DIFFERENTIATION AND ALTERNATION IN THE CALDWELL SILL, ONTARIO

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY EUGENE HIMIE SHANNON 1973



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ABSTRACT

DIFFERENTIATION AND ALTERATION OF THE CALDWELL SILL, ONTARIO

By

Eugene Himie Shannon

The extent of chemical differentiation and alteration of nine major elements and twelve trace elements in a vertical section of the Caldwell sill, Ontario, was conducted to determine variation in major and trace elements through differentiation in a vertical section of the Caldwell sill, and propose a crystallization model for their origin. An attempt is made to evaluate the effects of chemical weathering on this suite.

Analytical determinations of major and trace elements were done by emission spectrographic analysis, and rapid chemical analysis. The analytical values obtained were compared with those of the Logan sills, Karoo dolerites, Palisades sill, and other sills of the world to see if any similarities existed. It was found that in all the sills, calcium and magnesium showed a decrease from bottom to top. The chemical percentage plots versus height of the sill, the mafic index, and MgO do not show smooth trends possibly because of the high degree of deteuric alteration of this sill.

FKM and other distribution diagrams are drawn to show the degree of variation from the normal trend in basaltic differentiation. The author concludes that the Caldwell sill is composite, and that the associated granophyric rocks, the so-called red rocks resulted from the end product of a normal differentially fractionated basaltic magma, subjected to a high degree of deteuric alteration.

DIFFERENTIATION AND ALTERNATION IN THE

CALDWELL SILL, ONTARIO

Ву

Eugene Himie Shannon

A THESIS

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INTRODUCTION

The Caldwell sill which is within the area of the Logan sills, crops out between 89°30' and 89°00 West longitude and 48°00; 48°15' North latitude. Chemical analysis of the Logan sills are reported by Blackadar (1956). From the petrographic and mineralogical studies of the Logan sills, it is concluded by Blackadar (1956) that many of these sills are composite, and that the associated hybrid rocks, the so-called red rock, resulted from the assimilation of granite or rarely chert and quartzite. Differentiation was limited by the small size of the individual units composing multiple intrusions. However, there are no analyses reported on the Caldwell sill, which shows a vertical gradation from a diabase to a granophyre in a vertical section of approximately 90 feet. These latter rocks represent the last stage of a fractionated basaltic magma. Owing to the overprint of alteration the liquid line of descent has been obscured. However, this sill fits a model of a late stage tholeiitic differentiation sequence reminescent of the hornblende gabbro of the Duluth complex to the south, Cornwall (1951).

GEOLOGIC SETTING

Towards the close of the Precambrian time, the Lake Superior basin was subjected to the intrusion of vast amounts of basic magma. This activity gave rise to dikes, sheets, sills of diabase, one group of which is known as the Logan sills. From the similarity in petrology, mineralogy and field relations, the writer believes that the Caldwell sill is also the result of this intrusion. The large, differentiated, basic sill which outcrops in the vicinity of Duluth, Minnesota is thought to be derived from the same source. The Rove formation, a succession of interlayered shales and graywackes, underlie these sills.

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PREVIOUS INVESTIGATION

There has been no previous work carried out on the Caldwell sill, but the Logan sills which are within the region have been studied by Sir William Logan, T. Macfarlane, E. D. Engall, and A. C. Lawson. The results of the field work by T. L. Tanton were published in 1951 as memoir 167 of the Geological Survey of Canada. An Ontario Department of Mines field party headed by Dr. W. W. Moorehouse carried out further geological investigation during the field seasons of 1950. Blackadar (1956) carried out chemical analysis of the Logan sills.

PRESENT INVESTIGATION OF

THE CALDWELL SILL

In this study, twelve samples of the Caldwell sill, ranging from 5 feet to 90 feet, above the contact with the Rove formation, were collected by Dr. Charles Spooner (Table 1). The writer studied the extent of chemical differentiation during fractionation of nine major and twelve trace elements of eleven of these samples over a short vertical section of about 71 feet of this composite Chemical values are reported in Tables 3, 4, 5, and sill. It was found that the possibility for end stage vapor 6. phase reactions increases the closer one gets to the roof. The chemical values of the Caldwell sill in Tables 3, 4, 5, and 6 are compared with values determined from the Logan sills, the rocks of Duluth, the Keweenawan Series to see if these rocks, of basically the same mineralogical composition, follow the normal differentiation trend. The normal trend is a strong concentration of Na, K, Si, P, S, Ti, Cu, and Mn in the residual magma, or last stage of differentiation, and a decrease of Ca, Mg, and Al in the magma during differentiation and solidification. It is

TÆ	BLE	<pre>1Samples of the Caldwell Differentiated Sill, S-l to S-l2 (Collected by Dr. C. Spooner).</pre>
S	JITE	2 Differentiated Sill 62 4804 25 174 Air Photo #
Co	511:	C. M. Spooner
S	1	5' above base of cliff (probably 5' above contact with Rove)
S	2	7' above base of cliff
s	3	10' above base of cliff
S	4	12.5' above base of cliff
s	5	15' do
S	6	20' do
S	7	25' do
S	8	38' do
S	9	48' do
S	10	56' do 30' lateral displacement to west between
S	11	71' do
S	12	90' above base

considered that SiO_2 and Na_2O increase gradually, MgO and CaO decrease, Al_2O_3 declines in latter stages, FeO, TiO₂, $P_2\text{O}_5$, and Cu increase to a peak and fall off. If the above statements are true, it would be expected that the chemical analysis of the Caldwell sill will show the same trends.

THE DIABASE--GRANOPHYRE

The general geology of the area is given by Tanton (1931). According to Tanton, the Logan sills which are also within this area are most commonly found in the shaly members of the Rove formation. Fig. 1 is an index map showing the locations of the Logan sills and the Caldwell sill.

These rocks represent the last stage of a basaltic magma differentiate which has been extremely altered deuterically. This type of alteration was brought in by late stage water-rich fluids, presumably residual solutions from the granophyre precursor. These water-rich liquids superimposed a new low temperature mineralogy on the rocks with some change in bulk chemistry composition, especially magnesium and calcium.

Such alteration the author assumes affected particularly the upper parts of the sill (such as the section studied) owing to the tendency of this volatile-rich late fraction to rise in the partly consolidated crystal mush.

The evidence for making this extensive alteration deuteric includes:



Fig. 1. Index map (Fort William and Port Arthur, and Thunder Cape map areas, Thunder Bay District, Ontario, Department of Mines) showing the location of the Caldwell sill and the Logan sills.

- The trend of major element enrichment shown by the variation diagrams parallel the known magmatic trends in basalts; hence the alteration probably took place during the later stages of, and as a direct consquence of the consolidation of the magma.
- The fact that the data points are co-linear and deviation from the curve is small suggests similar degree of deuteric alteration throughout the sequence.
- 3. The fact that the minerals of the late stage granophyre are much less altered than the earlier minerals of the diabase indicate that the altering fluids were nearly in equilibrium with the early formed diabase minerals.
- 4. Many of the analysed altered rocks from the Logan sills contain up to 7.0% water total and 1.0% CO₂ and are even more extensively altered than the Caldwell sill. In spite of this alteration, the Logan rocks are co-linear, and show only moderate scatter, and fit the pattern of magmatic FeO enrichment followed by alkalic enrichment. This suggests that (1) the alteration is deuteric, and (2) the deuteric alteration is provincial in character affecting in some degree all diabase sills in the region.

