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K_2O/Na_2O CONTENT AS A POSSIBLE INDEX TO THE CHRONOLOGICAL SEQUENCE OF SOME PRECAMBRIAN IGNEOUS ROCKS OF MISSOURI

BY

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A

THESIS

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Approved by

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ABSTRACT

Flame photometric analyses for K_2O and Na_2O were run on 31 samples of the Precambrian igneous rocks of Missouri. Samples were collected from the field, physically prepared and dissolved by a standard method and a modified standard method of rapid silicate analyses. The K_2O, Na_2O values obtained are averages between two methods of analyses. The modified method reduces by 80% the time required to chemically digest a rock sample. The results for both methods are not significantly different. Curtin and Company Advanced Flame Photometer was used.

Results have been plotted on graphs and a chronological sequence for the named Precambrian igneous rock units of Missouri is indicated. It is suggested that the Middlebrook Group belongs to a separate magmatic cycle; that the Van East, Musco, and Bevos Groups belong to the same magmatic cycle; and that the basic intrusive rocks belong to a separate magmatic cycle.

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INTRODUCTION

Purpose and Scope of Investigation

Theoretically, as a magma differentiates it changes in chemical composition. Na^+ has a stronger ionic potential than K^+ and will form a stronger bond with oxygen, in the silica tetrahedron, and therefore will be relatively enriched and concentrated at an earlier phase of the differentiation than will K^+. This relationship is implied in the Rock Reaction Series (Bowen, 1928). On these same theoretical grounds, the K_2O/Na_2O ratio will increase as the melt differentiates, and the first rock units formed in a differentiating magma will have the lowest K_2O/Na_2O ratio, while the last formed units will have the largest K_2O/Na_2O ratio (Rankama Sahama, 1949, pp. 429-431). It is recognized, however, that several factors could influence and even interrupt the normal differentiation trends, i.e., orogenic activity, crustal contamination, and others.

Since age relationships of rock units within the five main groups of the Precambrian rocks of Missouri are not well known, the principle objective of this investigation was to determine if it is possible to assign to these rock units a chronological sequence based on the K_2O/Na_2O ratio, $K_2O + Na_2O$ sum, or individual K_2O, Na_2O values.

Flame photometric analysis is a rapid, an exact, and a relatively inexpensive way of obtaining the K_2O, Na_2O analysis. In many ways it surpasses the wet methods of quantitative chemical analysis. Titration is unnecessary in flame photometric work. Instead, standard solutions of K_2O and Na_2O are prepared from inexpensive A. C. S. grade NaCl, KCl, and $Li_2SO_4 \cdot H_2O$. Ten grams of each of NaCl and KCl, and 300 grams of $Li_2SO_4 \cdot H_2O$ is sufficient for nearly 1000 K_2O and Na_2O determinations. Other necessary items are gas, air, HF, H_2SO_4, HNO_3, and a water demineralizing apparatus, all of which are relatively inexpensive.

A secondary purpose of this investigation was to improve, if possible, the digestion time necessary for rock samples as outlined by rapid silicate analysis techniques (Shapairo and Brannock, 1956). The method of sample digestion used represents a modification of the standard method proposed by these authors. Results of the two methods do not greatly differ (Table I, p. 38).

It was beyond the scope of this investigation to directly use other correlation techniques, e.g., petrology-petrography. As a result, this work has been almost entirely restricted to rock chemistry and laboratory techniques.

Location of Area

Samples were collected from the area between T. 29-36 N., and R. 2-7 E., in the counties of Wayne, Reynolds, Iron, Madison, and St. Francois, in the southeastern portion of Missouri in the St. Francois Mountains of the Ozark Plateau (Figure 1, p. 4).

One sample, the Stegall Mountain rhyolite located farther west in T. 28 N., R. 3 W. on Stegall Mountain, was too far west to be included on the geologic map (Figure 2, p. 10). Its location, however, is shown on the index map. Specific locations for collected samples are given in Table 1, p. 38 . As far as is known, all but two of Missouri's named outcropping Precambrian igneous rocks are represented in the collected samples.

