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OF TERRESTRIAL STRONTIUM.

The Ohio State University, Ph.D., 1969
Geology

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THE EVOLUTION OF THE ISOTOPE COMPOSITION
OF TERRESTRIAL STRONTIUM

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Michael Dwight Fenton, B.S., M.S.

* * * * * *

The Ohio State University
1969

Approved by

[Signature]
Adviser
Department of Geology
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PUBLICATIONS


Fenton, M.D. and Faure, C., 1969, The age of the igneous rocks of the Stillwater Complex of Montana: Bull. Geol. Soc. of America, v. 80, no. 8
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>11</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>ILLUSTRATIONS</td>
<td>vii</td>
</tr>
<tr>
<td>TABLES</td>
<td>ix</td>
</tr>
</tbody>
</table>

## Chapter

<p>| I. INTRODUCTION | 1 |
| II. RUBIDIUM-STRONTIUM WHOLE-ROCK METHOD OF GEOCHRONOMETRY | 3 |
| III. COLLECTION OF SAMPLES AND ANALYTICAL TECHNIQUES | 6 |
| Collection of Samples | 6 |
| Sample Preparation | 7 |
| Analysis of Strontium Isotope Ratios | 9 |
| Analysis of the Rubidium and Strontium Concentration | 10 |
| IV. OCEANIC AND CONTINENTAL MAFIC IGNEOUS ROCK | 18 |
| Introduction | 18 |
| Skaergaard Intrusion, Greenland | 30 |
| Stillwater Complex, Montana | 39 |
| Bushveld Complex, South Africa | 48 |
| Great Dyke, Southern Rhodesia | 58 |
| Deccan Plateau Basalt, India | 62 |
| Columbia River Basalt, Oregon | 67 |
| Summary | 71 |
| V. ALKALIC IGNEOUS COMPLEXES AND ASSOCIATED CARBONATITES | 72 |</p>
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>72</td>
</tr>
<tr>
<td>Iron Hill Complex, Colorado</td>
<td>84</td>
</tr>
<tr>
<td>McClure Mountain Complex, Colorado</td>
<td>98</td>
</tr>
<tr>
<td>Rainy Creek Complex, Montana</td>
<td>106</td>
</tr>
<tr>
<td>Port Coldwell Complex, Ontario</td>
<td>112</td>
</tr>
<tr>
<td>Summary</td>
<td>119</td>
</tr>
<tr>
<td>VI. THE ISOTOPIC COMPOSITION OF STRONTIUM IN</td>
<td></td>
</tr>
<tr>
<td>CARBONATE ROCKS</td>
<td>120</td>
</tr>
<tr>
<td>Introduction</td>
<td>120</td>
</tr>
<tr>
<td>The Casper Formation, Wyoming</td>
<td>129</td>
</tr>
<tr>
<td>The Carbonate Rocks of the Belt Series,</td>
<td>135</td>
</tr>
<tr>
<td>Montana</td>
<td>135</td>
</tr>
<tr>
<td>The Bulawayan Limestone, Southern Rhodesia</td>
<td>138</td>
</tr>
<tr>
<td>Conclusions</td>
<td>140</td>
</tr>
<tr>
<td>VII. THE EVOLUTION OF THE MANTLE AND THE</td>
<td></td>
</tr>
<tr>
<td>CONTINENTAL CRUST</td>
<td>142</td>
</tr>
<tr>
<td>VIII. CONCLUSIONS</td>
<td>158</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>159</td>
</tr>
<tr>
<td>Figure</td>
<td>Illustration Title</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------</td>
</tr>
<tr>
<td>1.</td>
<td>Distribution of Tertiary basalt and the location of the Skaergaard Intrusion, East Greenland</td>
</tr>
<tr>
<td>2.</td>
<td>Cross section of the Skaergaard Intrusion, Greenland</td>
</tr>
<tr>
<td>3.</td>
<td>Cryptic layering in the Layered Series, Skaergaard Intrusion, Greenland</td>
</tr>
<tr>
<td>4.</td>
<td>Geologic map of the Stillwater Complex, Montana</td>
</tr>
<tr>
<td>5.</td>
<td>Rb-Sr isochron for the Stillwater Complex, Montana</td>
</tr>
<tr>
<td>6.</td>
<td>Geologic map of the Bushveld Complex, South Africa</td>
</tr>
<tr>
<td>7.</td>
<td>Cryptic layering in the Bushveld Complex, South Africa</td>
</tr>
<tr>
<td>8.</td>
<td>Geologic map of the Great Dyke, Southern Rhodesia</td>
</tr>
<tr>
<td>9.</td>
<td>The distribution of Deccan Plateau Basalt, India</td>
</tr>
<tr>
<td>10.</td>
<td>The distribution of Columbia River Basalt, Oregon and Washington</td>
</tr>
<tr>
<td>11.</td>
<td>The Kapuskasing Gravity High, Ontario</td>
</tr>
<tr>
<td>12.</td>
<td>Geologic map of the Powderhorn District, Gunnison County, Colorado</td>
</tr>
<tr>
<td>13.</td>
<td>Geologic map of the Iron Hill Complex, Colorado</td>
</tr>
<tr>
<td>14.</td>
<td>Rb-Sr isochron for the Iron Hill Complex, Colorado</td>
</tr>
<tr>
<td>15.</td>
<td>Geologic map of the McClure Mountain Complex, Colorado</td>
</tr>
</tbody>
</table>

vii
<table>
<thead>
<tr>
<th>Figure</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.</td>
<td>Rb-Sr isochron for the McClure Mountain Complex, Colorado</td>
<td>104</td>
</tr>
<tr>
<td>17.</td>
<td>Geologic map of the Rainy Creek Complex, Montana</td>
<td>107</td>
</tr>
<tr>
<td>18.</td>
<td>Rb-Sr isochron for the Rainy Creek Complex, Montana</td>
<td>111</td>
</tr>
<tr>
<td>19.</td>
<td>Rb-Sr isochron for the Port Coldwell Complex, Ontario</td>
<td>117</td>
</tr>
<tr>
<td>20.</td>
<td>Isotopic composition of strontium in water solutions of limestone of</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>the Casper Formation</td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td>Isotopic composition of strontium in hydrochloric acid solutions of</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>limestone of the Casper Formation</td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>The evolution of the isotopic composition of strontium in the Upper</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>Mantle</td>
<td></td>
</tr>
<tr>
<td>23.</td>
<td>The evolution of the isotopic composition of strontium in the Upper</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>Mantle and the Crust of the Earth</td>
<td></td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>1. Analyses of SrCO$_3$ standard</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>2. Sr$^{86}$ spike isotope abundances</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>3. Calibrations of Sr$^{86}$ spike solutions</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>4. Rb$^{87}$ spike isotope abundances</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>5. Calibrations of Rb$^{87}$ spike solutions</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>6. Rb-Sr data on G-1 and W-1</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>7. Rb-Sr blank measurements</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>8. Rb-Sr analytical data for the Skaergaard Intrusion, Greenland</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>9. Modal analyses, Stillwater Complex, Montana</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>10. Rb-Sr analytical data, Stillwater Complex, Montana</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>11. Modal analyses of a gabbro, Bushveld Complex, South Africa</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>12. Rb-Sr analytical data, Bushveld Complex, South Africa</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>13. Rb-Sr analytical data, Great Dyke, Southern Rhodesia</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>14. Rb-Sr analytical data, Deccan Plateau, India</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>15. Rb-Sr analytical data, Columbia River basalt, Oregon</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>16. Modal analyses, Iron Hill Complex, Colorado</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>17. Rb-Sr analytical data, Iron Hill Complex, Colorado</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>18. Modal analyses, McClure Mountain Complex, Colorado</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>19. Rb-Sr analytical data, McClure Mountain Complex, Colorado</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>20. Modal analyses, Rainy Creek Complex, Montana</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>21. Rb-Sr analytical data, Rainy Creek Complex, Montana</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>22. Modal analyses, Port Coldwell Complex, Canada</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>23. Rb-Sr analytical data, Port Coldwell Complex, Canada</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>24. The isotopic composition of strontium in Phanerozoic sea water</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>25. Isotopic composition of strontium in water solution of carbonate rocks</td>
<td>133</td>
<td></td>
</tr>
<tr>
<td>26. Isotopic composition of strontium in hydrochloric acid solution of carbonate rocks</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>27. Ages and initial Sr$^{87}$/Sr$^{86}$ ratios of mafic-ultramafic intrusions, plateau basalts, and alkaline intrusions</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>28. Ages and Sr$^{87}$/Sr$^{86}$ ratios of marine and continental carbonate rocks</td>
<td>153</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Geochemical models based on observations of the evolution of lead and strontium isotopes in crustal rocks have been devised to determine the history of differentiation in the upper mantle and consequent formation of the continents. There are two alternatives: Major differentiation of the mantle may have occurred early in the earth's history and the continents may have formed within a short time-span with little subsequent growth. Alternately, differentiation may have been a continuous process within the upper mantle during the past 4.5 billion years.

As a contribution to an understanding of the earth's history, it is proposed to document the change in the \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio of the upper mantle and the surface of the earth as a function of geologic time. The evolution of radiogenic \( \text{Sr}^{87} \) in the upper mantle can be documented by measuring the strontium-isotope composition of igneous rocks of different ages whose magmas can be reasonably assumed to have originated in the upper mantle.

It is assumed that strontium isotopes are not fractionated during partial melting of upper mantle rock and
contamination by assimilation of crustal rock is minimal. Large, layered mafic-ultramafic intrusions, plateau basalts, and carbonatite-alkalic igneous complexes have been chosen for analysis. In a similar fashion, the change in the strontium-isotope composition of the earth's surface can be measured by analyzing the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of marine and non-marine carbonate rocks of different ages.
CHAPTER II
RUBIDIUM-STRONTIUM WHOLE-ROCK METHOD
OF GEOCHRONOMETRY

The Rb-Sr method of geochronometry is based on the spontaneous decay of naturally-occurring Rb$^{87}$ to stable Sr$^{87}$ by beta emission at a constant rate of $1.39 \times 10^{-11}$ per year (Aldrich et al., 1956). Since Rb$^{87}$ is continually decaying the abundance of Sr$^{87}$ increases with time. In any rock sample, the present-day Sr$^{87}$ abundance is a result of the initial abundance at the time the rock became a closed system, the age of the rock, and the present Rb/Sr ratio of the rock. The abundance of Sr$^{87}$ is generally expressed as a ratio relative to the similarly abundant isotope Sr$^{86}$. Therefore, the Sr$^{87}$/Sr$^{86}$ ratio of a system is a function of time, its Rb/Sr ratio, and the initial Sr$^{87}$/Sr$^{86}$ ratio.

The fundamental law of radioactive decay, the basis of the Rb-Sr method of geochronometry, states that the number of atoms, N, disintegrating per unit time, t, is proportional to the number of radioactive atoms present. This may be expressed as:

$$-\frac{dN}{dt} = \lambda N$$  (1)
where $\lambda$ is the decay constant, and on integration from $t_0$ to $t$, equation (1) gives:

$$N = N_0 e^{-\lambda t}$$  \hspace{1cm} (2)

where $N_0$ is the number of atoms present at $t = 0$ (i.e. when the system became closed).

Since $N_0$ is not known, equation (2) must be rewritten in terms of radiogenic daughter products present at time $t$. These daughter atoms, $^aD$, equal the number of disintegrated parent atoms,

$$^aD = N_0 - N$$

By substitution, equation (2) becomes:

$$^aD = N(e^{\lambda t} - 1)$$  \hspace{1cm} (3)

In practice, the quantity of daughter products measured in any sample is a combination of radiogenic atoms, $^aD$, and non-radiogenic atoms, $D_0$, produced at the time of element synthesis and initially present in the sample, so that

$$D_{total \, measured} = D_0 + ^aD.$$  

Therefore, equation (3) must be expanded to account for the initial daughter atoms to give

$$D_{total} = D_0 + N(e^{\lambda t} - 1).$$  \hspace{1cm} (4)
for each of the rocks. The age of the suite of rocks is computed by using equation (5) with variables taken from the isochron.

Age determinations for the igneous complexes discussed in this report were made using a value of $1.39 \times 10^{-11}$ yr.$^{-1}$ for the decay constant of Rb$^{87}$, which was derived originally by Aldrich et al. (1956). The slopes and zero intercepts of the best straight lines were calculated by regression of $x$ on $y$ and $y$ on $x$. The error estimates of the ages were calculated from one standard deviation of the estimated slopes of the isochrons.
CHAPTER III

COLLECTION OF SAMPLES AND ANALYTICAL TECHNIQUES

Collection of Samples

The most important consideration in selecting igneous complexes and limestone formations suitable for this geochemical study was that their geologic histories should be reasonably well-established by previous field and laboratory studies. In addition, the selection depended on the availability of samples and the accessibility of localities to the author.

The following alkalic complexes with associated carbonatites were selected: (1) Iron Hill, Gunnison Co., Colorado; (2) McClure Mountain, Fremont Co., Colorado; (3) Rainy Creek Complex, Lincoln Co., Montana; and (4) Port Coldwell Complex, Ontario, Canada. With the exception of the Port Coldwell Complex, these intrusions were sampled by the author during the summer of 1967. Rock samples from Port Coldwell were collected by Dr. O. Faure in 1962 and by Dr. S. Chaudhuri in 1969.

The mafic and ultramafic rocks used in this study are from (1) the Skaergaard Intrusion, Greenland; (2) the Bushveld Complex, Republic of South Africa; (3) the
Stillwater Complex, Montana; (4) the Great Dyke, Southern Rhodesia; (5) the Deccan Plateau, India; and (6) the Columbia River Plateau, Oregon and Washington. These samples were taken from the collections of the Laboratory for Isotope Geology and Geochemistry of the Geology Department, The Ohio State University.

In 1967, the author also collected limestones from the Pennsylvanian-Permian Casper Formation, Wyoming, and from the Precambrian Belt Series, Montana. Samples of the Bulawayan limestone were provided by Dr. J. M. Schopf, U. S. Geological Survey, The Ohio State University. Samples of the Transvaal limestone, Africa, were donated by Dr. S. R. Hart of the department of Terrestrial Magnetism, Carnegie Institution of Washington. Limestones from Antarctica and northern Michigan were provided by G. Faure.

Sample Preparation

A slab sawed from the unweathered portion of a silicate rock to be analyzed was pulverized in a steel mortar to a size of -140 mesh. A portion of the powder was dissolved overnight at a low temperature in a Teflon crucible in a solution of 15 ml. hydrofluoric acid and five ml. sulfuric acid. The residue was dissolved in about 20 ml. of 2N hydrochloric acid. This was then filtered and tagged with radioactive Sr\textsuperscript{89} tracer. The solution was placed in an
ion-exchange column containing Dowex 50W-X8 resin and eluted through the column with 2.25 N Vycor-distilled hydrochloric acid. During elution, the position of the strontium cations was monitored with a geiger counter and the strontium-fraction was collected in several 15 ml. beakers. Two 15 ml. fractions having the highest radioactivity were evaporated in a Vycor dish. The strontium chloride residue was transferred into a 5 ml. Vycor beaker with a small amount of hydrochloric acid and a few drops of perchloric acid were added in order to oxidize the resin. The contents of this beaker were dried and stored for later analysis on the mass spectrometer. The procedure for collecting rubidium was the same as for strontium except that the rubidium in the eluate was identified by a flame test, using a platinum wire. Reagent grade hydrochloric and nitric acids were distilled in Vycor glass and water was double-distilled and demineralized. All Teflon-, glass-, and plastic-ware were thoroughly soaked and rinsed in demineralized water and 2.25 N hydrochloric acid.

Samples of carbonatite were pulverized, dissolved in 2N hydrochloric acid in order to remove the carbonate fraction, and decanted from the Teflon crucibles. Fifteen ml. of hydrofluoric acid and five ml. of sulfuric
acid were used to dissolve the insoluble silicate residues. The residue and the decanted hydrochloric acid solution of each sample was thoroughly mixed in the crucible, evaporated to a 20 ml. volume, and filtered. Limestone powders were either dissolved in continuously agitated demineralized water or in hydrochloric acid of known normality. The procedure for separating strontium is the same as that described above.

The mass spectrometric analyses were made on a 6-inch radius, 60° sector, single-tantalum-filament, solid-source, Nier-type mass spectrometer (Nuclide Corp. Model 6-60-S). Operating pressures for strontium analyses varied from $4 \times 10^{-8}$ to $3 \times 10^{-7}$ mm. of mercury, while rubidium analyses were done at less than $5 \times 10^{-7}$ mm. of mercury pressure. In order to minimize the effect of irregular emission, the peaks recorded on the strip chart were summed in sets of six and the ratios were determined for each group. Generally 10 to 12 sets of peaks were averaged for a Sr$^{87}$/Sr$^{86}$ analysis. About six sets were adequate for a rubidium or strontium concentration analysis.

**Analysis of Strontium Isotope Ratios**

Isotopic fractionation occurs during sample emission as a result of mass differences between isotopes and, therefore, must be adjusted by an appropriate factor.
Since the $\text{Sr}^{86}/\text{Sr}^{88}$ ratio in natural strontium is believed to be constant at 0.1194, all measured $\text{Sr}^{87}/\text{Sr}^{86}$ ratios were multiplied by a factor, $f$, where

$$f = \frac{(\text{Sr}^{86}/\text{Sr}^{88})_{\text{measured}} + 0.1194}{2 \times 0.1194}$$

To determine the accuracy and reproducibility of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for a sample, replicate analyses were made of the Eimer and Amend SrCO$_3$ standard (Lot 492327). Nineteen measurements made on the mass spectrometer are listed in Table 1. These analyses have a corrected mean of 0.7083 $\pm$ .0010 (2 S.D.). In addition, 68 duplicate and triplicate analyses of 31 rock specimens were made during the course of this investigation. According to these data from the rock specimens, replicate analyses of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for the same rock sample made under similar conditions are expected to fall inside a zone of $\pm$ .0016 (2 S.D.) about the mean.

