocrysts. The original age of the unit is unknown but is inferred to be Triassic or Permian on the basis of regional evidence. The age of metamorphism is inferred to be late Cretaceous.

The western metamorphic belt has long been recognized as having significant mineral-resource potential, and the unit studied here is the host rock for several known deposits, the most important of which are the Point Astley zinc-silver deposit and the Windham Bay lode gold deposit (both shown on fig. 1). These deposits consist of sulfide minerals, either disseminated through the unit or concentrated in lenses and stringers along the foliation within bleached or altered zones in phyllite. Although these deposits are within the greenschist and greenstone unit, these specific rock types are not common hosts.

#### SAMPLE COLLECTION, PROCESSING, AND ANALYSIS

The sample collection, processing, and analysis consisted of five successive stages: (1) selection of traverses for sampling within the bedrock unit (the

highest geologically significant level in the hierarchical analysis), (2) the selection of sampling sites along these traverses, (3) collection of several samples at each of those sites, (4) processing of the samples for analysis, and (5) analysis by emission spectrography and by chemistry.

In selecting traverses (or in places portions of traverses), the distribution of the bedrock unit was considered first; all areas known or inferred to be influenced by local intrusions were eliminated from consideration, as were areas with heavy brush and timber. Then, all possible continuous traverses of about 1.5 km length were evaluated in the field, and the five crossing the greatest breadth of the metavolcanic rock unit were selected for study. The longest traverse was subdivided into four subtraverses (subtraverses 2-5). Data on the eight traverses and subtraverses selected are given in table 1.

Geologic features that might differentially affect samples on the five traverses are (1) the increase in metamorphic grade to the east-southeast; (2) the Coast Range megalineament (zone of prominent, parallel, closely spaced joints, foliation surfaces, and compositional layering several kilometers wide), which passes through part of the sampled area; and (3) an unexplained aeromagnetic anomaly (Brew and others, 1977, p. 79), near subtraverses 2-5, which could be generated by a narrow, shallow,

steeply dipping granitic dike. However, the influence of the metamorphism can be discounted because field evidence shows the unit is continuous throughout, and in the absence of evidence to the contrary, the metamorphism is assumed to have been isochemical. The megalineament probably had little influence because the bleaching and alteration of rocks parallel to it are consistently local, and such areas were avoided in the selection of sample sites. Calculations show that an aeromagnetic anomaly like the one described could be caused by a 600-m-wide body reaching to within about 700 m of the surface (Brew and others, 1977).

Sample sites along each traverse were selected according to the following criteria: (1) Each site had to be within a relatively large outcrop of greenstone and greenschist; (2) between-site spacing was about that commonly used (0.4-0.8 km) in reconnaissance geologic mapping and geochemical sampling in wilderness-type studies; and (3) several square meters of almost continuously exposed bedrock had to be present at each site. Four to seven samples were collected at each site; each sample was at least 1 meter and generally a few meters apart from another. This spacing was the only criterion used in selecting the exact sample positions. Each sample weighed about 50-100 g and consisted of chips taken from parts of about a square meter of rock.

The samples were bagged on the outcrop. They were submitted for preparation and analysis to U.S. Geological Survey laboratories in Denver, Colo. They were crushed and split. Each split was ground to about 75  $\mu$ m (200 mesh) and analyzed for 30 elements by emission spectrography and for 5 elements by chemistry using routine procedures (Grimes and Marranzino, 1968; Ward and others, 1969). Altogether, 156 samples were collected, processed, and analyzed for the experiment. All analyses were performed in random order, and no replicate analyses were performed.

**STATISTICAL ANALYSIS PROCEDURES**

The results of the spectrographic and chemical analyses were statistically analyzed on the U.S. Geological Survey's DEC-10 computer in Denver, Colo., using STATPAC programs for Fisher-K statistics, graphic analysis, correlation, and analysis of variance (VanTrump and Miesch, 1977). The analysis of variance program permits estimation of sample variances at each level of the sampling hierarchy. The statistical procedures used calculate (1) the

TABLE 1.—Information on the eight traverses along which samples were collected for this experiment

[Spacing between sites is 0.4 to 0.8 km. Spacing between samples is 1 to 10 m]

Traverse number	Number of		Total traverse length (km)	Distance to next traverse (km)
	Sites	Samples		
1	6	29	1.1	4.4
2	3	13	1.9	
3	3	14		
4	3	14		
5	3	16		
6	4	17	1.3	3.0
7	6	29	1.8	2.9
8	5	24	1.5	6.6
				1.5
Total	33	156	7.6	

properties of the frequency distribution of each element, (2) the correlation between each pair of elements, (3) the geochemical variability within each level of the sampling hierarchy, (4) the statistical significance of this geochemical variability, by calculation of  $F$ -ratios, at each level of the hierarchy, and (5) the percentages of the total variance for each element at each level of the hierarchy.

Of the 35 separate elemental determinations on each sample, only 18 were used for statistical analysis. Because determinations of the other 17 elements included a large number of values (more than 20 percent) below the detection limit for the element, the conventional statistical analysis of these elements could yield biased results. Even after exclusion of these 17 elements from the data set, determinations for a few samples were below the detection limits for some elements (Co, Cr, Cu, Ni); in these cases, such determinations were replaced by a value equal to half the detection limit. This widely used procedure is arbitrary, and its sole justification is the belief that substitution of any value at or below the detection limit would not materially change any geochemical conclusions drawn from the statistical analysis.

Determinations in the data set used in this study are for Fe, Mg, Ca, Ti, Mn, Ba, Co, Cr, Cu, Ni, Sc, Sr, V, Y, and Zr (determined by emission spectrography) and for Cu, Pb, and Zn (determined by atomic absorption spectrophotometry). In text and tables, elements with the prefix "AA" have been determined by atomic absorption; those without, by emission spectrography.

The hierarchical sampling procedure used is as follows: The study area is divided into three 20-minute quadrangles, which constitute the first, or highest, hierarchical level. The eight traverses (and subtraverses) are contained within these three quadrangles and compose the second hierarchical level. Along these eight traverses are 33 sites, which are the third hierarchical level. The 156 individual samples within the 33 sites constitute the fourth, or lowest, hierarchical level.

## RESULTS AND INTERPRETATIONS

The means, standard deviations, and relative standard deviations of each element are shown in table 2. Graphic analysis and moments about the mean (Fisher- $K$  statistics) indicate that Fe, Mg, Ca, Ti, Co, Sc, Sr, Zr, AA-Pb, and AA-Zn are essentially normally distributed. Significant positive, or right, skewness exists for Ba, Cr, Cu, Ni, and V

TABLE 2.—Means, standard deviations, and relative standard deviations for 18 elements in 156 rock samples from the Tracy Arm-Fords Terror Wilderness study area, Alaska

Element	Mean	Standard deviation	Relative standard deviation (percent)
Fe (percent)---	7.0	2.6	37
Mg (percent)---	2.8	1.1	39
Ca (percent)---	3.9	2.1	54
Ti (percent)---	0.6	0.3	50
Mn (ppm)-----	1075	497.6	46
Ba (ppm)-----	248	513.4	207
Co (ppm)-----	25	12.9	52
Cr (ppm)-----	203	223.9	110
Cu (ppm)-----	58	54.3	94
Ni (ppm)-----	58	60.8	105
Sc (ppm)-----	32	12.3	38
Sr (ppm)-----	288	191.1	66
V (ppm)-----	217	176.1	81
Y (ppm)-----	20	8.9	46
Zr (ppm)-----	54	29.7	56
AA-Cu (ppm)----	58	15.1	26
AA-Pb (ppm)----	7	4.5	64
AA-Zn (ppm)----	36	20.0	56

(fig. 2). Log-transformations were performed on the determinations of these five elements to determine if this approach would normalize the data (Davis, 1973). Graphic analysis of the transformed data yielded vastly improved distributions for V, suggesting that this element is lognormally distributed. Graphic analysis of the log-transformed data for Ba, Cr, and Ni showed significant improvement of the distributions of these elements, but log-transformation of Cu data yielded no useful improvement (fig. 2).

However, only nontransformed data are used in the statistical interpretation; differences in interpretation due to use of the lognormal data for some elements (Ba, Cr, Cu, Ni, and V) and the normal data for others are considered to be insignificant in the context of geochemical exploration. (An example of the statistical treatment of the log-transformed data is given in table 4). Moreover, statistical evidence indicates that if the relative standard deviation of a sample population is less than 120 percent, the greater efficiency of using log-normal data to estimate the mean of that population is outweighed by the possibility of introducing bias if the lognormal distribution is inappropriate. Further Finney's efficiency curve (Koch and Link, 1971) would not suggest the use of log-transformations, as the use of the raw data yields a statistical efficiency greater than 90 percent for all elements in the data set except Ba. (That is, the sample mean of the nontransformed data is an estimator of the population mean more

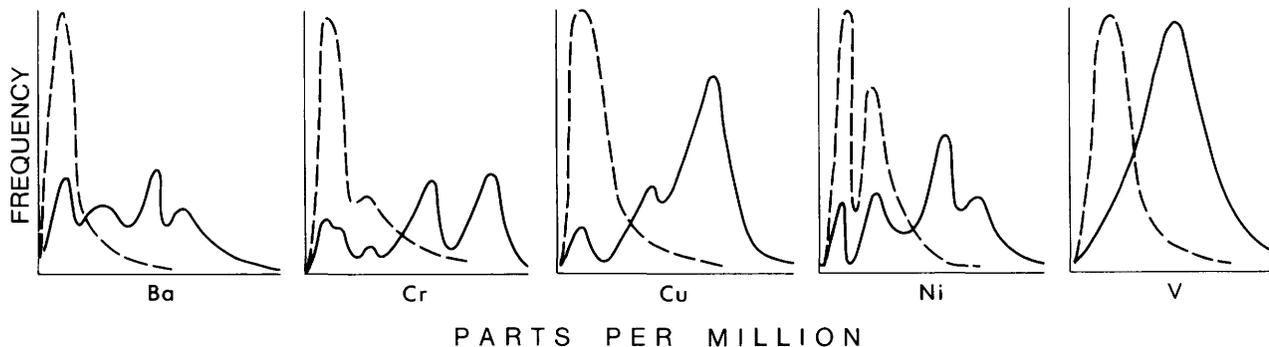


FIGURE 2.—Frequency distributions of the abnormally distributed elements, before (dashed line) and after (solid line) log-transformation of raw data.

than 90 percent of the time, even if the population is lognormally distributed.) Only Ba has a relative standard deviation higher than 120 percent.

Table 3 shows the variance components for each element at each level of the hierarchy. The computer program used to estimate these statistics is unable to distinguish very small variance components and may express this inability by the generation of

TABLE 3.—Computer generated variance components for elements determined in samples from the Tracy Arm-Fords Terror Wilderness study area, Alaska

[Inc., Inconsequential; component is so small that the computer generated a negative number for it, a statistical impossibility ]

Element	Between quadrangles	Between traverses	Between sites	Between samples
Fe----	Inc.	$0.274 \times 10^0$	$0.431 \times 10^0$	$0.644 \times 10^{-1}$
Mg----	Inc.	$.576 \times 10^0$	$.881 \times 10^{-1}$	$.819 \times 10^0$
Ca----	$0.583 \times 10^0$	Inc.	$.243 \times 10^{-1}$	$.181 \times 10^{-1}$
Ti----	Inc.	$.651 \times 10^{-2}$	$.321 \times 10^{-1}$	$.550 \times 10^{-1}$
Mn----	Inc.	$.212 \times 10^{-5}$	Inc.	$.245 \times 10^{-6}$
Ba----	$.213 \times 10^{-5}$	Inc.	$.510 \times 10^{-5}$	$.243 \times 10^{-6}$
Co----	Inc.	$.676 \times 10^{-2}$	$.214 \times 10^{-1}$	$.133 \times 10^{-3}$
Cr----	Inc.	$.264 \times 10^{-5}$	$.720 \times 10^{-4}$	$.320 \times 10^{-5}$
Cu----	Inc.	$.126 \times 10^{-4}$	Inc.	$.295 \times 10^{-4}$
Ni----	Inc.	$.270 \times 10^{-4}$	$.696 \times 10^{-3}$	$.182 \times 10^{-4}$
Sc----	Inc.	$.333 \times 10^{-1}$	$.510 \times 10^{-1}$	$.146 \times 10^{-3}$
Sr----	$.155 \times 10^{-4}$	Inc.	$.187 \times 10^{-5}$	$.235 \times 10^{-5}$
V-----	$.257 \times 10^{-4}$	Inc.	$.216 \times 10^{-4}$	$.308 \times 10^{-5}$
Y-----	$.265 \times 10^{-1}$	$.603 \times 10^{-2}$	$.425 \times 10^{-1}$	$.631 \times 10^{-2}$
Zr-----	Inc.	$.902 \times 10^{-3}$	$.166 \times 10^{-3}$	$.203 \times 10^{-4}$
AA-Cu--	Inc.	$.902 \times 10^{-3}$	$.166 \times 10^{-3}$	$.203 \times 10^{-4}$
AA-Pb--	$.156 \times 10^{-1}$	$.180 \times 10^{-1}$	$.436 \times 10^{-1}$	$.134 \times 10^{-2}$
AA-Zn--	$.144 \times 10^{-3}$	$.609 \times 10^{-2}$	$.543 \times 10^{-2}$	$.177 \times 10^{-3}$

negative variance components. These negative components suggest that an unusual sampling event occurred or, more likely, that the hierarchical analysis of variance program employed is unable to distinguish extremely small components of variance at hierarchical levels above the lowest level. If these components are small enough, they will contribute no significant variance and may be set to zero.

Table 4 and figure 3 display the variance components as percentages of the total variance at each hierarchical level. The data in this table indicate that for Fe, Mg, Ti, Mn, Co, Cr, Cu, Ni, Sc, Zr, and AA-Cu, the unit studied is essentially homogenous at the quadrangle hierarchical level, Ca, Ba, Sr, and V are homogeneously distributed at the traverse level, and Mn and Cu are homogeneously distributed at the site level. More than 50 percent of the total variance is explained at the sample level for Fe, Mg, Ti, Mn, Ba, Co, Cu, Sc, Sr, V, Y, AA-Cu, and AA-Pb. Mg, Co, Cu, Cr, Ni, and AA-Cu exhibit an interesting trend: low percentages of the total variance are contained in the quadrangle and site levels; much higher percentages of the total variance are explained at the traverse and sample levels. At the site level, this trend may be due to variation in the original composition of the metavolcanic rock unit sampled for the experiment.