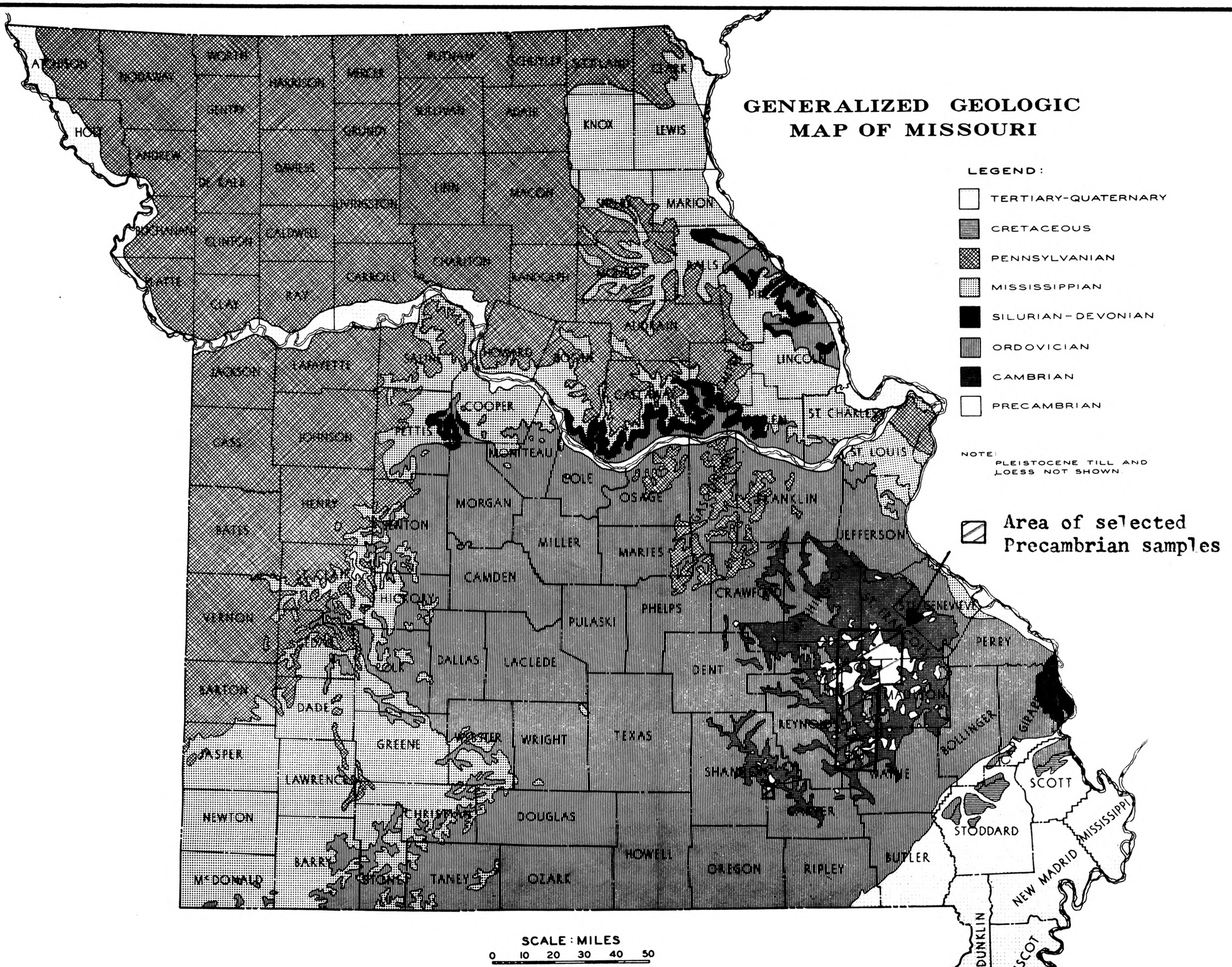
Field Collection of Samples to be Analyzed

Thirty-one rock samples were collected from the Precambrian rock outcrops of the St. Francois Mountains. In the sampling procedure an effort was made to collect representative samples from the various rock units. Dr. William C. Hayes of the Missouri Geological Survey and Water Resources selected most of the sample sites. Care was taken to avoid excessively altered rock material. Samples were broken directly from the outcrop. Sample locations, sampled units, and rock types are shown in Table 1, p. 38 .

Samples collected ranged from hand specimen to larger in size. Some weighed as much as five or six pounds. All samples were labeled and placed in paper bags and taken to the Missouri School of Mines Geology laboratory for further preparation and analysis.