In Fig. 2 the contents of CaO and MgO in the Caldwell and Logan sills and their differences have been plotted against FeO throughout the differentiation history of these sills. By looking at the FKM diagram in Fig. 12 it appears as though the FeO content of both the Caldwell sill and the Logan sills is constant. Assuming that this is true throughout differentiation, the amount of CaO and MgO of the Caldwell sill decrease as those of the Logan sills remained constant.

The curves of these diagrams explain the offset in the alkali lines of decent shown in the FMK diagram of Fig. 12. The interpretation of this offset of the Caldwell sill curve from the Logan sill curve is due to the continuous removal of MgO and CaO contents as FeO remained constant throughout differentiation. This type of alteration which the author has termed deuteric was brought about by late stage water rich fluids which superimposed a new low temperature mineralogy on these rocks causing some change in bulk chemistry, mostly in the MgO and CaO contents.

Petrography

Eleven thin sections of the sill were examined. The modal compositions are given in Table 2. The texture which is similar to the rocks of Duluth, Grout (1918), varies from sugary to very coarse. It is micropegmatitic, varying to granitic in some large mases. The chief red mineral is feldspar stained with considerable hematite,



Fig. 2. % CaO and MgO Lost During Differentiation of the Caldwell Sill. (The % of CaO and MgO are considered Const. in the Logan Sills.)

	S-1	s-2	s-3	s-4	s-5	s-6	s-7	s - 8	s -9	s-10	s - 11	
Height	5'	7'	10'	12.5'	15'	20'	25'	38'	48'	56'	71'	
Plagioclase	40	40	30	15	10	5	5	10	10	10	3	
K-spar	-	-	10	15	37	35	40	40	41	40	43	
Pyroxene	20	20	1	1	1	1	1	1	-	-	-	
Amphibole	10	10	19	21	15	5	6	3	3	4	2	
Biotite	3	3	3	4	5	5	4	-	-	-	-	
Chlorite	3	3	3	3	-	-	-	-	-	-	-	
Quartz	5	16	25	20	25	40	40	40	40	40	42	
Muscovite	2	2	2	2	Tr	Tr	Tr	-	-	-	-	
Sericite	15	15	20	15	15	10	5	5	5	3	3	
Magnetite	3.	55	5	2	1	1	1	1	1	1	Tr	
Ilmenite	5	2	3	2	1	1	1	1	1	1	Tr	
Pyrite	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	
Leucoxene	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	
Apatite	1	1	1	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	
Epidote	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	
Spinel	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	

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TABLE 2.--Estimated Modal Composition Per Cent of the Caldwell Sill.

often badly kaolinized. Probably most of the red rocks contain two feldspars, orthoclase and plagioclase. Zoning is especially common in the phases grading into the diabase. Quartz, though abundant is rarely visible except with the microscope as an intergrowth. Hornblende is the chief ferromagnesian mineral, but it is fibrous and mixed with secondary minerals as if itself secondary. Biotite is secondary.

Mineralogy

The rocks of the Caldwell sill are relatively simple mineralogically though extremely altered. Feldspar, and pyroxene comprise about 65 per cent of the mineral content in most thin sections examined. Olivine is absent throughout the sill due to extreme alteration. Biotite, chlorite, amphibole are abundant in most sections. Magnetite, ilmenite, pyrite, apatite, potash feldspar, carbonate and micropegmatite are found in variable amounts. This precambrian diabase sill, similar to the Mamainse diabase in the Canadian shield studied by Friedman (1954) has been greatly altered by hydrothermal deuteric action as the composition of pyroxenes and feldspars cannot be determined. Major and trace elements have been analysed by the writer to provide a tool for studying differentiation trends of basaltic magma, and to evaluate effects of differentiation.

Feldspars

Because of the high degree of alteration of the plagioclase feldspars to sericite and clay their compositions cannot be determined. In thin sections of the granophyre untwinned alkali feldspar forms extensive intergrowths with quartz displaying a graphic texture.

Olivine

Crystals of olivine are absent from these samples. Because of the extent of alteration, relict structures of olivine are not discernible.

Pyroxenes

Unfortunately, the pyroxenes like the plagioclase are extremely altered to serpentine, hornblende, clay minterals, etc. In thin sections where gragments could be seen the pyroxenes were mainly diopside and hyperstheme.

Amphiboles

Almost all of the amphiboles are hornblende. They are replacement products of the pyroxenes.

Biotite

The author believes that the biotite present is also a replacement product of the amphibole since it appears to be forming around the outer rims of the amphibole.

Magnetite and Ilmenite

Magnetite and Ilmenite are mostly concentrated in the diabasic part of the section. Higher in the more felsic part of the section the opaques seem to decrease considerably.

Quartz

Quartz though abundant, is rarely visible except with the microscope as an intergrowth in the granophyre.

Pyrite, leucoxene and apatite are only found in trace amounts.

Chemical Data

Major and trace elements analyses were done by the writer through the courtesy of the U.S.G.S. The procedures used were those outlined by Leonard Shapiro (Rapid Analysis of Silicate, Phosphate and Carbonate Rocks), Helz, Walthall and Berman (Spectrographic Computer Analysis of the U.S.G.S. chemical laboratory), W. Slavin (Atomic Absorption Spectroscopy). The chemical values are reported in Tables 3, 5, and 6 and in Table 4 as dry weight per cent.

Major Elements

The MnO content of the sill ranged from .11 per cent to .20 per cent (\pm .02%). According to Deer Howie and Zussman (1963) both the dark silicates which contain the hydroxyl groups, and the pyroxenes are the probable carriers of this element. The chemical analysis of these TABLE 3.--Analytical Results of Rapid Silicate Analysis of the Caldwell Sill, Caldwell, Ontario, Canada. Rapid Chemical Analysis of 12 Felsic Diabase (Sill) Samples From Caldwell, Ontario, Canada.

								1				
Field No.	S-1	S-2	S - 3	S-4	s-5	s-6	S-7	S-8	6-S	S-10	S-11	s-12
Height	5	. 7	10.	12.5'	15'	201	25'	38	48'	56'	71'	,06
sio ₂	53.3	53.2	54.6	58.7	62.6	62.8	63.7	67.0	67.7	67.7	67.9	55.8
	14.6	14.5	12.8	12.5	12.3	12.5	12.6	13.1	12.8	12.8	12.7	13.4
Fe203	2.1	2.0	2.7	1.5	1.7	2.8	3 . 3	2.2	2.6	2.7	3.0	2.7
FeO	9.7	10.5	10.4	9.6	8.0	6.9	6.0	4.5	4.0	4.3	3.5	10.5
MgO	2.6	2.7	2.6	1.9	1.2	1.1	66.	.70	.52	.45	.57	2.6
CaO	5.0	4.9	3.9	3.6	2.6	2.4	2.2	1.3	1.3	1.3	1.4	3.6
Na ₂ 0	3.2	3.8	2.7	2.8	3.1	3.7	3.8	3.5	3.4	3.5	3.6	3.3
K2O	2.9	1.9	3.2	3.7	3.8	3.1	3.1	4.3	4.6	4.0	4.2	2.5
H ₂ 0 ⁺	2.5	2.5	2.9	2.4	2.3	2.0	2.1	2.0	1.9	2.0	1.7	1.1
H ₂ 0 ⁻	.46	.47	.73	• 58	• 50	.67	.70	.50	.48	.41	.64	.71
rio ₂	2.8	2.8	2.6	1.9	1.3	1.2	1.1	.60	•55	.60	.54	2.6
P205	.61	•59	.68	.51	.35	• 30	.27	.08	•08	•08	.07	.71
MnO	.19	.21	.20	.19	.16	.16	.15	.13	.11	.12	.11	.22
co ₂	<.05	<.05	<.05	.12	<.05	<.05	< "05	<.05	<.05	.12	<.05	<.05
Sum	100	100	100	100	100	100	100	100	100	100	100	100