Analysis of the Rubidium and Strontium Concentration

All concentrations of rubidium and strontium were determined by isotope dilution. With this method, the quantity of an element is measured from the change produced in its isotopic composition by the addition of a known...
<table>
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<th>Date</th>
<th>( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} ) (corr.)</th>
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### TABLE 2
**Sr$^{88}$ SPIKE ISOTOPE ABUNDANCES**

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<td>0.97544</td>
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<td>0.01658</td>
<td>0.00658</td>
<td>0.97642</td>
<td>0.00015</td>
<td>O.S.U.</td>
</tr>
<tr>
<td>0.0173</td>
<td>0.0068</td>
<td>0.976</td>
<td>-0.0005</td>
<td>O.R.</td>
</tr>
</tbody>
</table>

### TABLE 3
**CALIBRATIONS OF Sr$^{86}$ SPIKE SOLUTIONS**

<table>
<thead>
<tr>
<th>Date</th>
<th>Sr Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/27/66</td>
<td>23.35 $\mu g/ml.$</td>
</tr>
<tr>
<td>3/3/66</td>
<td>23.54</td>
</tr>
<tr>
<td>7/14/66</td>
<td>23.61</td>
</tr>
<tr>
<td>1/5/67</td>
<td>23.52</td>
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<tr>
<td>5/20/67</td>
<td>23.93</td>
</tr>
<tr>
<td>5/25/67</td>
<td>24.01</td>
</tr>
<tr>
<td>6/1/67</td>
<td>23.68</td>
</tr>
<tr>
<td>6/17/67</td>
<td>23.85</td>
</tr>
<tr>
<td>6/23/67</td>
<td>24.14</td>
</tr>
<tr>
<td><strong>average:</strong></td>
<td><strong>23.74</strong></td>
</tr>
<tr>
<td>12/20/67</td>
<td>5.05 $\mu g/g.$</td>
</tr>
<tr>
<td>12/20/67</td>
<td>5.06</td>
</tr>
<tr>
<td><strong>average:</strong></td>
<td><strong>5.06</strong></td>
</tr>
<tr>
<td>3/28/68</td>
<td>5.085</td>
</tr>
<tr>
<td>3/29/68</td>
<td>5.062</td>
</tr>
<tr>
<td><strong>average:</strong></td>
<td><strong>5.073</strong></td>
</tr>
<tr>
<td>8/29/68</td>
<td>5.203</td>
</tr>
<tr>
<td>8/29/68</td>
<td>5.183</td>
</tr>
<tr>
<td>8/30/68</td>
<td>5.192</td>
</tr>
<tr>
<td><strong>average:</strong></td>
<td><strong>5.186</strong></td>
</tr>
</tbody>
</table>
quantity of a stable isotope of that element. For a strontium determination, a known quantity of spike solution enriched in Sr$^{86}$ is added to a solution containing a known quantity of the sample to be analyzed and a measurement of the resulting Sr$^{86}$/Sr$^{88}$ ratio is made. The equation is:

$$\frac{\text{Sr}^{86}}{\text{Sr}^{88}} = \frac{\text{Ab}_{N}^{86}N + \text{Ab}_{S}^{86}S}{\text{Ab}_{N}^{86}N + \text{Ab}_{S}^{86}S}$$

where

- $N =$ total number of Sr atoms in a known amount of of rock
- $S =$ total number of Sr atoms in the spike solution
- $\text{Ab}_{N}^{86}$ = abundances of the Sr$^{86}$ and Sr$^{88}$ in the rock
- $\text{Ab}_{N}^{88}$ = abundances of the Sr$^{86}$ and Sr$^{88}$ in the spike solution

The $N/S$ atomic ratio is converted into a weight ratio by multiplication with the ratio: (atomic weight of rock strontium/atomic weight of spike strontium). The weight ratio is then solved for $N$, the weight of strontium in the sample, by substituting the known value for $S$.

For rubidium analysis, the Rb$^{87}$/Rb$^{85}$ ratio is measured and applied to the same equation:
\[
\frac{\text{Rb}^{87}}{\text{Rb}^{85}} = \frac{\text{Ab}_N^{87N} + \text{Ab}_S^{87S}}{\text{Ab}_N^{85N} + \text{Ab}_S^{85S}}
\]

The calibration of a spike solution consists of the determination of both isotopic composition and its concentration. The isotopic composition of Sr\textsuperscript{86} spike (Oak Ridge Batch No. LH1368-A) was measured twice in this laboratory and the atomic abundances are compared with those determined at Oak Ridge in Table 2.

The concentration of the strontium spike solution was determined by isotope dilution, using a standard, or "shelf solution," of normal isotopic composition. This shelf solution was made from "spec-pure" strontium nitrate obtained from Johnson, Mathey, & Co., Ltd. The results of isotope dilution analyses and the average concentrations of the four Sr\textsuperscript{86} spikes used are listed in Table 3. The isotopic composition of Rb\textsuperscript{87} spike (Oak Ridge Batch No. LY1448-A) was measured in this laboratory and the atomic abundances are compared with those determined at Oak Ridge in Table 4. Two Rb\textsuperscript{87} spike solutions were used in this study. The concentrations of the rubidium spike solutions were measured by the isotope dilution method using a rubidium shelf solution of normal isotopic composition and of known concentration. The analyses and average concentrations for the two spike solutions are listed in Table
### TABLE 4

**Rb\(^{87}\)** SPIKE ISOTOPE ABUNDANCES

<table>
<thead>
<tr>
<th>Rb(^{87})</th>
<th>Rb(^{85})</th>
<th>Lab</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.99195</td>
<td>0.00805</td>
<td>O.S.U.</td>
</tr>
<tr>
<td>0.9916</td>
<td>0.0084</td>
<td>O.R.</td>
</tr>
</tbody>
</table>

### TABLE 5

**CALIBRATIONS OF Rb\(^{87}\)** SPIKE SOLUTIONS

<table>
<thead>
<tr>
<th>Date</th>
<th>Rb Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/21/67</td>
<td>1.166 μg/ml.</td>
</tr>
<tr>
<td>9/21/67</td>
<td>1.066</td>
</tr>
<tr>
<td></td>
<td>average: 1.112</td>
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<tr>
<td>8/30/68</td>
<td>5.167 μg/g.</td>
</tr>
<tr>
<td>8/31/68</td>
<td>5.251</td>
</tr>
<tr>
<td>11/1/68</td>
<td>5.134</td>
</tr>
<tr>
<td></td>
<td>average: 5.184</td>
</tr>
</tbody>
</table>
5. Prior to the start of this study, rubidium and strontium analyses were made on samples of G-1 and W-1 in order to check the accuracy of isotope dilution analyses and the spike calibrations (Table 6). These data agree closely with the values recommended by Fleischer (1969).

It is desirable to make a "blank" analysis for rubidium and strontium to establish the level of contamination, so that a correction may be made to rubidium and strontium determinations for rocks having very low concentrations of these elements. A blank analysis is made by the isotope dilution method, using the usual reagents, ion-exchange column, glass-ware, spike solutions, etc., except that no rock sample is added. The calculated rubidium or strontium concentration is, therefore, the amount of contamination which may be assumed to occur during all other isotope dilution analyses. Data for three strontium and three rubidium blank measurements made during this study are recorded in Table 7.
### TABLE 6

**Rb AND Sr CONCENTRATIONS IN G-1 AND W-1**

<table>
<thead>
<tr>
<th>Analyst</th>
<th>G-1</th>
<th>W-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Fleischer (1969) O.S.U.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb (ppm)</td>
<td>220.</td>
<td>22.</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>250.</td>
<td>180.</td>
</tr>
<tr>
<td>Rb/Sr</td>
<td>0.88</td>
<td>0.12</td>
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<tr>
<td>O.S.U.</td>
<td>215.8</td>
<td>21.6</td>
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<tr>
<td></td>
<td>248.8</td>
<td>191.8</td>
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<tr>
<td></td>
<td>0.86</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>216.5</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>254.8</td>
<td>187.8</td>
</tr>
</tbody>
</table>

### TABLE 7

**Rb AND Sr BLANK MEASUREMENTS**

<table>
<thead>
<tr>
<th>Date</th>
<th>Sr (µg/g)</th>
<th>Rb (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9/67</td>
<td>0.167</td>
<td>0.148</td>
</tr>
<tr>
<td>12/67</td>
<td></td>
<td>0.061</td>
</tr>
<tr>
<td>4/68</td>
<td>0.108</td>
<td>0.019</td>
</tr>
<tr>
<td>8/68</td>
<td>0.108</td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>0.128</td>
<td>0.076</td>
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</table>
CHAPTER IV

OCEANIC AND CONTINENTAL MAFIC IGNEOUS ROCKS

Introduction

Rocks from large, layered, mafic-ultramafic intrusions and from continental basalt plateaus have been chosen as representative of magmas derived from regions within the upper mantle. Evidence justifying this premise is reviewed below.

The primary source of basalt magma is perhaps most obvious in ocean basin environments, where the most direct evidence is the association of volcanic activity with earthquake swarms. An earthquake swarm is a sequence of shocks grouped in space and time with no one single principal event. Most such swarms are concentrated in areas of present or recent volcanism (Richter, 1958; Minikami, 1960). This relationship between volcanism and earthquakes is most impressively illustrated along the mid-oceanic ridge system. This system, first recognized as one of the major tectonic features of the world by Ewing and Heezen (1956), is a zone of intense seismic activity. Most of the earthquakes occur as swarms, have foci at shallow depths of less than 70 kilometers, and are narrowly confined to the ridge
crests or along transverse faults (Sykes, 1967). The discovery of linear magnetic anomalies parallel to the ridge crests (Vine and Matthews, 1963; Pitman and Heirtzler, 1966), when considered with these seismic data and other data in the fields of marine geology and geophysics, support the sea-floor-spreading hypothesis of Hess (1962) and Dietz (1961). It is now commonly accepted that the rifts extend into the upper mantle and serve as vertical, tabular conduits for rising basaltic magma.

A few days prior to eruptions of the volcano Kilauea on Hawaii, swarms of several thousand discrete earthquakes originate between 45 and 60 kilometers beneath the summit. The source of magma is presumed by Eaton and Murata (1960) to be at these depths. These authors have also estimated the minimum depth at which lava can enter the volcanic system and be forced to the summit by assigning densities to the basaltic lava column and to the various crustal layers in the Hawaiian region. In this manner, they found that the lava source regions must be from 39 to 57 kilometers below sea level. More recent seismic refraction and gravity data have led to an interpretation that supports the belief that the upper mantle below Kilauea and Mauna Loa volcanoes is tapped during eruptions. Major fault zones, passing through the Kilauea and Mauna Loa caldera regions in a northeasterly direction, have a total vertical
movement of 7.5 kilometers. These rift zones appear to be transcrustal and are closely related to fundamental processes of uplift and magma production in the upper mantle (Ryall and Bennett, 1968).

The spatial distribution of most deep-focus earthquakes shows a close correlation with island arc structures. Zones of intermediate and deep earthquake foci dip beneath the arcs at angles reaching 60 degrees and to depths of as much as 700 kilometers. The occurrence of deep-focus earthquakes indicates that materials as deep as 700 kilometers are involved in the development of island arcs (Sykes, 1966).

Seismic studies and field relationships of the various basalt types suggest that the zone of earthquake foci within the upper mantle is the primary source of the basaltic material that constitutes island arcs. Evidence suggestive of partial melting was reported by Gershkov (in Holmes, 1965, p. 951), who was unable to record S-waves originating beneath the Japanese or Aleutian arcs when the P-waves which did arrive had passed through the mantle at depths of 55 to 60 kilometers beneath the volcanic belt of Kamchatka and the Kurile Islands. The volcanic belt seemed to be underlain by pockets of molten rock, which allowed passage of P-waves but not of S-waves. On the basis of field relationships between alkali basalts, aluminum-rich
basalts, and tholeiites in Japan, Kuno (1960, 1959) suggested a definite link between the depth of earthquake foci and the basalt magma type. Green and others (1967), in basic agreement with Kuno, suggest that deep earthquake foci may be related to the upward movement of mantle material that eventually melts at higher levels to produce the various types of basalt. Alternaty, Oliver and Isacks (1967) have suggested that earthquake activity is directly related to the underthrusting of a rigid "lithosphere", having a thickness of as much as 200 kilometers, below the island arc system.

The source of continental basalts is much more difficult to determine. Numerous authors (Ross et al., 1954; Hess, 1955; Wilshire and Binns, 1961) have stressed the remarkable uniformity of composition of the ultramafic nodules, called lherzolites, found in undersaturated basalt. The mineral assemblage is olivine (Fo85-92), aluminous enstatite, aluminous chrome-diopside, and a minor amount of spinel (MgAl2O4 - rich). The world-wide occurrence of these nodules is strongly suggestive that there is an abundant source of ultramafic rock beneath both continents and ocean basins, such as in the upper mantle. An alternate explanation is that the xenoliths are crystal accumulates, products of differentiation of the basalts in which they are found.
It is possible that the lherzolite nodules are xenoliths from the upper mantle incorporated into a rising basalt. Comparison of the mineralogy and bulk chemical composition of lherzolite nodules with the chemical compositions of high temperature peridotite intrusion (Green, 1963, 1964) and with other peridotites (Green and Ringwood, 1963) demonstrates that the mineral assemblage of the lherzolite inclusions is unstable at high temperatures at upper crustal levels. Experimental work has shown the olivine-aluminous pyroxene-spinel assemblage to be stable at pressures greater than about eight kilobars at 1100°C. in compositions close to those of lherzolite nodules (Green and Ringwood, 1967). Also, the low CaO content of most orthopyroxenes (less than one percent) and of olivine (less than 0.1 percent) suggests temperatures less than volcanic temperatures, i.e., less than 1000°C, before inclusion into their host basalts (Green and Ringwood, 1967). In addition to the experimental evidence, the nodules commonly show cataclasis, dimensional or crystallographic orientation of minerals, and grainboundary recrystallization between clinopyroxene and spinel forming plagioclase, olivine, and chrome spinel aggregates. This evidence of internal disequilibrium suggests that the xenoliths were consolidated rocks prior to incorporation by the basalt (Den Tex, 1963; Green and Ringwood, 1967).
A Rb-Sr isotope study of lherzolite nodules and their host basalts from Massif Central, France does not support a genetic relationship between nodules and basalts. The nodules are depleted in rubidium and strontium and have high Sr$^{87}$/Sr$^{86}$ ratios relative to the host basalts (Leggo and Hutchison, 1968). Stueber and Murthy (1966), in a similar study, also found nodules to be depleted in rubidium and strontium relative to basalts. However, they were unable to show a difference in Sr$^{87}$/Sr$^{86}$ ratios between nodules and basalts. The nodules used by Stueber and Murthy included dunites and eclogites in addition to peridotites, and the authors do not indicate that any lherzolites were used.

Green et al. (1968) have noted that K/Th, K/U, Th/U, and lead isotopic ratios are distinctly different for lherzolite nodules and their enclosing basalts. The authors suggest that nodules and basalts are chemically distinct systems accidently brought into juxtaposition and that they have not attained chemical or mineralogical equilibrium.

Perhaps the depth of the source regions of basalt magma under continents may be estimated, if a reasonable estimate of the geothermal gradient can be made. Since basaltic material reaches the earth's surface almost
entirely as a liquid, the pressure-dependant liquidus curve can be projected until it intersects the geothermal curve. Unfortunately, estimates of the geothermal gradient vary widely, depending on the distribution of radioactive elements, the thermal conductivity values assumed, and the rock types presumed to be within the crust and upper mantle. Clark (1961) suggested that melting of basalt can occur at about 50 kilometers. On the other hand, some believe that the geothermal curve may not intersect the liquidus curve at any depth, because the adoption of a geothermal curve assumes that the sole mechanism of heat loss to the earth surface is conduction at a steady rate over hundreds of millions of years. Holmes (1965) showed that temperatures within the crust and upper mantle are hundreds of degrees below the melting temperatures of basalt. An elegant model of the temperature distribution in the upper mantle, devised earlier by Clark and Ringwood (1964), taking into account surface heat flow, heat production in the crust and mantle by radioactive elements, and thermal conductivity, showed that the temperature separation of the geothermal gradient from the melting curve to be greatest beneath the continents. A transfer of heat to overcome the temperature gap can not, therefore, be achieved by conduction alone and another mechanism, perhaps some form of mass transfer (convection), must be postulated.
Green and Ringwood (1967) envision a solid mass of peridotite rising diapirically from depths of 100 to 400 kilometers. The cause of the movement is attributed to gravitational instability, combined with a suitable combination of horizontal inhomogeneity and rheological properties. Stresses associated with earthquake activity are not essential as an initial triggering mechanism. Partial melting does not begin until the solid diapir, which is cooling adiabatically, rises to about 140 kilometers from the earth surface. Basaltic magma segregates when about 20 to 40 percent of the peridotite volume melts. It is their opinion, therefore, that the parent material of all basalts is peridotite of the upper mantle.

The problem of identifying the basalt which originated in the upper mantle was approached from a geochemical viewpoint by Faure and Hurley (1963). They proposed the hypothesis that the value of the initial Sr$^{87}$/Sr$^{86}$ ratio of igneous rocks at the time of crystallization can be used as a criterion for the origin of the material. If so, the mean initial Sr$^{87}$/Sr$^{86}$ ratio of young oceanic basalts, which are derived from the upper mantle, can be measured and used as a standard of comparison with the ratios measured for continental basalts. A compilation of 98 published initial ratios for basalts from 13 areas in the ocean basins gives a mean Sr$^{87}$/Sr$^{86}$ ratio of 0.7041 ±
0.0006 (1 S.D.). The mean initial Sr\textsuperscript{87}/Sr\textsuperscript{86} for 52 continental basalts from 12 areas is 0.7050 ± 0.0013 (1 S.D.). The means of the two types of basalt are not significantly different, but continental basalts have a much wider range of ratios. Continental basalts have ratios as high as 0.7116, whereas the highest ratio in this compilation for an oceanic basalt is 0.7060. (All ratios have been adjusted to a value of 0.7083 for the Elmer and Amend standard carbonate.) Apparently, ratios less than about 0.705 may indicate an upper mantle locally rich in radiogenic strontium, or they may be a result of contamination by assimilation of crustal rock.

Isotopic inhomogeneity within the upper mantle has been observed in oceanic and continental environments. Gast et al. (1964) found consistent differences in the initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratios for basalts of Gough Island (0.7045) and Ascension Island (0.7025). Manton and Leeman (1969) reported high initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratios averaging 0.707 for basalts of the eastern Snake River Plain, Idaho. High initial ratios there are attributed to inhomogeneity within the upper mantle rather than contamination because Hill and Pakiser (1966) reported the absence of the sialic crustal layer under the Snake River plain. Leggo and Hutchison (1968) reported ratios averaging 0.7038 for
basalts of central France which contain lherzolite xenoliths.

Despite the evidence suggesting that the upper mantle is isotopically homogeneous, the high initial Sr$^{87}/$Sr$^{86}$ ratios for continental basalts are most easily explained by some process of contamination of the magma as it rises through 30 to 40 kilometers of old sial, rich in radiogenic strontium. According to the model by Green and Ringwood (1967) for magma formation by fractional melting of the mantle, the initial source region of the rising peridotite diapir is much deeper than the point at which the earliest liquid forms by fractional melting. Since the chemical composition of the newly-formed liquid is dependent partially upon pressure (depth), and since crystals and liquid in the rising diapir remain in chemical equilibrium, the nature of the liquid will change continuously as pressure decreases. Therefore, the chemistry of the magma is not established until the magma separates from the crystal residue, which is generally below the M-Discontinuity.

Presumably, strontium isotopes are not fractionated during partial melting of the peridotite and the Sr$^{87}/$Sr$^{86}$ ratio for the newly formed liquid should equal that of the crystal residue, but there is the potentially serious problem of contamination of the liquid by strontium in the wall
rocks of different isotopic composition. Green and Ringwood (1967) discussed the process of contamination as it might occur at depths greater than 35 kilometers (below the M-Discontinuity). A rising magma may cool in two ways: (1) heat transfer by conduction to cooler wall rock without intermixing of material, and (2) by reaction with and/or solution of crystalline material incorporated into the magma. At shallower depth, the large temperature contrast between magma and wallrock should usually result in a chill zone that would isolate the magma and prevent contamination. At greater depths, where the temperature contrast is much less, solution of low-melting components in the wall rock peridotite might occur. The abundance of low-melting components, such as biotite, phlogopite, K-feldspar, is low, but these minerals are enriched in rubidium and radiogenic strontium, which are not easily accepted into the peridotite pyroxene and olivine. Therefore, a slowly rising and fractionating magma could be enriched in radiogenic Sr\(^{87}\) by selective absorption of low-melting minerals containing this isotope, but any wall-rock reaction will still reflect the Sr\(^{87}/Sr^{86}\) ratio of the upper mantle.

Wall-rock reaction within the continental crust may be negligible for slowly rising basalt magmas that reach the surface as lava flows or crystallize at depth in the crust to form layered complexes. First, the temperature
contrast between magma and sialic crust may cause a chill zone to form, thereby reducing the probability of contamination ever occurring. Second, the immense volumes of these magmas (Deccan: 700,000 Km³; Columbia and Snake River: 300,000 Km³; Holmes, 1965, p. 301) that have relatively high strontium concentrations tend to reduce the effects of contamination. Finally, in the lower crust, strontium-rich plagioclase is a stable mineral that will not readily release strontium into an invading magma (Green and Ringwood, 1967). Wallrock-reaction within the sialic crust is also thought to be minimal for carbonatite-alkaline complexes because of the rapid, explosive way that these magmas penetrate the crust.