Previous Work

One of the first reports which discusses the Precambrian rocks of Missouri was written by Broadhead (1874). He concluded that the



MISSOURI GEOLOGICAL SURVEY AND WATER RESOURCES
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DECEMBER 1958
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Figure 1

oldest rocks in Missouri were the granites and porphyries of Archean age. A contribution of major importance was made by Erasmus Haworth (1894). Using petrographic, chemical, and mineralogical analyses, field studies, and geologic mapping, he concluded that the granites and porphyries (rhyolites and felsites) were gradational in their relationships, and had different textures due to the different stages of solidification of the magma. He cited many locations where these gradational relationships were observable. However, Haworth thought that many of the porphyry hills were the result of different eruptions. Keyes (1896) observed that nowhere was there a sharp boundary between the granite and porphyry. He further concluded that the chemical composition of the granites and rhyolites were similar and were differentiates of the same magma.

Very little work was done on the Precambrian igneous of Southeast Missouri in the period from 1896 to 1930. Tarr (1931) questioned the gradational nature of the granites and porphyries as proposed by Haworth. Tarr found field evidence on Knoblick Mountain and in surrounding areas to confirm that the granites of Southeast Missouri were intruded into the eruptive porphyries and hence were younger.

Additional studies have been made of the Precambrian igneous rocks of Southeast Missouri. French (1956) discussed the granites in the Washington County area. Hayes (1959) compiled chemical analyses for 93 Precambrian igneous samples. Kisvarsanyi (1960) completed an excellent study of the petrographic and spectrochemical character of the granites and granite porphyries of St. Francois, Washington, Iron, and Madison Counties.

Robertson and Tolman (1960) compiled a geologic map of the Precambrian outcrops in Missouri. They subdivided the Precambrian rocks into five groups and 29 units. Hayes (1961) edited a guidebook to the geology of the St. Francois Mountain area. In this Snyder and Wagner discuss basic rocks, granites, granite porphyries, and felsites along with the status and problems of the Precambrian of Southeast Missouri (pp. 84-94). Detailed field mapping by R. E. Anderson (1961-1962) gives promise of important contributions to a better understanding of the igneous age relationships of Southeast Missouri.

Acknowledgments

Thanks are given to Dr. A. H. Brownlow, who originally proposed the problem to the author, but who was called into the military service before the study was begun. Many thanks are given to Professor R. R. Kennedy of the Geology Department at the Missouri School of Mines and Metallurgy, whose counseling and advice were helpful.

The author extends his appreciation to the personnel of the State of Missouri Geological Survey and Water Resources. Their help in providing samples and maps have greatly facilitated this study. Special thanks go to Dr. William C. Hayes, Assistant State Geologist, for his interest and helpful suggestions concerning this investigation.

Appreciation is given to Mr. Don Knapp of the Missouri Geological Survey and Water Resources, who collected many of the rock samples.

To the other members of the Geology Department staff at Missouri School of Mines and Metallurgy, and to those who have helped him in any way, the author expresses his graditude.

GEOLOGY

Geologic Setting

Precambrian igneous rocks are exposed in the southeastern and eastern portions of Missouri. These form what is called the St. Francois Mountains, a portion of a broad, oval upwarped dome called the Ozark Plateau. This dome has a topographic axis trending southwest through South Central Missouri and into Oklahoma.

According to Snyder and Wagner (1961), the earliest known geologic event to take place in this area was the extrusion of early volcanic felsites. Younger extrusions of felsites formed and together with the older extrusives were folded and faulted, the fold axis trending almost north - south. Granites and granite porphyries later intruded these felsites. The holocrystalline rocks are chemically very similar to the younger felsites. Iron mineralization possibly took place next. Intrusion of basic rocks is considered one of the latest events in the area.

Later, this Precambrian area was faulted. Erosion occured, streams cut deeply into the old igneous rocks, exposed the granites and produced a rugged topography with a relief of 2000 feet or more in places.

Transgressions and regressions of the Paleozoic sea in this area deposited sandstones and limestones of Cambrian to Carboniferous age and consist of magnesian limestones with interbedded sandstones. In general, these sediments dip away in all directions from the central crystalline igneous area called the St. Francois Mountains. Generally, younger and younger strata successively form the surface rocks as the distance increases from the porphyry hills.