Table 4 shows that for all but one of the elements, the percentage of the total variance explained by the variance between quadrangles is small. AA-Zn is the exception; the high variance at this level indicates that the distribution of Zn in the study area is unlike that of any other element. The distribution of Zn, in general, has not been fully explained (Park and MacDiarmid, 1975), and in these rocks it may represent either an original distribution, a secondary Zn (and Pb?) mineralization event, or even a later redistribution of this mobile element from

TABLE 4.—Variance components as percentages of total variance and the significance of *F*-ratios derived from the variance components

[Differences between hierarchical levels are nonsignificant if no asterisk appears between columns ]

Element	Hierarchical Level			
	Quadrangle	Traverse	Site	Sample
Variance components of normal data				
Fe-----	0	3.8	6.8	90.1
Mg-----	0	38.8	** 5.9	* 55.2
Ca-----	12.1	0	50.3	** 37.6
Ti-----	0	6.9	34.3	** 58.7
Mn-----	0	8.0	0	92.0
Ba-----	7.0	0	16.2	** 76.9
Co-----	0	33.3	** 1.1	65.6
Cr-----	0	40.2	** 11.0	** 48.8
Cu-----	0	29.9	** 0	70.1
Ni-----	0	51.7	** 13.3	** 35.0
Sc-----	0	2.2	3.3	94.5
Sr-----	3.5	0	49.2	** 53.6
V-----	7.2	* 0	6.1	86.7
Y-----	9.4	7.4	5.3	77.9
Zr-----	0	13.0	39.9	** 47.1
AA-Cu--	0	29.1	** 5.4	65.5
AA-Pb--	7.4	8.5	20.6	** 63.4
AA-Zn--	13.1	** 14.0	12.4	** 40.5
Variance components of log-transformed data				
Cu-----	5.7	2.5	6.3	* 85.4
V-----	7.7	0	14.9	** 77.4

\* The difference between hierarchical levels is significant at the 0.10 alpha level.

\*\*The difference between hierarchical levels is significant at both the 0.10 and 0.05 alpha levels.

either of these sources. The primary feature of this distribution is that it is regional in extent, and any explanation of Zn origin must take this into account.

Fe is evenly distributed throughout the study unit, as is demonstrated by the lack of significant differences at all levels (table 4). More than 75 percent of the total variation in Fe, Mn, Ba, Sc, V, and Y lies at the sample hierarchical level, indicating essentially homogeneous distribution for these elements; therefore, intense sampling over a large number of sites and traverses is not statistically

necessary to characterize the distribution of these elements (in the rock unit analyzed in this study). More intense site sampling will be required to establish the distribution of Co, Ti, Ni, Sr, Zr, AA-Pb, and AA-Zn, as a significant percentage of the total variance of these elements is at the traverse hierarchical level.

The significance of *F*-ratios derived from the variances within each level of the hierarchy is also shown in table 4. These ratios are tabulated for (1) traverses within quadrangles, (2) sites within traverses, and (3) samples within sites. There is no significant difference in variance between hierarchical levels in the distributions of Fe, Mn, Sc, and Y (see table 4); the distribution of the variances of these elements is even at all hierarchical levels. For 16 elements, there is no significant difference between the quadrangle and traverse levels at either of the two alpha levels tested (0.05 and 0.10). The two exceptions are V at the 0.10 level and Zn at both alpha levels.

The statistical significance of the correlation coefficients (table 5) can be obtained using the standard normal (*z*) statistic:

$$Z = (\sqrt{n-3}/2) \ln((1+r)/(1-r)),$$

where *n* is the number of samples, and *r* is the correlation coefficient. For this experiment, in which *n* equals 156, it can be shown that *r* values (alpha  $\leq 0.05$ ) beyond about  $\pm 0.16$  are statistically significant.

From these findings (lacking replicate analyses to evaluate analytical variation) the writers conclude that the distribution of almost all the elements in the data set for this study unit could be adequately evaluated by (1) collecting more than one sample at any given site, in order to better characterize the distribution of the variances at the sample level because the largest variance component for all the 18 elements except Ca and Ni occurs at this level, (2) using significantly fewer sites along each traverse, as the site hierarchical level contains a relatively small variance component (less than 15 percent of the total variance) for 12 of the elements in the data set, and (3) using a traverse spacing of 3-7 km, the spacing used in this study. For example, statistically valid information on the bedrock background values for most of the 18 determinations in the data set could probably be obtained with just two sites along each of the eight traverses and subtraverses used and two samples at each site or with just one site on each traverse and four samples at each site. Either of these methods would yield a

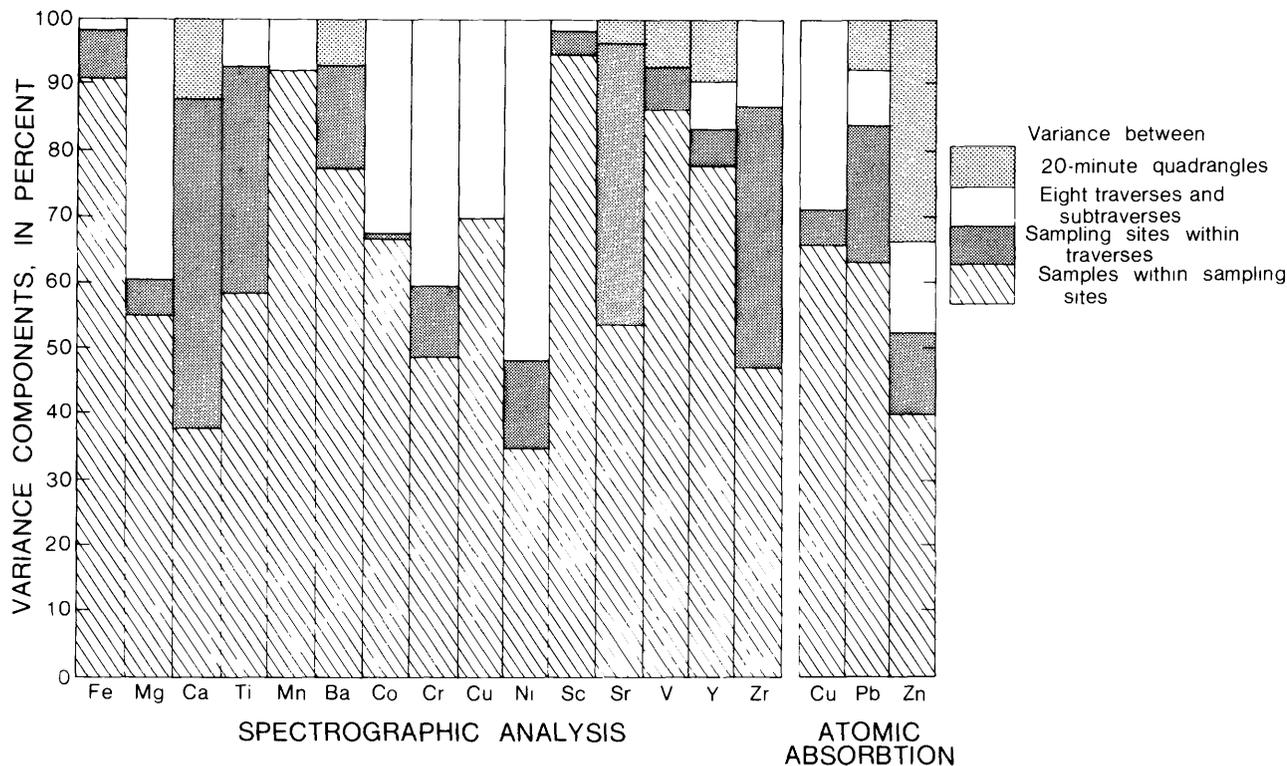


FIGURE 3.—Variance components, as percent total variance.

TABLE 5.—Correlation coefficients of element concentrations in rock samples from the Tracy Arm-Fords Terror Wilderness study area, Alaska

[Significant correlations (i.e.  $\geq \pm 0.16$ ) are underscored]

Fe	Mg	Ca	Ti	Mn	Ba	Co	Cr	Cu	Ni	Sc	Sr	V	Y	Zr	AA-Cu	AA-Pb	AA-Zn	Element
1.00	<u>0.40</u>	0.08	<u>0.41</u>	<u>0.62</u>	-0.02	<u>0.28</u>	0.07	<u>0.23</u>	<u>0.23</u>	0.09	-0.10	<u>0.63</u>	-0.02	-0.11	0.07	-0.03	0.08	Fe
	1.00	0.14	<u>0.31</u>	<u>0.38</u>	-0.04	<u>0.47</u>	<u>0.57</u>	0.09	<u>0.60</u>	0.10	-0.06	<u>0.26</u>	-0.04	-0.01	0.02	0.13	-0.03	Mg
		1.00	0.11	<u>0.39</u>	-0.14	0.06	<u>0.16</u>	-0.15	<u>0.16</u>	<u>0.18</u>	<u>0.50</u>	<u>0.18</u>	0.06	-0.11	-0.10	<u>-0.19</u>	<u>-0.48</u>	Ca
			1.00	<u>0.30</u>	0.01	<u>0.37</u>	<u>0.28</u>	0.14	<u>0.42</u>	0.09	<u>0.20</u>	<u>0.17</u>	<u>0.36</u>	<u>0.42</u>	-0.01	0.06	0.12	Ti
				1.00	-0.10	<u>0.20</u>	0.12	0.14	<u>0.25</u>	-0.02	0.01	<u>0.54</u>	-0.12	-0.15	0.01	-0.15	<u>-0.16</u>	Mn
					1.00	0.10	0.09	-0.08	0.09	-0.07	-0.10	-0.04	0.08	<u>0.33</u>	-0.08	<u>0.33</u>	<u>0.17</u>	Ba
						1.00	<u>0.57</u>	0.09	<u>0.62</u>	<u>0.18</u>	0.03	0.06	<u>0.24</u>	<u>0.27</u>	0.05	0.10	-0.01	Co
							1.00	-0.14	<u>0.85</u>	0.13	0.01	-0.03	0.06	0.16	-0.14	<u>0.23</u>	-0.14	Cr
								1.00	-0.06	-0.11	-0.12	<u>0.17</u>	-0.15	-0.15	<u>0.84</u>	-0.07	0.13	Cu
									1.00	0.08	0.05	0.09	<u>0.22</u>	-0.10	<u>0.23</u>	-0.09	0.00	Ni
										1.00	0.14	0.01	<u>0.27</u>	0.00	-0.10	0.00	0.00	Sc
											1.00	-0.10	<u>0.28</u>	<u>0.29</u>	-0.02	-0.02	-0.16	Sr
												1.00	<u>-0.20</u>	<u>-0.34</u>	0.09	-0.07	-0.05	V
													1.00	<u>0.60</u>	<u>-0.16</u>	0.09	0.15	Y
														1.00	<u>-0.18</u>	<u>0.23</u>	<u>0.18</u>	Zr
															1.00	-0.11	0.07	AA-Cu
																1.00	<u>0.50</u>	AA-Pb
																	1.00	AA-Zn

total of 32 samples, instead of the total of 156 samples used in this study. For background information on a rock unit such as that described herein, a typical U.S. Geological Survey wilderness-type bedrock sampling program would involve 50-60 samples.

The conclusions from this experiment may apply to other areas with similar lithologies and can probably be used for general guidance, but experiments of the same type, done early in the geochemical study of a given area, could help establish an

effective system for determining background values and thus aid in the organization of an effective sampling program.

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# Efficient Stream-Sediment Sampling Design: An Experiment at Tracy Arm, Alaska

By BRUCE R. JOHNSON, CARL L. FORN, JAMES D. HOFFMAN,  
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SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-E

*An application of analysis-of-variance techniques  
to the problem of sampling design for  
regional stream-sediment geochemical surveys*





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**EFFICIENT STREAM-SEDIMENT SAMPLING DESIGN:  
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ABSTRACT

A total of 371 stream sediment samples were collected from a 150-km<sup>2</sup> drainage north of Tracy Arm, Alaska. The basin contains approximately 45 km of first- and second-order active stream channels. Nearly 1,700 splits of these samples were analyzed for 30 elements by spectrograph and for 4 elements by atomic absorption using standard U.S. Geological Survey techniques. Variance components, derived from a four-level hierarchical-design analysis of variance, were found to vary widely among the elements. For most elements included in the study, variations among samples spaced less than 1.5 km along active stream channels are insignificant compared with variations at 1.5-km spacings (the largest spacings tested by the model). For many of the elements analyzed in this study, particularly those determined by spectrograph, approximately one-half of the total variation is a result of sample preparation and analysis in the laboratory. This is an indication that the study area did not contain large geochemical anomalies. To reduce the effects of this analytical noise, it is necessary to collect more than one sample at each sample location or to run replicate analyses of each sample.

INTRODUCTION

A stream-sediment sampling experiment was undertaken as part of the U.S. Geological Survey wilderness resource evaluation program in the Tracy Arm-Fords Terror Wilderness study area, southeastern Alaska (Brew and others, 1977). The primary objective was to develop sampling plans and data analysis techniques that make the most effective use of the time and resource available for sampling active stream sediments. These techniques may be useful in improving the quality of future resource evaluation programs in southeastern Alaska and other areas of similar terrain and bed-rock geology.

Geochemical information is usually presented in the form of contour maps of the abundance of one

or more elements of interest. Such maps are intended to show background amounts of the element in question as well as areas of anomalously high amounts of that element. The size, intensity, and location of these anomalies form the basic information useful to a resource evaluation program. With the increased efficiency of computer-generated statistical analysis and automatic contour plotting, it is much easier to generate anomaly maps than it is to assess their quality. Therefore, a second objective of the sampling experiment was to assess the stability, or reproducibility, of maps generated by current procedures.

Previous studies of this problem have generally stressed the need for formal randomization procedures at all stages of the analysis to ensure the validity of subsequent statistical procedures (Eisenhart, 1947; Krumbein and Slack, 1956; Miesch, 1976). Although such procedures are ideal in terms of statistical theory, they are often impractical for large resource-assessment programs. This study is designed to help bridge the gap between more formal statistical techniques and the real world of deadlines and budgets.