Consideration of the various lines of evidence presented above has led to the premise adopted for this study that continental flood basalts, basaltic magmas which formed the mafic-ultramafic layered intrusions, and magmas which formed the alkaline complexes with their associated carbonatites were derived from material originating in the upper mantle. Although the possibility of contamination of the magma by assimilation of sialic rock can not be easily dismissed, it is assumed that the effects of contamination are negligible.
The Skaergaard Intrusion, one of a series of Tertiary plutonic complexes along 1000 kilometers of the east Greenland coast opposite Iceland, was discovered by L. R. Wager, when he was a member of the 1930 Danish East Greenland Expedition. Since then, he and W. A. Deer have studied the intrusion and published its original description (Wager and Deer, 1939). A review of the geology was subsequently published in *Layered Igneous Rocks* (Wager and Brown, 1967).

Along the coast of east Greenland, Cretaceous sedimentary rocks and Tertiary basalts and tuffs cover a metamorphic complex (Fig. 1). During early Tertiary time, the Skaergaard basaltic magma was emplaced and solidified. It was then injected by massive dike swarms which were feeders for the surface basalt flows. Soon after the eruptive activity occurred, about 52 million years ago (Hamilton, 1963), a major flexure developed at the edge of the continent with its axis parallel to the coast. As a result of the flexuring, the Skaergaard Intrusion was tilted and erosion has gradually exposed a vertical cross section of 2.4 kilometers.

Three major rock units have been delineated within the cone-shaped mass of the Skaergaard Intrusion (Fig. 2; Wager and Brown, 1967). These are the Layered Series surrounded by the Marginal and Upper Border groups. The
Figure 1. The distribution of Tertiary basalt and the location of the Skaergaard Intrusion, East Greenland (after Wager and Brown, 1967).
Figure 2. North-south cross section of the Skaergaard Intrusion showing its appearance prior to monoclinal folding (after Wager and Brown, 1967).
Marginal Border group consists of a fine-grained, massive chilled-zone at the outer edge and an inner series of layered rock dipping inwards at angles up to 70°. The Layered Series, surrounded by the Marginal Border group, now dips 15° to 30° to the south, but prior to the flexuring, the layers were nearly horizontal. The Upper Border group is distinguished from the Layered Series below by an abundance of country rock xenoliths and granophyre sheets. In addition, the anorthite concentrations of plagioclase increase in an upward direction, which is opposite to the trend in the Layered Series.

The Skaergaard Layered Series, like the other major igneous intrusions of basaltic parentage discussed in this report, has distinctive features that set it apart from other non-basaltic plutonic complexes. These are rhythmic layering, igneous lamination, and cryptic layering. Within the chamber, the magma cooled slowly and, as the appropriate temperatures of crystallization were reached, olivine, pyroxene, plagioclase, and other minerals crystallized and sank at rates determined by their densities. These minerals, which settled as deposits on the chamber floor, are called the cumulus crystals. The relative proportion of plagioclase and ferromagnesian crystals changes at different stratigraphic levels, giving a conspicuous color-banding to the rock. This texture is called rhythmic
layering. Quite often the rocks exhibit a crude fissility
due to the parallel arrangement of tabular plagioclase,
and occasionally pyroxene, crystals (Wager and Deer, 1939).
This texture, called igneous lamination, seems most preva-
 lent near the bottom of the Layered Series and near the
top of the Upper Border group. Currents in these regions
may have been considerably stronger, as the mass congealed,
and plastered successive sheets of crystals against the
walls surrounding the magma chamber.

Not readily apparent in the field is a hidden or
"cryptic", vertical variation in chemistry within the in-
trusion (Fig. 3). Toward the top of the Layered Series,
plagioclase is more sodic and pyroxenes and olivine are
increasingly iron-rich and magnesium-impoverished. Addi-
tionally, magnetite, apatite, quartz, and pyrrhotite ap-
ppear at different levels within the intrusion.

The initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the Skaergaard magma
at the time of solidification may be computed, if the pre-
sent $\text{Sr}^{87}/\text{Sr}^{86}$ ratio, the $\text{Rb}^{87}/\text{Sr}^{86}$ ratio, and the age of
a representative sample are known. For this purpose,
sample 4306 (O.S.U. No. R4887), a hortonolite ferrogabbro
from 1700 meters above the base of the Layered Series,
donated by R. W. Wager, was selected for analysis (Table
8). The weighted mean for three analyses of the $\text{Sr}^{87}/\text{Sr}^{86}$
ratio, in which each weight is the reciprocal of the
Figure 3. Cryptic layering in the Layered Series, Skaergaard Intrusion, Greenland. Continuous vertical lines indicate cumulus minerals. Broken vertical lines indicate intercumulus minerals. (After Wager and Brown, 1967)
<table>
<thead>
<tr>
<th>Metres</th>
<th>Plagioclase</th>
<th>Clinopyroxene</th>
<th>Inverted Nepheline</th>
<th>Olivine</th>
<th>Ilmenite</th>
<th>Magnetite</th>
<th>Apatite</th>
<th>Quartz and Micronemaitite</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>62</td>
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<tr>
<td>1000</td>
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<td>57</td>
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<td>2000</td>
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<td>45</td>
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<td>59</td>
<td>57</td>
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<td>2500</td>
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<td>27</td>
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<td>33</td>
<td>35</td>
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</tbody>
</table>
### TABLE 8

**Rb AND Sr ANALYTICAL DATA**

**SKAERGAARD INTRUSION, GREENLAND**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>$\frac{\text{Rb}^{87}}{\text{Sr}^{86}}$</th>
<th>$\frac{\text{Sr}^{87}}{\text{Sr}^{86}}$ (corr)</th>
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<tbody>
<tr>
<td>R4887</td>
<td>2.37</td>
<td>214.1</td>
<td>0.032</td>
<td>0.7056</td>
</tr>
<tr>
<td></td>
<td></td>
<td>215.3</td>
<td></td>
<td>0.7031</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7054</td>
</tr>
</tbody>
</table>
variance of the corresponding ratio, is 0.7043. Duplicate strontium analyses and one rubidium analysis give a Rb$^{87}$/Sr$^{86}$ ratio of 0.032. Assuming an age of 52 million years for the Skaergaard Intrusion (Hamilton, personal comm. in Wager and Brown, 1967), the initial Sr$^{87}$/Sr$^{86}$ ratio is 0.7043. The abundance of radiogenic Sr$^{87}$ has not increased significantly since the time of solidification because of the very low Rb$^{87}$/Sr$^{86}$ ratio.

Hamilton (1963) measured the Sr$^{87}$/Sr$^{86}$ ratios of nine rocks from the Layered Series. These ratios ranged from 0.7044 to 0.7089 and had a mean of 0.7065. One of the Layered Series rocks that he analyzed was a hortonolite ferrogabbro (E.G. 5181) collected 1800 meters from the base of the Layered Series. The mineralogy of E.G. 5181 is similar to that of R4887 and was collected 100 meters stratigraphically above the location of R4887. Sample E.G. 5181 has a Sr$^{87}$/Sr$^{86}$ ratio of 0.7079, that is 0.2 percent higher than the average of the Layered series. This suggests that the ratio 0.7043 for R4887 may be as much as 0.2 percent higher than the average for the Skaergaard magma at the time of solidification. The best estimate for the initial Sr$^{87}$/Sr$^{86}$ ratio of the intrusion is 0.7029.
Stillwater Complex, Montana

The Stillwater Complex is a layered igneous intrusion of ultramafic to mafic composition located at the northern edge of the Beartooth Mountains in southwestern Montana (Fig. 4). Jones et al. (1960) have described the structural relationships between the Complex and surrounding Precambrian and Paleozoic rocks. The western end of the Complex dips steeply to the north, 60° to 70°; the central part dips moderately to the northeast; the eastern third is vertical or overturned. The contact between the Complex and the younger sedimentary rocks appears to be an unconformity because igneous layering is not parallel to the sedimentary bedding and the northerly dip of the igneous layering appears to be 25° to 30° steeper than the dip of the sedimentary bedding. Also, boulders of the igneous rock from the Complex occur in the overlying Wolsey shale of Middle Cambrian age (Vhay, 1934). The difference between the dip of the igneous layering and sedimentary bedding is attributed to either a pre-Middle Cambrian tilt of the Complex to the north during an arching of an ancestral Beartooth range, or to a primary inclination of igneous layering in a lopolith structure.

Bonini et al. (1968, p. 31) have reported the results of an extensive gravity survey in the region within Wyoming and Montana containing the Complex. A series of gravity
highs occurring in an area of almost 4000 km² may be accounted for by the five mile thick, flat-lying sheet of buried, high density Stillwater rocks. They estimate that the present exposures of the Complex represent less than 10 percent of its original exposure, whereas Hess (1960) sets the figure at about 60 percent. In either case, the total quantity of magma, of which the exposed Stillwater Complex is only a fraction, must have been immense.

The oldest rocks in the region occur at the base of the Complex (Jones et al., 1960; Hess, 1960). Field studies of these rocks have been limited to reconnaissance. They are Precambrian metasedimentary rocks, including gneiss, schist, a bluish, sugary-textured quartzite, hornfels, which was produced by contact metamorphism at the time of the Stillwater intrusion, and what may represent a metamorphosed sedimentary iron formation, containing quartz, fayalite, iron-rich pyroxene, grunerite, and magnetite. Concordancy of the Stillwater igneous intrusive to the original Precambrian sedimentary rocks has been assumed, because of the distribution of this iron formation (Jones et al., 1960). Granitic intrusive rocks of unknown age containing xenoliths of metasedimentary rocks cross-cut the base of the Stillwater Complex and the metasedimentary rocks on the east and west sides of the base of the Complex.

The mineralogy of the Stillwater Complex is relatively
simple, consisting of only four essential minerals: olivine, orthopyroxene, clinopyroxene, and calcic plagioclase. On the basis of layering and mineralogy, Peoples (1932) subdivided the Complex into stratigraphic units as shown in Figure 4. The lower two-thirds of the basal Ultramafic zone consists of the Peridotite member, which is composed of coarsely crystalline, interlayered harzburgite, chromitite, bronzitite, and dunite. The Bronzitite member of the Ultramafic zone is a single layer of bronzitite stratigraphically above the Peridotite member and below the Banded zone. The contact between the Ultramafic zone and Banded zone is either a distinct, sharp bronzitite-norite contact, or a series of alternating layers of these two rock types over a few feet. The Banded zone and the overlying Upper zone consist of layers of gabbro, troctolite, anorthosite, and norite. As in other layered intrusions, cryptic layering is well-developed in the Stillwater Complex.

Serpentinization is widespread in the Ultramafic zone and is most intense within the lower portion of this zone (Hess, 1960). Serpentine often has completely replaced the olivine in harzburgites, but pyroxenes show a greater resistance to serpentinization. In most of the bronzitite little serpentinization is apparent (Hess, 1960).

Recent work by investigators using the K-Ar and Rb-Sr methods on various minerals stimulated speculation that the
Complex could be one of the oldest of the world's known igneous intrusions. A K-Ar analysis of biotite from the contact metamorphic zone below the complex suggested that the magma intruded the area at least 3200 million years ago (Kulp, quoted by Donn et al., 1965). This minimum age seemed confirmed when Kistler et al. (1969) measured an apparent age of 3200 million years for a whole-rock sample of the chilled border phase using the K-Ar method. K-Ar and Rb-Sr analyses of pyroxenes and whole rocks of the complex by Kistler et al. (1969) suggested an age perhaps as great as 3800 million years. However, Schwartzman and Giletti (1968) have reported much different results from their study of rocks and minerals using the K-Ar method. As expected, they found pyroxene to be unreliable as an age indicator because of excess argon which had been incorporated into the crystal lattice at the time of crystallization. They also found biotite from the contact metamorphic zone having an apparent age of only 2330 million years.

In an attempt to resolve this problem, Fenton and Faure (1969) applied the Rb-Sr whole-rock method to four harzburgites, one norite, and two anorthosites donated by H. H. Hess. The modal analyses of these rocks are shown in Table 9 and Rb-Sr analytical data are listed in Table 10. The whole-rock isochron defined by these data is
## Table 9

**Modal Analyses of Rocks from the Stillwater Complex, Montana**

<table>
<thead>
<tr>
<th>Sample</th>
<th>R4961</th>
<th>R4967</th>
<th>R4964</th>
<th>110</th>
<th>R4971</th>
<th>R4969</th>
</tr>
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<tbody>
<tr>
<td>olivine</td>
<td>5</td>
<td>68</td>
<td>63</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>clinopyroxene</td>
<td>79</td>
<td>19</td>
<td>19</td>
<td>20</td>
<td>26</td>
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<td>orthopyroxene</td>
<td>7</td>
<td>1</td>
<td>8</td>
<td>71</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>plagioclase</td>
<td>8 (An77)</td>
<td>8 (An72)</td>
<td>8 (An73)</td>
<td>3</td>
<td>58 (An73)</td>
<td>91 (An60)</td>
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<td>chromite</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>6</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>serpentine</td>
<td>T</td>
<td>T</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>iddingsite</td>
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<td>biotite</td>
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<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
<td></td>
</tr>
<tr>
<td>amphibole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chlorite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T</td>
<td></td>
</tr>
</tbody>
</table>

T = Present

- **TABLE 9**
- **MODAL ANALYSES OF ROCKS FROM THE STILLWATER COMPLEX, MONTANA**
- **Sample**
- **R4961**
- **R4967**
- **R4964**
- **110**
- **R4971**
- **R4969**
- **Olivine**
- **Clinopyroxene**
- **Orthopyroxene**
- **Plagioclase**
- **Chromite**
- **Serpentine**
- **Iddingsite**
- **Biotite**
- **Amphibole**
- **Chlorite**
- **Table continues...**
<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Sr$^{87}$/Sr$^{86}$ (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4961</td>
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<td>27.1 *</td>
<td>0.272</td>
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<td></td>
<td>2.33*</td>
<td>25.2 *</td>
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<td></td>
<td>2.34</td>
<td>24.66</td>
<td></td>
<td>0.7189</td>
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<tr>
<td>R4967</td>
<td>0.72*</td>
<td>39.4 *</td>
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<td></td>
<td>0.58</td>
<td>37.45</td>
<td></td>
<td>0.7076</td>
</tr>
<tr>
<td>R4971</td>
<td>1.21</td>
<td>70.7 *</td>
<td>0.048</td>
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</tr>
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<td></td>
<td>1.07*</td>
<td>70.31</td>
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</tr>
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<td>65.48</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>0.7048</td>
</tr>
<tr>
<td>R4964</td>
<td>0.54*</td>
<td>14.6 *</td>
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<td></td>
<td>0.47</td>
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</tr>
<tr>
<td>R4186</td>
<td>6.59*</td>
<td>155.9 *</td>
<td>0.113</td>
<td>0.7072</td>
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<td></td>
<td>5.55</td>
<td>156.5</td>
<td></td>
<td>0.7077</td>
</tr>
<tr>
<td>R4969</td>
<td>3.9 *</td>
<td>158.0 *</td>
<td>0.072</td>
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</tr>
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<td></td>
<td>0.7052</td>
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<td>18.30</td>
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<td></td>
<td>1.54</td>
<td>18.08</td>
<td></td>
<td>0.7111</td>
</tr>
</tbody>
</table>

* Analyst: G. Faure
shown in Figure 5. It is apparent that five of the rocks form a linear array on the isochron diagram. The slope of the isochron indicates an age of 2450 ± 210 million years for the Complex. The initial Sr$^{87}$/Sr$^{86}$ ratio is 0.7029 ± .0006. A recent analysis by Stueber and Murthy (1968) of an unaltered peridotite from the Stillwater Complex is plotted on this isochron diagram and fits this isochron within experimental error.

Two serpentinized harzburgites do not fit the isochron. A possible explanation for this anomalous behavior is that these rocks became contaminated with radiogenic Sr$^{87}$ during serpentinization at the time of crystallization and consequently had initial Sr$^{87}$/Sr$^{86}$ ratios of 0.7060 and 0.7094, respectively. If this explanation is correct, the position of R4967 on the isochron diagram may be accounted for by the addition of 1.61 x 10^{-7} moles of excess Sr$^{87}$ (a 0.4 percent increase of Sr$^{87}$) during contamination. Similarly, 4.72 x 10^{-7} moles of Sr$^{87}$, added to R4961 (a 1.8 percent increase), would produce similar results.
Figure 5. Whole-rock Rb-Sr isochron for the Stillwater Complex, Montana
Bushveld Complex, South Africa

The Bushveld igneous complex consists of a varied assemblage of lavas, pyroclastic rocks, sills, and plutonic phases, grouped within an area of 25,000 square miles in the Republic of South Africa (Fig. 6; Wager and Brown, 1967). The Bushveld layered intrusion occupies over 40 percent of the area and may be the largest known basic intrusion in the world.

The immense size of the layered intrusion, along with the extensive overlying rock formation, which include the Red Granite, and the paucity of exposures of the intrusion's basal contact, are factors which have inhibited an understanding of the mechanism of intrusion and shape of the mass. Although generally thought of as a prime example of a lopolith, continuing studies of structural relationships at the floor and margins of the intrusion have shown that the intrusion transgresses folded and fractured country rock. In addition, gravity and mine data suggest that some marginal contacts are steeply dipping. It would seem that the relationship between intrusion and country is far from conformable and the intrusion may be a cone-sheet rather than a lopolith (Wager and Brown, 1967; Willemse, 1964). The hypothesis of a single mass of magma, solidifying to form the layered intrusion, is losing support. As study proceeds, more credence is attached to the
Figure 6. Geologic map of the Bushveld Complex, South Africa. (After Wager and Brown, 1967)
hypothesis of at least four magma chambers, separated by low country rock barriers. Detailed studies of extensive marker units, such as magnetite, platinum-mineral, and chromite layers, suggest that a main chamber had spilled over into subsidiary basins.

The bulk of the Bushveld intrusion consists of a layered series of ultramafic to mafic rocks, ranging from peridotite and pyroxenite near the base, through gabbro, norite, and anorthosite, to diorite and mafic granophyre toward the top. As in the Skaergaard intrusion, gravity is generally thought to have been the major factor in the differentiation of a basaltic magma into a sequence of layered rocks. There are no exposures of an extensive marginal zone comparable to the Marginal and Upper Border group rocks of the Skaergaard intrusion. A fine-grained hypersthene gabbro, which appears to underlie the eastern edge of the layered series, may represent a chilled margin.

One of many schemes of subdivision of the Layered Series at the Bushveld was devised by Wager and Brown (1967), based on laterally-extensive and easily mappable magnetite, chromite, or platinum mineral-layers. The four main units of the Layered Series are the Basal, Critical, Main, and Upper Zones (Figure 7).
Figure 7: Stratigraphic sequence of cryptic layering in the eastern part of the Bushveld Complex, South Africa. (After Walker and Brown, 1967)
The Basal zone consists of bronzitite, harzburgite, and dunite, with minor thin layers of chromitite near the top, totaling about 4000 feet. The layering of this zone is on a large scale and is comparable to the Ultramafic zone of the Stillwater Complex. Typically, thin layers of cumulus olivine with poikilitic bronzite alternate with thicker layers of cumulus bronzite with poikilitic augite. Olivine composition varies little within this zone, the range being Fo_{88} to Fo_{86}. Similarly, bronzite compositions vary only from En_{86} to En_{83}. Plagioclase is An_{80} and augite is Ca_{45}Mg_{50}Fe_{5}.

Overlying the Basal Series is 3500 feet of the Critical Series. Physical conditions within the magma at the time of deposition of the Critical Series must have been highly unusual, because the series is characterized by the development of very thin layering that is not found elsewhere in the intrusion. The layers, which may be as thin as a few millimeters, consist of accumulations of varying proportions of chromite, plagioclase, bronzite, augite, and olivine. The most spectacular layering consists of alternating layers of cumulus chromite and plagioclase, minerals of very different densities.