						Salic Gro	đņ				
	s-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	6- 3	S-10	S-11
Quartz Corundum Zircon orthoclase Albite Albite Leucite Kaliophylite Nepheline Thenardite Sodium Carbonate Sodium Carbonate	6.06 0.00 0.00 0.00 0.00 0.00 0.00 0.00	5.71 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	1 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	14.12 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	19.50 87.00 87.00 0.00 0.00 0.00 0.00 0.00	20.57 0.00 82.12 0.00 0.00 0.00 0.00 0.00 0.00	21.63 0.00 82.93 0.00 0.00 0.00 0.00 0.00 0.00	24.00 0.000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.00000 0.0000 0.00000 0.0000 0.00000 0.00000 0.00000 0.0000000 0.00000000	25.34 0.00 29.58 0.01 0.00 0.00 0.00 0.00	26.00 26.00 26.00 20	26.50 00.002 00.002 00.002 000000 0000000000
Acmite Sodium Metasilicate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	00.0	0.00
Potassium Metasilicate Mollopside Wollastonite Hypersthene Olivine	0.00 4.30 0.00 16.67 0.00	0.00 3.70 0.00 18.80	0.00 1.93 0.00 19.18	0.00 4.04 16.90 0.00	0.00 2.39 0.00 13.47 0.00	0.00 1.84 0.00 10.75 0.00	0.00 0.00 8.05 0.00	0.00 0.00 7.55 0.00	0.00 .52 5.63 0.00	0.00 0.00 0.100 0.120 0.02	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0
Calcium Orthosilicate Magnetite Hematite Sphene Perovskite Rutile Fluorite Pyrite Calcite Chromite	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	9.00 9.00 9.00 9.00 9.00 9.00 9.00 9.00	04000000000000000000000000000000000000	00000000000000000000000000000000000000	00000000000000000000000000000000000000	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	••••••••••••••••••••••••••••••••••••••	0.000 0.00 0.00 0.00 0.00 0.00 0.00 0.	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	040400000000 0004000000000000000000000	04010000000 0100000000 0000000000000000

TABLE 4.--Analytical Results: Rapid Analysis and Trace Analysis, 100 Per Cent Water Free (CIPW Norm, Weight Per Cent).

rocks shows that the content of manganese varies very little from the bottom to the top of the sill. This means that both the primary pyroxenes and secondary hydroxyl minerals carried the oxide (Fig. 3). P_2O_5 is mainly tied up with the mineral apatite. Generally speaking about 95 per cent of the P_2O_5 content of igneous rocks is in this form. P_2O_5 ranges from .08 per cent-.68 per cent. This oxide gradually increased during the earlier stages of differentiation, then it decreased and remained constant up to the top of the sill (Fig. 3).

TiO₂ is present in amounts up to 2.8 per cent. Undoubtedly, this is mainly tied up with illeminite or titaniferous magnetite. This oxide ranges from .54 per cent to 2.8 per cent. It shows a steady trend during the early stages of differentiation, then it decreases a little, and therefore remained almost constant up to the top of the sill (Fig. 4).

 ${\rm SiO}_2$ is exceedingly high in this sill, ranging from 53.3 per cent (bottom) to 67.9 per cent (top). The ${\rm SiO}_2$ content in this sill is higher than the values of the Logan sills and other diabase sills throughout the world. This high content of ${\rm SiO}_2$ is due to the presence of an acid residum which is dominantly quartzo-feldspathic, and charged with soda and lime. Kennedy (1933) classifies these rocks as the last differentiate of a tholeiitic basalt.
at 177

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Fig. 3. Graph illustrating the variation in chemical composition of the Caldwell sill with respect to elevation.



Fig. 4. Graph illustrating variation in chemical composition of the Caldwell sill with respect to elevation.

CaO and MgO decreased with differentiation from bottom to the top of the sill (Fig. 3). These elements are mostly concentrated within pyroxenes, olivine and plagioclase, which come out very early in a differentiated basaltic sill. Al₂0, decreased during the early stages of differentiation and thereafter remained almost steady to the close of differentiation (Fig. 4). K₂O and Na₂O increased with differentiation from the bottom of the sill to the top (TOp.). The alkalies are mobile and travel upwards, tending to concentrate in the valatile phases becoming enriched during the later stages of differenti-Unlike the Caldwell sill, the Logan sills though ation. lower in K₂O and Na₂O, are higher in MgO and CaO. Combined water is more abundant in these granophyric rocks. Figs. 5 and 6 are variation diagrams showing the chemical composition of the Logan sills.

Trace Elements

The results of the trace element studies are presented according to element behavior during differentiation (Fig. 7). The trace elements tend to follow the major elements in their distribution. They enter the sites that might normally be occupied by major cations in the lattice structure. This means that the trace cation successfully competes with the major cation for the available site. The cation of a trace element tends to enter the mineral lattice site normally occupied by a



Fig. 5. Graph illustrating the chemical composition of the major elements of the Logan sills with respect to MgO.



Fig. 6. Graph illustrating the variation in chemical composition of the Logan sills magma.

major cation whose chemical properties are closest; for example, where $Rb^+(1.48A)$ enters a K^+ (1.33A) site. Some trace elements are only accommodated with difficulty in the lattice sites of the major elements in minerals, and these tend to behave independently; for example Zr and Cu. Thus, where trace elements have no similar major elements with which they can associate, they tend to concentrate in the magma until they can form a separate mineral phase, i.e., Zr. Their behavior then switches from that of a trace to that of a major mineral-forming element, with which other suitable matched trace elements may then associate (Kenneth R. Walker, 1969). Distribution trends of trace elements of the Caldwell sill are shown in Fig. 7.

Strontium

Some recent estimates of the strontium content of basaltic rocks are 440 ppm Faure and Hurley (1963), 440 ppm, Vinogradov (1962), 461 ppm, Gast (1960), and 300 ppm, Fairbairn and others (1953). The Sr within the rocks of the Caldwell sill as reported by the author ranges from 882 ppm in the more basic samples to 144 ppm in the more felsic. There is an average of 376 ppm for both felsic and basic samples of this diabase-granophyre. It appears as though most of the strontium was contained within the



Fig. 7. Graph illustrating the variation in chemical composition of the trace elements of the Caldwell sill with respect to elevation.

Ca-rich minerals such as plagioclase and clinopyroxene which have been extremely altered. In the Palisades sill, Walker (1969), Sr content shows a steady increase with fractionation in the middle and late fractionation stages, whereas the Ca content progressively decreases. This might be true because of the early removal of Ca in Cabearing phases. In the Caldwell sill, Sr does not show a steady increase with fractionation. This might be due to the depletion of Sr as fractionation proceeded or the lack of available sites, like (K + Ca) for Sr. Another possibility could be the early removal of Sr in Ca rich phases. Hier (1962) shows that the ratio of Sr in K feldspar to plagioclase is close to unity and ranges from 0.5 to 2.0. Heier and Taylor (1964) have noted that high Ba and Sr contents of many alkaline rocks. Wager and Mitchell (1951) found that Sr increased in the residual magma until about 60 per cent solidification, and then dropped off. The present day study shows that alkali basalts contain much more Sr than do tholeiites. The enrichment of Sr in alkali basalts may be due to higher average K contents. Variation diagram with respect to height is drawn to show the trend of Sr with differentiation. Sr showed an increase during the initial stages of differentiation, then it began to fluctuate during later stages of differentiation. It shows an overall decrease (Fig. 7).