To generate a data set for testing current procedures, a drainage area north of Tracy Arm (fig. 1) was sampled intensively. A hierarchical- or nested-design analysis of variance was used to estimate the components of total sample variance that are related to different sample spacings as well as the analytical variance. For many elements analyzed by spectrographic techniques in this study, approximately one-half of the total sample variance is the analytical component. To reduce this component so that small anomalies may be differentiated from the analytical noise, it is necessary to collect more than one sample

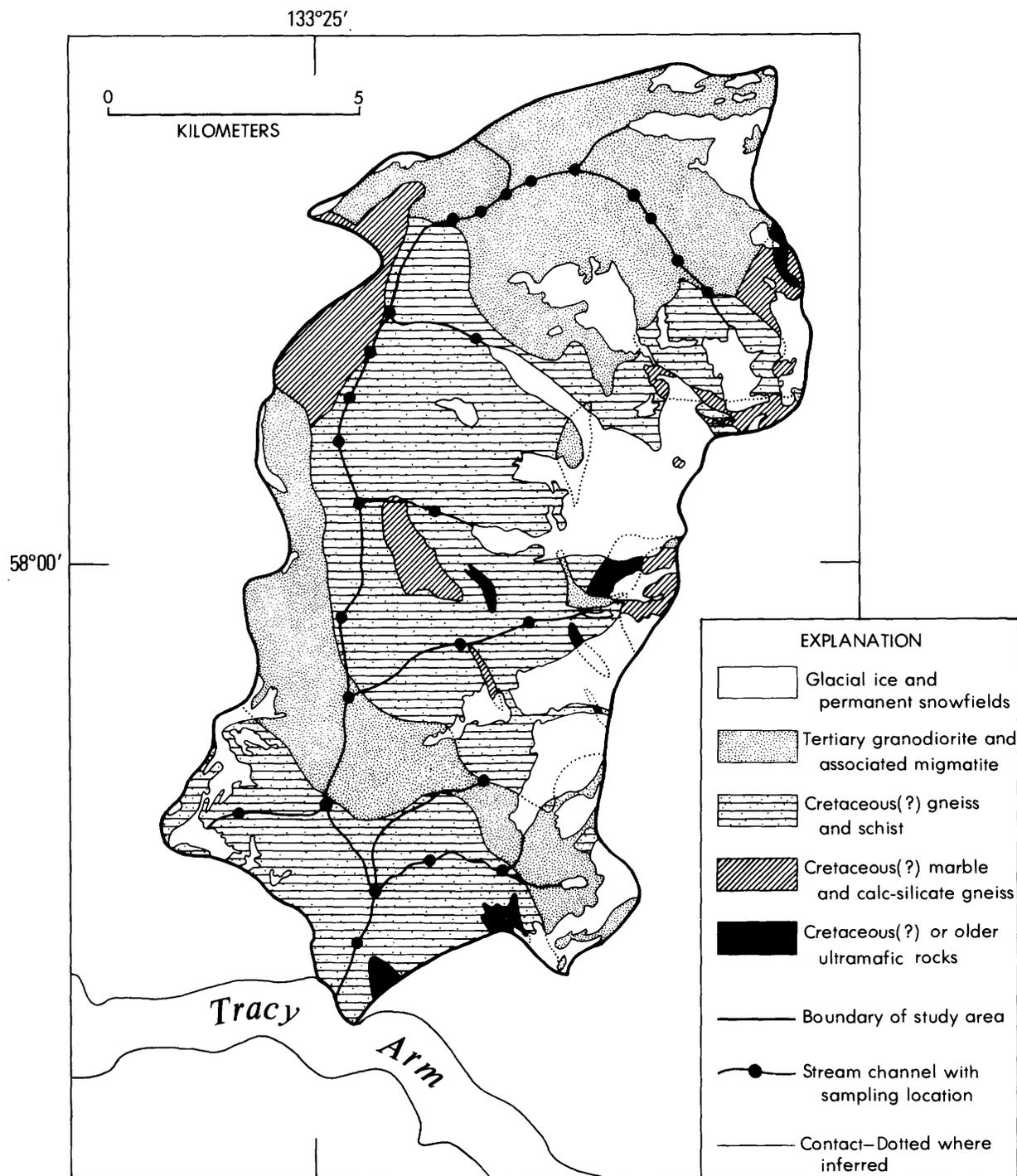


FIGURE 1.—Geologic map of study area at Tracy Arm. Geology from Brew and others (1977).

from each sample location and (or) analyze each sample more than once.

#### SAMPLING AND CHEMICAL ANALYSIS

The drainage basin chosen for this study lies on the north side of Tracy Arm and covers an area of

approximately 150 km<sup>2</sup> (fig. 1). The bedrock underlying the basin is composed primarily of hornblende-biotite granodiorite and associated migmatite and host rocks of amphibolite-grade gneiss and schist. Small areas of marble and calc-silicate gneiss are included in the host rocks as are several small ultramafic bodies (Brew and others, 1977). Elevations in

the drainage basin range from boundary peaks approximately 2000 m high to sea level at the mouth of the main stream. In addition to the main stream, eight first-order tributaries are contained within the basin.

To perform a hierarchical analysis of variance, the basin was first divided into 27 sampling locations (fig. 1). Each location was subdivided into sites, and sample points were randomly located within each site (fig. 2). A sampling location was defined as a few hundred square meters of active stream sediments that could be sampled by hand. The average distance between the centers of sampling locations, measured along the stream course, was about 1.5 km.

Within each sampling location, one to five sites were selected at random. If the location included a stream junction, all tributaries were sampled. A site was defined as an area of several square meters from which active stream sediment could be collected. It should be emphasized that formal randomization procedures were not followed for site selection. The collecting geologist was instructed to select sites within a location at random and to include all tributaries. Because the possible number of sites that could be selected was virtually unlimited and the statistical techniques used are believed to be robust (Cochran, 1947), lack of formal randomization should not seriously affect the results. Originally three sampling sites were to be chosen within each location, but the realities of accessibility limited the number to one or two at some locations, whereas within others four or five sites could be selected. The average distance between the centers of sites within a location was about 100 m.

Within each site, samples were collected from one to four separate points. Again, random selection of sampling points within each site was left to the geologist. At each collection point, both a normal,

fine-grained sample and a visibly coarser grained sample were collected. The samples were dried in the field and shipped to the U.S. Geological Survey's Mobile Analytical Lab in Juneau, Alaska, for processing.

At the laboratory, the samples were each sieved at 80 mesh to separate coarse and fine fractions. At this stage, there were four sample fractions from each sampling point: a coarse (+80 mesh) and a fine (-80 mesh) fraction of both the normal and the coarser samples. Each fraction was then pulverized and split so that replicate chemical analyses could be performed. Three splits were obtained from the fine fraction of the normal samples, and two splits were obtained of all other fractions. In all, 1,669 splits were analyzed by standard Geological Survey procedures for 30 elements by spectrographic techniques and for an additional 4 elements by atomic absorption techniques (Grimes and Marranzino, 1968; Ward and others, 1969).

STATISTICAL ANALYSIS

Frequency curves of the results reported by the analytical laboratory were plotted as an initial step in the data analysis. The curves were examined to determine which of the four combinations of sample collection and treatment produced the greatest mean concentration of each element. The common technique of collecting fine-grained samples and analyzing the fine fraction produced the greatest concentration of most, but not all, elements. If the intended survey were aimed specifically at magnesium and calcium, for example, a greater concentration would probably be found (in this study area) in a coarser original sample (table 1).

TABLE 1.—Sampling and separation procedures which yield the greatest mean concentration of selected elements

[Spec, analysis by emission spectrography. A. A., analysis by atomic absorption]

Sample	Split (mesh)	Greatest mean concentration
Fine	+80	Spec: Be A.A.: Pb
	-80	Spec: Ba, Co, Cr, Cu, Fe, Ni, Sc, Sr, Ti, Zn A.A.: Cu, Zn
Coarse	+80	Spec: Pb
	-80	Spec: Ca, La, Mg, Mn, V, Y

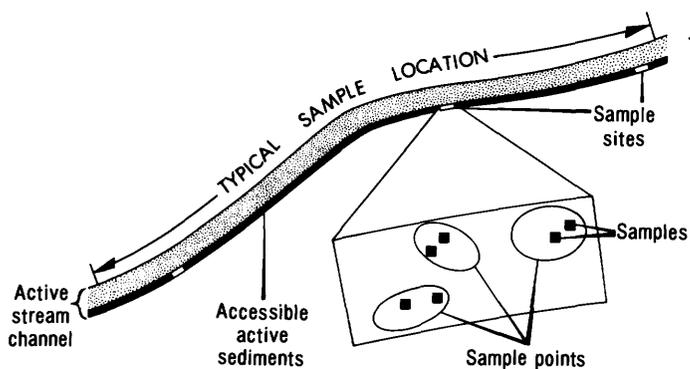


FIGURE 2.—Design of sampling program at Tracy Arm.

However, for a multielement geochemical survey, the -80 mesh fraction of a fine-grained sample seems to be preferable.

Subsequent statistical analyses were carried out simultaneously and separately on data from each of the four sample fractions. Because the -80 mesh fraction of the fine samples appeared to produce the best data, the rest of this discussion will concentrate on the data obtained from these samples.

All spectrographic analytical data were reported either as a six-step logarithmic scale, with the following numbers representing the centers of the intervals, . . . 1, 1.5, 2, 3, 5, 7 . . . , or by an alphabetic code (Ward and others, 1963; Grimes and Marranzino, 1968). The number of analyses falling into each of the coded classes as well as the detection limits in use are tabulated in table 2. Because distributions with a large number of values above or below detection limits are not compatible with analysis of variance techniques, all sample distributions with more than 25-percent coded values were eliminated from the remainder of the analysis. Thus, spectrographic analyses of 13 elements (table 2) were eliminated, as was atomic absorption analysis of gold. However, there is no evidence that distributions of these elements differ substantially from those of the remaining elements. The other 20 elements had less than 25-percent coded values and were used in the hierarchical analysis of variance.

Examination of the frequency curves showed the sample distributions to be positively skewed almost without exception. Because logarithmic transformation of the data removes much of the skewness, the original population distribution was assumed to be closer to lognormal than normal. Because analysis-of-variance techniques assume a normal sample distribution, all sample data were converted to their logarithms before performing the analysis of variance.

All coded values must be replaced by numeric values for the analysis of variance. For this analysis all values coded N and L (table 2) were replaced with a numeric value one step below the detection limit for that element, and all values coded G were replaced with a numeric value one step above the maximum comparison limit (see Miesch, 1967, for more exact methods of treating censored data).

A four-level hierarchical-design analysis of variance was performed on the data for each element using the U.S. Geological Survey's STATPAC program D0038 (Sower and others, 1971; George Van Trump, unpub. data, 1972). This program generates variance components for each hierarchical level

TABLE 2.—Detection limits of analyses and number of coded values reported for each element

[Number of analyses, 555; except for Au by atomic absorption, 185 analyses. Analyses of fine fraction of fine samples. N, not detected; L, detected but below comparison limit; G, greater than maximum comparison limit]

Element <sup>1</sup>	Analytical limits		Analytical values reported			
	Lower	Upper <sup>2</sup>	Within analytical limits	N	L	G
SPECTROGRAPHIC ANALYSES						
Fe-----	9.05%	20%	554	0	0	1
Mg-----	.02	10	548	0	0	7
Ca-----	.02		555	0	0	0
Ti-----	.002	1	539	0	0	16
(Ag)-----	0.5 ppm		7	537	11	0
(As)-----	200		0	555	0	0
(Au)-----	10		0	555	0	0
(B)-----	10		84	257	214	0
Ba-----	20	5,000 ppm	549	0	0	6
(Be)-----	1		211	40	304	0
(Bi)-----	10		0	555	0	0
(Cd)-----	20		0	555	0	0
Co-----	5		555	0	0	0
Cr-----	10		555	0	0	0
Cu-----	5		555	0	0	0
La-----	20		452	76	27	0
Mn-----	10		555	0	0	0
(Mo)-----	5		4	550	1	0
(Nb)-----	20		4	375	176	0
Ni-----	5		555	0	0	0
Pb-----	10		428	13	114	0
(Sb)-----	100		0	555	0	0
Sc-----	5		555	0	0	0
(Sn)-----	10		0	555	0	0
Sr-----	100		555	0	0	0
V-----	10		555	0	0	0
(W)-----	50		0	555	0	0
Y-----	10		555	0	0	0
(Zn)-----	200		2	552	1	0
Zr-----	10	1,000	554	0	0	1
ATOMIC ABSORPTION ANALYSES						
(Au)-----	0.05 ppm		1	184	0	0
Cu-----	5		555	0	0	0
Pb-----	5		524	0	31	0
Zn-----	5		555	0	0	0

<sup>1</sup>Elements in parentheses were not used for analysis of variance.

<sup>2</sup>Upper comparison limit shown only where G codes were reported.

along with the total sample variance for each element. A variance component is that portion of the total sample variance that can be attributed to variations at a particular hierarchical level (Krumbein

TABLE 3.—Variance components, means, and approximate confidence limits for selected elements

Element	Total variance of log(X)	Variance components <sup>1</sup>				Geometric mean <sup>2</sup>	Analytical standard deviation	Approximate 95% confidence limits (steps) <sup>3</sup>
		Location	Site	Sample	Analytical			
SPECTROGRAPHIC ANALYSES								
Fe ----	0.028	16.8	17.2	4.8	61.1	5.1%	0.13	1.5
Mg ----	.027	23.6	9.7	0	66.7	2.8	.15	2
Ca ----	.031	19.8	11.2	0	69.0	5.7	.15	2
Ti ----	.055	3.9	8.2	0	87.9	.47	.24	3
Ba ----	.047	36.3	10.9	5.1	47.8	1500 ppm	.16	2
Co ----	.032	41.6	8.1	9.2	41.1	20	.11	1.5
Cr ----	.090	49.8	14.1	2.1	34.0	180	.18	2
Cu ----	.083	11.2	7.5	15.9	65.4	32	.23	3
La ----	.096	12.3	10.4	21.9	55.4	54	.30	3.5
Mn ----	.021	6.8	4.5	0	88.7	1100	.14	1.5
Ni ----	.083	54.7	12.8	10.5	22.0	62	.14	1.5
Pb ----	.009	4.6	13.3	0	82.1	12	.17	2
Sc ----	.022	16.0	17.7	9.5	56.9	24	.11	1.5
Sr ----	.043	26.3	24.9	0	48.8	380	.14	1.5
V ----	.016	2.5	9.3	0	88.2	150	.12	1.5
Y ----	.042	1.1	4.9	24.6	69.4	29	.17	2
Zr ----	.069	7.4	7.3	28.3	57.1	150	.20	2.5
ATOMIC ABSORPTION ANALYSES								
Cu ----	0.031	36.4	8.5	36.0	19.1	28 ppm	0.08	1
Pb ----	.025	31.6	2.9	8.6	57.0	7	.13	1.5
Zn ----	.034	33.1	32.8	26.4	7.7	39	.05	.5

<sup>1</sup>Percent total variance of log(X).