The Main zone, above the Critical Series, is the thickest unit of the intrusion, varying between 10,000 and 17,000 feet. Main zone rocks are gabbro with plagi-
clase, clinopyroxene, and minor orthopyroxene or inverted pigeonite. In contrast to the Critical and Upper Zones, the Main Zone is massive, but pyroxene and plagioclase alternately increase and decrease in relative abundance, producing a sequence of layers throughout the zone. Although this layering may be obscure, igneous lamination is best developed in the Main Zone (Van den Berg, 1946).

The first significant accumulation of magnetite, which is the lowest of a series of spectacular magnetite layers, marks the base of the Upper Zone. This zone, which has a maximum thickness of 6300 feet, has iron-rich olivine and apatite as important rock constituents. Occurring in minor amounts are quartz, alkali feldspar, hornblende, and biotite. The extreme iron enrichment of the zone is marked by the magnetite layers and high Fe/Mg ratio in olivine and pyroxene, making it comparable to the Upper Zone of the Skaergaard intrusion.

A number of different investigations have been conducted in order to determine the absolute age of the Bushveld complex. Schreiner (1958) made a Rb-Sr age determination of the Red Granite, overlying the Bushveld layered rocks, based on a whole-rock sample, four feldspars, and a biotite. He assigned an age of $1920 \pm 130$ million years to the Red Granite. Nicolaysen et al. (1958) made Rb-Sr age determinations on micas from four Bushveld igneous rocks, U-Pb age determination on three zircon concentrates
<table>
<thead>
<tr>
<th>Mineral Description</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Augite with hypersthene lamellae</td>
<td>11</td>
</tr>
<tr>
<td>Augite</td>
<td>22</td>
</tr>
<tr>
<td>Bronzite with augite lamellae</td>
<td>2</td>
</tr>
<tr>
<td>Plagioclase (An_{69})</td>
<td>66</td>
</tr>
</tbody>
</table>
from the Red Granite in the central Bushveld, and lead isotope age determinations of galenas in sedimentary rocks of the Transvaal System. They assigned an age of 1950 ± 150 million years to the intrusion of the Bushveld Complex.

In order to determine the initial Sr$^{87}$/Sr$^{86}$ ratio of the Bushveld magma at the time of solidification, a sample of bronzite-bearing gabbro was selected for Rb-Sr analysis. This sample (R4193) was collected from Waterkop 602 by the Shaler Memorial Expedition of Harvard University (Harvard No. 13444X) and was donated by Dr. J. B. Thompson of Harvard University. The sample was in a zone of anorthosite with sharp bands of pyroxene (Table 11). The weighted mean of two Sr$^{87}$/Sr$^{86}$ ratio analyses is 0.7055 (Table 12). Even though the Rb$^{87}$/Sr$^{86}$ ratio is a low 0.090, over a period of 1950 million years (Nicolaysen et al., 1958) the Sr$^{87}$/Sr$^{86}$ ratio has increased significantly from an initial value of 0.7030. Since a thin section does not indicate post-crystallization alteration of the sample, 0.7030 is considered to be the true initial Sr$^{87}$/Sr$^{86}$ ratio for the sample and is representative of the initial ratio of the Layered Complex.
Great Dyke, Southern Rhodesia

The Great Dyke of Southern Rhodesia consists of layered dunite, pyroxenite, and chromitite with minor gabbro and quartz gabbro. It has a total length of about 330 miles and an average width of 3.5 miles (Fig. 8). Although the intrusion appears to be a dike cutting Precambrian granites and gneisses, detailed field relationships suggest that it is the remains of four intersecting lopoliths preserved in a graben (Worst, 1958). The original mass may have had dimensions comparable to the Bushveld Complex.

The layered intrusion may be divided into two main zones: the Ultramafic Zone and the Gabbro Zone. The central area of the Great Dyke, near the town of Hartley, contains a total exposed thickness of 7,000 feet of layered rocks in the Ultramafic Zone. Seven, thick pyroxenite layers alternate with serpentinized dunite and harzburgite layers and ten thin chromitite seams. A maximum thickness of 3000 feet of Gabbro-Zone rocks is preserved in the Hartley area, where 500 feet of gabbro and norite is overlain by 700 feet of quartz gabbro. Typical rhythmic layering, igneous lamination, and cryptic layering are well developed in the Great Dyke.

The isotopic composition of strontium and concentrations of rubidium and strontium were measured by Faure et
Figure 8. Geologic map of the Great Dyke, Southern Rhodesia. (After Allsopp, 1965)
al. (1963) for two whole-rock samples of gabbro from the Wedza Complex of the Great Dyke. The age assigned to the Great Dyke is $2243 \pm 350$ million years \(\text{yr.}^{-1}\). Later, Allsopp (1965) reported Rb-Sr whole-rock analyses for five samples from the Wedza, Selukwe, and Hartley Complexes of the Great Dyke. After correcting the measured $\text{Sr}^{87}/\text{Sr}^{86}$ ratios according to a $\text{Sr}^{86}/\text{Sr}^{88}$ value of 0.1194, his data indicates an age of $2537 \pm 92$ million years. This age agrees very well with K-Ar and Rb-Sr ages of biotite samples separated from two of the whole-rocks used for Rb-Sr analysis. It appears that the Great Dyke is significantly older than the Bushveld layered intrusion which has an age of 1950 million years.

A gabbro (R4936) collected from the Great Dyke by G. B. Worst was selected for Rb-Sr analysis. Since a thin section was not available, it is assumed that post-crystallization alteration has not occurred to any significant degree. The weighted mean of three analyses for the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio is 0.7050 (Table 13). Duplicate analyses for the rubidium and strontium concentrations give a $\text{Rb}^{87}/\text{Sr}^{86}$ ratio of 0.07 for this sample. Assuming an age of 2537 million years, the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for the sample is 0.7025.
### TABLE 13

**Rb AND Sr ANALYTICAL DATA**

**GREAT DYKE, SOUTHERN RHODESIA**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Sr$^{87}$/Sr$^{86}$ (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4936</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>0.7045</td>
</tr>
</tbody>
</table>
Deccan Plateau Basalt, India

The area now occupied by the Deccan Plateau Basalts is about 200,000 square miles in western, central, and southern India (Fig. 9; Krishnan, 1960, p. 470). The maximum total thickness for the flows is over 7,000 feet near the Bombay coast; individual flows range in thickness from a few feet to as much as 120 feet. In contrast with their thickness, the flows have a great horizontal extent. Individual flows have been traced for distances of over 60 miles. The lavas are generally horizontal, but gentle warping has occurred locally, producing dips up to 20 degrees.

The basalts of the Deccan Plateau are strikingly uniform in composition and are classified as tholeiitic basalt (Turner and Verhoogen, 1960, p. 205). The mineral assemblage consists of: (1) two pyroxenes, augite with pigeonite or hypersthene, which are often strongly enriched in iron; (2) magnesian, unzoned olivine; (3) labradorite; (4) residual glass charged with magnetite, and (5) abundant deuteric zeolite, carbonate, and chalcedony.

The age of the Deccan basalts is based on fossil flora and fauna preserved in sedimentary rocks below the basalts and interlayered between individual flows (Krishnan, 1960, p.482). An angular unconformity separates the basalts from
Figure 9. Map of India showing the distribution of Deccan Plateau Basalts. (After Holmes, 1965)
underlying marine sedimentary rocks which contain a nautilus, lamellibranchs, and gastropods. There is an absence of any characteristic genera, but these fossils show a close affinity with Cretaceous fossils found in eastern India. Several algae have been found and one of them, Acicularia, has not been recorded from any beds older than Paleocene. In another locality, strata of the Ranikot Series, which contain Eocene Nummulites rest unconformably on basalt flows. Interlayered throughout the basalt flows are fluvial and lacustrine deposits of small horizontal extent which are generally two to ten feet thick. They include cherts, limestones, and pyroclastic sandstones. These units contain Eocene algae, ostracods, crustaceans, frogs, turtles, plants (including palm leaves), and fish. In Pakistan, basalt flows are interstratified with shales and sandstones, the latter containing volcanic ash and basalt fragments. These sedimentary rocks contain assemblages of corals, echinoids, gastropods, and Nautilus bouchardianus, all of Late Cretaceous age. It is reasonable to conclude on the basis of this evidence that volcanism began in the latest Cretaceous and continued well into the Eocene.

A sample of Deccan basalt was analyzed for rubidium and strontium concentrations and also for the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio (Table 14). This sample was collected along the
### TABLE 14

**Rb AND Sr ANALYTICAL DATA**

**DECCAN PLATEAU**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>$\frac{\text{Rb}^{87}}{\text{Sr}^{86}}$ (corr.)</th>
<th>$\frac{\text{Sr}^{87}}{\text{Sr}^{86}}$ (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1864</td>
<td>16.2</td>
<td>206.8</td>
<td>0.226</td>
<td>0.7060</td>
</tr>
</tbody>
</table>
Kogna River, Bombay state, between Pophali (17°26'N., 73°41'E.) and Navja (17°26'N., 73°46'E.). Duplicate analyses of the Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio are identical, 0.7060, and single measurements of Rb and Sr give a Rb\textsuperscript{87}/Sr\textsuperscript{86} ratio of 0.226. Faure and Hurley (1963) previously reported a Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio of 0.7055 and a Rb\textsuperscript{87}/Sr\textsuperscript{86} ratio of 0.0685. The Sr\textsuperscript{87}/Sr\textsuperscript{86} ratios are in close agreement. There is a discrepancy between the Rb\textsuperscript{87}/Sr\textsuperscript{86} ratios, but this should not have a significant influence in the calculation of the initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio. If the age of this sample is between 40 and 70 million years, the calculated initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio is in the range 0.7058 - 0.7059. This value is the highest initial ratio measured during this study for layered intrusions and plateau basalts and may indicate an upper mantle locally enriched in radiogenic Sr\textsuperscript{87} or contamination by assimilation of crustal rock.
Columbia River basalt, Oregon and Washington

The name Columbia River basalt was given to the basaltic lavas of Eocene to Recent age which spread over eastern Washington, eastern Oregon, southern Idaho, and northeastern California (Russell, 1901). However, since that time, the name has been restricted to the dominantly Miocene flows in northern Oregon, southeastern Washington, and western Idaho (Fig. 10; Waters, 1961; Heitanen, 1963).

Waters (1961) reported on the stratigraphic and lithologic variations in the Columbia River basalt and divided the rocks into two distinct varieties. The older variety is characterized by about five percent olivine, a silica content of 47 to 50 percent, and by notably higher Al₂O₃, MgO, and CaO than the younger variety (Yakima basalt). The younger Yakima basalt is over 20 percent tachylite and has little or no olivine, a silica content of 54 percent, and greater amounts of K₂O and TiO₂. A late variant of the Yakima basalt contains more olivine and plagioclase and a distinctly high iron and titania content than normal Yakima flows.

The age of the older basalt is probably early or middle Miocene because in Grant County, Oregon, it lies unconformably upon the John Day Formation (Oligocene - early Miocene) and is overlain by the middle to late Miocene Mascal Formation (Waters, 1961). The Yakima basalt overlies,
Figure 10. Map of Washington, Oregon, and Idaho showing the extent of the Columbia River basalt.

(After Waters, 1961)
or is intercalated with fluvial and lacustrine beds which contain middle or late Miocene flora. The Ellensburg Formation, which contains early Pliocene fossil vertebrates and plants, rests on the Yakima basalt. The age of the Columbia River basalts is probably early Miocene to early Pliocene.

A sample of Columbia River basalt (RL443) was selected for rubidium, strontium, and strontium isotope analyses (Table 15) in order to determine the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the magma at the time of solidification. This sample was collected by P. M. Hurley and H. W. Fairbairn from the center of a flow at the base of a 1000-foot-thick stratigraphic section located on the Wahkeenah Trail, Rte. U. S. 30, just east of Portland, Oregon. Since a thin section is not available, the sample is assumed to be unaltered. A single rubidium analysis and duplicate strontium analyses give a $\text{Rb}^{87}/\text{Sr}^{86}$ ratio of 0.513. Duplicate analyses of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio give a weighted mean value of 0.7036.

Faure and Hurley (1963) reported analyses of two other basalts from the same location (RL428 and RL435). The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for RL428 is 0.7037 and the $\text{Rb}^{87}/\text{Sr}^{86}$ ratio for RL435 is 0.510. Their results are in excellent agreement with analyses of RL443. If the age of the sample is between 15 and 25 million years (Evernden and James, 1964),
**TABLE 15**

Rb and Sr ANALYTICAL DATA

COLUMBIA RIVER BASALT, OREGON

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Sr$^{87}$/Sr$^{86}$ (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1443</td>
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<td>307.8</td>
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<td></td>
<td></td>
<td>316.8</td>
<td></td>
<td>0.7048</td>
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</tbody>
</table>
the minimum value for the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the three samples is 0.7034.

Summary

The initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios have been determined for a series of mafic-ultramafic intrusions and continental plateau basalts. These ratios are thought to indicate the isotopic composition of strontium in the magmas and their parent rocks at the time they left the source regions in the upper mantle. The initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios are: (1) Skaergaard intrusion, 0.7029; (2) Stillwater Complex, 0.7029; (3) Bushveld Complex, 0.7030; (4) Great Dyke, 0.7025; (5) Deccan basalt, 0.7058; and (6) Columbia River basalt, 0.7034. In addition, an age of 2450 ± 210 million years has been measured for the Stillwater Complex, using the Rb-Sr whole-rock method. These data will be used to define a strontium growth-curve for the upper mantle.
CHAPTER V

ALKALIC IGNEOUS COMPLEXES
AND ASSOCIATED CARBONATITES

Introduction

There has been considerable discussion about the origin and history of alkalic igneous complexes and associated carbonatites because of their diverse and unusual mineralogy and chemistry. The available field and laboratory data are presented in order to justify the premise that the alkalic rocks and associated carbonatites are differentiates of a magma derived from the upper mantle.

In general, most complexes consist of a variety of undersaturated and saturated rocks. The main rock groups are ultramafic, feldspathoidal, feldspathic, and carbonatitic. The ultramafic rocks often found are pyroxenites, peridotites, alkalic pyroxenites, and kimberlites. Pyroxenites and peridotites contain diopside, less commonly augite, but never orthopyroxenes. The olivine is forsterite and is often serpentinized. Accessory minerals are usually apatite, magnetite, and calcite. Alkalic pyroxenites contain titanaugite or aegirine-augite with perovskite as a common accessory. Biotite and phlogopite pyroxenites, often altered to vermiculite, are common. Kimberlites,
often associated with carbonatites, will be discussed later.

Especially characteristic of the alkalic complexes are feldspathoidal rocks of the urtite-ijolite-melteigite series, and the melilite-rich rocks. Particularly common are the ijolites, such as occur at Iron Hill, Colorado, containing the essential minerals nepheline and calcium-rich diopside or aegirine-augite. Melanite, apatite, perovskite, sphene, biotite, and calcite are accessories. Uncompahgrite at Iron Hill, containing 68 percent melilite and 15 percent diopside, is typical of the melilite-rich rocks.

Nepheline syenites and related magnite, juvite, and sodalite syenite have been observed at numerous localities including McClure Mountain and Iron Hill, Colorado, and the Rainy Creek Complex, Montana. Nepheline, commonly altered to cancrinite and muscovite, is the most common feldspathoid. Sodalite is less common and secondary analcrite corrodes feldspar. Associated alkali feldspars are generally sodic and the more common accessories are magnetite, apatite, sphene, garnet, and calcite. There is a wide variety of syenitic rocks and where these rocks are demonstrably intrusive, as opposed to metasomatized country rock formed in place, they are closely related to the feldspathoidal rocks.
With few exceptions, plugs, dikes, and veins of carbonate rock are located either within alkalic igneous complexes or in the surrounding country rock. A complex may have one or two centrally located plugs of carbonate rock, which may be surrounded by cone sheets, ring-dikes, or radial, tangential, or irregularly distributed dikes, composed of carbonate rock. Iron Hill is typical of the type of complex that contains a central plug of carbonate rock, surrounded by a radiating array of carbonate dikes. McClure Mountain in Colorado lacks the central carbonate mass but does have numerous carbonate dikes.

Usually a variety of minerals are present in these plugs, dikes, and veins, including carbonates, silicates, oxides, sulfides, and halides. The dominant minerals are dolomite, calcite, ankerite, siliceous dolomite, and siderite. Also common in lesser amounts are ilmenite, pyrochlore, fluorite, and many others.

The origin of these carbonate rocks has been a difficult problem. Hög bom (1895) is credited as the first to state that the "limestone" associated with nepheline syenite at Alnö, Sweden, was magmatic. Workman (1911) supported Hög bom's conclusion in a discussion of primary (i.e., magmatic) calcite and Brøgger (1921) later verified the existence of carbonate magma at the Fen Complex in Norway.
Considerable evidence is now available that shows that carbonate magmas can exist. Perhaps the most convincing evidence is the occurrence of carbonate lava from Oldoinyo Lengai volcano, Tanzania. Two analyzed samples contain 78-80 percent \( \text{CaO} \), \( \text{Na}_2\text{O} \), and \( \text{CO}_2 \); less than two percent \( \text{SiO}_2 \); and minor \( \text{BaO} \), \( \text{SrO} \), \( \text{Cl} \), and \( \text{SO}_3 \) (DuBois et al., 1963). Partially assimilated xenoliths in these lavas and in carbonate plugs and dikes argue for a fluid origin of the carbonates. The carbonates may be foliated, granitoid, porphyritic, or brecciated -- textures typical of igneous rocks. Also, carbonate rocks within a complex may show a differentiation series with age, such as at Iron Hill, where fine to medium grained dolomite contains younger and coarser lenses of slightly ankeritic dolomite and even younger phases of ankerite (Heinrich, 1966, p. 149).

As students of these "carbonatites," as they were later called, gradually accepted a magmatic origin, they became divided over the question of the source of the large quantity of carbon dioxide that is associated with a carbonatite magma. Both Brögger (1921) and Högbohm (1895) believed that the carbon dioxide source was limestone, below the intrusion, which was assimilated by a rising alkalic magma. Both Daly (1910, 1918, 1925, 1933) and Shand (1947) were strong advocates of limestone syntexis as a mechanism for the production of alkalic igneous rocks and as a source of
carbon dioxide. Some authors went a step farther and suggested that carbonatite plugs are actually huge limestone xenoliths. Larsen (1942) concluded this after his study of Iron Hill, as did Landes (1931) for the carbonatite of Magnet Cove, Arkansas.

An alternate hypothesis for the origin of carbonatites is that they are an end-product of extreme differentiation and that the carbon dioxide is juvenile. Such a hypothesis could not be easily accepted when only field evidence was available. During the past decade, experimental evidence has accumulated demonstrating the possible existence of carbonate magmas at low temperatures and pressures. Wyllie and Tuttle (1959b) found carbon dioxide to be only slightly soluble in granitic melts, but markedly soluble in magmas of more alkaline compositions. They also stated the possibility that carbon dioxide could become more soluble in alkaline liquids with progressive crystallization of the magma, so that a complete transition from normal alkaline magmas to carbonatite magmas could be produced.