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TABLE	

Field No. Sample Spectrum	W-178062 S-1	w-1 78063 S-2	W-178064 S-3	W-178065 S-4	W-178066 S-5	W-178067 S-6	W-178068 S-7	w-178069 S-8	W-1 78070 S-9	W-178071 S-10	W-178072 S-11	
Be ppm	2	2	2	е	£	e	m	4	'n	4	£	
Co ppm	27	30	27	16	8	٢	S	2	7	7	2	
Cr ppm	15	13	12	6 0	13	14	6	42	13	19	29	
Cu ppm	87	80	131	22	48	24	17	13	п	21	Q	
mqq nM	1520	1680	1730	1470	0611	1170	1140	970	869	920	812	
mq ppm	4	4	7	4	ŝ	٢	ę	7	9	7	E	
mdd qu	6	13	20	17	25	26	22	31	33	34	30	
Ba ppm	637	430	1000	864	597	480	513	862	967	696	662	
Ni ppm	22	20	13	ę	8	4	4	10	£	4	11	
mqq dq	5	7	12	8	6	7	Q	7	10	30	4	
Sr ppm	882	606	841	450	260	178	180	183	176	193	144	
udd uz	108	213	165	122	136	159	141	82	135	168	104	
Zr ppm	226	327	460	341	401	681	549	653	681	649	603	

Barium

Recent estimates of Ba in basaltic rocks include 300 ppm, Vinogradov (1962), 330 ppm, Turekian and Wedepohl (1961), 33 ppm, Gast (1960), 310 ppm for one activation analysis, Hamaguchi and others (1957), and 280 ppm, Fairbairn (1953). The wide range of values of Ba may partly reflect poor inter-laboratory correlation. The Caldwell sill is very high in barium. The value range from 430 ppm to 1000 ppm, with an average of 720 ppm. This high content of Ba is due to the presence of a high amount of feldspar present as intergrowth. K-feldspars are richer in Ba (2000-3000) than coexisting plagioclase owing to a strong coherence of K and Ba. Heier (1964) shows that alkalic rocks are usually rich in Ba, indicating high barium content in feldspathoids. The high content of Ba could also be due to the high degree of alteration that these rocks have suffered. The present study shows that alkale basalts have about twice as much barium than do tholeiites. The coherence of K and Ba is reflected in the increase of Ba in alkali basalts that have more alkalies. The sharp increase in the barium content in the barium content in the late fractionation stages probably resulted from the increase in the K content of the orthoclase with fractionation. Variation diagram with respect to height is drawn to show the trend of barium with differentiation (Fig. 7). Barium shows a steady increase during differentiation of the Caldwell sill.

Chromium

Fleischer and Stevens (1962), Ahrens and Fleischer (1960), and Fleischer and Chao (1960) find only fair agreement in Cr content of W-1 (+50% and -33%) from various laboratories. There is a great deal of uncertainty about absolute values of chromium. Recent estimates of chromium content in basaltic rocks are: 172 ppm Turekian and Carr (1963), 200 ppm, Vinogradov (1962), 170 ppm, Turekian and Wedepohl (1961), 100 to 400 ppm, Goldschmidt (1954). Chromium usually shows the greatest dispersion of all the spectrographically determined elements, which reduces the significance of an average value. The study of basalt gives an arithmetic mean of 162 to 168 ppm and a median value of 140 ppm for 245 analyses (Poldervaart and Hess, 1968). The range of accepted values from the study of basalt was between 0-550 ppm, Poldervaart and Hess (1968).

The author assumes that most of the chromium was separated from the magma with the olivines and pyroxenes. Early pyroxene incorporates great amounts of chromium causing chrome spinels to cease crystallization. Later pyroxenes and magnetite usually have lesser amounts of chromium because the magma is now depleted in chromium. Carstens (1958) finds that feldspar, feldspathoids, ilmenite and other minerals in basaltic rocks contain little or no chromium. Alkali basalts are therefore

usually low in chromium. Variation diagram is drawn with respect to height is drawn to show the trend of chromium with differentiation (Fig. 7). Chromium does not show a continuous decreasing trend as expected during differentiation. This might probably be due to spectrographic dispersion of chromium. Chromium was determined in nearly all of the analysis made, although in amounts never exceeding 42 ppm. According to Rakama and Sahama (1950) chromium occurs in trace amounts in many silicates. It has been detected in augite, hornblende and olivine. Mason (1952) states that 1.2 per cent of some augites may be CR_2O_3 . It is particularly abundant in magnesian-olivine. In the Caldwell sill, it ranges from 8.05-29 ppm. In this sill chromium shows a random trend with differentiation.

Cobalt

Some recent estimate of cobalt in basaltic rocks included 45 ppm, Vinogradov (1962), 48 ppm, Turekian and Wedepohl (1961), Carr and Turekian (1961), and 35 ppm, Unksov and Lodochinikova (1961). The cobalt of the Caldwell sill as reported by the author ranges from 1.6 ppm to 30.3 ppm. Co tends to follow the pyroxenes and olivines which have Fe^{+2} and Mg^{+2} . These cations provide appropriate sites for cobalt. Since the pyroxenes and olivines are almost completely absent from this late stage differentiate, it is not surprising that cobalt is this

low. Cobalt decreases with differentiation as expected
(Fig. 7).

Nickel

Nickel enters the same minerals as cobalt. Turekian (1963) and others show that nickel is enriched in early olivine and to a lesser extent in early orthopyroxene. It is also present in lesser amounts in magnetite, clinopyroxene, amphibole, and biotite. Since nickel enters most abundantly into the olivine structure, this mineral has a marked influence on the nickel distribution in basaltic rocks. In general nickel is rapidly depleted by early ferromagnesian silicates and opaque ores and has low abundance in late-stage basalts. The author therefore believes that the low amount of nickel is due to its early extraction from the magma with olivine, and pyroxenes. The author reports that nickel ranges from 2.39 ppm to 22 ppm in the Caldwell sill. There appears to be no systematic decreases with differentiation as expected. This is probably due to the extreme alteration of the olivines and pyroxenes of these rocks, and the removal of certain cations, like Fe and Mg which act as favorable lattice sites for nickel. The distribution trend of nickel is shown in Fig. 7. Nickel shows an overall decrease with differentiation.

Zirconium

Recent estimates of zirconium in basaltic rocks include 110 ppm, Vinogradov (1962), 140 ppm, Turekian and Wedepohl (1961), and 110, Degengardt (1957). In the Caldwell sill as reported by the author, the value of zirconium ranges from 226 ppm to 681 ppm (from bottom to The average value of 498.4 ppm is much higher than top). any other result reported in the literature. However, this high value of zirconium in the residual magma could be due to the fact that zirconium has its highest concentrations in products of residual fractionation; the granophyre. According to Chao and Fleischer (1960), zirconium increases rapidly from mafic to silicic compositions. The main feature of zirconium behavior as reported by Walker (1969) is that it forms its own silicate phase, zircon, rather that entering other mineral lattices. This accounts for its somewhat irregular distribution in the whole rock. The size of $2r^{+4}$ (0.80A), in addition to the problem of charge balance, makes entry into major cations sites of minerals difficult. Ringwood (1955b) has indicated that zirconium may also form complexes. As (ZrO₄) is large with respect to (SiO4), it concentrates in residual melts. The distribution trend of zirconium is shown in Fig. 7. Zirconium shows a great increase from the bottom of the sill to the top.