<sup>2</sup>Geometric mean is the antilog of the mean of log(X).

<sup>3</sup>Atomic absorption results were not reported on the six-step scale. For purposes of comparison, the confidence limits have been converted to equivalent scale steps.

and Graybill, 1965, p. 209). The four levels used in this study were (1) sampling locations, (2) sites, (3) sample points, and (4) repeat analyses. The results of the analysis are tabulated in table 3, and the variance components are displayed in figure 3.

The most striking aspect of the variance components is the lack of pattern or uniformity from element to element. There are large differences in the variance distribution among levels from one element

to another and also significant differences in total variation between elements. Some patterns do emerge, however. In general, about one-half of the total sample variation is generated during the sample preparation and analysis, about one-fourth of the variance is due to differences between sample locations, and the remaining one-fourth is due to differences between sites within sampling locations and between sample points within sites. The fact that

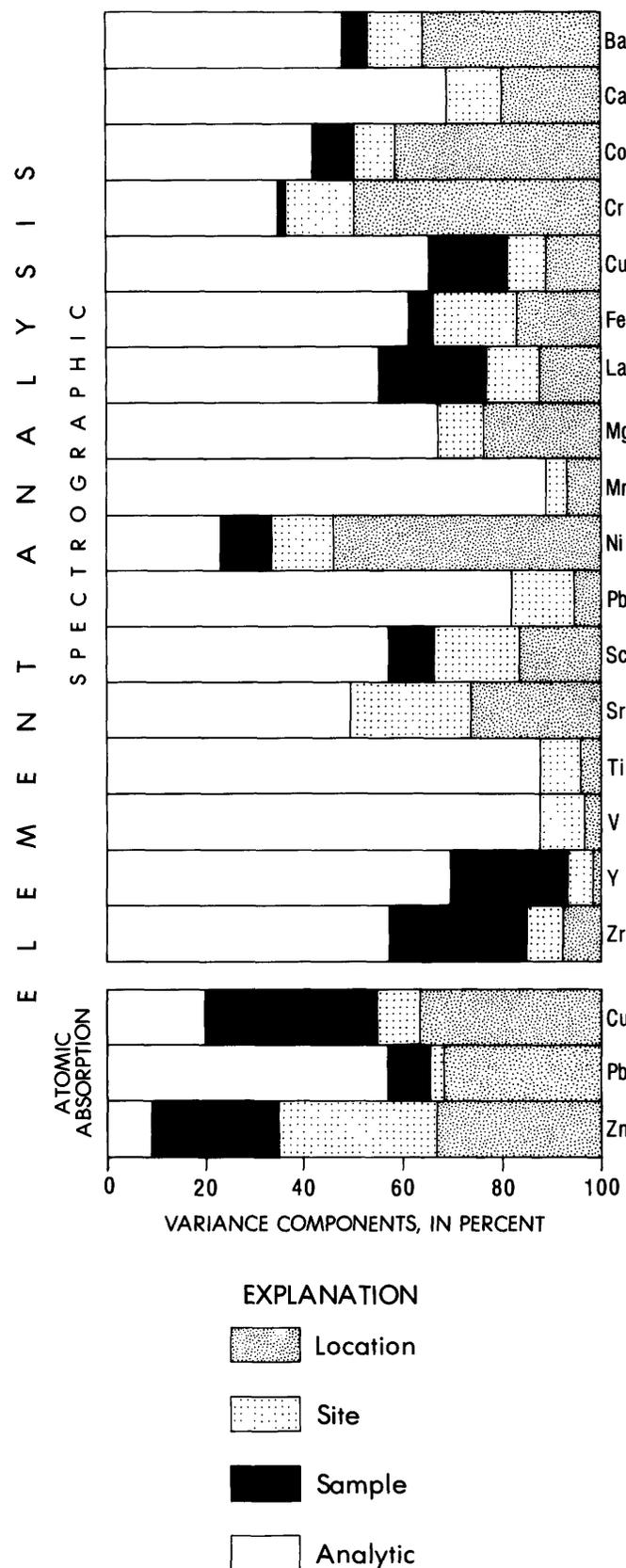


FIGURE 3.—Variance components, as percentage of total variance, by element.

components of variance for site and sample point levels are generally significantly smaller than the components for locations is encouraging because the sampling locations are spaced typically for a regional analysis project. Thus, spacing sample locations any more closely is probably not necessary in this area for defining geochemical background levels and detecting significant anomalies.

The generally large analytical variance may cause a great deal of information to be lost if normal  $1 \times 1$  (one sample per location, one analysis per sample) sampling techniques are used. There are exceptions, however, so that each element and each analytical technique must be considered separately.

The fact that the analytical variance accounts for about one-half of the total variance in this data should not be considered a criticism of the analytical technique. It is an indication that the analytical variance and the remaining sample variance are approximately the same magnitude. If the sample population were totally homogeneous, for example, the analytical variance would account for all the total variance. Because the study area did not contain any large anomalies, the sample variance was small. Large anomalies would have shown up despite the analytical noise in a  $1 \times 1$  sample design. However, much of the background information would have been lost.

The precision of the analytical techniques can be estimated from the analytical variance components. Using standard statistical techniques, 95-percent confidence limits can be estimated for each element by doubling the analytical standard deviation and adding to and subtracting from the log of the value in question (Krumbein and Graybill, 1965). Antilogs of these values can be found to convert the confidence limits to parts per million or percentages. Conversion can also be made to the number of steps up or down the six-step spectrographic scale at which the approximate 95-percent confidence limits lie. These limits are given in table 3.

The interpretation of these limits is best explained by an example: From table 3, the 95-percent confidence limits for copper analyzed spectrographically are plus and minus 3 steps. If the laboratory reported a single analysis of a single sample as having 100 ppm copper, we would expect the true amount of copper in the sample to lie between 30 and 300 ppm with probability 0.95. That is, we would expect the true value to be more than 3 steps away from the reported value 1 time in 20 for all such analyses of copper. The analytical precision values reported here appear consistent with a recent study by Motooka and Grimes (1976), in which they analyzed 22 dif-

ferent samples over 2,700 times using the same analytical techniques.

A comparison with the confidence limits for copper measured by atomic absorption points out the need to study the problem separately for each element and each technique. The 95-percent confidence limits in this instance are plus and minus 1 step. For a sample reported as having 100 ppm copper by this technique, we would expect the true amount of copper to be between 70 and 150 ppm with probability 0.95.

### SAMPLING DESIGN

The approach used in this experiment is obviously not suited to routine large-scale geochemical sampling programs, but it does provide a test of such programs. Such a program uses only one suite of samples to detect anomalous occurrences of 20 or more elements. For each element of interest, a contour plot is normally generated that shows areas above some threshold value as being anomalous.

One measure of the quality of such a map is its stability. If repeating the entire experiment, including resampling and reanalyzing, would produce a map that was essentially the same as the original map, then the original would be considered quite stable. Fortunately, it is not necessary to actually repeat the experiment to measure the map stability. Miesch (1976) devised a statistical procedure for measuring map stability based on calculation of the variance mean ratio ( $v_m$ ). He concluded that if  $v_m$  is less than 1, the geologic pattern of the area will not be stable. If  $v_m$  is greater than 1, the pattern is more stable, and, as  $v_m$  approaches 3, the map becomes quite stable (Miesch, 1976, p. 102). An example of the calculation of  $v_m$  is shown as follows:

According to Miesch (1976),

$$v_m = N_v / D_m,$$

where

$v_m$  is the variance mean ratio,

$N_v$  is the sampling location variance component, and

$D_m$  is the variance of sampling locality means.

$D_m$  is estimated by

$$D_m = (s_s^2/n_s) + (s_A^2/(n_s n_A)),$$

where

$s_s^2$  is the combined site and sample point variance components,

$s_A^2$  is the analytical variance component,

$n_s$  is the number of samples per sampling location, and

$n_A$  is the number of analyses per sample.

Assuming a hypothetical average element with  $N_v$  of 0.012, site and sample-point variance components of 0.006 each ( $s_s^2 = 0.012$ ), and  $s_A^2$  of 0.028,  $v_m$  may be calculated for any combination of  $n_s$  and  $n_A$ , as follows:

$n_s$	$v_m$			
	$n_A=1$	$n_A=2$	$n_A=3$	$n_A=4$
1	0.3	0.5	0.6	0.6
2	.6	.9	1.1	1.3
3	.9	1.4	1.7	1.9
4	1.2	1.8	2.3	2.5

Because variations at the site and sample-point levels in this study were found to be relatively insignificant, all map stability calculations are based on a sample location separation of approximately 1.5 km. Because one suite of samples must be collected for all elements, the calculations have been done using a hypothetical average element. The variance components for this average element were obtained by taking the mean components of all elements shown in table 3. Any single element or other combination of elements deemed to be more important could be used as well.

By using variance components of an average element and combining site and sample-point variances, the problem is resolved into a question of how many samples to collect at each sample location and how many replicate analyses to make of each sample.

It is clear from the calculations shown that the standard 1 × 1 sample design has very poor map stability for the average element used. If a  $v_m$  of approximately 1.0 is considered a minimal acceptable level of map stability for reconnaissance work, then the calculations show that either a 2 × 2 design or a 3 × 1 design might be sufficient. Even better would be a 4 × 1 design. These conclusions are valid for this particular study area, which has no large anomalies. An area with larger anomalies would have a larger sample variance and would allow a simpler sample design to maintain the same  $v_m$ .

To select the most cost-efficient sample design, the costs of sample collection and analysis must be known. Analytical costs are usually known as a constant per analysis as long as the total number of analyses is large. The cost of collecting each sample generally decreases as the number of samples collected at each location increases. Estimates of field collection expenses should be based on collecting up to about four samples per sampling location. At that point, it should be possible to estimate costs per sampling location for the various sampling designs. In the example above, the 2 × 2 design is more eco-

nomical if sample collection costs exceed analytical costs, whereas the  $3 \times 1$  design is more economical if analytical costs are higher.

Finally, an estimate of total costs for sampling and analysis can be made from the sample design chosen and the projected number of sampling locations within the project area. If this total exceeds the resources available, a few options remain. The first is to increase the spacing between locations. The effect will be to increase the areal size of the smallest details visible in the final maps. Another option may be to cut the analytical costs by limiting the number of elements. Finally, it may be possible to enhance anomaly contrast by selective concentration of specific minerals. This procedure might make a simpler and cheaper sample design possible.

The specific goals of the survey must always be kept in mind. Generally, a geochemical survey is intended to (1) detect large anomalies, (2) estimate geochemical background levels, (3) detect subtle broad halos, or some combination of these. Spacing between locations and map stabilities that are adequate for one set of goals may not be for another. In any case, using a sample design that produces a map stability ( $v_m$ ) of less than 1 in an attempt to cut costs is undoubtedly a false economy, unless the only objective is the detection of large anomalies.

### CONCLUSIONS AND RECOMMENDATIONS

The stream sediment experiment based on data from a stream drainage near Tracy Arm, southeastern Alaska, has pointed out some problems inherent in the standard reconnaissance geochemical survey. Most of these problems are related to the collection of a single sample at each location and the lack of replicate analyses. This  $1 \times 1$  sampling design produces geochemical anomaly maps that are, in general, highly unstable. Information obtained from a geochemical survey can be maximized by careful consideration of the natural variations in samples and the expected analytical variation, and by the choice of a sample design that best fits these factors.

The following are some recommended procedures for reconnaissance stream-sediment surveys aimed at developing an understanding of background geochemistry and delimiting areas of anomalous metal concentrations:

1. A small-scale pilot study in the area to be surveyed is invaluable. A hierarchical-sampling design should be used and an analysis of variance should be performed on the data to obtain variance components for each level of the sampling design, including the replicate-analysis level (Krumbein and Slack, 1956). This study will produce the best possible data for determining the sampling design for the major study.
2. If a pilot study is impossible, use the data generated by this study and others like it with extreme caution. The more an area differs from the area of this study in terms of terrain, climate, bedrock geology, and other factors, the less useful the specific data generated by this study are likely to be.
3. Set the spacing of sample locations on the basis of the variance components generated by the pilot study and the size of the smallest expected important anomaly.
4. Select a sampling design based on variance components and sample-collection and analytical costs. Use a sample design that keeps  $v_m$  above 1 for all major elements of interest. At this point, the total cost of the survey can be estimated and adjustments made to the spacing of sample locations and (or) the scope of the survey. For more help in establishing location spacing and calculating  $v_m$ , see Miesch (1976).
5. Before going into the field, prepare a detailed description of sampling procedures for each geologist. The target population being sampled should be identified, and procedures for randomly selecting samples at each location should be standardized.
6. If possible, use a randomizing technique when assigning numbers for analysis, and ship all samples for analysis to the laboratory at one time. Both procedures help to minimize variable bias (Miesch, 1976).
7. When plotting anomaly maps, plot location means only. Geometric means are more stable than arithmetic means.
8. When interpreting the anomaly maps, the most stable anomalies are those which involve more than one element over areas of at least several sample locations. Anomalies generated by only one element or at a single location should be considered suspect.

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# Indirect Determination of Chloride in Plants by Atomic-Absorption Spectrophotometry

By JOHN B. McHUGH *and* JAMES H. TURNER

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-F

*A new rapid instrumental method  
for determining chloride  
in plant materials*





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## INDIRECT DETERMINATION OF CHLORIDE IN PLANTS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

By JOHN B. McHUGH and JAMES H. TURNER

### ABSTRACT

Chloride in plant materials is extracted by dilute nitric acid, and an appropriate aliquot of the acid solution is reacted with a known amount of standard silver-nitrate solution. The amount of chloride is calculated from the chloride equivalent of the difference in the amount of silver added and that remaining in solution after precipitation of silver chloride. The excess silver is determined by atomic-absorption spectrophotometry. The method is extremely fast with good precision and has a detection limit of 0.01 percent chloride in the bulk plant. The results compare favorably with those obtained by the Mohr titrimetric method.