Wyllie and Tuttle also discovered low-temperature liquids that may be considered to be simple carbonatite magmas (1959a,b, 1960a,b; Tuttle and Wyllie, 1958). At 683°C and 1000 bars, a liquid consisting of 68 percent CaO, 19 percent CO₂, and 13 percent H₂O coexists with calcite,
portlandite, and solid CaO. Between 27 and 4000 bars, the minimum liquidus temperature varies between 685°C. and 640°C. At 1000 bars, with an addition of magnesium, the minimum liquidus temperature drops to 625°C. Similar synthetic liquids were found to exist at pressures of less than 10 bars, particularly with the addition of alkali carbonates (Wyllie and Tuttle, 1962). On the basis of their experimental results, they concluded that a carbonatite magma could reach a near-surface level as a liquid and then violently erupt as tuffaceous material and gas-charged carbonatitic lava. Subsequently, Van Groos and Wyllie (1965) reported immiscibility between a silicate melt and a liquid consisting of 90 percent Na₂CO₃ within the system CaO-Na₂O-Al₂O₃-SiO₂-CO₂-H₂O at about 750°C. Liquid immiscibility could explain the occurrence of a highly reactive carbonate magma that is not significantly contaminated with silicates.

If, from the preceding review of field and laboratory evidence, we accept that alkalic rocks and carbonatites of a complex are genetically related products of magmatic differentiation, we should consider the evidence that suggests that the fractionating magma originated in the upper mantle and explosively pierced the continental crust.

Examination of the country rock invariably shows the
effects of rapid intrusion of carbonatite-alkaline complexes at high pressure. The intrusion is discordant to foliation or stratification of the wall rocks. Some complexes have caused a doming of the host rock. Davies (1947) recognized doming as the initial tectonic development at some east African complexes and McCall (1959) estimated a 2000-foot rise of the Precambrian erosion surface at Rangwa, western Kenya. Generally a "shock" zone has formed around the intrusion. The shock zone, originally recognized by von Eckermann (1948) at Alnö, consists of quartz granulation, jointing, fenitization, brecciation, and mylonitization.

Carbonatites and alkaline rocks tend to occur in readily definable petrographic provinces which are recognized on the basis of geographic, geologic, or petrologic affinities, but not necessarily with respect to time. In some provinces, such as southern Colorado, it is possible that intrusions of two different ages are present. There, the Iron Hill Complex is 1481 million years old while the age of the nearby McClure Mountain Complex is between 517 and 704 million years old (these new age determinations are discussed below).

Backlund (1932), in discussing the distribution of plutonic carbonatite-alkaline rock provinces, pointed out that most of these are located within, or close to the edges of, stable continental platforms. Intrusion of these
distinctive complexes seems to be typically associated with crustal instability and large scale vertical faulting in non-orogenic areas. Rarely do orogenic zones contain these complexes.

Numerous authors have discussed the close relationship between zones of major faulting and carbonatite-alkaline complexes (McCall, 1959; King and Sutherland, 1960; Ginsburg, 1962; Gittons et al., 1967). The relationship of alkaline magmatism in Africa to the rift valleys is well known, but the exact nature of the relationship has not been established. By analogy with the African occurrences, Kumarapoli and Saull (1966) have postulated, on the basis of seismic evidence and the presence of alkaline and carbonatite rocks, the existence of a major rift zone from the Monte Region Hills in the St. Lawrence Valley westward to the Lake Superior region. Gittons et al. (1967) note a prominent linear distribution of Canadian carbonatites extending southward from James Bay. Nearly coincident with these intrusions is the anomalous gravity and magnetic feature known as the Kapuskasing High (Fig. 11), which was interpreted as indicative of a thin granitic crust (Garland, 1950). Later, Innes (1961) attributed this gravity high to a major tensional feature extending deep into the crust that has allowed basaltic magma to rise to a shallow level. He considered the Kapuskasing High to be a northeast extension of the Mid-Continent Gravity High described by Thiel
Figure 11. Areal extent of the Kapuskasing Gravity High, Ontario, Canada. (after Innes, 1961)
(1956) as extending 800 miles from Lake Superior toward Kansas. Innes (1961) further suggests that a tensio-nal, rift zone may extend from James Bay to Kansas which is similar to the African Rift Zone. There seems little reason to doubt that carbonatite-alkalic magmatism is often closely related to major structural features of the earth's crust.

The relationship between kimberlites and carbonatite-alkalic complexes that was postulated by von Eckermann (1961), among others, has been summarized by Dawson (1964). Many kimberlite provinces contain carbonatite-alkalic complexes, such as at Magnet Cove and in southwest Africa. At Fen, Norway, and Alnö, Sweden, kimberlites appear as co-genetic units with the carbonatites. At the Premier Pipe, South Africa, carbonatite dikes cut serpentinized kimberlite. Like the carbonatite-alkalic complexes, kimberlites occur as small, circular, steep-sided pipes localized in clusters along major fault zones or aligned with the structural trend of Precambrian rocks. Intrusion of kimberlite occurs explosively as evidenced by the occurrence of considerable brecciation.

Most kimberlites contain carbonate as matrix material, either anhedral and poikilitic, or as a replacement mineral of melilite, phlogopite, olivine, pyroxene, and antigorite. The interstitial anhedral crystals and poikilitic crystals
are considered to be of late-magmatic origin, while calcium-rich pseudomorphs are thought to be deuteritic in origin. Kimberlites characteristically contain trace element assemblages similar to those of alkalic rocks. These include relatively high concentration of Ti, P, Cr, Mn, Co, Nb, Ba, Sr, Zr, V, Ni, and Th.

A question remains, concerning the ultimate origin of kimberlites, carbonatites, and the associated alkalic igneous rocks. It is generally believed that the upper mantle is of ultramafic composition and that various basaltic magmas that penetrate the earth's crust are products of partial melting of the parent ultramafic rock (Yoder and Tilley, 1962; Kushiro and Kuno, 1963; Ringwood et al., 1964). Many lines of evidence suggest that the parent material of kimberlites originated in an upper mantle of ultramafic material: (1) the association of kimberlites and rifts, (2) the general composition of kimberlite, which is carbonated, hydrated, alkalic peridotite, (3) the presence of diamonds and eclogite xenoliths, and (4) the stability fields of some kimberlite minerals, such as aluminum-rich enstatite. Evidence indicating that kimberlites originated from a depth of at least 100 kilometers was reported by Birch (1963) and Boyd and England (1965). Steuber and Murthy (1966) found that Sr^{87}/Sr^{86} ratios of ultramafic xenoliths in kimberlites, continental basalts, and oceanic
basalts are in general agreement confirming the conclusion of Nixon et al. (1963) that basalts and kimberlites originate in the upper mantle.

Because of the close relationship in time and space between kimberlites and carbonatite-alkaline complexes, the latter may also evolve in some way from an ultramafic parent material. A significant study of the peralkaline residua system Na$_2$O-Al$_2$O$_3$-Fe$_2$O$_3$-SiO$_2$ made by Bailey and Schairer (1966) strongly supports the hypothesis that ijolite, nepheline syenite, and carbonatite are members of a fractionation series, beginning with an alkali basalt formed by partial melting of ultramafic rocks in the upper mantle.
Iron Hill Complex, Colorado

The small stock of alkaliic rocks and carbonatite of the Iron Hill Complex is located in southwestern Colorado, about 22 miles south-southwest of the town of Gunnison (Fig. 12).

Much of the region surrounding the Iron Hill Complex is underlain by Precambrian rocks, which were divided by Hunter (1925) into the Black Canyon schist, the Dubois greenstone, and the Powderhorn granite group. The Black Canyon schist is predominantly biotite schist, quartz-mica schist, micaceous quartzite, with minor amounts of granite gneiss and amphibole schist. The Dubois greenstone consists chiefly of hornblende schist, hornblende gneiss, amphibolite, metadiorite, and chlorite schist. The host rock for the Iron Hill Complex is the Powderhorn granite group, which is relatively uniform in composition except for a few diverse textural types such as schistose metarhyolite porphyry, porphyritic granite, and aplite. Gently dipping strata of the Jurassic Morrison Formation overlie the Precambrian rocks. Rhyolite and quartz latite flows and tuffs of the Miocene Potosi Series rest on an erosion surface that cuts across the Jurassic sedimentary rocks.

Larson (1942) published the first thorough study of the rocks of the Iron Hill Complex and Temple and Grogen
EXPLANATION

Precambrian

Tv
Volcanic rocks

Jurassic

Jm
Morrison Formation

Carbonatite

Alkalic-rock Complex

Igneous and metamorphic rocks

Figure 12. Generalized geologic map of the Powderhorn district, Gunnison County, Colorado. (after Hunter, 1925; Cross and Larsen, 1935)
(1965) later made a study which included core-drilling. The following descriptions are taken from these publications. The area of outcrop of the Iron Hill Complex is about 12 square miles (Fig. 13). Drilling near the edges of the complex has shown that it is roughly funnel-shaped and consists of somewhat concentric masses of uncomphagrite, pyroxenite, ijolite, syenite, and nepheline syenite surrounding a central core of carbonatite. At the surface, the concentric shapes of the rock units, fracture zones, flow banding within the carbonatite plug, and carbonatite cone sheets within the alkalic rocks and country rock. Cutting across these arcuate rock units are carbonatite dikes which radiate from a common point on the north side of Iron Hill.

The uncomphagrite occurs as irregular bodies of very-coarse-grained rock made up chiefly of melilitite, with lesser amounts of pyroxene, biotite, garnet, perovskite, magnetite, and apatite. The pyroxenite mass is extremely variable and includes pyroxenite, pegmatitic pyroxenite, and pyroxenite bearing orthoclase, garnet, or nepheline. The typical pyroxene varies from green pleochroic aegirine-augite to an almost colorless, nonpleochroic diopsidic type. Accessory minerals include sphene, perovskite, magnetite, ilmenite, apatite, potash feldspar, and biotite. Cross-cutting relationships demonstrate that the pyroxenite is the oldest unit of the complex. The pyroxene-nepheline rocks called
Figure 13. Geologic map of the Iron Hill Complex, Gunnison County, Colorado. (after Larsen, 1942)
EXPLANATION

<table>
<thead>
<tr>
<th>Precambrian</th>
<th>Q</th>
<th>Alluvium</th>
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<td>Jurassic</td>
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<td>Potosi volcanic rocks</td>
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<tr>
<td></td>
<td>Jm</td>
<td>Morrison Formation</td>
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<tr>
<td></td>
<td>qg</td>
<td>Quartz gabbro</td>
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<tr>
<td></td>
<td>ng</td>
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<tr>
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<td>Soda syenite</td>
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<tr>
<td></td>
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<td>Carbonatite</td>
</tr>
<tr>
<td></td>
<td>pc</td>
<td>Igneous and metamorphic rock</td>
</tr>
</tbody>
</table>
ijolites intrude the pyroxenite and may also be younger than the uncomphagnet. Although the proportions of minerals vary considerably, generally these coarse-grained rocks consist of one third each of nepheline, pyroxene, and titaniferous garnet, with apatite, primary calcite, sphene, and lesser amounts of biotite, and rarely orthoclase or albite.

A small plug and a few dikes of soda-syenite intrude pyroxenite, ijolite, and uncomphagnet. At least 90 percent of the syenite consists of microperthite. Either aegirine or soda amphibole make up most of the remainder of the rock. A mass of nepheline syenite cuts pyroxenite and country rock near the border of the complex and in part forms a dike along the border. Over 75 percent of this rock is albite, orthoclase, and microperthite. The remainder includes interstitial nepheline, aegirine, and melanite. Other accessories include magnetite, biotite, sphene, and apatite.

The carbonatite of Iron Hill underlies an area of about two and one-half square miles and rises a thousand feet above the immediate vicinity. There are several varieties of carbonatite, the dominant type being a foliated brown ankeritic dolomite. Non-foliated, coarse-grained dolomite is common and other types are magnetite-bearing, sideritic carbonate and jasperized carbonate. In addition to
carbonates, other minerals, all in minor amounts, are ilmenite, pyrochlore, pyrite, rutile, zircon, monazite, fluorite, biotite, and apatite.

Numerous carbonatite dikes occur within and near the complex. The most common type of dike consists of carbonatite similar to that of Iron Hill. Many dikes contain pyrochlore and fluorite. Other dikes are either primarily siderite with minor pyrite and chalcopyrite or biotite-rich carbonatite.

In addition to the intrusive rocks of the Iron Hill Complex, many dikes and irregular masses of igneous rock intrude the Precambrian terrane, including the Powderhorn granite. These igneous rocks include diorite, quartz diorite, gabbro, and syenite. These rocks have chemical and structural features which are similar to those of the main complex and are considered to be related to it, rather than to the Tertiary volcanics (Olson and Wallace, 1956).

Samples of ijolite, carbonatite, uncomphagrite, and soda-syenite were collected by the author from the Iron Hill Complex for a Rb-Sr whole-rock age determination (Fig. 13, Table 16) Two other samples are from the augite syenite intrusion at Lot Mine, that is located five and one-half miles north-northwest of Iron Hill (Fig. 12). The soda syenite (I-14) consists of 84 percent perthite, 15
TABLE 16

MODAL ANALYSES OF ROCKS FROM IRON HILL COMPLEX, COLORADO

<table>
<thead>
<tr>
<th>Sample</th>
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<th>I - 14</th>
<th>I - 15a</th>
<th>I - 16</th>
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<td>25</td>
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<tr>
<td>melilitte</td>
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<td>alteration after melilitte</td>
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<td></td>
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<td>8</td>
</tr>
<tr>
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</tr>
<tr>
<td>apatite</td>
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<td>T</td>
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<tr>
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</tr>
<tr>
<td>biotite</td>
<td></td>
<td>T</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>nepheline</td>
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<td></td>
<td></td>
<td>9</td>
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<tr>
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<td></td>
<td>1</td>
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<tr>
<td>epidote</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
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<tr>
<td>quartz</td>
<td></td>
<td></td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>
percent clinopyroxene, and minor apatite and sphene. Alteration of the perthite to clays is very minor. The sample of ijolite (I-15a) is unusually rich in orthoclase, 35 percent, and poor in nepheline, 9 percent. Clinopyroxene and iron oxide are major constituents, while apatite, calcite, biotite are present in minor amounts. Alteration to clays, sericite, and carbonate is negligible. Almost 70 percent of the uncomparable (I-15) is melilite and clinopyroxene. Other minerals are garnet, enstatite, phlogopite, and apatite. Much of the melilite in this sample is replaced by fine-grained aggregates of hydrothermal minerals. These minerals are diopside, garnet, idocrase, calcite, mica, sphene, amphibole, juanite, cebollite, and others (Larsen, 1942). Aside from this late-stage hydrothermal alteration, the uncomparable shows no sign of alteration resulting from weathering. The two samples from Lot Mine (I-18 and I-18A) are almost identical in mineralogy. Over three-fourths of each rock is quartz with the remainder being epidote. Clay is present in minor amounts.

The isochron defined by these six samples (Fig. 14, Table 17) has a slope indicating an age of 1481 ± 59 million years for the Iron Hill Complex. The initial Sr$^{87}/$Sr$^{86}$ ratio is 0.7025 ± 0.0009. The deviations of the carbonatite (I-17) and the ijolite (I-15a) from the linear array of the other four samples are the major causes of the uncertainty in the age and initial ratio. An isochron defined
<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Rb(^{87})/Sr(^{86})</th>
<th>Sr(^{87})/Sr(^{86}) (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I - 14</td>
<td>60.1</td>
<td>704.1</td>
<td>0.246</td>
<td>0.7078</td>
</tr>
<tr>
<td>I - 15a</td>
<td>43.28</td>
<td>634.2</td>
<td>0.201</td>
<td>0.7042</td>
</tr>
<tr>
<td>I - 16</td>
<td>44.23</td>
<td>629.3</td>
<td>0.012</td>
<td>0.7042</td>
</tr>
<tr>
<td>I - 16</td>
<td>7.77</td>
<td>1937.</td>
<td>0.012</td>
<td>0.7023</td>
</tr>
<tr>
<td>I - 17</td>
<td>61.9</td>
<td>118.7</td>
<td>1.51</td>
<td>0.7274</td>
</tr>
<tr>
<td>I - 18a</td>
<td>64.1</td>
<td>151.5</td>
<td>1.21</td>
<td>0.7283</td>
</tr>
<tr>
<td></td>
<td>61.16</td>
<td>149.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 14. Whole-rock Rb-Sr isochron for the Iron Hill Complex, Colorado

Age: 1481 ± 59 m.y.

Sr$^{87}$/Sr$^{86}$: 0.7028
by I-16, 14, 18, and 18A has a slope indicating an age of 1487 ± 9 million years and an initial Sr$^{87}$/Sr$^{86}$ ratio of 0.7027 ± 0.0001. The correlation coefficient for this isochron is 0.99999. A possible cause of these deviations is contamination by assimilation of country rock during intrusion of the carbonatite and ijolite units. However, the high strontium content of about 630 ppm for the ijolite and a very low initial Sr$^{87}$/Sr$^{86}$ ratio of about 0.7000 indicates that assimilation of country rock enriched in radiogenic Sr$^{87}$ has not occurred to any significant degree. The carbonatite also has a very low initial Sr$^{87}$/Sr$^{86}$ ratio of about 0.705 and an extremely low Rb/Sr ratio which does not indicate contamination. A preferred alternative suggestion is that the magma was not isotopically homogeneous at the time of intrusion.
McClure Mountain Complex, Colorado

About 10 miles southwest of Canon City, Colorado, is the center of an igneous province having an area of about 400 square miles, that contains three major carbonatite-alkalic complexes and associated dike swarms. These complexes are the McClure Mountain Complex, the Democrat Creek stock and the Gem Park stock. Rocks of this igneous province have intruded Precambrian igneous and metasedimentary rocks, including the Idaho Springs Formation. The largest complex of the region, at McClure Mountain, occupies an area of 20 square miles (Fig. 15). It is circular in plan view and its component rock units are distributed in a roughly concentric fashion.

The principal rock types, described by Parker and Hildebrand (1962), are nepheline syenite, mafic nepheline-bearing rocks, biotite-hornblende syenite, pyroxene-olivine-plagioclase rocks, and carbonatite. Nepheline syenite, the most abundant rock, is composed of sodic orthoclase, variable quantities of nepheline, and some sodalite, sphene, and biotite or hornblende. The mafic nepheline-bearing rocks consist of variable proportions of nepheline, orthoclase, amphibole, biotite, and sphene. Biotite-hornblende syenite is a strongly foliated, coarse-grained rock, consisting mostly of perthite and albite-oligoclase with lesser amounts of biotite and hornblende. The pyroxene-
EXPLANATION

<table>
<thead>
<tr>
<th>Layer</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>Alluvium</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>Nepheline syenite</td>
<td></td>
</tr>
<tr>
<td>mn</td>
<td>Mafic nepheline-bearing rocks</td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>Biotite-hornblende syenite</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>Gabbro</td>
<td></td>
</tr>
<tr>
<td>im</td>
<td>Igneous and metamorphic rock</td>
<td></td>
</tr>
</tbody>
</table>

Figure 15. Geologic map of the McClure Mountain Complex, Fremont County, Colorado. (After Parker and Hildebrand, 1962)
olivine-plagioclase rocks vary from pyroxenites to anorthosites. Magnetite and apatite are accessory minerals. Carbonatite dikes occur within the complex and extend into the country rock. The dominant minerals are calcite and dolomite with minor amounts of apatite, magnetite, ilmenite, and riebeckite.