Niobium

Niobium was detected in the Caldwell sill to range from 9 ppm to 34 ppm (from bottom to top). This means that niobium increased from bottom to top during magmatic differentiation. One of the most important features of the geochemistry of niobium and tantalum are their strong coherence with titanium (Rankama, 1944, 1948; Fleischer et al., 1952). Quantitative studies of the distribution of niobium in minerals in some basalts (Huckenholtz, 1965; Cornwall and Rose, 1957), and in gabbroic rocks (Gottfried, unpublished data) indicate that the iron-titanium oxides (magnetite and ilmenite) contain most of the niobium in major rocks. This means that the content of niobium depends on the concentration of titanium. The distribution trend of niobium is shown in Fig. 7. Niobium increases from bottom to the top, while titanium decreases with differentiation. This trend might be due to the fact that perhaps niobium followed other cations as titanium was depleted from the magma.

Copper

Recent estimates of copper in basaltic rocks include 100 ppm (Vinogradov, 1962), 88 ppm (Wedepohl, 1962), 87 ppm (Turekian and Wedepohl, 1961), 56 ppm for gabbros, 87 ppm for basalts (Monita, 1955), and 72 ppm (Fairbairn and others, 1953). Present day studies show an arithmetic mean of 119-123 ppm and a median of 100 ppm

for 156 analysis. Copper ranges from 5.97-131 ppm in the Caldwell sill. It has an average of 44.3 ppm. Copper decreases from bottom to top in these rocks. The author believes that this decrease is due to the fact that copper might have separated earlier as a sulphide phase. The dominant characteristic of copper behavior is its tendency to complex in the magma rather than form independent ions if enough sulfur is available. When sufficiently concentrated, copper forms an immiscible liquid, which in turn separates as a sulphide phase. At low concentration copper can be camouflaged by olivine, pyroxene or biotite. This behavior was identified in the Skaergaard intrustion by Wager and Mitchell (1951). Avariation diagram of copper with respect to height is shown in Fig. 7, and chemical values in Table 5.

Beryllium

The author did not encounter any literature on the chemical analysis of beryllium in basaltic rocks. However, from the periodic chart, beryllium, with a valence of 2, might behave like some of the other alkaline earth metals. In the Caldwell sill, beryllium ranges from 1.81-4.39 ppm. Though slightly irregular, it shows an overall increasing trend from bottom to top. It drops slightly in S-11 to 2.79 ppm. This slight irregular trend with differentiation of beryllium could be due to the presence or absence of available cation sites, or insufficient amount of beryllium

in the original magma. Distribution trend of beryllium is shown with respect to height in Fig. 7. Spectrographic results are recorded in Table 5.

Molybdenum

Mo in the granophyre-disbase of the Caldwell sill range from 3 ppm to 7 ppm. It has an overall average of 6 ppm. According to Walker (1969) Mo enters the opaque iron minerals, and its presence in these minerals show a progressive, but irregular increase in concentration with fractionation. Molybdenum shows a strong tendency to complex and concentrate in residual magmas, as the complexes formed are larger than SiO_4 (Ringwood, 1955b), Zr (0.80A), or Fe (0.64A), which is consistant with its presence mainly in the opaque iron minerals. The irregular increase in concentration of molybdenum could also be due to its early separation from the magma as a sulphide phase. The distribution trend of molybdenum with respect to height is shown in Fig. 7.

Lead

Lead distribution in the Caldwell sill is irregular. Lead shows a slight general increase in concentration with differentiation. The average composition is 10 ppm. It ranges from 4 ppm to 30 ppm. Distribution trend is given in Fig. 7, and values are given in Table 5. Lead tended to concentrate in the residual melt as expected, though

some of it might have entered crystal lattices, such as the K-feldspars proxying for potassium ion, or might have separated earlier as sulphide phases.

Zinc

The distribution of zinc, like beryllium in basaltic rocks are not reported in any recent literature that the author has read. However, from the geologic occurrence of zinc the author believes that zinc crystallizes out as a sulphide mineral similar to lead. Zinc ranges from 226 ppm to 681 ppm. It seemed to be mostly concentrated in the residual magma. Zinc also shows a slight irregular trend with differentiation, but overall it seems to increase in concentration from bottom to top. The distribution trend of zinc is shown in Fig. 7, and spectrographic values are reported in Table 5.

Comparisons of the ratios of Sr/Ca, Ba/Ca, Pb/K and Co/Ni of the palisades sill and Caldwell sill are shown in Figs. 8, 9, 10, and 11. The curves were made to see whether the trace elements were controlled by differentiation, favorable lattice sites, or whether trace elements followed major elements because of their chemical sililarities. These curves were also drawn to see if alternation played a significant role in the differentiation of these elements. According to the Sr/Ca ratio curves of both the Palisades sill and the Caldwell sill, it seems that Sr follows Sr very closely up to a point in



Fig. 8. Sr/Ca plotted with respect to height in the Caldwell sill and Logan sills.



Fig. 9. Ba/K plotted with respect to height in the Caldwell sill and Logan sills.



Fig. 10. Pb/K plotted with respect to height in the Caldwell sill and Logan sills.



Fig. 11. Co/Ni plotted with respect to height in the Caldwell and Logan sills.

the differentiation sequence, after which Ca was fractionated out or removed and Sr followed potassium, a cation with a favorable lattice site.

The Ba/K curves show that Ba closely follows potassium throughout the sill, and is mostly concentrated in the residual where there is an abundance of potassium rich feldspars. The analytical results of trace elements of both sills show a high content of barium in the residual magma.

The Pb/K ratio curves in both the Palisades and Caldwell sills are irregular and do not show any regular trend towards enrichment in the residual magma as expected. However, Pb values in both sills tended to concentrate in the residual magma, though some of it might have entered sulphide phases.

The Co/Ni curves of the Palisades sill tended to build up in the magma during the early and middle fractionation stages, and entered late stage rocks. The magma was depleted in Co/Ni and the values decreased. The Co/Ni in the Caldwell sill built up gradually to a peak and then became depleted in the magma, and fell drastically. The Co/Ni curve of the Caldwell sill does not parallel that of the Palisades until near the point when the Co/Ni became depleted and the values decreased.

Error bars have been plotted to indicate the precision and accuracy limits (+50% and -33%) of the

spectrographic methods, of the U.S.G.S. analytical laboratories, Washington, D.C.