### INTRODUCTION

Atomic-absorption spectrophotometry offers a rapid, simple method for indirect determination of chloride in plants, whereas determining chloride by the classic Mohr titrimetric method entails a tedious sodium-carbonate fusion, a filtration, and a titration with a standardized silver-nitrate solution (Brown and others, 1970, p. 69). By using an adaptation of Ezell's method (Ezell, 1967), the amount of excess silver added to the sample is measured by atomic absorption, and the percent chloride is calculated from this measurement.

To determine chloride in plants by atomic-absorption spectrophotometry, the simple method described as follows is used: The sample is digested in 5 percent nitric acid, a known amount of standard silver-nitrate solution is added, chloride present is precipitated by the silver nitrate, and the excess silver is determined by the atomic absorption spectrophotometer. Slavin (1968, p. 158) reported that silver analyses is sensitive and interference free. Approximately 80 plant samples, against 20 for the Mohr method, can be determined per day by the atomic-absorption method.

### ACKNOWLEDGMENT

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### LABORATORY REAGENTS AND APPARATUS

All standards and reagents used in this method are stable and must be chloride free; the atomic-absorption silver standards, especially the lower ones, should be made up fresh every week.

Standard silver solution, 1,000  $\mu\text{g}/\text{mL}$  (micrograms per milliliter): Dissolve 1.575 g reagent-grade silver nitrate in water; add 20 mL concentrated nitric acid; cool and dilute to 1,000 mL with demineralized water. Store in amber glass container.

Dilute standard silver solution, 100  $\mu\text{g}/\text{mL}$ : Dilute 10.0 mL of the 1,000  $\mu\text{g}/\text{mL}$  silver standard solution with 2 mL concentrated nitric acid and dilute to 100 mL with demineralized water. Store in amber glass container.

Nitric acid, concentrated, reagent-grade, chloride-free.

Hotplate, oscillating: with temperature control from 90° to 370° C.

Centrifuge, International Model K,<sup>1</sup> variable speed to 2,300 revolutions per minute.

Atomic-absorption spectrophotometer.

### PROCEDURE

#### SAMPLE PREPARATION AND DETERMINATION

Weigh a 1-g sample of oven-dried, ground plant material and transfer the sample to a 50-mL volu-

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metric flask; add 25 mL of 5 percent nitric acid to the sample; place flask on a steam bath or hot plate; and heat for 1 hour without boiling. Cool the solution and dilute to 50 mL with demineralized water, mix, and allow to stand until undigested sample settles out. Take an aliquot, usually from 25 to 0.5 mL, depending on the chloride content of the sample, and transfer to a 100-mL volumetric flask; then add sufficient deionized water to bring the volume to 40 mL, and add 2 mL of concentrated nitric acid. Accurately measure 3.0 mL standard silver-nitrate solution, add to the sample solution, mix, and dilute to 100 mL with demineralized water. Place the solution in the dark until ready to be read on the atomic-absorption spectrophotometer. Mix the sample solution and transfer a portion to a 16×150 mm test tube and centrifuge for 15 min at 2,000 r/min. Measure the silver in the supernatant liquid on the atomic-absorption spectrophotometer.

#### STANDARD PREPARATION AND CALIBRATION

Working standards of 1, 5, 10, 20, and 30  $\mu\text{g}/\text{mL}$  silver are made from 100 and 1,000  $\mu\text{g}/\text{mL}$  standard silver solutions. These working standards are made in 100-mL volumetric flasks by adding 1.0 mL, 5.0 mL of the 100  $\mu\text{g}/\text{mL}$  stock solution and 1.0 mL, 2.0 mL, 3.0 mL of the 1,000  $\mu\text{g}/\text{mL}$  stock solution to volume. All working standards for calibrating the atomic-absorption spectrophotometer are made up in 2 percent chloride-free nitric-acid solutions.

The optimum working range for silver is 2 to 20  $\mu\text{g}/\text{mL}$  (Perkin-Elmer Corp., 1968, p. Ag-1). Curvature correction technique (Perkin-Elmer Corp., 1970, p. 2-8) is used to set working standards to a linear line on the Perkin-Elmer Model 403 atomic-absorption spectrophotometer.

#### INSTRUMENTATION

This work is performed on a Perkin-Elmer Model 403 atomic-absorption spectrophotometer. Operating conditions used (Perkin-Elmer Corp., 1968, p. Ag-1) are listed as follows:

- burner (4-inch flat head)
- Perkin-Elmer silver hollow-cathode lamp operating at 12 mA (milliamperes)
- wavelength = 328.1 nm
- slit width = set at "4" (0.7 nm)
- acetylene = 34 flow-meter setting
- air = 64 flow-meter setting

#### RESULTS

Chloride percent is calculated on the basis of the chloride equivalent of the difference in silver added

and the amount remaining after precipitation. The following formula is employed to calculate the percent chloride by using this procedure:

$$\text{Percent Cl}^- = ((30.0 - b) \times 0.1643) / a,$$

where

30.0 =  $\mu\text{g}/\text{mL}$  silver added to the sample solution,

$b$  =  $\mu\text{g}/\text{mL}$  silver remaining after precipitation, value obtained from atomic-absorption reading,

0.1643 = chloride equivalent factor time dilution factor, and

$a$  = aliquot taken.

#### DISCUSSION

An aliquot should be chosen that will consume a moderate amount (2  $\mu\text{g}/\text{mL}$  or more) of the silver added. With a high-chloride sample, use a small aliquot so that a sufficient amount of silver is left over to determine accurately; with a low-chloride sample, use a large aliquot (as much as 25 mL), enabling a more accurate and sensitive measurement of the chloride content of the sample. Sensitivity of 0.01 percent chloride can be measured by use of a 25-mL aliquot.

#### PRECISION

Table 1 shows the arithmetic mean of five determinations per sample, comparing the Mohr titration method with the atomic-absorption method. The plant material *Bebbia juncea* was from Death Valley, Calif.; all other plant materials were from Nevada. Table 2 shows the repeatability of the five plant samples by atomic-absorption spectrophotometry.

#### CONCLUSION

The atomic-absorption method offers a fast, simple, accurate way to analyze for chlorides in

TABLE 1.—A comparison of the chloride content of plant materials determined by the Mohr titrimetric method with that determined by atomic-absorption methods

Sample Number D-	Material	Chloride (percent)	
		Mohr	Atomic absorption
403648	<i>Bebbia juncea</i> -----	0.63	0.52
408134	<i>Sarcobatus vermiculatus</i>	1.90	1.65
411477	<i>Atriplex confertifolia</i> ---	8.57	8.08
411478	<i>Baccharis glutinosa</i> ----	.06	.09
412069	<i>Lycium pallidum</i> -----	4.84	4.28

TABLE 2.—*Repeatability of chloride-content determinations by atomic-absorption method*

Sample Number D-	Range of values (percent)	Standard deviation	Relative standard deviation
403648	0.50-0.54	0.017	3.2
408134	1.62-1.68	.022	1.4
411477	7.97-8.22	.094	1.2
411478	0.08-0.11	.016	17.7
412069	4.05-4.40	.143	3.3

plant materials. With the exception of low-chloride samples, the reproducibility of the atomic-absorption method is good (table 2). Five to 10 times as many samples per day can be determined by the atomic-absorption method as by the Mohr method. Indirect determination of chloride by atomic-absorption spectrophotometry in plant materials is a useful new method.

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# Determination of Iridium and Ruthenium in Geological Samples by Fire Assay and Emission Spectrography

By JOSEPH HAFFTY, A. W. HAUBERT, and N. J. PAGE

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-G

*Detailed description of a method for determining  
trace amounts of iridium and ruthenium*





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## DETERMINATION OF IRIDIUM AND RUTHENIUM IN GEOLOGICAL SAMPLES BY FIRE ASSAY AND EMISSION SPECTROGRAPHY

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By JOSEPH HAFFTY, A. W. HAUBERT, and N. J. PAGE

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### ABSTRACT

Microgram quantities of iridium and ruthenium are determined in geological materials by a combination fire-assay and emission-spectrographic method. The method described is rapid and convenient as compared with other methods applied to these two metals. As little as 0.5 micrograms ( $\mu\text{g}$ ) iridium and 1.5  $\mu\text{g}$  ruthenium can be detected. Based on a 15-g sample, this represents about 0.030 parts per million (ppm) iridium and 0.1 ppm ruthenium.

### INTRODUCTION

Iridium, ruthenium, and osmium occur as alloys in alluvial and eluvial placer deposits, but knowledge of the residence and geochemical cycle of these elements in the parent rocks is poorly understood because of the lack of techniques to analyze rapidly large numbers of rock samples for these metals. Fewer analyses of Ru in rocks are available in the literature than are those for Ir and Os. For this reason, less is known about ruthenium's distribution in geologic materials and thus about its geochemical significance. The placer deposits of Ir, Ru, and Os appear to be derived from alpine-type ultramafic and mafic rocks (ophiolitic sequences), whereas Pd and Pt placer deposits appear to originate from stratiform and concentrically zoned ultramafic and mafic complexes. Evidence for the different geochemical behavior for the two groups of platinum-group metals was reported by Cabri and Harris (1975), who used the  $\text{Pt} \times 100 / (\text{Pt} + \text{Ir} + \text{Os})$  ratios in concentrates from alluvial and eluvial deposits to relate deposits with low ratios to alpine-type parents and those with high ratios to stratiform and concentric environments. More recently, Rajamani and others (1977) demonstrated that Ir and Os are distributed differently than Pt and Pd in sulfide and basaltic melts and thus emphasized the need for

data on the distribution of these metals in geologic materials.

Methods for the determination of Ir and Ru using fire assay and Pt as a collector have been described (Broadhead and others, 1972; Page and others, 1976; Haffty and others, 1977). The neutron-activation method described by J. J. Rowe *in* Page and others (1976) and by Haffty and others (1977), although more sensitive, is tedious and time consuming. This method is also subject to fission product interference from  $^{103}\text{Ru}$  produced from U, unless sample pretreatment consisting of separating the Ru as the tetroxide, as described by Koda (1970), is employed.

As more analytical techniques become available for determining Ir, Ru, and Os, we hope that the geochemistry of these three elements will become better understood and that exploration for possible lode deposits will be a reality. Although similar to the method reported by Broadhead and others, the method described here for the determination of Ir and Ru is, overall, more convenient to apply.

### EXPERIMENTAL METHOD

#### FIRE ASSAY

Ten milligrams of Pt (99.999 percent pure), in the form of 0.254-mm (0.01-in.) -diameter wire, is used as a collector for Ir and Ru. The wire is weighed to an accuracy of  $\pm 0.002$  mg. A piece of lead foil 20 mm by 13 mm and 0.2 mm thick is sharply folded lengthwise at the center with pliers. The fold is then opened, the platinum wire placed in the center of the crease, and the fold closed on the wire and again folded lengthwise at the center to give a thickness of four layers. All edges are then crimped

with pliers to ensure enclosure of the wire. This lead envelope is added as the last step in the preparation of the fusion mixture.

The fusion mixture consists of a flux formed by combining  $\text{Na}_2\text{CO}_3$ ,  $\text{PbO}$ ,  $\text{SiO}_2$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ , and  $\text{CaF}_2$ , together with household flour as a reducing agent or  $\text{KNO}_3$  as an oxidizing agent, depending on the chemical and mineralogical composition of the sample. These are combined in a "30-g" fire-clay crucible; 15 g of sample is added, followed by the lead foil containing the platinum wire. The contents are thoroughly mixed, after which the crucible is placed in the muffle of an assay furnace preheated to a temperature of  $1,000^\circ\text{C}$ . The fusion and cupellation steps are described in detail by Haffty and others (1977). However, there is one modification to the cupellation step. After the buttons are "open," the temperature is decreased to  $860^\circ\text{C}$ , rather than  $840^\circ\text{C}$ , and finished at  $920^\circ\text{C}$ . The platinum beads obtained after cupellation are weighed, and the increase in weight over that of the Pt added is noted.

#### SPECTROGRAPHIC ANALYSIS

The noble metals from 15 g of sample are contained in the platinum beads obtained after cupellation. The beads are transferred to cupped graphite electrodes. The sample-bearing electrodes are then placed in the arc-spark stand, the beads are excited, and the spectra are recorded using the apparatus and operating conditions listed in table 1.

The emulsion is calibrated by means of an iron bead arced at 5.5 A dc and exposed for 25 s at a transmission of 25 percent. The iron lines and rela-

TABLE 1.—Apparatus and spectrographic operating conditions for the determination of iridium and ruthenium

Excitation source	dc arc at 300 V (open circuit) and 20 A.
Electrodes	Anode: 3.2-mm (0.125-in.) -diameter graphite with 6.35-mm (0.25-in.) -deep cup, Ultra Carbon <sup>1</sup> stock no. 213202. Cathode: ASTM type C-1, Ultra Carbon stock no. 111202.
Spectrograph	Jarrell-Ash 3.4-m, Wadsworth mounted grating with 5,906 grooves per centimeter (15,000 grooves per inch), giving a reciprocal linear dispersion of 0.524 nm/mm in the first order.
Wavelength region	225–350 nm.
Slit width	15 $\mu$ .
Illumination	Arc image focused on grating.
Analytical gap	4 mm, maintained during burn.
Transmission	40 percent.
Exposure	40 s.
Emulsion	Kodak SA-1.

<sup>1</sup> Any use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

TABLE 2.—Iron lines used for plate calibration

Fe line (nm)	Intensity	Fe line (nm)	Intensity
315.789	73	321.738	165
317.545	125	322.207	625
317.802	94	322.599	770
319.693	470	323.944	285
320.540	210	325.124	62
321.594	225	326.824	29

tive intensities used for plate calibration were selected from a list of homologous lines (Crosswhite, 1950; Bastron and others, 1960) and are reproduced in table 2 for the convenience of the reader. The calibration curve is established by plotting transmission (ordinate) versus intensity (abscissa) on log-log paper.

The spectra of standards and unknown samples are recorded on separate photographic plates. The iron bead spectrum, which is used for plate calibration, is always put on the unknown-sample plate. After the plates have been processed, transmittance measurements of selected analytical and internal standard lines (table 3) are obtained by means of a microphotometer. From the calibration curve, intensity values are obtained for the standards and are used in constructing the analytical curves. Once the transmittance values for the standards are established, they are used repeatedly for obtaining the intensities from succeeding calibration curves for plates bearing the unknown samples. The analytical curves are established by plotting the ratio of the intensities of the analytical and internal standard lines against concentration, in micrograms, on logarithmic coordinates. The concentration of the elements in the unknown samples are read from the analytical curves. This concentration, in micrograms, is then divided by the weight of sample taken to give parts per million or parts per billion ( $10^{-9}$ ) in the sample.