Samples of hornblende syenite, nepheline syenite, cancrinite syenite, and shonkonite were collected by the author from the McClure Mountain Complex (Table 18). A sample of a carbonatite body which intrudes the biotite syenite unit was donated by E. W. Heinrich. The localities of these samples are shown in Figure 15, the Rb-Sr analytical data are listed in Table 19, and isochron-A for the five samples is shown in Figure 16. With the exception of the cancrinite syenite, MM-5, the rocks have $\frac{Rb^{87}}{Sr^{86}}$ ratios of less than 0.4. Sample MM-5 expands the range of $\frac{Rb^{87}}{Sr^{86}}$ ratios to 3.064. The slope of isochron-A indicates an age of 517 ± 14 million years and an initial $\frac{Sr^{87}}{Sr^{86}}$ ratio of 0.7059. Thin sections of MM-2,3,4, and 5 show that the feldspars have been replaced to various degrees by clays, sericite, and carbonate. In particular, sample MM-5 was highly altered to clays, which may have had the effect of significantly altering the Rb/Sr ratio of the rock. Even incipient weathering has a tendency to cause the rapid release of strontium from a rock, resulting
TABLE 18
MODAL ANALYSES OF ROCKS
FROM THE MCLURE MOUNTAIN COMPLEX, COLORADO

<table>
<thead>
<tr>
<th>Sample</th>
<th>MM - 2</th>
<th>MM - 3</th>
<th>MM - 4</th>
<th>MM - 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-feldspar</td>
<td>35</td>
<td>15</td>
<td>59</td>
<td>72</td>
</tr>
<tr>
<td>perthite</td>
<td>52</td>
<td></td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>nepheline</td>
<td>1</td>
<td>1</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>clinopyroxene</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>hornblende</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>biotite</td>
<td></td>
<td>37</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>apatite</td>
<td></td>
<td>T</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>iron oxide</td>
<td>1</td>
<td>T</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>calcite</td>
<td>T</td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>sphene</td>
<td>T</td>
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<td>1</td>
<td></td>
</tr>
<tr>
<td>quartz</td>
<td>T</td>
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<td></td>
</tr>
<tr>
<td>scapolite</td>
<td></td>
<td></td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>cancrinite</td>
<td></td>
<td></td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>sodic plagioclase</td>
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<td></td>
<td></td>
<td>T</td>
</tr>
</tbody>
</table>
TABLE 19

Rb AND Sr ANALYTICAL DATA

McCLURE MOUNTAIN COMPLEX, COLORADO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Rb(^{87})/Sr(^{86})</th>
<th>Sr(^{87})/Sr(^{86}) (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM - 2</td>
<td>99.76</td>
<td>706.7</td>
<td>0.3628</td>
<td>0.7092</td>
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<td>MM - 3</td>
<td>67.23</td>
<td>1331.</td>
<td>0.1462</td>
<td>0.7073</td>
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<tr>
<td>MM - 4</td>
<td>177.2</td>
<td>1648.</td>
<td>0.3113</td>
<td>0.7081</td>
</tr>
<tr>
<td>MM - 5</td>
<td>149.0</td>
<td>140.8</td>
<td>3.064</td>
<td>0.7268</td>
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<tr>
<td>MM - 81</td>
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<td></td>
<td></td>
<td>0.7053</td>
</tr>
</tbody>
</table>
Figure 16. Whole-rock Rb-Sr isochron diagram for the McClure Mountain Complex, Colorado.

A: age: $517 \pm 14$ m.y.
$\text{Sr}^{87}/\text{Sr}^{86}$: 0.7059

B: age: $704 \pm 7$ m.y.
$\text{Sr}^{87}/\text{Sr}^{86}$: 0.7055
in an increase in the Rb/Sr ratio (Dasch, 1968). If this occurred to sample MM-5, the age and initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio for this suite of rocks are minimum values. Another isochron (B) which does not include MM-5 indicates an age of 704 ± 7 million years and an initial ratio of 0.7055. These two isochrons are thought to define the limits of the age and initial ratio of the intrusion.

The initial Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio of McClure Mountain Complex is high in contrast to the ratio of 0.7028 for nearby Iron Hill Complex. Assuming a similar mode of emplacement for the two complexes, it does not seem likely that only one of the complexes was contaminated by assimilation of sialic rock. A preferred explanation is that the initial ratios reflect an isotopically heterogeneous upper mantle.
Rainy Creek Complex, Montana

The Rainy Creek Complex of alkalic igneous rocks underlies a six-square-mile area located seven miles northeast of Libby, Montana. The most thorough descriptions of the Complex were reported by Larsen and Pardee (1929), Pardee and Larsen (1928), Perry (1948), and Boettcher (1967).

This alkalic complex intrudes metasedimentary rocks of the Precambrian Belt Series (Fig. 17). The main rock units of the complex are pyroxenite, syenite, and nepheline syenite. About two-thirds of the stock consists of coarse-grained pyroxenite, that grades locally into nearly pure biotite, or its alteration product, vermiculite. Microcline microperthite is present in the pyroxenite in amounts up to 15 percent. Accessory minerals are magnetite, ilmenite, sphene, and garnet. A fluorine-rich apatite commonly constitutes up to 10 percent of the rock.

The southwestern third of the stock consists of syenite, and small masses of syenite cut the pyroxenite. A typical sample contains about 85 percent microcline microperthite and 15 percent secondary muscovite, with accessory hornblende, fluorite, apatite, sphene, biotite, and garnet.

Nepheline syenite occurs only as a narrow dike about 0.1 mile southwest of the stock. It is composed chiefly
Figure 17. Geologic map of the Rainy Creek Complex, Lincoln County, Montana. (after Larsen and Pardee, 1929)
of albite and equal parts of nepheline and microcline. There are minor amounts of aegirine, apatite, magnetite, fluorite, and zeolites present.

A body of biotite-bearing rock, altered to vermiculite of economic quality, occurs at the center of the pyroxenite. This body is dike-like in shape and is at least 100 feet wide, 300 feet long, and 265 feet deep. In addition to the main vermiculite mass, there are smaller lens-like or tabular bodies nearby, most of which are separated from the wall rock by fault or slip planes. Vermiculite commonly constitutes more than 80 percent of the rock.

Samples of syenite and vermiculite-biotite rock were collected for Rb-Sr analysis by the author. Three of the syenites, LV-1, 2, and 4, are almost entirely perthite, with minor clinopyroxene and traces of sphene, sodic-plagioclase, and apatite (Table 20). These rocks show minor alteration to clays. Sample LV-3 is a phlogopite-rich syenite with traces of melilitc and iron oxide. The K-feldspar in this rock is highly altered to clays.

The Rb-Sr data are listed in Table 21. The four whole-rocks and a biotite from the vermiculite-biotite rock have a range of Rb$^{87}$/Sr$^{86}$ ratios between 0.3 to ten. The isochron (Fig. 18) indicates an age of 185 ± 3 million years. The initial Sr$^{87}$/Sr$^{86}$ ratio is 0.7038.
### TABLE 20

**MODAL ANALYSES OF ROCKS FROM THE RAINY CREEK COMPLEX, MONTANA**

<table>
<thead>
<tr>
<th>Sample</th>
<th>LV - 1</th>
<th>LV - 2</th>
<th>LV - 3</th>
<th>LV - 4</th>
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</thead>
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<tr>
<td>perthite</td>
<td>94</td>
<td>93</td>
<td></td>
<td>98</td>
</tr>
<tr>
<td>K-feldspar</td>
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<td></td>
<td>75</td>
</tr>
<tr>
<td>phlogopite</td>
<td></td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>clinopyroxene</td>
<td>5</td>
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<td></td>
<td>2</td>
</tr>
<tr>
<td>sphene</td>
<td>1</td>
<td>T</td>
<td></td>
<td>T</td>
</tr>
<tr>
<td>sodic-plagioclase</td>
<td>T</td>
<td>T</td>
<td></td>
<td>T</td>
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<tr>
<td>apatite</td>
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<td>T</td>
<td></td>
<td>T</td>
</tr>
<tr>
<td>melilite</td>
<td></td>
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<td>T</td>
</tr>
<tr>
<td>iron oxide</td>
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<td></td>
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<td>1</td>
</tr>
</tbody>
</table>
### TABLE 21

**Rb AND Sr ANALYTICAL DATA**

**RAINY CREEK COMPLEX, MONTANA**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Rb$^{87}$/Sr$^{86}$</th>
<th>Sr$^{87}$/Sr$^{86}$ (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LV - 1</td>
<td>164.7</td>
<td>860.4</td>
<td>0.558</td>
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<td></td>
<td>167.6</td>
<td>859.9</td>
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<td>0.7050</td>
</tr>
<tr>
<td>LV - 2</td>
<td>155.3</td>
<td>1394.0</td>
<td>0.324</td>
<td>0.7048</td>
</tr>
<tr>
<td></td>
<td>157.4</td>
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<td>0.7037</td>
</tr>
<tr>
<td>LV - 3</td>
<td>178.0</td>
<td>513.0</td>
<td>1.01</td>
<td>0.7060</td>
</tr>
<tr>
<td></td>
<td></td>
<td>509.8</td>
<td></td>
<td>0.7061</td>
</tr>
<tr>
<td>LV - 4</td>
<td>182.1</td>
<td>1209.0</td>
<td>0.425</td>
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</tr>
<tr>
<td></td>
<td>175.1</td>
<td>1217.0</td>
<td></td>
<td>0.7044</td>
</tr>
<tr>
<td>LV - 5</td>
<td>351.4</td>
<td>102.0</td>
<td>9.97</td>
<td>0.7295</td>
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</table>
Figure 18. Rb-Sr whole-rock isochron for the Rainy Creek Complex, Montana.
The syenites of the Coldwell district are located at the town of Coldwell, Ontario, on the northern shore of Lake Superior. The most complete study of this area was made by Kerr (1910). Later, Thomson (1935) reviewed the geology and discussed various hypotheses of the origin of the alkaline complex. There has recently been a revival of interest by the mining industry, but geologic data are generally not published. The Ontario Department of Mines has published a geologic map of the Port Coldwell Area (Preliminary Geological Map No. P. 114, 1967). The following geologic descriptions are taken from Kerr (1910) and Thomson (1935).

The Complex underlies an area of 125 square miles and is noted for its extreme diversity in composition and marked variation of rock types within short distances. Keewatin schists and greenstones bound the Complex on the east and west and occur as roof pendants. On the northern edge of the complex, these syenites gradually merge into a large area of biotite granites and gneisses. For the sake of simplicity, the rocks may be placed in four, fairly well-defined groups: hornblende syenite, augite syenite, quartz syenite, and nepheline syenite.

The hornblende syenite is a medium- to coarse-grained reddish rock, consisting of red soda-orthoclase and green
hornblende, with minor amounts of microperthite, albite, barkevikite, and riebeckite. An augite syenite, commercially known as "black granite," is a distinctive, dark, greenish brown, coarse-grained rock, which appears black at a distance. Microperthite is the chief feldspar with minor amounts of soda-orthoclase and soda-plagioclase present. Pale-brown augite is bordered by deep-green aegirine-augite. Arfvedsonite is often accompanied by barkevikite, and biotite occurs sparingly. Quartz syenite, a fine-grained quartz-rich phase of the red hornblende-syenite, contains quartz, soda-orthoclase, andesine, and lesser amounts of hornblende, augite, and biotite. The nepheline syenite has a medium- to coarse-grained texture and contains microperthite, anorthoclase, soda-orthoclase, albite, nepheline, augite, aegirine-augite, riebeckite, and biotite.

Fairbairn et al. (1959) measured the K-Ar and Rb-Sr ages for biotite and potassium feldspar from the Coldwell intrusion. For biotite in nepheline syenite, the K-Ar age is 1065 million years and the Rb-Sr age is 1070 million years. On the other hand, the Rb-Sr age of the potassium feldspar in augite syenite is 1225 million years. Fairbairn et al. were unable to account for the discrepancy. Twenty miles to the northwest of the Coldwell intrusion is the Prairie Lake carbonatite with an age of 1112 million years, determined by the K-Ar method (Gittins et al., 1967).
The results of these age determinations suggest a genetic relationship between the Coldwell alkalic complex and the Prairie Lake carbonatite.

Two pyroxene syenites, two hornblende syenites, and one syenite were collected on Rt. 17, eight miles east of Coldwell, Ontario, by G. Faure and S. Chaudhuri. Except for the syenite, these rocks are coarse-grained and consist of over 75 percent perthite and less than 21 percent ferromagnesian minerals (Table 22). Post-crystallization alteration is negligible. The syenite (50) is an aplite with a trachytic texture, consisting mostly of K-feldspar (sandi-dine?) and interstitial nontronite with minor calcite and fluorite. The nontronite is considered to be hydrothermal after glass. The K-feldspar is replaced to a considerable degree by clays.

The Rb-Sr analytical data are listed in Table 23. The pyroxene- and hornblende syenites have similar $\text{Rb}^{87}/\text{Sr}^{86}$ ratios that range from 1.6 to 2.4. The syenite, 50, has a very high ratio of 31.7 and is important in defining the slope of the isochron (Fig. 19). Unfortunately, this syenite is highly altered, which probably has significantly affected its $\text{Rb}^{87}/\text{Sr}^{86}$ and $\text{Sr}^{87}/\text{Sr}^{86}$ ratios. The isochron, which is defined by all five rocks, indicates an age of $999 \pm 9$ million years for the Fort Cordwell intrusion. This age is low in comparison with biotite and feldspar
TABLE 22  
MODAL ANALYSES OF ROCKS FROM THE  
PORT COLDWELL COMPLEX, CANADA

<table>
<thead>
<tr>
<th></th>
<th>Sample</th>
</tr>
</thead>
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<td></td>
<td>47</td>
</tr>
<tr>
<td>perthite</td>
<td>81</td>
</tr>
<tr>
<td>clinopyroxene</td>
<td>T</td>
</tr>
<tr>
<td>hornblende</td>
<td>12</td>
</tr>
<tr>
<td>biotite</td>
<td>2</td>
</tr>
<tr>
<td>apatite</td>
<td>T</td>
</tr>
<tr>
<td>quartz</td>
<td></td>
</tr>
<tr>
<td>iron oxide</td>
<td>2</td>
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<tr>
<td>iddingsite</td>
<td>3</td>
</tr>
<tr>
<td>chlorite</td>
<td>2</td>
</tr>
<tr>
<td>fluorite</td>
<td>T</td>
</tr>
<tr>
<td>K-feldspar</td>
<td></td>
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<tr>
<td>calcite</td>
<td></td>
</tr>
<tr>
<td>nontronite</td>
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</tr>
</tbody>
</table>

* * *
### Table 23

**Rb AND Sr ANALYTICAL DATA**

**PORT COLDWELL COMPLEX, CANADA**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>Rb(^{87})</th>
<th>Sr(^{86}) (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>118.8</td>
<td>146.5</td>
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<td>48</td>
<td>114.1</td>
<td>197.7</td>
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<tr>
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<td>111.7</td>
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</tr>
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<td>180.0</td>
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<td>0.7316</td>
</tr>
<tr>
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<td>0.7310</td>
</tr>
<tr>
<td>50</td>
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<td>16.8</td>
<td>31.7</td>
<td>1.147</td>
</tr>
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<td></td>
<td>17.46</td>
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</tr>
<tr>
<td>383</td>
<td>84.67</td>
<td>212.9</td>
<td>1.15</td>
<td>0.7203</td>
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<tr>
<td></td>
<td>213.0</td>
<td></td>
<td></td>
<td>0.7203</td>
</tr>
</tbody>
</table>
Figure 19. Rb-Sr whole-rock isochron for the Port Coldwell Complex, Canada.

age: 999±9 m.y.
Sr$^{87}$/Sr$^{86}$: .704
ages of 1070 and 1225 million years, respectively (Fairbairn et al., 1959). It is possible to evaluate these mineral ages by using them to calculate initial Sr$^{87}$/Sr$^{86}$ ratios of the four, unaltered whole-rocks. If the age of these rocks is 1225 million years, the average initial ratio is 0.6984. Since this value is the same as the primordial Sr$^{87}$/Sr$^{86}$ ratio of meteorites, the age of the rocks is probably much less than 1225 million years. An age of 1070 million years seems most reliable because the Rb-Sr and K-Ar ages of biotite from nepheline syenite are concordant (Fairbairn et al., 1959). The average initial Sr$^{87}$/Sr$^{86}$ ratio for the four syenite samples is 0.7021 when an age of 1070 million years is assumed. It follows that the Sr$^{87}$/Sr$^{86}$ ratio of the upper mantle where the magma was derived had a Sr$^{87}$/Sr$^{86}$ ratio of 0.7021.
Summary

Rb-Sr analyses of whole-rocks from a series of alkalic igneous complexes and associated carbonatites were made for determinations of their ages and initial Sr$^{87}$/Sr$^{86}$ ratios. The results are: (1) Iron Hill Complex, 1481 million years, 0.7028; (2) McClure Mountain Complex, 517 - 704 million years, 0.7057; (3) Rainy Creek Complex, 185 million years, 0.7038; and (4) Port Coldwell Complex, 1070 million years, 0.7021. These data will be used, in addition to the data for continental mafic and ultramafic igneous rocks (Chapter III), to construct a strontium growth-curve for the upper mantle.
CHAPTER V

THE ISOTOPIC COMPOSITION OF STRONTIUM
IN CARBONATE ROCKS

Introduction

The initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios for the mafic-ultramafic intrusions, plateau basalt flows, and carbonatite-alkalic complexes provides information regarding the isotopic evolution of strontium and the Rb/Sr ratio of the upper mantle. A complementary documentation of the evolution of strontium within rocks at the surface of the earth is important for an understanding of the chemical differentiation of the mantle and growth of continents in the past. An estimate of the isotopic composition of strontium in the rocks at the earth's surface may be obtained from the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the oceans. The oceans are a large reservoir of strontium, whose isotopic composition is affected by the age and Rb-enrichment of the rocks exposed on the continents. Changes in the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the ocean in the geologic past provide information concerning the growth of the sialic continents.

Interest in the isotopic composition of strontium in sea water and marine carbonate rocks was stimulated by
Wickman (1948), who suggested that oceanic strontium should be a representative sample of the isotopic composition of strontium in the crust of the earth at any given time. Similarly, Hedge and Walthall (1963) equated the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of sea water with the "weathering crust." Wickman suggested that the increase in the $\text{Sr}^{87}$ abundance by radioactive decay of $\text{Rb}^{87}$ be used to determine the absolute age of marine carbonates and shells, provided the strontium in the ocean represents an average isotope abundance for strontium in surface rocks. On the basis of rubidium and strontium abundances estimated for the crust of the earth, Wickmann calculated an increase of six percent per billion years in the $\text{Sr}^{\text{87}}/\text{Sr}^{\text{86}}$ ratio in limestones. However, more accurate data on the abundances of strontium and rubidium in the crust allow an increase of less than 0.4 percent per billion years for the $\text{Sr}^{\text{87}}/\text{Sr}^{\text{86}}$ ratio in limestones (Gast, 1955). Therefore, the method is not useful for dating marine limestones.

Before proceeding to a discussion of measurements of the $\text{Sr}^{\text{87}}/\text{Sr}^{\text{86}}$ ratio of sea water and associated carbonates, the sources of strontium in the oceans should be defined. Three different sources of strontium in the oceans have been recognized by Faure et al. (1965): (1) volcanic rocks and volcanic emanations, (2) carbonate and sulfate rocks of marine origin, and (3) old igneous and metamorphic rocks of
the Precambrian shield regions. Each of these sources contributes strontium of a specific isotope composition. Volcanic rocks and volcanic emanations contribute strontium derived from the upper mantle. The \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio of these rocks is about 0.704 ± 0.002. Carbonate and sulfate rocks of marine origin contribute much strontium to the oceans as a result of weathering. Turekian (1964) concluded that most of the strontium in the sea is derived from carbonate rocks on the continents. Similarly, Faure et al. (1965) suggested that as much as 80 percent of the strontium in the modern oceans is derived from weathering of marine carbonate rocks. They selected 0.708 as a reasonable value of the \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio of the strontium contributed to the oceans by weathering of the carbonate rocks of marine origin. Old igneous and metamorphic rocks of the Precambrian shield regions contribute strontium that is enriched in radiogenic \( \text{Sr}^{87} \) as a result of decay of \( \text{Rb}^{87} \) to \( \text{Sr}^{87} \). The isotopic composition of strontium of these rocks is extremely variable because of their diverse ages and \( \text{Rb}/\text{Sr} \) ratios; but it is enriched in radiogenic \( \text{Sr}^{87} \) relative to the strontium in young volcanic rocks. This enrichment was clearly demonstrated by Faure et al. (1963) who measured the isotopic compositions of strontium in calcareous shells of modern fresh water mollusks from the Canadian Shield. The observed \( \text{Sr}^{87}/\text{Sr}^{86} \) ratios ranged from 0.712 to 0.726 reflecting the presence of radiogenic \( \text{Sr}^{87} \).
in the ancient crystalline basement rocks. On this basis, Faure et al. (1965) later suggested that the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of strontium derived as a result of weathering of Precambrian shield rocks lies in the range 0.712 to 0.720.