Petrology

The presence of a quartzo-feldspathic groundmass, increasing graphic intergrowth of quartz and feldsparaparent eutectic proportions, and a trend towards soda, potash, and SiO, enrichment, indicate that the chemical changes are compatible with the differentiation of a tholeiitic magma of silica enrichment trend. The Logan sills which are within the same proximity and supposedly from the same magma are also tholeiitic, Blackadar (1956). The results of the chemical analyses tend to substantiate the classification of the Caldwell sill as a tholeiite. The Caldwell sill is more silica and alkali enriched than rocks of the Logan sills, Palisades sillKaroo dolerites, and some other sills that the author has compared with these rocks. On the FKM diagram (Fig. 12) the Caldwell sill shows a trend predominantly towards alkali enrichment. A comparison of the average composition of the Caldwell sill with other diabase sills of tholeiitic composition does not show a great amount of similarity. The SiO₂, Na₂O and K_2O contents are higher, and the CaO and MgO are much lower than other diabase sills. The intrusive Caldwell diabase has a greater amount of FeO and a lesser amount of Fe₂O₃. This proves that iron



Fig. 12. Graph illustrating iron and alkali enrichment during crystallization of the Logan sills and the Caldwell sill.

enrichment was insignificant. $\begin{array}{c} FeO+Fe_2O_3 \\ \hline MgO+FeO+Fe_2O_3 \end{array} X 100 \\ \mbox{increased steadily.} & TiO_2 \\ \hline FeO+Fe_2O_3+TiO_2 \end{array} X 100 \end{array}$

markedly and fell sharply. The FKM diagram shows the trend towards both alkali and iron enrichment. The Logan sills plots indicate that there was progressive enrichment in iron relative to magnesia until near the completion of the process when a rapid increase in the proportion of alkalies present occurred. The Caldwell sill on the other hand shows a trend predominantly towards alkali enrichment. If the present evidence is regarded in conjunction with Wager and Deer (1939), it may be regarded as established that enrichment in Fe_2O_3 is the normal trend of differentiation during the crystallization of some basaltic magmas. The Caldwell sill represents the alkaline line of descent. This sill represents the last stage of differentiation, as one constituent after another is removed. Alkali enrichment becomes the dominant trend with fractionation and increasing P_{02} and P_{H20} .

Iron enrichment trends are affected by both the partial pressure of oxygen and the content of water present. The oxidizing effect of escaping gases on the crystallized iron minerals in the Caldwell sill magma was infinitesimal due to the overprint of alteration. However, the effect of the vapor phase on the magma before crystallization must be considered. Experimental work by Kennedy (1948) has shown that the ferric-ferrous ratio of basaltic magma depends on the temperature of the melt and the P_{O2} of the vapor in equilibrium with the melt. The P_{O2} depends on the total pressures of the volatiles and the degree of dissociation of H_2O , the principal volatile constituent in equilibrium with the magma. The dissociation of H_2O into H^+ and OH^- is proportional to the temperature. Kennedy's data (1948) as shown elsewhere by Cornwall (1951), indicates that the decrease of dissociation of H_2O for a given temperature drop with constant total volatile pressure is more than offset by the increased oxidizing effect of $O^=$ on iron at the lower temperature. Thus, the net effect of a drop in temperature, the pressure remaining constant, is an increase in the ferric-ferrous ratio of the melt.

Discussion of Errors

Precision and Accuracy of Rapid Analysis

It is the practice in the Rapid Analysis laboratory of the U.S.G.S., Washington, D.C., to analyse each sample two times, each time by different analysts. Results of 1 per cent or higher are reported to the nearest tenth of a per cent; results below 1 per cent are reported to the nearest hundredth.

Major elements that are 10 per cent or above are plus or minus 1 per cent relative. Constituents that are 1-10 per cent are plus or minus .1 per cent absolute,

e.g., 6.7 per cent and 6.6 per cent are about the same. Constituents that are below 1 per cent are plus or minus .02 per cent absolute, e.g., .60 per cent or .62 per cent are about the same (Dr. Leonard Shapiro and W. W. Brannock, 1959).

For complete analysis, the averages of the summations are expected to be between 99.0 and 101.0. These methods are designed to give results that are comparable to those obtained by conventional gravimetric method. Two studies (Fairbairn and others, 1951, and Stevens and others, 1960) of the results of conventional analyses made by a number of laboratories show the range of results obtained for each constituent in two silicate rock samples. The Rapid methods described here provide data well within these ranges (Shapiro, 1959).

Accuracy and precision of concentration ranges of elements determined by computerized spectrographic analyses of silicate rocks are at least equal to the visual semiquantitative spectrographic analysis previously used (50%, -33%) (W. W. Helz, F. G. Walthall, and S. Berman, 1969).

A routine analysis includes all elements listed in Table 6 with limits. Values obtained by visual methods are supplied when possible for those listed above without limits. The standard deviation of any single answer is taken as plus 50 per cent, and minus 33 per cent. Third

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Oxide Formulas (Majors)	Concentration Limits (%)	Element	Limits (ppm)	Element	Limits (p	(unde	Element	Limits	(mqq)
S102	0.0068 - 73.4	BE	1.00 - 147	11	31.6 - 4	6,400	NS	3.16 -	215
AL203	0.0597 - 59.7	18	1.00 - 2150	3	3.16 -	464	SR	0.46 - 1	464,000
FE203	0.0723 - 33.6	8	14.7 - 681	W	1.00 - 46	4,000	TA	147 -	10,000
MGO	0.0036 - 49.7	CE	20.0 - 4310	MO	1.00 -	1,000	TB	14.7 -	1,000
CAO	0.0953 - 44.2	8	1.00 - 215	NB	2.15 -	1,000	TE	316 -	10,000
NA20	0.0063 - 9.18	CR	1.00 - 6810	QN	14.7 -	464	TH	21.5 -	6810
K20	0.0820 - 12.0	S	3160 -46,400	IN	1.00 -	1,000	71	3.16 -	6810
T102	0.0007 - 11.4	CG	1.00 - 1000	SO	1.00 -	1470	ML	3.16 -	147
P205	0.106 - 10.6	DY	3.16 - 1000	PB	1.00 -	1000	D	215 -	10,000
ONW	0.0001 - 60.0	ER	2.15 - 1000	DA	0.22 -	68.1	٨	1.47 -	215
		Eu	1.00 - 1000	PR	2.15 -	1000	м	10.0	4640
Element		5	2.15 - 1000	ΡT	6.81 -	1000	Y	3.16 -	464
Symbol	Concentration	8	3.16 - 1000	RB	681 - 10	000,000	ΥB	0.68 -	14.1
(Traces)	Limits (ppm)	ម	1.00 - 681	RE	10.0 -	681	NZ	14.7 -	3160
		ŦĦ	10.0 - 6810	RH	0.00 -	147	ZR	3.16 -	681
AG	0.10 - 10.0	ĐH	ı	RU	0.46 -	1470	Symbols Used in R	kepor t	
AS	100 - 10,000	đĦ	1.00 - 147	SB	68.1 -	3160 <	Less Than Lower L	.imit (4)	
AU	6.81 - 1000	NI	4.64 - 147	SC	1.00 -	68.1 >	Greater Than Uppe	er Limit (4)	
B	10.0 - 215	IR	6.81 - 2150	SE		H	Note 5		
BA	1.00 - 2150	Ŀ	14.7 - 1470	SM	4.64 -	1000	Note 6		

Notes:

A routine analysis includes all elements listed above with limits. Values obtained by visual methods are supplied, when possible, for those listed above without limits.
 The standard deviation of any single answer should be taken as plus 50 per cent, and minus 33 per cent. Of true value (accuracy) also

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Third significant figures, when reported, appear solely for programming convenience. The above limits apply under ideal conditions. In some cases interferences will narrow the limits. H denotes interference for an element which cannot be resolved by any routine method. An asterisk denotes a sample weight other than 15 mg was used. All answer were then adjusted by the appropriate multiple.

significant figures, when reported, appear solely for programming convenience.