TABLE 3.—Analytical lines used in determination of iridium and ruthenium

[The Pt 274.483-nm line was used as internal standard line throughout]

Element	Analytical Line (nm)	Concentration range ( $\mu\text{g}$ )
Iridium	284.973	0.5–25
	292.479	0.5–25
	295.126	15–100
Ruthenium	273.572	2.5–100
	287.498	1.5–50

## PREPARATION OF STANDARDS

Two sets of standards are prepared. One set is made using measured volumes of single-metal standard solutions containing 1,000, 100, 10, and 1 ppm in 2 M HCl. These standard solutions are made by serially diluting standard stock solutions calculated to contain 1,000 mg of the element per liter. The stock solutions are prepared by dissolving 229.5 mg of spectrographic grade ammonium chloroiridate ( $(\text{NH}_4)_2\text{IrCl}_6$ ) and 328.8 mg of ammonium aquochlororuthenite ( $(\text{NH}_4)_2\text{Ru}(\text{H}_2\text{O})\text{Cl}_5$ ) in 100-mL volumetric flasks and diluting to volume with 2 M HCl.

Micropipettes, used to measure the volumes of the standard solutions, are selected to give 100, 50, 25, 10, 5, 2.5, 1.0, 0.5, and 0.25  $\mu\text{g}$  of Ir and Ru in solution. Thirty grams  $\text{Na}_2\text{CO}_3$ , 50 g  $\text{PbO}$ , and 15 g  $\text{SiO}_2$  (used as sample blank) are weighed in that order into each of nine fire-clay crucibles. The standard solutions are transferred carefully to the top of the  $\text{SiO}_2$ , so that the solutions are kept away from the crucible walls. The solutions are dried by placing the crucibles under heat lamps for several hours. Then, 5 g  $\text{Na}_2\text{B}_4\text{O}_7$ , 1 g  $\text{CaF}_2$ , 3.0 g of household flour, and 10 mg of pure Pt (used as a collector, as in the samples) are added to complete the charge. The contents are mixed and then fused. The buttons are cupelled and the beads arced as described previously.

The second set of standards is prepared by using various weights of 0.025-mm (0.001-in.) -diameter wire consisting of 10 percent Ir and 90 percent Pt. The wire is cut in predetermined lengths and accurately weighed on a Cahn electrobalance. Then the pieces of wire are transferred from the weighing pan to lead foil for convenience of handling, as described previously for platinum wire. The weights of Ir are selected to approximate, as closely as possible, those weights obtained using the reciprocal of the cube root of 10 (0.4642) as a dilution factor, resulting in a 3-step breakdown per order of magnitude. The actual weights of Ir obtained were 0.34, 0.52, 1.22, 2.53, 5.34, 12.19, 21.13, 50.92, and 105.6  $\mu\text{g}$ .

Ruthenium alloyed with platinum (5 percent Ru and 95 percent Pt), in the form of wire 0.127 mm (0.005 in.) in diameter, is also added to this second set of standards in varying weights as described for Ir. These Ir-Pt and Ru-Pt weighed pieces of wire are added to blank fire-assay charges along with pure Pt as a collector—taking into account the weight of Pt contributed by both the Ir-Pt and Ru-Pt wire. The charges are processed and the beads arced as described previously.

## RESULTS AND DISCUSSION

Although this method is similar to that of Broadhead and others (1972), it varies in significant particulars so that the method described here is more convenient to apply. For example, the Pt, which is used as a collector for Ir and Ru, is introduced in the form of pure wire rather than by adding specific amounts of platinum stock solution to the fire-assay charge and waiting for the charge to dry overnight. Many pieces of wire can be cut beforehand and made available, particularly if many samples are to be analyzed for these two metals. The use of radio-tracers or yield-correction factors was found to be unnecessary if the standards were treated in the same way as the unknown samples. In addition, as a result of the standards being exposed on a separate photographic plate, the standards need only be prepared and excited occasionally. Having once obtained the transmittance values for the analytical lines, these values can be used repeatedly for obtaining the intensities from succeeding calibration curves established for unknown-sample plates.

Two sets of standards—one set using standard solutions, the other using Ir-Pt and Ru-Pt wire—were used in obtaining the data in table 4. When compared with the literature values for both Ir and Ru, the values obtained using solution and wire standards are both seen to be within acceptable limits. However, standard solutions are preferred for analysis because they are more convenient to prepare. In another study, known amounts of Ir-Pt and Ru-Pt wire were added to a flux contained in a fire-clay crucible and run as unknown samples; favorable results were obtained for both elements using either set of standards. This demonstrates that when Ir and Ru are present as an alloy, acceptable results can be obtained. Thus, it appears that the method is not significantly affected by the chemical form in which Ir and Ru exist in geological samples.

## PRECISION AND ACCURACY

The precision of the method is illustrated by the results shown in table 5. The standard deviations were obtained by running eight 15-g portions of the South African reference sample. Standard deviations for iridium and ruthenium using both solution and wire standards are comparable.

A measure of the accuracy is obtained by comparing the values obtained by this method with those obtained using other techniques (table 4), namely, atomic-absorption spectroscopy, optical emission spectroscopy, and neutron-activation analysis.

TABLE 4.—Comparison of iridium and ruthenium values obtained by this method with those quoted in the literature

[Data are in parts per million. For samples run more than once, values shown are averages.  
All samples weighed 15 g]

Sample	Sample runs	This method				Literature Values		
		Solution standards		Wire standards		Ir	Ru	Source
		Ir	Ru	Ir	Ru			
Merensky Reef ore, reference sample, (South Africa)-----	8	0.086	0.45	0.083	0.40	0.074	0.43	Steele and others (1975).
Rustenburg Pt ore (South Africa)-----	2	.11	.56	.11	.50	.14	.61	Broadhead and others (1972).
H chromitite (20MV68)-	1	.025	.15	.015	.17	.030	.232	Page and others (1976).
J chromitite (4BE68)--	1	.089	.59	.085	.53	.086	.482	Do.
A chromitite (8WF68)--	1	.64	.91	.61	.81	.530	.900	Do.
A chromitite (13WF68)-	1	.13	.35	.12	.31	.170	.270	Do.

TABLE 5.—Precision of the Ir-Ru method

[(S) = by solution standards; (W) = by wire standards; n = 8]

Element	Average Concentration (ppm)	Standard deviation <sup>1</sup>	Coefficient of variation <sup>2</sup>
Iridium (S)-----	0.086	0.0070	8.1
Iridium (W)-----	.083	.0065	7.8
Ruthenium (S)---	.45	.069	15
Ruthenium (W)---	.40	.061	15

<sup>1</sup>Standard deviation =  $\sqrt{\frac{\sum d^2}{n-1}}$  where n is the number of individual results, and d is the difference between individual results and their average.

<sup>2</sup>Coefficient of variation =  $\frac{\text{Standard deviation} \times 100}{\text{average of individual results}}$

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# Complexity of Titaniferous Magnetites from Essex County, New York, as a Hindrance to Beneficiation by a Method Based on Curie Temperature Differences

By HARRY KLEMIC *and* PATRICIA J. LOFERSKI

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-H

*The compositions of some titaniferous magnetite  
concentrates separated magnetically at high  
temperatures are presented*





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**COMPLEXITY OF TITANIFEROUS MAGNETITES FROM  
ESSEX COUNTY, NEW YORK, AS A HINDRANCE TO BENEFICIATION BY  
A METHOD BASED ON CURIE TEMPERATURE DIFFERENCES**

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By HARRY KLEMIC and PATRICIA J. LOFERSKI

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ABSTRACT

Titanium and some other elements that substitute for iron in magnetite lower the Curie temperature of the magnetite. We made high-temperature magnetic separations of magnetite concentrations from mineralogically complex magnetite-ilmenite ores from the Little Pond and Sanford Lake deposits, Essex County, N.Y., in an attempt to obtain separates having different titanium contents. Finely ground samples of magnetite concentrates were heated to temperatures of 500° C and higher and were separated magnetically while hot by means of a hand magnet. The magnetic and nonmagnetic fractions obtained contained 3-4 percent titanium and lesser amounts of aluminum, magnesium, manganese, and vanadium as determined by spectrographic analysis. However, the magnetic and nonmagnetic separates were almost identical in composition.

We concluded that the magnetites from the Little Pond deposit are too complex in mineralogic association and composition to be beneficiated by the methods we used. We believe, however, that the method is worthy of testing where more refined equipment and techniques are used and that it may be applicable to the beneficiation of some titaniferous magnetites and other magnetic minerals.

INTRODUCTION

The high titanium content of the magnetite in ilmenite ores of Essex County, N.Y., is a detriment in smelting the magnetites for iron. Although the titanium content of the iron-rich part of the ores can be reduced by magnetic separation of most of the magnetite from the ilmenite, the magnetite concentrates still contain excessive amounts of titanium. Examinations of samples of ore-grade material from the Little Pond deposits have shown compositional variations in the magnetite.

Titanium and some other elements that substitute for iron in magnetite serve to lower the Curie temperature below that of pure magnetite. Ideally, this effect might be used to advantage in the beneficiation

of titaniferous magnetite. It should be possible to separate titaniferous magnetite concentrates into fractions having different amounts of titanium by heating the magnetite concentrate feed to above the Curie temperature of part of the material, which will render that part nonmagnetic, and by performing a magnetic separation of the heated material.

We have tried such a method on material from the Little Pond and Sanford Lake deposits. Although separations of heated material into magnetic and nonmagnetic fractions were obtained well below the Curie temperature of pure magnetite, the compositions of separates of Little Pond material were almost identical, as determined by spectrographic analyses. We consider the results of the tests of the Little Pond material to be unsatisfactory. A sample of Sanford Lake magnetite concentrate tested at a furnace temperature of 500° C was nonmagnetic. No further tests or analyses of this material were made.

CHARACTERISTICS OF SOURCE MATERIALS

The magnetite-ilmenite ores of Essex County are mineralogically complex. The Little Pond ores occur in gabbro, and they contain gangue minerals such as plagioclase, pyroxene, hornblende, olivine, spinel, and garnet. Most magnetite grains in the ore-grade material are less than 3 mm in diameter, and many grains contain blebs and exsolution lamellae of gangue minerals. The magnetite also contains titanium and other impurity elements in solid solution.

Chemical analyses of the Little Pond magnetite ores reported by Kemp (1899) showed about 8 and 11 percent titanium in two samples. Spectrographic analyses by J. L. Harris and Leung Mei of the U.S.

TABLE 1.—Spectrographic analyses of magnetite-ilmenite ore and magnetite concentrates from Essex County, N.Y.

[Analyses by J. L. Harris and Leung Mei, U.S. Geological Survey. Elements looked for, but below minimum limits assigned for method used, are: As, Au, B, Be, Cd, Ce, Cu, Dy, Er, Eu, Gd, Ge, Hf, Ho, In, Ir, La, Lu, Nd, Os, Pd, Pr, Pt, Re, Rh, Sb, Sm, Ta, Tb, Tl, Tm, U, and W. H was not determined because of interference. The standard deviation of any single result should be taken as +50 percent and -33 percent]

Element	Little Pond Magnetite-ilmenite ore, sample No. 74Jy23-2, lab. No. W-187770, sample spectrum	Sanford Lake Magnetite con- centrate, sample No. HKSL-M, lab. No. W-192907, sample spectrum
	Percent	
Si -----	3.6	3.3
Al -----	2.8	1.8
Fe -----	>24	>24
Mg -----	4.6	0.59
Ca -----	0.83	0.12
Na -----	0.1	0.007
K -----	H	H
Li -----	H	H
Ti -----	5.3	3.4
P -----	<0.07	<0.07
Mn -----	0.33	0.13
	Parts per million	
Ag -----	0.5	0.97
Ba -----	17	9.7
Co -----	169	110
Cr -----	>6,800	<sup>1</sup> 300
Ga -----	64	110
Mn -----	3,270	1,300
Mo -----	<2.1	12
Nb -----	21	<22
Ni -----	420	180
Pb -----	50	62
Pr -----	34	68
Sc -----	13	9.5
Sn -----	<14.7	41
Sr -----	17	3.2
V -----	>1,000	<sup>1</sup> 1,500
Y -----	9.6	23
Yb -----	1.9	2.9
Zn -----	580	650
Zr -----	59	68

<sup>1</sup> Visual reading of plate.

Geological Survey in studies made for this report show 5.3 and about 6 percent titanium in two ore-grade samples. The results of these analyses and of an analysis of magnetite concentrate from the Sanford Lake deposits are shown in table 1.

The ilmenite-magnetite ores of the Sanford Lake deposits include two major types: anorthositic ore having a ratio of total Fe:TiO<sub>2</sub> of greater than 2:1, and gabbroic ore having a ratio of total Fe:TiO<sub>2</sub> of less than 2:1 (Gross, 1968; Kays, 1961). Granular magnetite and ilmenite occur together in the ores and are commonly coarse grained. The magnetite generally contains exsolution laths and blebs of titanium-bearing minerals, including ilmenite, rutile, ulvospinel, hercynite, and possibly coulsonite (FeV<sub>2</sub>O<sub>4</sub>). Some vanadium may also be in the magnetite lattice (Balsley, 1943; Gross, 1968). As much

as 35 percent of the volume of some magnetite grains consist of ilmenite intergrowths (Stephenson, 1945).

As shown in the results of the spectrographic analyses, the Little Pond ore specimen contains more magnesium, aluminum, calcium, silicon, and titanium than does the Sanford Lake concentrate, probably because of the presence of more of the gangue minerals in the ore.

Although some of the titanium in both samples is in ilmenite, which is mostly in discrete grains in the Little Pond specimen and in exsolution laths in the Sanford Lake magnetite concentrate, some of the titanium is in the magnetite. Electron microprobe studies of the Little Pond magnetite (Bird and Klemic, 1976) revealed compositional variations both within single grains and between different magnetite grains. The material was analyzed for eight elements: Fe, Ti, Al, Mg, Mn, Si, V, and Cr. Major variations were noted for Ti (4.5-13.4 percent) and Al (1.01-5.2 percent). Variations for the less abundant elements were also noted.