It may be questioned whether the strontium dissolved in groundwater and surface water has the same isotopic composition as the bedrock. Dasch (1968) has studied this problem in weathering profiles developed on igneous rocks and compared the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of weathered and unweathered rocks. He found that the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of weathered and fresh specimens of the same rock are indistinguishable. This observation suggests that the strontium that is released from the rock as a result of chemical weathering has essentially the same isotopic composition as the total strontium present in the rock. However, limited data from the Hubbard Brook watershed, New Hampshire, where early Paleozoic gneiss and monzonite and Pleistocene till are exposed to erosion, show that water contains less radiogenic strontium than the bedrock. Similarly, Hart and Tilton (1966) found the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of Lake Superior water to be low (0.718) relative to sediments in the lake (0.739), and Faure et al. (1967) found a similar situation after analyzing Lake Huron water. Contrary to the results of these studies, Jones and Faure (1967) found agreement between $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of water and associated sediment
in Lake Vanda, Antarctica.

With the data currently available, it is not possible to assume that dissolved strontium entering the oceans today has a $\text{Sr}^{87}/\text{Sr}^{86}$ ratio exactly equal to that of the average bedrock being eroded. However, a minor discrepancy between the two ratios is not expected to be serious. Since we are interested in the change of the isotopic composition of strontium in the rocks at the earth's surface as a function of time, knowledge of the actual value of the average $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in the crust of the earth is not necessary. The strontium which is carried into the oceans by rivers will eventually be thoroughly mixed because the residence time of strontium in the oceans, which is about one million years, is long compared to the mixing time of about a thousand years (Dasch, 1968).

Measurements of $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of ocean water have been reported by Gast (1961), Compston and Pidgeon (1962), Herzog, et al. (1958), Hedge and Walthall (1963), Faure et al. (1965), and Murthy and Beiser (1968). Faure et al. (1965) analyzed strontium in ten samples of surface water from the North Atlantic and found that the average $\text{Sr}^{87}/\text{Sr}^{86}$ ratio is 0.7093 ± 0.0005. They suggested that this value is a constant for present-day ocean water. Later, Murthy and Beiser (1968) reported an average $\text{Sr}^{87}/\text{Sr}^{86}$
ratio of 0.7094 ± 0.0006 for analyses of 21 water samples, one manganese nodule, and one oolite sample from the Atlantic, Pacific, and Indian oceans. Jones (1969, personal comm.) obtained an average of 0.7094 for two samples of water from the Ross Sea and also 0.7095 for one analysis of sea water from Littleton Harbor, New Zealand. There appears to be good reason, therefore, to accept a value of 0.7093 for the \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio of modern marine strontium. This ratio probably has had different values in the past depending on the changing relative quantities of strontium contributed to the oceans by the three different sources listed above.

Calcium carbonate precipitated from sea water contains strontium with the same isotopic composition as strontium in sea water because strontium isotopes are not measurably fractionated in nature. The \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio of marine limestones for practical purposes is not modified by decay of \( \text{Rb}^{87} \) because the \( \text{Rb}/\text{Sr} \) ratio of carbonate rocks is generally low (about 0.005, Turekian and Wedepohl, 1961). Before the variation of the \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio of sea water can be determined on the basis of analyses of calcium carbonate, it must first be demonstrated that modern marine carbonate has the same isotopic composition of strontium as sea water. This demonstration has been provided by Peterman et al. (1967) who showed that eight modern mollusks have a mean \( \text{Sr}^{87}/\text{Sr}^{86} \)
ratio of 0.7092 ± 0.0002, which is virtually identical to that of the sea water. In addition, Faure et al. (1967) found the Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio for strontium in water and shells of the pelecypod *Mytilus edulis*, Linné from the Hudson Bay to be 0.7093 ± 0.0003.

Peterman et al. (1967) analyzed a suite of carbonate fossils of known age in order to establish the variation of the Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio of sea water as a function of geologic time (Table 24). These ratios are essentially constant from Ordovician to Mississippian time at about 0.7078. The ratios then gradually decreased to a low of 0.7068 in the Late Jurassic Period followed by a rapid increase with time to the present value of sea water.

Peterman et al. (1967) attributed the changing Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio of strontium in sea water to changes in the relative proportions of strontium derived from penecontemporaneous volcanic and plutonic rocks and strontium derived from the old crust. The Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio of Precambrian seas can be determined by measuring the Sr\textsuperscript{87}/Sr\textsuperscript{86} ratio of unmetamorphosed carbonate rocks. A serious problem is the paucity of unmetamorphosed carbonate rock available for analysis. In addition, it is often difficult to fix the time of deposition accurately of Precambrian carbonate rocks.

Inherent in the analysis of carbonate rocks is the serious problem of demonstrating that the measured Sr\textsuperscript{87}/Sr\textsuperscript{86}...
TABLE 24

THE ISOTOPIC COMPOSITION OF STRONTIUM IN PHANEROZOIC MARINE FOSSILS

(After Peterman et al., 1967)

<table>
<thead>
<tr>
<th>Age</th>
<th>Sr$^{87}$/Sr$^{86}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>0.7092 ± 0.0002</td>
</tr>
<tr>
<td>Early Pliocene</td>
<td>0.7087 ± 0.0003</td>
</tr>
<tr>
<td>Late Miocene</td>
<td>0.7088 ± 0.0004</td>
</tr>
<tr>
<td>Early Eocene</td>
<td>0.7074 ± 0.0004</td>
</tr>
<tr>
<td>Late Cretaceous</td>
<td>0.7074 ± 0.0002</td>
</tr>
<tr>
<td>Early Cretaceous</td>
<td>0.7072 ± 0.0001</td>
</tr>
<tr>
<td>Late Jurassic</td>
<td>0.7068 ± 0.0001</td>
</tr>
<tr>
<td>Late Permian</td>
<td>0.7072 ± 0.0003</td>
</tr>
<tr>
<td>Late Mississippian</td>
<td>0.7076 ± 0.0003</td>
</tr>
<tr>
<td>Late and Middle Devonian</td>
<td>0.7078 ± 0.0002</td>
</tr>
<tr>
<td>Late and Middle Ordovician</td>
<td>0.7072 ± 0.0003</td>
</tr>
</tbody>
</table>

*All ratios are adjusted according to a value of 0.7083 for the Eimer and Ament standard carbonate.
ratio represents the isotopic composition of strontium of the carbonate fraction only. The clay-size fraction may contribute radiogenic Sr\(^{87}\) when the limestone is dissolved during sample preparation. The effect of this on an analysis of strontium from the carbonate fraction may be appreciable, but is difficult to evaluate.

The isotopic composition of strontium of the clay-size fraction in modern deep sea sediment appears to be closely related to their geologic provenance. These fine-grained sediments are mostly continental detritus and contain the isotopic record of the bedrock from which they were derived. The mineralogy of the clay fraction also affects the strontium isotopic composition. Illite is the principal rubidium-bearing clay-mineral and has the highest Rb/Sr ratio. It would be expected to have the highest Sr\(^{87}/\text{Sr}^{86}\) ratio, especially if derived from old bedrock. Consequently, a clay fraction with a high content of illite may have a high Sr\(^{87}/\text{Sr}^{86}\) ratio.

No systematic study has previously been made to determine the best technique for preferentially extracting strontium from the carbonate fraction of a sample while avoiding strontium from the clay-size fraction. Such a study is reported here. The samples that were analyzed are from the Pennsylvanian-Permian Casper Formation of southeastern Wyoming, from the Siyeh and Alty Formations
of the Precambrian Belt Series of Montana, and from the Precambrian Bulawayan limestone of the Zwankendaba Group in Southern Rhodesia.

The Casper Formation, Wyoming

Reviews of the stratigraphy and depositional environment of the Casper Formation in southeastern Wyoming have been published by Thomas et al. (1953) and Agatston (1954). During Middle Pennsylvanian time, southeastern-most Wyoming was exposed as land while the remainder of Wyoming was submerged beneath a shallow sea. Fusulinids and brachiopods indicate a sea water depth of less than 200 feet in eastern Wyoming. The region was a stable shelf area, but gradually, the western half of Wyoming rose above sea level as the sea withdrew to the east. Southeastern Wyoming sank and received sediments as the ancestral Rockies of Colorado, the Bighorn region of northern Wyoming and Montana, and the Wind River region in central Wyoming became strongly positive elements. By Wolfcampian time (Early Permian), the eastern third of Wyoming was occupied by an open shallow sea.

Along the margins of the Laramie Mountains the Casper Formation varies considerably in lithology. It is composed predominantly of alternating thick sandstones and thin limestones. The limestones, in general, are light-colored, almost white, but some are marked by pale tints of pink, lavender, or purple.
The samples used in this study are from the upper part of the stratigraphic section in Rogers Canyon, located eight miles north-northeast of Laramie, and are Wolfcampian in age on the basis of fusulinids (Thompson and Thomas, 1953). According to the radiometric time scale of Holmes (1960), deposition occurred about 270 million years ago. One of the two samples, LC-4, was collected nine feet from the top of the highest limestone unit, while the other, LC-6, was located six feet below LC-4.

Samples of powdered LC-4 (one gram each, -140 mesh) were agitated in separate 100 ml. volumes of double-distilled, demineralized water for time periods of five minutes to eight hours. After filtering the remaining undissolved limestone, each of the water solutions was evaporated to a volume of 20 ml. and passed through an ion-exchange column to separate the strontium for isotope analysis. The strontium isotope data are shown in Table 25. Measured Sr\textsuperscript{87}/Sr\textsuperscript{86} ratios ranged from 0.7073 to 0.7108. With the exception of the low ratio for the half-hour solution (0.7073, Fig. 20) longer dissolution times resulted in higher ratios.

In order to verify the expectation that the Sr\textsuperscript{87}/Sr\textsuperscript{86} ratios within a stratigraphic interval of six feet would not differ significantly, two other samples of Casper limestone, LC-6, were dissolved in water for 15- and 30-
Figure 20. Isotopic composition of strontium in water solutions of limestones of the Casper Formation.

Figure 21. Isotopic composition of strontium in hydrochloric acid solutions of limestones of the Casper Formation.
minute periods. The 15-minute solution had an unusually high ratio of 0.7119, but the 30-minute solution had a ratio of 0.7083, which is in the range of values for LC-4 (Table 25, Fig. 20).

Acid solutions of LC-4 having different normalities were made by dissolving powdered samples for five minutes in 20 ml. volumes of 0.1N, 2N, and 6N hydrochloric acid. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for the three solutions were essentially alike, 0.7091, 0.7091, and 0.7092 (Table 26, Fig. 21). These values are virtually the same as the value obtained for the 5-minute water solution.

The insoluble fraction of LC-4 was separated from the carbonate by dissolving a powdered sample in 2N hydrochloric acid. The insoluble fraction, 28 percent by weight of the total fraction, is primarily quartz and feldspar sand with a trace of chlorite. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of this fraction is 0.7132.

The data for water solutions of LC-4 and LC-6 which are listed in Table 25 include the anomalous 0.7119 which must be considered. In the previous discussion of analytical precision (Chapter II), it was pointed out that 95 of 100 replicate values of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of a rock sample are expected to lie inside a zone of $\pm 0.0016$ around the mean ratio. This estimate is based on 68 duplicate
<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation and age</th>
<th>Insoluble Fraction</th>
<th>Dissolution time (hrs.)</th>
<th>Sr$^{87}$ (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC - 4</td>
<td>Casper Fm. 270 m.y.</td>
<td>quartz, feldspar, chlorite</td>
<td>8, 3, 1/2, 1/4, 1/12</td>
<td>0.7105, 0.7108, 0.7073, 0.7099, 0.7093</td>
</tr>
<tr>
<td>LC - 6</td>
<td>Casper Fm.</td>
<td>quartz, feldspar, chlorite</td>
<td>1/2, 1/4</td>
<td>0.7083, 0.7119</td>
</tr>
<tr>
<td>GP - 1</td>
<td>Siyeh Ls. 1325 m.y.</td>
<td>illite, chlorite, quartz</td>
<td>1/2, 1/4</td>
<td>0.7744, 0.7741</td>
</tr>
<tr>
<td>GP - 3</td>
<td>Altyn Ls. 1325 m.y.</td>
<td>illite, chlorite, quartz</td>
<td>24, 24</td>
<td>0.7380, 0.7162</td>
</tr>
<tr>
<td>154</td>
<td>Bulawayan Ls. 2950 m.y.</td>
<td>quartz, chlorite, carbon</td>
<td>20, 20</td>
<td>0.7070, 0.7043</td>
</tr>
</tbody>
</table>

**TABLE 25**
ISOTOPIC COMPOSITION OF STRONTIUM IN WATER SOLUTIONS OF CARBONATE ROCKS.
and triplicate analyses of 31 rock specimens. Therefore, the 0.7119 value for sample LC-6 is considered anomalous to the trend of decreasing ratios with decreasing time.

Four water solutions of LC-4 and LC-6, having a duration of less than 30 minutes (excluding 0.7119), and one hydrochloric acid leach of LC-4 give a mean \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio for the Casper Formation of 0.7088. This is considered to be the best estimate of the isotopic composition of strontium in this Permian carbonate unit. It is of interest to compare this value with analyses by Brookins (1967) of Permian limestones of eastern Kansas and with analyses by Peterman et al. (1967) of fossils of similar age. Brookins dissolved carbonate samples from the Towanda, Threemile, and Ells Formations using 2N hydrochloric acid and found the average \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio to be 0.7087 (adjusted to a value of 0.7083 for the Eimer and Amend standard), which agrees with the value for the Casper limestone. According to the analyses of Peterman et al., late Permian sea water had a \( \text{Sr}^{87}/\text{Sr}^{86} \) ratio of about 0.7072 (Table 24). If we accept the assumption that fossils are the best indicators of the isotopic composition of strontium of ancient sea water, the most likely explanation for the higher ratios for the limestones is that the clay-size fraction contributed radiogenic strontium during dissolution.
The Carbonate Rocks of the Belt Series, Montana

The geosynclinal argillite, quartzite, and carbonate of the Precambrian Belt series crop out in western Montana, northern Idaho, and British Columbia. The Siyeh and Altyn limestones, which were sampled for study, are part of the estimated 26,000 to 36,000 feet of rock exposed in Glacier National Park (Ross, 1959).

The Siyeh limestone consists of limestone, dolomite, sandstone, and argillite. Individual units may appear to be massive, but are often finely laminated, oolitic, and stromatolitic (Ross, 1959). The Altyn limestone is predominantly dolomite with minor dolomitic siliceous, and ferruginous limestone and quartzite. The Altyn limestone also contains stromatolites.

A minimum age of sedimentation of the Belt Series has been determined by Obradovich and Peterman (1968) on the basis of Rb-Sr whole-rock analyses of the Newland limestone and Chamberlain shale in the Big Belt and Little Belt Mountains to the southeast. The Newland limestone and Chamberlain shale are correlative with the Siyeh and Altyn limestones, respectively (Ross, 1959). The age is 1325 ± 15 million years.

Two powdered samples of Siyeh limestone (GP-1) were agitated in demineralized water for 30 and 15 minute
periods. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of the resulting solutions are 0.7744 and 0.7741 (Table 25), respectively, and are identical within experimental error. The insoluble fraction, which is 85 percent by weight of GP-1, consists of illite, chlorite, and quartz. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for this fraction is 1.041 indicating appreciable enrichment in radiogenic $\text{Sr}^{87}$, presumably as a result of decay of $\text{Rb}^{87}$ in the illite.

Two strontium isotope analyses were made of two separate 24-hour water solutions of the Altyn limestones (GP-3), which contains 25 percent insoluble fraction of illite, chlorite, and quartz. The analyses, 0.7380 and 0.7162 differ significantly, but both are lower than the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of GP-1 (Table 25).

Samples of GP-1 were dissolved with 0.1N, 2N, and 6N hydrochloric acid to determine whether acid strength affects the measured $\text{Sr}^{87}/\text{Sr}^{86}$ ratio. The three ratios differ considerably within a wide range from 0.7710 to 0.7755 (Table 26).

Perhaps the most obvious conclusion to be derived from these data is that clays may effectively mask the isotopic composition of strontium of the carbonate fraction by contributing radiogenic $\text{Sr}^{87}$ during dissolution of the carbonate fraction. The average $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.7743 for
<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation</th>
<th>HCl Normality</th>
<th>Dissolution time (min.)</th>
<th>Sr$^{87}$ (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC - 4</td>
<td>Casper Fm.</td>
<td>0.1</td>
<td>5</td>
<td>0.7091</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>5</td>
<td>0.7091</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>5</td>
<td>0.7092</td>
</tr>
<tr>
<td>GP - 1</td>
<td>Siyeh Fm.</td>
<td>0.1</td>
<td>5</td>
<td>0.7755</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>5</td>
<td>0.7647</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>5</td>
<td>0.7710</td>
</tr>
<tr>
<td>154</td>
<td>Bulawayan</td>
<td>0.1</td>
<td>15</td>
<td>0.7029</td>
</tr>
<tr>
<td></td>
<td>Ls.</td>
<td>0.1</td>
<td>15</td>
<td>0.7031</td>
</tr>
</tbody>
</table>

TABLE 26

ISOTOPIC COMPOSITION OF STRONTIUM
IN HCl ACID SOLUTIONS OF CARBONATE ROCKS
water solutions of GP-1 (85% insoluble fraction) is attributed to the removal of radiogenic $\text{Sr}^{87}$ from illite by water. The three ratios of the acid solutions were also very high compared to ratios of the water solutions. Water solutions of GP-3 also had high ratios, but these ratios were much lower than those of GP-1, perhaps because of a smaller clay fraction (25%).

The study of the effects of different acid strength on the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of LC-4 gave results which could have been predicted, considering that the clay content of the insoluble fraction of the sample amounted to only a trace of chlorite. A similar study using GP-1 with 85 percent insoluble fraction (mostly clay minerals) showed great inconsistency. The 2N hydrochloric acid solution was much lower than either the weaker 0.1N or stronger 6N hydrochloric acid solutions. There is, then, no measurable correlation between the strength of acid used and the measured $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for a carbonate rock having a high content of insoluble minerals.

The Bulawayan Limestone, Southern Rhodesia

The Zwankendaba Group in Southern Rhodesia consists of banded ironstone, graywacke, arkose, volcanic conglomerate, and the dolomitic, carbonaceous Bulawayan limestone. This group is interbedded with a sequence of volcanic
greenstone. Algal structures containing as much as 1.08 percent free carbon are well developed near Turk Mine, 33 miles north-northeast of Bulawayo (Macgregor, 1940). The minimum age for the Bulawayan limestone is 2950 ± 100 million years, based on a Rb-Sr whole-rock age determination for the G-4 granite which intrudes the stratigraphically younger Moodies system (Nicolayson, 1962).

Three separate water solutions of 20 hours duration had Sr$^{87}$/Sr$^{86}$ ratios that average 0.7057 (Table 25). Two solutions of 15 minute duration, using 0.1N hydrochloric acid had ratios of 0.7029 and 0.7031, which are lower than the ratios of the water leaches (Table 26). The insoluble residue of the Bulawayan limestone, which consists of quartz, chlorite, and carbon, has a Sr$^{87}$/Sr$^{86}$ ratio of 0.7378.