The results of the analyses of 149 samples and 682 comparisons are summarized in Table 7 (A. T. Myers, R. G. Havens, and P. J. Dunton, 1961). These comparisons show that 69.3 per cent of the semiquantitative results included the quantitative results within the reported one-third order of magnitude. The per cent missed by one-third of an order is 29.9 per cent, while only 0.7 per cent is missed by more than one-third of an order. These results are shown graphically in Fig. 13. A diagonal line is drawn through the squares in which the results of the two methods are in the same order of magnitude. There are 133 misses by one-third of an order above the quantitative value. This small positive bias has not been resolved.

The samples used for the data were selected to show the effects on accuracy and precision caused by various factors within the method. Several years of experience in applying this method to many routine determinations indicate that similar precision and accuracy are obtained for all the elements included in this procedure, that is, the assigned one-third order of magnitude includes the quantitative value at least 60 per cent of the time.

Tables 8 and 9 show the analytical data for Ag, Co, Mn, Mo, Ni, Pb, U, V, and Zn in 30 samples of veins and mineralized metamorphic rocks, and compares the semiquantitative one-third of an order results with quantitative

Element	Agreement Within 1/3 Order	Miss by 1/3-Order	Miss by 2/3-Order	Miss by 1-Order	Total Number of Comparison
	30 samples of	veins and m	ineralized m	etamorphic	rocks
Ag	41.7	45.8	8.3	4.2	24
Co	80.0	20.0	0	0	15
Cu	73.3	26.7	0	0	30
Mn	56.7	43.3	0	0	30
Mo	66.7	33.3	0	0	30
Ni	73.3	23.3	3.3	0	30
Pb	66.7	30.0	3.3	0	30
U	85.2	14.8	0	0	27
v	66.7	33.3	0	0	30
Zn	61.1	38.9	0	0	18
Average	67.1	30.9			
Total					264
8 sa	mples of igne	ous minerals	and 2 sampl	es of igne	ous rocks
Co	68.3	31.7	0	0	60
Cr	80.4	19.6	0	0	56
Mn	78.1	21.9	0	0	64
Ni	51.7	48.3	0	0	60
Ti	70.3	29.7	0	0	64
Average	69.8	30.2			
Total					304
	104 sampl	es of soils	from the Mal	achite min	e
Cu	75	25	0	0	104
	5 sampl	es of low-gra	ade thorium	type ores	
Th	60	40	0	0	10

TABLE 7.--Comparisons of the Results of the Analyses of 149 Samples and 682 Comparisons.



Figure 13. Comparison of semiquantitative spectrochemical results with chemical and spectrochemical quantitative results. Elements determined: Ag, Co, Cr, Cu, Mo, Mo, Ni, Pb, Th, Ti, U, V, and Z. Source of samples analyzed veins, mineralized metamorphic rocks, igneouis minerals, and soils. Total number of paired results, 682 in agreement, 478; missed by onethird, 204; missed by more than one-third order, 5.

	Ag		Co		Cu		м	In	Mo	
Sample	Fire Assay	Spectro- Chemi- cal ²	Wet Chemi- cal ²	Spectro- Chemi- cal ²	Wet Chemi- cal4	Spectro- Chemi- cal ²	Wet Chemi- cal ¹	Spectro- Chemi- cal ²	Wet Chemi- cal ³	Spectro- Chemi- cal ²
1	0.00014	0.00015	<0.005	0.003	0.03	0.03	0.15	0.15	0.04	0.07
2	.00054	.0015	<.005	.007	.15	.15	.20	.3	.22	.3
3	.00014	.0015	<.005	.003	.14	.15	.17	.3	.038	.03
4		0	<.005	.003	.0095	.015	1.80	3.	.018	.015
5	.0046	.007	.018	.015	.15	.15	.63	.7	.60	.7
6		.0003	<.005	.007	.02	.015	1.45	1.5	.060	.07
7	.0014	.0015	<.005	.007	.09	.07	. 56	.7	.18	.15
8	.00008	.0015	<.005	.007	.08	.07	.50	.7	.072	.07
9	Tr.	Tr.	<.005	.003	.03	.03	4.12	3.	.062	.07
10	.00014	.0003	<.005	.003	.03	.03	. 59	.7	.060	.07
11	.0062	.007	.017	.015	.87	1.5	.08	.15	.56	.7
12	.0042	.007	.008	.015	.14	.15	.10	.07	.43	.3
13	.00014	.0007	<.005	.003	.11	.15	.05	.07	.04	.03
14	.0015	.003	.012	.015	.19	.3	.08	.15	.14	.15
15		Tr.	<.005	.003	.03	.03	.12	.15	.006	.007
16	.0062	.007	.021	.015	.23	.3	.09	.15	.31	.7
17	.0048	.007	.007	.015	.09	.15	.47	.7	.42	.7
18	Tr.	.0015	<.005	.003	.09	.07	1.8	3.	.058	.07
19	.0178	.015	.04	.03	1.07	1.5	.22	.15	.22	.3
20	Tr.	.0015	<.005	.007	. 22	.3	.09	.15	.054	.15
21	.0056	.015	.018	.015	.95	1.5	.12	.13	.21	.3
22	.0095	.015	.016	.015	.62	.7	.05	.07	.15	.3
23	.0012	.003	.006	.007	.46	.7	.02	.03	.07	.15
24	.0120	.015	.016	.015	1.16	1.5	.04	.03	.22	.3
25	.0241	.015	.05	.03	.89	1.5	.21	.3	.84	.7
26	.0036	.007	.012	.015	. 32	.3	.28	.3	.17	.15
27	.00068	.003	<.005	.007	.10	.15	.18	.15	.092	.15
28	.0031	.003	.013	.015	.16	.15	.58	.7	.14	.3
29	.0016	.003	<.005	.007	.43	.7	.41	.3	.17	.3
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TABLE 8.--Comparison of Semiquantitative Spectrochemical Results With Quantitative Results by Other Methods for 10 Elements in 80 Samples of Vein Material and Mineralized Metamorphic Rocks From the Front Range, Colorado.

¹Analyst, D. L. Skinner. ²Analyst, N. M. Conklin.

³Analysts, R. F. Dufour and Claude Huffman, Jr.

⁴Analyst, W. D. Goss.

TABLE 8.--Continued.