Because of these compositional variations, we inferred that in grinding the grains to finer particle sizes, the fine particles would have a spectrum of compositions and that they would have a related spectrum of Curie temperatures.

#### MAGNETIC PROPERTIES

The principal oxide minerals that are commonly present in titaniferous iron deposits are magnetite (Fe<sub>3</sub>O<sub>4</sub>) and ilmenite (FeTiO<sub>3</sub>). Maghemite (Fe<sub>2</sub>O<sub>3</sub>), ulvospinel (Fe<sub>2</sub>TiO<sub>4</sub>), and hematite (Fe<sub>2</sub>O<sub>3</sub>) may also be present. Magnetite and ulvospinel form a compositional series, and hematite and ilmenite form another compositional series. In major titaniferous magnetite deposits, the bulk of the magnetite is nearer in composition to the magnetite end member than to ulvospinel, and the bulk of the ilmenite is nearer in composition to the ilmenite end member than to hematite. The magnetic susceptibilities of these two minerals differ considerably at room temperature.

The temperatures above which the minerals of the magnetite-ulvospinel series and the ilmenite-hematite series are nonmagnetic (Curie points) are shown in figure 1. The curves in figure 1 are based on data reported by Syono (1965, p. 79, fig. 2) and Stacey and Banerjee (1974, p. 37) and are in part from earlier reports by Akimoto (1962), Ishikawa and Akimoto (1958), Nagata and Akimoto (1956), and Bozorth and others (1957).

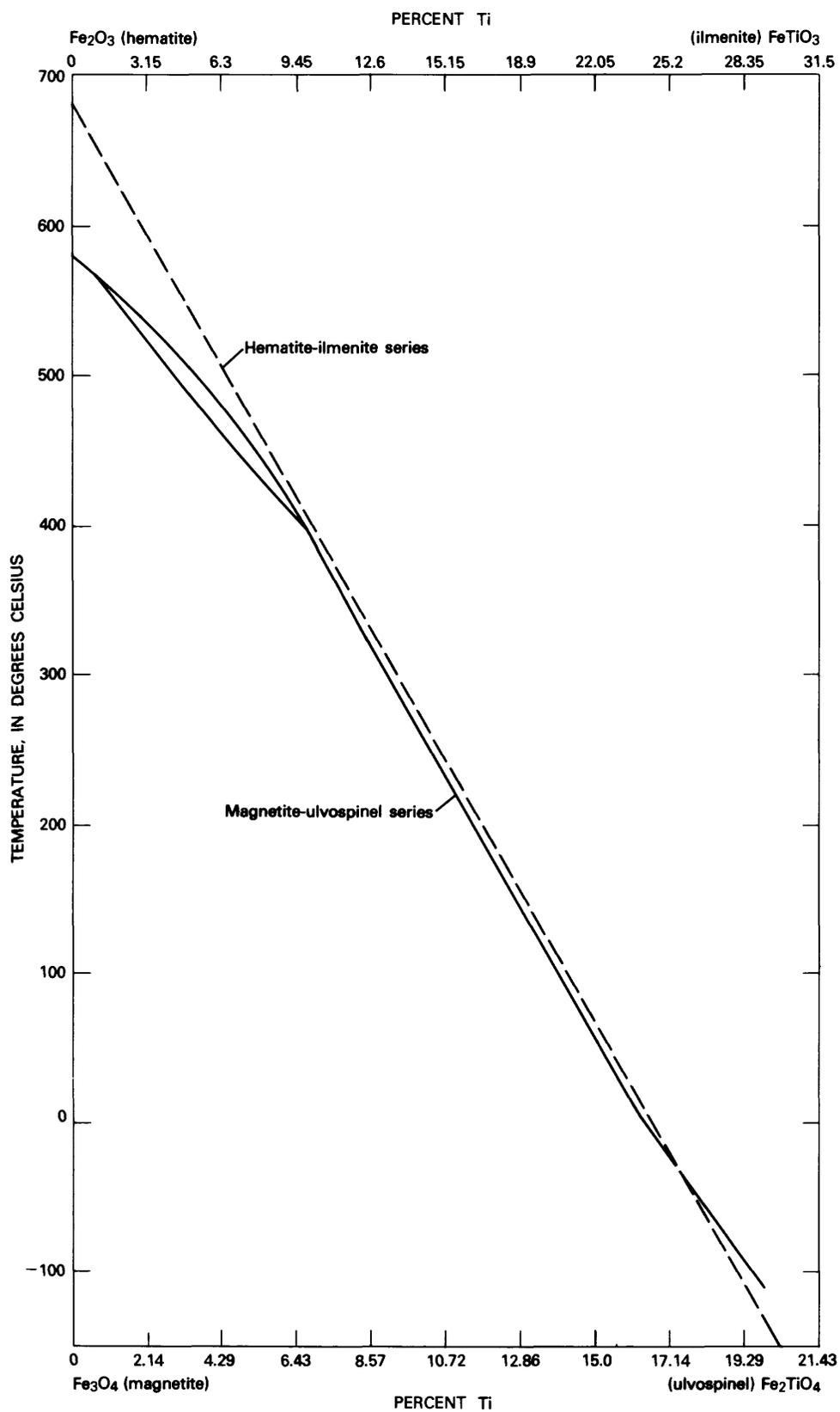


FIGURE 1.—Curie points of minerals in magnetite-ulvospinel series and in hematite-ilmenite series. Different temperature have been reported by different authors for magnetites near the upper part of the curve.

In both series, the Curie temperatures decrease as titanium content increases. Magnetite from the deposits of interest to us in this study probably contains less than 25 percent of the ulvospinel in solid solution (about 5 percent Ti); therefore, the Curie points of the magnetite should be higher than 430° C.

#### SAMPLE PREPARATION AND SEPARATION PROCEDURES

The Little Pond "ore" was crushed and ground, and the Sanford Lake magnetite concentrate was also ground. Both samples were sieved, and the fractions between 170- and 325-mesh sizes were selected for tests. These samples were repeatedly separated magnetically by a hand magnet to eliminate nonmagnetic minerals. Some of the material was ground to minus 325-mesh size and again separated magnetically. X-ray analyses indicated that a small amount of ilmenite, probably less than 5 percent, was still present in the magnetic samples.

After some preliminary trials in which we noted problems related to cooling of the samples during separation tests and other undesired effects, we decided to use Pyrex<sup>1</sup> test tubes as sample holders. The samples were spread thinly in the test tubes, which were laid on their sides in grooves on pieces of insulation bricks in an electric furnace. The furnace was heated to desired temperatures for the different test runs. Prior to removal of the tubes from the furnace for magnetic tests, the tubes were tapped and rolled to reduce the sintering effect of heating. Some magnetic tests were made while the tubes were inside the furnace but near the mouth of the furnace. In other tests, the test tubes and the pieces of insulation bricks were removed from the furnace for convenience of handling. The heat of the enclosing tubes tended to reduce the rate of cooling of the samples during the time necessary to make the magnetic separations.

The use of the tubes as sample holders also made it possible to maintain fairly uniform distances between the magnet and the hot samples. The magnet was placed against the upper side of the sample tube and moved along the length over which the sample was spread. Any material that had retained its magnetism at the test temperature was attracted to the upper side of the tube and was drawn along the tube to a separate place and dropped by removal of the magnet. The magnet was again placed

above the remaining nonmagnetic part of the hot sample. As the sample cooled, it recovered its magnetism, and the time lag for recovery could be noted.

#### RESULTS OF HIGH-TEMPERATURE MAGNETIC TESTS

After a few tests using the Pyrex tubes as sample holders, we concluded that placing the samples in the preheated furnace at temperatures of 410° C or more and heating to higher temperatures in runs of less than an hour duration gave desired results in the altering of part of the material to a nonmagnetic state. Nonmagnetic material was present in all but one of the Little Pond samples tested magnetically at a furnace temperature of 500° C or higher, but that one sample may not have reached furnace temperature before the magnetic test was made. In some of the tests, the amount of nonmagnetic material was greater than the amount of material that retained its magnetism at the test temperatures.

Only one test was performed on Sanford Lake material after the preliminary tests. That sample, tested at 500° C, was nonmagnetic.

Magnetic and nonmagnetic separates obtained from Little Pond "ore" in separations made at furnace temperatures of 520° C were analyzed by X-ray diffraction, primarily to compare their ilmenite contents. In two pairs of separates, no obvious difference in their ilmenite contents was found. In one other pair of separates, the nonmagnetic fraction contained slightly more ilmenite.

The results of the magnetic tests show that parts of the Little Pond concentrates became nonmagnetic at 500° C, and other parts remained magnetic at 540° C, the highest furnace temperature used in the final tests.

Magnetic and nonmagnetic fractions of Little Pond concentrates from four heating runs were analyzed spectrographically by J. L. Harris, of the U. S. Geological Survey. The ranges, reported in abundance of 19 elements that were present in most of the fractions, are shown in table 2. The Sanford Lake separates were not analyzed spectrographically after heating.

The amounts of the more abundant elements that are likely to proxy for iron in magnetite in each of the separates, as determined by spectrographic analysis, are shown in table 3 for convenience of comparison. These elements are titanium, aluminum, magnesium, manganese, and vanadium. The standard deviation of +50 percent and -30 percent of

<sup>1</sup>Any use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

**TABLE 2.**—Range in composition of separates of heated magnetite concentrates from Little Pond deposit, Essex County, N.Y., as determined by spectrographic analyses

[Analyst: J. L. Harris, U.S. Geological Survey. Other elements looked for but below minimum limits assigned for method used are Ag, As, Au, B, Ba, Be, Bi, Cd, Ce, Dy, Er, Eu, Gd, Ge, Hf, Ho, In, Ir, La, Lu, Mo, Nb, Nd, Os, Pd, Pr, Pt, Re, Rh, Ru, Sb, Sm, Sn, Ta, Tb, Te, Th, Tl, Tm, U, W, Y, and Yb. The standard deviation of any single result should be taken as +50 percent and -33 percent]

Element	Range, in percent	Element	Range, in parts per million
Ti	2.88-4.18	Co	127 -155
Al	1.66-2.48	Cu	29.2- 62.2
Mg	1.40-1.91	Ga	48.5- 75.2
Mn	.30- .36	Ni	309 -400
Si	2.50-3.73	Pb	110 -154
Fe	>23.5	Sc	7.1- 9.0
Ca	.67- .85	Sr	8.7- 17
Na	.02- .05	Zn	452 -643
V <sup>1</sup>	.15- .3	Zr	54 - 74
Cr <sup>1</sup>	about 1	K	interference

<sup>1</sup> Visual reading of plate.

the amounts reported for elements analyzed by the spectrographic method greatly exceeds the reported differences in compositions.

**CONCLUSIONS**

On the basis of our tests and the analytical results, we believe that the titaniferous magnetite of the Little Pond deposit is too complex, both in composition and in content of gangue minerals in the form of exsolution lamellae and minute blebs, to be beneficiated by magnetic separations made on the basis of differences in Curie temperatures.

We believe, however, that the method of mineral separation based on Curie temperature differences is worthy of further testing. The construction and development of a magnetic separator for operation at controlled temperatures and through a broad range of magnetic intensities may make it possible to separate not only titaniferous magnetites but also other more weakly magnetic minerals that are dif-

icult to separate at ordinary temperatures. Success in the application of this method to mineralogically complex magnetite concentrates may depend on the use of very fine particle sizes.

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**TABLE 3.**—Partial results of spectrographic analyses of separates of heated magnetite concentrates from Little Pond deposit, Essex County, N.Y.

[Analyst: J. L. Harris, U.S. Geological Survey. Results are in percent. Chromium estimated to be about 1 percent in all separates by visual examination of spectrographic plate. Vanadium content estimated by visual examination of spectrographic plate. The standard deviation of any single result should be taken as +50 percent and -33 percent. mg, magnetic; nmg, not magnetic]

Element	Run 8			Run 11		Run 12			Run 16	
	A mg	B nmg	C nmg	D mg	E nmg	F mg	G nmg	H nmg	J mg	K nmg
Ti	3.1	3.6	3.7	4.1	2.9	3.3	3.0	3.3	3.5	4.2
Al	2.0	2.3	2.4	2.2	2.5	2.1	2.5	1.7	2.3	2.2
Mg	1.7	1.8	1.7	1.9	1.8	1.6	1.6	1.8	1.4	1.9
Mn	0.3	.4	.4	.3	.4	.3	.3	.3	.3	.3
V	0.3	0.2	0.2	.2	.2	.3	.2	.2	.2	.2

Run 8.—Sample put in furnace at 480° C, heated to 500° C. Total heating time, 50 minutes.  
 Run 11.—Sample put in furnace at 460° C, heated to 510° C. (All magnetic at 500° C.) Total heating time, 25 minutes.  
 Run 12.—Sample put in furnace at 500° C; furnace kept at 500° C. Total heating time, 15 minutes.  
 Run 16.—Sample put in furnace at 480° C, heated to 500° C. Total heating time, 15 minutes.

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# A Technique for the Decomposition and Dissolution of Rocks and the Determination of Lithium, Calcium, and Magnesium Using Atomic-Absorption Spectroscopy

By ALLEN L. MEIER

SHORTER CONTRIBUTIONS TO GEOCHEMISTRY, 1979

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 1129-I

*This technique eliminates fluoride precipitation  
encountered during hydrofluoric acid  
decomposition of rocks*





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## A TECHNIQUE FOR THE DECOMPOSITION AND DISSOLUTION OF ROCKS AND THE DETERMINATION OF LITHIUM, CALCIUM, AND MAGNESIUM USING ATOMIC-ABSORPTION SPECTROSCOPY

By ALLEN L. MEIER

### ABSTRACT

Hydrofluoric acid is used in the proposed technique for the decomposition of rocks; a combination of hydrochloric acid and boric acid is used for sample dissolution prior to the determination of lithium, calcium, and magnesium using atomic-absorption spectroscopy. Results obtained using the proposed technique compare favorably with results obtained using other techniques. The problem of fluoride precipitation encountered in techniques using hydrofluoric acid for sample decomposition is eliminated with the use of boric acid.

### INTRODUCTION

The decomposition of silicate rocks is usually accomplished by fusion with carbonate or borate fluxes or by using hydrofluoric acid with a mixture of other acids. The flux or hydrofluoric acid attacks the silicate, rendering the rock soluble in acid or water. The solution produced is used for subsequent analysis.