The average Sr$^{87}$/Sr$^{86}$ ratios for the Bulawayan limestone reported in the literature is about 0.702 (Powell, 1966). Since a dissolution time of 20 hours in water is unnecessarily long and because the Sr$^{87}$/Sr$^{86}$ ratios measured are higher than those measured for the acid solutions, suggesting the influence of the clay fraction during this long time period, these analyses probably are not valid for the isotopic composition of the Bulawayan carbonate. The Sr$^{87}$/Sr$^{86}$ ratio of 0.7030 for the 0.1N hydrochloric acid solution is accepted as the more likely value.
Conclusions

Some reasonable conclusions may be drawn concerning the analysis of carbonate rocks. In order to avoid leaching radiogenic Sr$^{87}$ from the clay fraction during dissolution of a carbonate rock, samples as clay-free as possible must be used and dissolution time in hydrochloric acid or water must be kept to a minimum, less than five minutes. Because of the anomalous ratios which may be obtained, confidence in Sr$^{87}$/Sr$^{86}$ ratios for limestone formations will be increased if the value is based on duplicate or triplicate analyses of at least two different samples from the same formation.

On the basis of these measurements on the Casper limestones and the data of Brookins (1967) for limestones of eastern Kansas, a Sr$^{87}$/Sr$^{86}$ ratio of 0.7038 is accepted for Permian carbonate rocks. This value is higher than ratios measured by Peterman et al. (1967) for Permian carbonate fossils and may indicate the influence of the clays in the limestone analyses.

Consideration of the data for acid and water solutions of the carbonate rocks of the Belt Series lead to the conclusion that no value for the Sr$^{87}$/Sr$^{86}$ ratio can be accepted as representative of the sea water in which these carbonate sediments were deposited.
The value of 0.7030 is accepted as the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for Bulawayan carbonate. However, because of a likely contribution of radiogenic $\text{Sr}^{87}$ from the clay fraction having a high $\text{Sr}^{87}/\text{Sr}^{86}$ ratio (0.7378), the isotopic composition of strontium in sea water three billion years ago may have been lower than 0.7030. Similarly, the ratios measured for other carbonate and clay fractions suggest that the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of a solution containing dissolved marine carbonate rock is higher, by an unknown amount, than the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the sea water which precipitated this carbonate.
CHAPTER VI

THE EVOLUTION OF THE MANTLE
AND THE CONTINENTAL CRUST

The rate and time of formation of the continents has been a fundamental problem to those concerned with the history of the earth. During the last decade, this problem has received considerable attention from geochemists who have offered several possible solutions. Observations of lead and strontium isotopes from rocks of the earth's crust have shown that the continents formed quickly and have not grown appreciably since, and, also, that they have been growing at a continuous, constant rate through geologic time.

Since Faure and Hurley (1963) showed that the Rb/Sr ratio of the average sialic crust is from three to five times greater than the subsialic source regions of basalt magmas, it seemed possible to Hurley et al. (1962) that the rate of growth of sialic continents could be determined by documenting the rate of enrichment within the continents of rubidium relative to strontium. Their approach to this problem was to determine the excess radiogenic Sr$^{87}$ in the
sialic crust over that necessary for the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the source region of sial. Their observations of excess radiogenic strontium in igneous and metamorphic rocks having a wide range of geologic ages (times of intrusion or metamorphism) indicated to them that these rocks had little, if any, history within the continental crust prior to their final emplacement. Therefore, material differentiated directly from the subsialic source regions was added to the sialic crust at a constant rate during the past 2800 million years. The amount of material in the sialic crust which is reworked by melting and differentiation is thought to be relatively low.

The conclusion, that a constant rate of growth has occurred for the sialic crust, is based on the assumption that the enrichment of rubidium during differentiation of the upper mantle is accompanied by enrichment of silica, alumina, sodium and potassium relative to calcium and magnesium. Evidence supporting this assumption is gained from suites of differentiated igneous rocks (Faure, 1961; Nockolds and Allen, 1956; and Turekian and Wedepohl, 1961) which show this trend of enrichment.

Patterson and Tatsumoto (1964) also considered the problem of continental development by studying lead isotope concentrations in K-feldspars from rocks of the Canadian Shield. They prepared composites of hundreds of beach and
river sands which represent samples of large areas of the North American continent at different times in the past. Six of the seven feldspar concentrates were taken from the North American continent and had ages from 90 to 2400 million years. They reasoned that the K-feldspar fraction of each concentrate should be representative of igneous and metamorphic rocks at thousands of locations and the lead within this fraction should have an isotopic composition unchanged since the rocks were formed because of the insignificant quantity of uranium present in K-feldspar. One concentrate was obtained from volcanic sediments of "zero" age dredged from one location on the East Pacific Rise.

The isotopic composition of lead in each of these seven concentrates was then compared with that of a hypothetical mixture of lead of the same age which had evolved in a closed system of uranium and lead. The detrital K-feldspar leads clearly evolved in open systems because there is a progressive enrichment of Pb$^{206}$ in the observed lead relative to the hypothetical ideal lead as a function of age. Also, there is a progressive increase in the U$^{238}$/Pb$^{204}$ ratio of the observed lead as a function of age.

To account for the enrichment of Pb$^{206}$ and the increase of the U$^{238}$/Pb$^{204}$ ratio, they considered a "two-phase dynamic model." Prior to the time of segregation of the earth's core, about 4.55 billion years ago, the earth was homogeneous with respect to uranium and lead. During
the first 100 million years after the core and mantle separated, there was a very rapid migration of uranium and lead toward the earth's surface. The migration of lead was essentially completed, but uranium continued to migrate at a lower, but still appreciable rate.

This two phase model did not satisfactorily account for the observed data, however, because continuing migration of uranium would result in lead that is more radiogenic than that observed in the feldspars. This model was modified by adding a third phase (sialic continental crust) which separated from the protocrust at an early time in the earth's history. From the time of sial formation, lead within the sial evolved in an environment insulated from further enrichment of uranium from the mantle by a residual layer of mantle material. According to this model, the earth's mantle fractionated into an outer phase and an inner phase within 100 million years after the core segregated from the mantle. This new outer phase is considered a "protocontinental layer" which may have been about 150 km thick. Between 3.5 and 2.5 billion years ago, major, continent-forming events occurred within the protocontinental layer, resulting in the accumulation of a continental crust, tens of kilometers thick. The remaining protocontinental layer below the new continental crust is a residual unit of mantle material about a hundred kilometers thick.
In an attempt to explain the apparent incompatibility of these two models, Armstrong (1963) developed a mathematical model that had as its prime character the process of continued mixing of crust and mantle materials in orogenic zones at the borders of continents. This process, which is assumed to have continued through geologic time, is the result of sea-floor spreading and the consequent under-thrusting of sialic sediment into the upper mantle below the continents. In the upper mantle, the sediment is mixed with mantle material and then returned to the crust as sialic magma. As a result of mixing, this new sialic magma has an isotopic composition between that of the crust and mantle.

Armstrong suggested that for a short time early in the earth's history, probably as core segregation proceeded, evolution of both lead and strontium isotopes occurred throughout the mantle. During this short time interval, the mantle was being thoroughly mixed by subcrustal currents extending to the base of the mantle. Subsequently, mantle differentiation began and proceeded at a rate which resulted in an appreciable volume of continental crust by three billion years ago. Most continental growth occurred before 2.5 billion years ago, as Patterson and Tatsumoto (1964) also suggested, and since that time material eroded from the continents has been continuously recycled through
through the mantle. In effect, there has not been a net increase in the volume of the continental crust over the past 2.5 billion years as Hurley et al. (1962) suggested.

As a new approach to the problem of determining the time and rate of separation of the continents from the mantle, Hurley (1968 a,b) described a method to establish the abundances of rubidium, potassium, and strontium in the earth. He was also interested in determining the degree of partitioning of these elements between the continents and mantle. He began by using a model of the crust suggested by Poldervaart (1955) with modifications according to seismological data (Pakisor and Robinson, 1967). Estimates of rubidium, strontium, radiogenic Sr$^{87}$, and argon abundances in crustal rocks led first to reasonable estimates of the masses of rubidium, potassium, and strontium in the earth and the crust, and finally to the conclusion that a thin, unstable protocrust amounting to one-quarter of the present crust existed 3800 million years ago. Additional separation of the sial from the upper mantle began 3300 million years ago and continued to the present at a constant rate. If, as Armstrong (1968) suggested, part of the radiogenic Sr$^{87}$ generated in the crust were lost to the mantle during convective cycling, the separation of the crust would be extended proportionately back in time, but a linear growth rate would still prevail.
Prior to publication of these reports, Gast (1960) had remarked that initial Sr\(^{87}/Sr^{86}\) ratios of Keewatin pillow lavas and Stillwater Complex anorthosite were not much different from those of Recent mafic rocks. Consideration of this observation along with the assumption that strontium isotopes are not fractionated during magma generation in the upper mantle, led Faure et al. (1962) to suggest the possibility that the initial Sr\(^{87}/Sr^{86}\) ratios of mafic magmas of different ages record the changing isotopic composition of strontium within the upper mantle, provided the rising magmas did not become contaminated by assimilation of crustal rock. If the upper mantle has been a closed system with respect to rubidium and strontium, the initial Sr\(^{87}/Sr^{86}\) ratios plotted against time should define a linear strontium growth-curve, extending from the primordial value of 0.6985 to the present value of about 0.704. The slope of the line would reflect the Rb/Sr ratio for the upper mantle. Preliminary measurements of the initial ratios of several mafic intrusions ranging in age from two billion years to Tertiary did not define such a linear strontium growth curve. Apparently, the mantle had not been a closed system and the Rb/Sr ratio of the mantle had changed in the past. This promising beginning by Faure et al. (1962) warranted further investigation and led to the present study, part of which is an attempt to accurately define the shape of the strontium growth-curve for the upper mantle and to
determine the rate at which the Rb/Sr ratio of the upper mantle has changed.

The initial Sr$^{87}$/Sr$^{86}$ ratios and ages of the ten mafic-ultramafic, alkaline intrusion with associated carbonatites, and plateau basalts analyzed during this study are listed in Table 27 and these data are plotted on a strontium evolution diagram (Fig. 22). Allowing for possible isotopic heterogeneity in the mantle and possible contamination by assimilation of sialic rock, and assuming that the upper mantle has always been an open system with respect to rubidium and strontium, a best-fitting strontium growth curve is one which begins at 0.7035 for the present day Sr$^{87}$/Sr$^{86}$ ratio for the upper mantle and has a slope indicating a Rb/Sr ratio of 0.007. This growth-curve is not linear, but has a constantly changing slope between 2.5 billion years to the present. Even with this changing slope, the curve will not extrapolate to the primordial Sr$^{87}$/Sr$^{86}$ ratio of 0.6985 at 4.5 billion years. Apparently, the Rb/Sr ratio of the mantle has changed rapidly between 4.5 and 2.5 billion years ago. These data suggest that the models of Patterson and Tatsumoto (1964) and Hurley et al. (1962) do not really conflict. Perhaps after the core and mantle segregated 4.5 billion years ago, intensive differentiation continued which resulted in the formation of a major volume of sialic crust.
### TABLE 27
AGES AND INITIAL Sr\(^{87}/\)Sr\(^{86}\) RATIOS OF MAFIC-ULTRAMAFIC INTRUSIONS, PLATEAU BASALTS, AND ALKALICINTRUSIONS WITH ASSOCIATED CARBONATITES

<table>
<thead>
<tr>
<th>Intrusion</th>
<th>Age (m.y.)</th>
<th>Initial Sr(^{87}/)Sr(^{86})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Great Dyke</td>
<td>2537</td>
<td>0.7025</td>
</tr>
<tr>
<td>(2) Stillwater Complex</td>
<td>2450</td>
<td>0.7029</td>
</tr>
<tr>
<td>(3) Bushveld Complex</td>
<td>1950</td>
<td>0.7030</td>
</tr>
<tr>
<td>(4) Iron Hill Complex</td>
<td>1481</td>
<td>0.7028</td>
</tr>
<tr>
<td>(5) Port Coldwell Complex</td>
<td>1070</td>
<td>0.7021</td>
</tr>
<tr>
<td>(6) McClure Mountain Complex</td>
<td>517-704</td>
<td>0.7057</td>
</tr>
<tr>
<td>(7) Rainy Creek Complex</td>
<td>185</td>
<td>0.7038</td>
</tr>
<tr>
<td>(8) Deccan basalt</td>
<td>40-70</td>
<td>0.7058</td>
</tr>
<tr>
<td>(9) Skaergaard Intrusion</td>
<td>52</td>
<td>0.7029</td>
</tr>
<tr>
<td>(10) Columbia River basalt</td>
<td>15-25</td>
<td>0.7034</td>
</tr>
</tbody>
</table>
Figure 22. Diagram showing the change in the isotopic composition of strontium in the upper mantle through geologic time. Numbers refer to localities listed in Table 27.
The limits of this period of intensive differentiation, as documented by the rapid change in the Rb/Sr ratio of the upper mantle, may be better defined by considering the rate of change of the Rb/Sr ratio of the earth's surface. The average Sr$^{87}$/Sr$^{86}$ ratios measured for carbonate rock formations and their respective ages are listed in Table 28. The sample of Transvaal limestone is from the Dolomite Series in the Transvaal System of South Africa. This limestone is younger than rocks of the Venterdorp System System (2300 m.y.) and older than the Bushveld Complex (1950 m.y.) according to radiometric studies by Nicolaysen (1962) and van Niekerk and Burger (1964). A limestone sample was collected by S. Chaudhuri from the Parting Shale Member in the Nonesuch Shale, located in Ontonagon County, Michigan. Near the base of the Parting Shale Member is a limestone layer that is persistently one-quarter to one inch thick over a wide lateral extent. Although the environment of deposition of the Nonesuch Shale is problematic, White and Wright (1954) suggest that the sediments were deposited in a deltaic or near-shore environment. A Rb-Sr radiometric study of the Nonesuch Shale and associated felsite by Chaudhuri and Faure (1967) suggests an age of about 1075 million years for the limestone unit. A marine origin and Middle Cambrian age of the Leverett Formation in the Byrd Mountains, Antarctica, has been established on the basis of trilobite fragments
<table>
<thead>
<tr>
<th>Sample</th>
<th>Environment of Deposition</th>
<th>Age (m.y.)</th>
<th>Sr\textsuperscript{87} / Sr\textsuperscript{86} (corr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(11) Bulawayan Ls.</td>
<td>marine</td>
<td>2950</td>
<td>0.7030</td>
</tr>
<tr>
<td>(12) Transvaal Ls.</td>
<td>marine</td>
<td>2000</td>
<td>0.7044</td>
</tr>
<tr>
<td>(13) Parting Sh., Nonesuch Fm.</td>
<td>marine</td>
<td>1000</td>
<td>0.7083</td>
</tr>
<tr>
<td>(14) Leverett Fm.</td>
<td>marine</td>
<td>550</td>
<td>0.7089</td>
</tr>
<tr>
<td>(15) Casper Fm.</td>
<td>marine</td>
<td>270</td>
<td>0.7088</td>
</tr>
<tr>
<td>(16) Mackello Fm.</td>
<td>non-marine</td>
<td>250</td>
<td>0.7182</td>
</tr>
<tr>
<td>(17) Buckley Fm.</td>
<td>non-marine</td>
<td>250</td>
<td>0.7164</td>
</tr>
<tr>
<td>(18) Weaver Fm.</td>
<td>non-marine</td>
<td>250</td>
<td>0.7150</td>
</tr>
</tbody>
</table>
Limestones in the Peruvian Mackello, Buckley, and Weaver Formation in the Transantarctic Mountains are generally accepted as continental (Barrett, 1965; Wade et al., 1965; Minshew, 1966).

These data are plotted on a strontium evolution diagram (Fig. 23) and a strontium growth-curve (AC) for the surface of the earth has been constructed according to the following assumptions: (1) The curve must intersect the "zero time" ordinate within the range of estimates for the Sr$^{87}$/Sr$^{86}$ ratio of the surface of the continental crust. A Sr$^{87}$/Sr$^{86}$ ratio of 0.716 is compatible with the suggestion by Faure et al. (1965) that the Sr$^{87}$/Sr$^{86}$ ratio of strontium derived as a result of weathering of rocks of the Precambrian Shield is 0.716 ± 0.004. Armstrong (1968) accepted a value of about 0.720, as did Hurley (1968). (2) At the ordinate, the curve must have a slope indicating a maximum Rb/Sr ratio of 0.35 for the surface of the continental crust. This value for the Rb/Sr ratio is a result of recent analyses of rocks of the Canadian Shield by Shaw et al. (1968). (3) The slope of the curve must change at a constant rate as it extends back in time in order to be consistent with the changing slope of the curve for the upper mantle. (4) The curve must be below the data points because solutions of carbonate rock tend to contain radiogenic Sr$^{87}$ that is leached from the clay-size fraction in
THE EVOLUTION OF THE ISOTOPIC COMPOSITION OF TERRESTRIAL STRONTIUM

- Intrusions and plateau basalts
- Carbonate rocks
the rock.

The changes in the isotopic composition of strontium in Precambrian seas from three to one billion years ago, as documented by the three Precambrian limestones, closely parallel the changes in composition of the surface of the continental crust (curve AB). The rate of change of the isotopic composition of strontium in Precambrian sea water appears to be a reliable indicator of the rate that sial separated from the mantle and is, therefore, a record of the growth-rate of the continents during Precambrian time. According to the configuration of the strontium growth-curves for the upper mantle and the continental crust, the early period of intense differentiation of the mantle ended about three billion years ago. By this time a significant portion of sialic crust had separated from the mantle. The Rb/Sr ratios of the upper mantle and the surface of the earth three billion years ago may be calculated from the slopes of the two curves. The Rb/Sr ratios are 0.009 and 0.021 for the upper mantle and the earth's surface, respectively. From this time on, radiogenic Sr$^{87}$ increased at a faster rate in the sialic crust than it did in the mantle because of a higher Rb/Sr ratio in the sial. The difference in the growth-rate of radiogenic Sr$^{87}$ in the two units is illustrated by the diverging growth-curves at three billion years. Sialic material continued to
separate from the mantle, but at a slower rate during the past three billion years. The continuous growth of the continents is indicated by the constant change in slope of the two strontium growth-curves.

On the evolution diagram, the strontium growth curve for Phanerozoic sea water (Peterman et al., 1967) is drawn (curve BP) and extrapolated to join curve AB at about one billion years. The isotopic composition of strontium in sea water younger than one billion years does not seem to represent an average for the isotopic composition of strontium in the continental crust. Turekian (1964) argued that the constancy of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in limestones of Phanerozoic age implies a significant strontium supply from weathering limestone. Following Turekian's conclusion, since significant deposition of limestone began at least one billion years ago (e.g. Greeville limestone), the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of sea water after this time can not be expected to be that of the continental crust. A recycling of strontium by uplift and weathering of carbonate rocks would tend to lower the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of strontium in sea water relative to that of the sialic continents. Instead, the record of the changing isotopic composition of strontium in the sialic crust during the past billion years is in carbonate rocks precipitated from water which had drained large areas of sialic bedrock, such as East Antarctica or the Canadian Shield.
CHAPTER VII

CONCLUSIONS

The distribution of initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of magmas derived from the upper mantle and $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of marine and non-marine carbonate rocks on a strontium-evolution diagram provides important information concerning the history of differentiation of the mantle and the formation of continents. The changing isotopic composition of strontium in the upper mantle is the record of rapid differentiation of the upper mantle during a 1.5 billion year period after segregation of the earth's core, followed by three billion years of constant, continuous differentiation at a much lower rate. During the first 1.5 billion years of earth history, a significant portion of the sialic crust formed. The changing isotopic composition of strontium in marine and fresh water from three billion years to the present time is the record of a continuous, but much slower, growth of the sialic crust.
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