Ni		i	P	מי		U		7	Zn		
Sample	Wet Chemi- cal ³	Spectro- Chemi- cal ²	Wet Chemi- cal4	Spectro- Chemi- cal ²	Wet Chemi- cal ⁴	Spectro- Chemi- cal ²	Wet Chemi- cal ³	Spectro- Chemi- cal ²	Wet Chemi- cal ⁷	Spectro- Chemi- cal ²	
1	0.0065	0.007	0.10	0.07	0.63	0.7	0.02	0.015	0.013	<0.03	
2	.010	.015	.46	.7	. 58	.7	.03	.07	.014	<.03	
3	.0075	.007	.06	.07	.26	.3	.03	.03	.012	<.03	
4	.0065	.007	.009	.007	.017	<.07	.03	.01	.020	Tr.	
5	.006	.03	.81	.3	5.57	7.	.03	.07	.086	.07	
6	.002	.007	.21	.15	. 33	.3	.04	.05	.030	<.03	
7	.011	.007	.23	.3	.58	.3	.08	.03	.030	<.03	
8	.0075	.007	.08	.07	.56	.7	.03	.03	.023	<.03	
9	.0085	.003	.05	.015	.067	.07	.02	.015	.019	<.03	
10	.008	.007	.07	.03	.684	.07	.04	.03	.022	<.03	
11	.022	.03	1.05	1.5	.79	.7	.03	.03	.19	.07	
12	.011	.015	.46	.7	1.95	1.5	.02	.03	.056	.03	
13	.0065	.007	.11	.07	.033	.07	.01	.015	.062	.03	
14	.016	.015	.63	.7	.72	.7	.02	.015	.16	.15	
15	.009	.007	.03	.03	.009	<.07	.02	.015	.11	.07	
16	.039	.03	.73	.7	1.59	1.5	.03	.03	.068	.07	
17	.022	.03	.69	.3	4.59	7.	.03	.03	.020	<.03	
18	.009	.007	.13	.07	.50	.3	.03	.03	.046	Tr.	
19	.035	.03	.62	.7	3.61	3.	.05	.07	.11	.07	
20	.0085	.015	.06	.07	.28	.3	.03	.03	.044	.03	
21	.018	.015	. 29	.3	. 58	.7	.03	.03	.092	.07	
22	.018	.03	. 37	.7	1.15	1.5	.02	.03	.052	.07	
23	.014	.015	.08	.15	.11	.15	.02	.03	.076	.07	
24	.016	.015	.70	.7	2.79	3.	.03	.03	.089	.07	
25	.053	.07	.60	.7	3.70	3.	.08	.07	.10	.03	
26	.017	.015	.16	.3	1.11	.7	.04	.03	.045	Tr.	
27	.009	.007	.10	.15	.29	.3	.03	.03	.041	.03	
28	.016	.015	. 28	.3	2.49	3.	.05	.03	.16	.07	
29	.019	.03	.73	.7	1.37	1.5	.03	.03	.16	.15	
30	.011	.07	1.45	1.5	6.36	7.	.06	.07	.084	.07	

⁵Analysts, H. M. Nakacawa and C. E. Thompson. ⁶Analysts, H. H. Lipp, J. P. Schuch, and J. S. Wahlberg.

7 Analyst, J. S. Wahlberg.

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chemical results. The author compared the emission spectrographic results of Co, Mn, Pb, and Zn of the Caldwell sill with the above analysis by A. T. Myers, R. G. Havens, and P. J. Dunton (1961). Comparisons were close enough to say that they fall within the same order of magnitude.

In Table 9, the author reports a series of numbers reported (per cent) as compared with limits of concentration defined by standard (per cent).

Error bars have been plotted at analytical points to show that the standard deviation for every single answer is taken as +50 per cent, and -33 per cent.
Number Reported (Per Cent)	Limits of Concentration Defined by Standards (Per Cent)		
7	10	- 4	1.6
3	4.6	- 2	2.2
1.5	2.2	-]	L.O
.7	1.0	-	.46
.3	.46	-	.22
.15	.22	-	.10
.07	.10	-	.046
.03	.046	-	.022
.015	.022	-	.010
.007	.010	-	.0046
.003	.0046	-	.0022
.0015	.0022	-	.0010
.0007	.0010	-	.00046
.0003	.00046	-	.00022
.00015	.00022	-	.00010

TABLE 9.--Concentration Ranges of Reported Semiquantitative Spectrographic Results Based on One-Third Order of Magnitude.

Note: In addition to the above the following symbols are used in reporting results: M: major constituent greater than 10 per cent. Tr: barely detected and concentration uncertain. O: looked for but not found (for limits of detection see Table 2). -: not looked for. < with number: less than number shown; here standard detectabilities do not apply. .

CONCLUSION

Differentiation in the Logan sills, Palisades sill and other similar sills led to an enrichment in iron. The Caldwell sill shows a trend towards alkali enrichment. This sill represents the close of magmatic differentiation, characterized by an enrichment in alkalies and silica and a deficiency in magnesium, calcium, iron, and aluminum.

The author therefore concludes that these rocks are a result of the last residue of a basaltic magma differentiate which have been extremely altered deuterically by water-rich fluids.



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APPENDIX

APPENDIX

Analytical Procedures

Rapid Method Analysis

The methods described here are those that are currently in use by the U.S. Geological Survey for rapid rock analysis. They are an outgrowth of the scheme of analysis originally presented by Shapiro and Brannock (1952) and revised by Shapiro and Brannock (1956). Since 1956 approximately 800 samples per year have been analyzed. During this period the methods for analyzing silicate rocks have been modified and extended to include methods for carbonate and phosphate rocks.

Provision is made for the determination of SiO_2 , Al₂O₃, total iron, FeO, MgO, CaO, TiO₂, MnO, P₂O₅, K₂O, Na₂), H₂O, CO₂, F, and S. The complete scheme for the analysis of silicate, carbonate and phosphate rocks is shown by the flow diagram in Fig. 14.

Silica and Alumina were determined spectrophotometrically on alliquots of a solution prepared by fusing the sample with NaOH; a molybdenum blue method was used for SiO₂; and alizarin red-S was used in the determination of Al₂O₃. A second portion of the sample was digested



Figure 14. Schematic diagram for the rapid analysis of rocks.

with $HF - H_2SO_4 - HNO_3$ in teflon beakers. This solution was used for the photometric determination of total iron with orthophenathroline, TiO_2 with tiron, P_2O_5 with molybdivanadophosphoric acid, MnO as permanganate after a persulfate oxidation, and low-level MgO with thiazol yellow. Automatic photometric titrations were used for CaO, MgO, and CaO-MgO. Flame photometry was used for Na₂O and K₂O. Separate portions of samples were used for the determination of FeO by titration with $K_2Cr_2O_7$ after decomposition with HF and H_2SO_4 ; H_2O by its weight when evolved by heating a mixture of sample plus flux; CO_2 by evolution with acid, high or low levels of CO_2 being measured either by change in volume upon alkaline absorption or by direct volume measurement.

Spectrographic Analysis

The methods described here are those that are currently in use by the U.S.G.S. for analytical work.

15mg. of sample plus 30mg. of graphite were mixed throughly in order to make the burn smooth. The mixed samples were placed in carbon electrodes. Carbon electrode was used because of its capability in determining all elements. The elements were raised to an excited state and as they were returning to ground state, mostly ultraviolet light was given off. This light was dispersed by grating into component wave lengths which were recorded on a photographic plate. Atmosphere was used instead to prevent the combination of C and N which gives cyanogen bands that make the wave length area 3500-4200A not useable. Ar/O_2 enhances sensitivity of some elements and gives detectability for others. The wavelength of light (line) gave which element was present and the darkness of the line proportional to concentration compared your plate to standards of known concentrations.

The advantages of this method is that small amount of sample is used, and many trace elements of low levels are detected.

Computer Analysis of Photographed Optical Emission Spectra

A recording system and computer were used for the complete spectrochemical analysis of the photographed spectra. Transmission values were taken at equal intervals of travel along the spectrum. These values were transferred to a magnetic tape with high precision, high speed, and in a form suitable for computer processing. This processing included wave length determination, line identification, and plate calibration.

A microphotometer moves the spectrum through a scanning beam at a velocity of 5mm per sec. At 5µ intervals of distance traveled, the analog photomultiplier output is digitized and stored in a buffer. When a predetermined number of readings have accumulated, they are transferred to a magnetic tape as a group without interrupting incoming readings. The number of the reading (not recorded) determines the wave length coordinate. Transmission values are recorded in three digits.

Computer line finding starts with a known strong line and an approximate value of dispersion. The position of the line in the spectrum expressed as a reading number is determined automatically and is stored with the related transmission value.

Lines for chemical analysis are found by the computer using a wavelength list of such lines. An IBM 360-65 computer was used in this work with Fortran 1V language.