Fusion with carbonate or borate fluxes has been used for the decomposition of silicate rocks by Ingamells (1964), Suhr and Ingamells (1966), Shapiro (1967), Van Loon and Parissis (1969), Medlin and others (1969), Abbey (1970), O'Gorman and Suhr (1971), Abbey and others (1974), and Saavedra and others (1974). Cremer and Schlocker (1976) reported that the use of lithium borate-mineral acid in the decomposition and dissolution of silicate rocks was unsatisfactory in attacking some accessory minerals. Other problems with fusion techniques are that a high salt concentration is added to the solution to be analyzed and that the determination of the ion used in the flux is precluded (Bernas, 1968).

Langmyhr and Sveen (1965) investigated the decomposition of silicate rocks in hydrofluoric acid and found that 21 of 28 major and some minor minerals that may be present in silicate rocks were decom-

posed effectively at 95° C. The remainder of the minerals, with the exception of topaz, decomposed at higher temperatures in a Teflon<sup>1</sup>-lined bomb. Langmyhr and Sveen (1965) also reported that hydrofluoric acid alone was more effective than a mixture of acids.

Decomposition of rocks with hydrofluoric acid leads to the precipitation of slightly soluble fluorides (Langmyhr and Sveen, 1965; Dolezal and others, 1968; Bernas, 1968; Meier, 1976). Langmyhr and Sveen (1965) used an aluminum salt to complex and dissolve precipitated fluorides. Bernas (1968) reported the use of boric acid to dissolve precipitated fluorides. Fluoride removal can also be accomplished by evaporation to dryness with perchloric acid or sulfuric acid (Langmyhr and Sveen, 1965; Langmyhr and Paus, 1968; Ward and others, 1969). Sulfuric acid should not be used if atomic-absorption determinations are to be made because sulfate may cause interference (Langmyhr and Paus, 1968).

The proposed decomposition and dissolution procedure provides a rapid and efficient technique to dissolve rocks for atomic-absorption analysis. This technique has the advantages of hydrofluoric-acid decomposition without the use of perchloric acid for fluoride removal, particularly when a laboratory is not equipped with the fume hoods that are necessary for the safe use of perchloric acid. The decomposition and dissolution procedure used to provide a solution for the determination of lithium, calcium, and magnesium can also be used for the determination of other major and minor metal constituents of silicate rocks. Silicon cannot be determined, however, be-

<sup>1</sup>Any use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

cause it is removed as a volatile tetrafluoride during the decomposition of the rock.

## PROCEDURE

### APPARATUS AND EQUIPMENT

Teflon beakers: 50 mL [molded of TFE Teflon].

Volumetric flasks: 100 mL and 10 mL.

Hot plate.

Wash bottle.

Atomic absorption spectrophotometer.

Hollow cathode lamps, Ca, Mg, Li.

### REAGENTS

Boric acid solution: Dissolve 50 g of reagent-grade boric acid in 1 liter of demineralized water.

Hydrochloric acid (6 normal): Dilute 500 mL concentrated hydrochloric acid to 1 liter with demineralized water.

Hydrofluoric acid: 48 percent.

Lanthanum chloride solution (10 percent La): Weigh 58.7 g lanthanum oxide ( $\text{La}_2\text{O}_3$ ) into a 1,000-mL beaker and wet with demineralized water. Cautiously add 100 mL of concentrated hydrochloric acid in small portions. When the oxide is completely dissolved, slowly dilute to 500 mL with demineralized water while stirring to avoid overheating.

Lanthanum chloride solution (1.1 percent La): Dilute 110 mL of lanthanum chloride solution (10 percent La) to 1,000 mL with demineralized water.

### STANDARDS

Calcium stock solution,  $1,000 \mu\text{g mL}^{-1}$ : Dissolve 2.497 g of dried calcium carbonate (overnight at  $100^\circ \text{C}$ ) in a mixture of 50 mL of demineralized water and 10 mL of 6 N hydrochloric acid. Dilute to 1,000 mL with demineralized water.

Lithium stock solution,  $1,000 \mu\text{g mL}^{-1}$ : Dissolve 9.9349 g of lithium nitrate in demineralized water and dilute to 1,000 mL with demineralized water.

Magnesium stock solution,  $1,000 \mu\text{g mL}^{-1}$ : Dissolve 1.000 g pure metallic magnesium in a minimum amount of 6 N hydrochloric acid (approx. 15 mL) and dilute to 1,000 mL with demineralized water.

Calcium working-standard solution: Prepare a series of standard solutions containing 0 to  $100 \mu\text{g mL}^{-1}$  by dilution of the calcium stock solution. For each mL of working standard to be prepared, add 0.1 mL of lanthanum-chloride solution (10 percent La), 0.05 mL of 6 N hydrochloric acid, and 0.05 mL of boric-acid solution.

Lithium working-standard solution: Prepare a series of standard solutions containing 0 to  $10 \mu\text{g mL}^{-1}$  by dilution of the lithium stock solution. For each milliliter of working standard to be prepared, add 0.05 mL of 6 N hydrochloric acid, and 0.05 mL of boric-acid solution.

Magnesium working standard solution: Prepare a series of standard solutions containing 0 to  $10 \mu\text{g mL}^{-1}$  by dilution of the magnesium stock solution. For each milliliter of working standard to be prepared, add 0.1 mL of lanthanum-chloride solution (10 percent La), 0.05 mL of 6 N hydrochloric acid, and 0.05 mL of boric-acid solution.

### SAMPLE DECOMPOSITION AND DISSOLUTION

1. Weigh 0.20 g of powdered rock or soil in a 50-mL Teflon beaker.
2. Add 15 mL of hydrofluoric acid to the beaker.
3. Place the beaker on a hot plate set on high (approx.  $250^\circ \text{C}$ ), and heat until all of the acid has been boiled off and all fumes have dissipated.
4. Add 5 mL of 6 N hydrochloric acid, and heat until acid begins to boil.
5. Add 5 mL of boric acid solution, and heat until the solution comes to a slight boil.
6. Remove the beaker from the hot plate, and transfer the solution to a 100-mL volumetric flask. Dilute to volume with demineralized water. Mix well by shaking, and use for lithium determination.
7. Transfer a 1-mL aliquot of the solution used for lithium determination to a 10-mL volumetric flask, and dilute to volume with lanthanum-chloride solution (1.1 percent La). Mix well by shaking, and use for calcium and magnesium determination.

### ESTIMATION

An atomic-absorption spectrophotometer is set to the operating conditions recommended by the manufacturer and calibrated using prepared working standards for each element. Lithium is determined by aspirating the solution contained in the 100-mL volumetric flask; calcium and magnesium are determined by aspirating the solution in the 10-mL volumetric flask. Concentration in the samples is calculated as follows:

$$\text{ppm Li} = \text{instrument reading in } \mu\text{g mL}^{-1} \times 500, \text{ and}$$

$$\text{percent Ca or Mg} = \text{instrument reading in } \mu\text{g mL}^{-1} \times 0.5$$

Sensitivity and detection limits vary from one atomic absorption instrument to another; therefore, absolute limits of detection and working ranges are not stated. The working range for each element is limited to the linear portion of a curve plotted from concentration versus absorbance. This range can be extended by using an instrument with scale-expansion and curve-correction capabilities, reducing sensitivity by rotating the burner, or by diluting the sample. Any or all of these techniques should be used to fit the concentration range of the samples to be

analyzed to the capabilities of the instrument to be used. The operating conditions listed in table 1 were used with a Perkin-Elmer model 603 atomic-absorption instrument, and the readings obtained using those conditions are given in table 2.

Typical working ranges, using the described procedure without use of curve correction, are as follows:

- Lithium concentration in sample*
- 0- 500 ppm ----- Burner in line with sample beam.  
 500-5000 ppm ----- Burner rotated 90° to sample beam.  
 >5000 ppm ----- Dilution.
- Calcium concentration in sample*
- 0- 2 percent ----- Burner in line with sample beam.  
 2-50 percent ----- Burner rotated 90° to sample beam.  
 >50 percent ----- Dilution.
- Magnesium concentration in sample*
- 0 -0.5 percent ----- Burner in line with sample beam.  
 0.5-5 percent ----- Burner rotated 90° to sample beam.  
 >5 percent ----- Dilution.

TABLE 1.—Operating conditions used with the atomic-absorption instrument

	Lithium	Calcium	Magnesium
Grating	VIS	VIS	UV
Wavelength counter	335	211	285.
Slit	3	4	4.
Scale expansion	1 ×	1 ×	1 ×
Lamp current	10 ma	10 ma	10 ma.
Source lamp	Li	Ca	Mg.
Integration	3 sec	3 sec	3 sec.
Burner	10 cm	10 cm	10 cm.
Fuel	Acetylene	Acetylene	Acetylene.
Oxidation	Air	Air	Air.
Flame type	Lean, blue	Lean, blue	Lean, blue.
Filter	In	Out	Out.

TABLE 2.—Readings obtained for lithium, calcium, and magnesium on the atomic-absorption instrument

Concentration ( $\mu\text{g mL}^{-3}$ )	Absorbance	
	Burner in line	Burner rotated 90°
<b>Lithium</b>		
0.1	0.017	( <sup>1</sup> )
1	.172	0.007
2	.337	.013
3	.488	.020
5	.766	.034
10	1.313	.068
<b>Calcium</b>		
0.7	0.009	( <sup>1</sup> )
1	.101	0.003
2	.191	.006
3	.424	.015
10	.835	.031
25	1.502	.071
50	1.843	.146
100	1.905	.292
<b>Magnesium</b>		
0.1	0.082	0.003
1	.753	.029
2	1.242	.059
3	1.724	.089
5	1.939	.149
10	( <sup>2</sup> )	.291
25	( <sup>2</sup> )	1.741
50	( <sup>2</sup> )	1.405

<sup>1</sup> Below absorbance range of the instrument.  
<sup>2</sup> Above absorbance range of the instrument.

### RESULTS AND DISCUSSION

Using the technique discussed in this paper, five replicate analyses were made on each of five selected samples to establish a mean value and a confidence interval for lithium, calcium, and magnesium. The same samples were also analyzed by two other methods. One of the methods, described by Ward and others (1969), uses a combination of nitric, perchloric, and hydrofluoric acids for sample decomposition, followed by hydrochloric-acid dissolution of the residue. The other method employs the decomposition procedure of Ward and others (1969) but was followed by the proposed hydrochloric- and boric-acid dissolution. Table 3 compares results obtained by these three methods.

Five replicate analyses were made on each of six standard rock samples to establish a mean value and to determine the standard deviation for lithium, calcium, and magnesium by the proposed method. Comparisons of the results to recommended values are shown in table 4.

The low values obtained for calcium on sample MAG 638 and for magnesium on sample MAG 754 using a combination of nitric, perchloric, and hydrofluoric acids (Ward and others, 1969) indicate that perchloric acid is not completely effective in the removal of fluorides when high concentrations of calcium or magnesium are present. The addition of boric acid in the dissolution procedure effectively redissolves these precipitated fluorides. The relatively good agreement of values obtained by the technique proposed in this paper with the other tech-

TABLE 3.—Comparison of replicate analyses using three techniques for decomposition and dissolution of rocks

[Values shown are averages of replicate analyses and limits at the 95 percent confidence level]. Lithium analyses in ppm, calcium and magnesium analyses in percent]

Technique <sup>1</sup>	Element	Sample number and material									
		MAI 180 Clay		MAI 413 Clay		MAH 430 Tuff		MAG 754 Carbonate		MAG 638 Carbonate	
1	Li	840	+14	135	+3	705	+23	574	+6	787	+30
2	Li	802	+11	148	+7	709	+21	584	+14	758	+17
3	Li	790	+16	140	+3	714	+12	542	+25	775	+28
1	Ca	3.10+	.05	3.90+	.27	7.43+	.64	2.14+	.09	25.0	+1.3
2	Ca	3.01+	.09	4.10+	.18	7.42+	.27	2.20+	.11	25.7	+ .3
3	Ca	2.98+	.18	3.88+	.19	7.36+	.10	2.18+	.07	23.8	+ .9
1	Mg	3.25+	.05	3.27+	.16	1.48+	.13	25.1	+ .1	3.88+	.32
2	Mg	3.10+	.04	3.40+	.16	1.45+	.07	25.2	+ .1	3.98+	.11
3	Mg	3.07+	.16	3.24+	.14	1.47+	.01	19.6	+ .1	3.94+	.18

<sup>1</sup>Techniques:

- 1, HF decomposition, HCl-H<sub>3</sub>BO<sub>3</sub> dissolution (proposed in this paper).
- 2, HF-HNO<sub>3</sub>-HClO<sub>4</sub> decomposition, HCl-H<sub>3</sub>BO<sub>3</sub> dissolution.
- 3, HF-HNO<sub>3</sub>-HClO<sub>4</sub> decomposition, HCl dissolution.

TABLE 4.—Comparison of lithium, calcium, and magnesium as determined by the proposed technique, with recommended values for some standard rocks

Sample No. and material	Lithium			Calcium			Magnesium		
	Average, proposed technique (ppm)	Standard deviation	Recommended value (ppm)	Average, percent, proposed technique	Standard deviation	Recommended value, in percent	Average, percent, proposed technique	Standard deviation	Recommended value, in percent
NBS 97a, flint clay-----	517	2.39	<sup>1</sup> 511	0.072	0.002	<sup>1</sup> 0.079	0.090	0.002	<sup>1</sup> 0.090
NBS120a, phosphate rock--	6.4	.89	---	29.9	.50	<sup>1</sup> 30.3	.13	.002	<sup>1</sup> 1.19
G-2, granite-----	29.0	1.00	<sup>2</sup> 34.8	1.29	.080	<sup>2</sup> 1.39	.44	.008	<sup>2</sup> 1.46
D7S-1, dunite-----	<1	---	<sup>2</sup> <2	.095	.009	<sup>2</sup> 1.107	30.1	.45	<sup>2</sup> 30.0
PCC-1, peridotite-----	<1	---	<sup>2</sup> <2	.32	.047	<sup>2</sup> 1.36	26.1	.45	<sup>2</sup> 26.0
GSP-1, granodiorite----	28.4	.55	<sup>2</sup> 32.1	1.34	.026	<sup>2</sup> 1.44	.59	.025	<sup>2</sup> 1.58

<sup>1</sup>Certified value, U.S. National Bureau of Standards.

<sup>2</sup>Value recommended by Flanagan (1973).

niques discussed shows it to be a useful procedure for decomposition and dissolution of rocks for atomic-absorption analysis, especially when perchloric acid cannot be used.

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