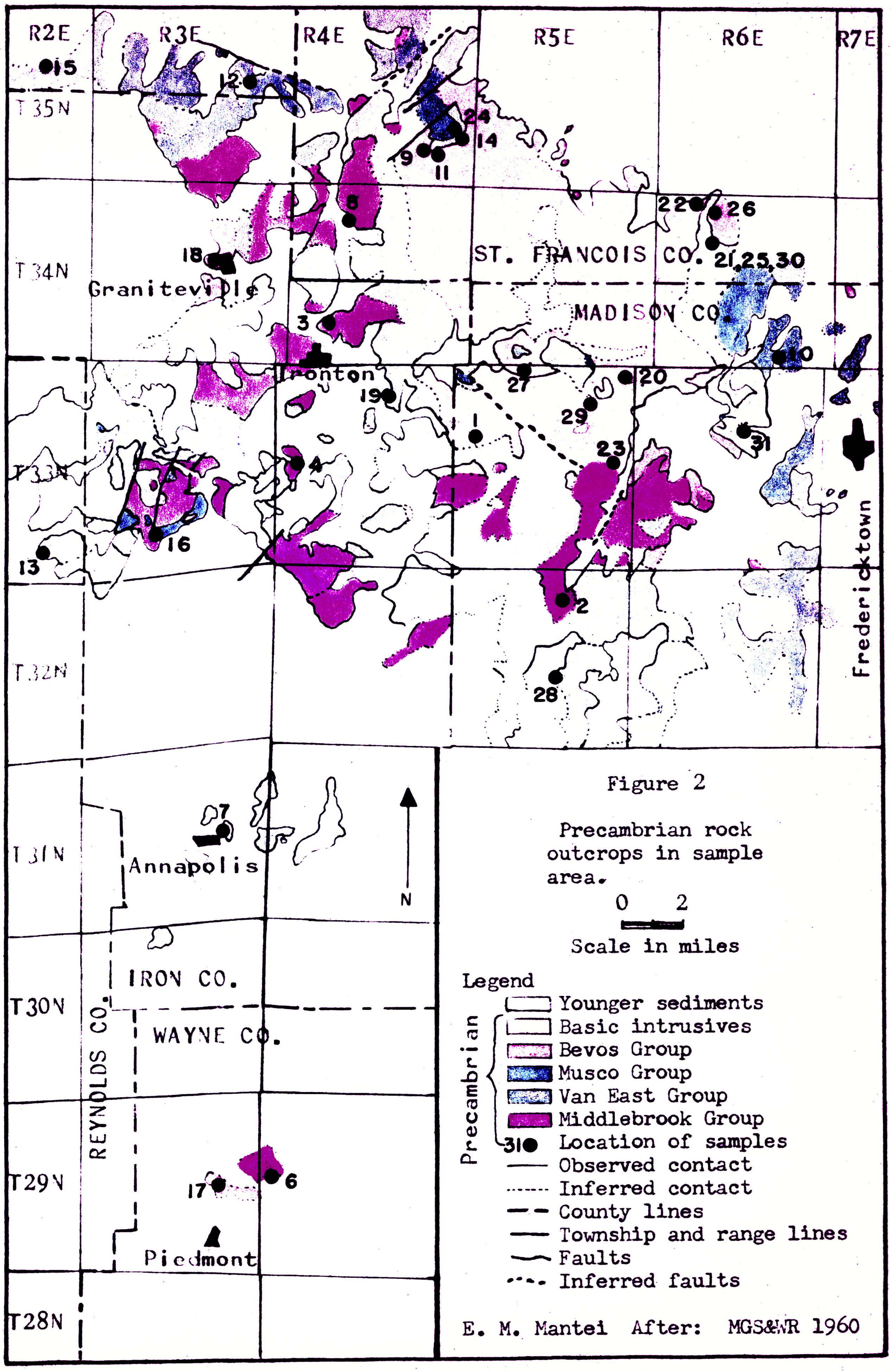

Figure 2

Precambrian rock outcrops in sample area.

General Description of the Igneous Rocks of Missouri

Precambrian igneous rocks occur as scattered outcrops over an area of more than 1000 square miles in the southeastern part of Missouri (Snyder and Wagner, 1961, p. 93). The rocks consist of rhyolites, felsites, granites, granite porphyries, and basic intrusives.

The rhyolites are generally reddish, but show a wide range from light pink to a dark gray or purple. Their texture shows considerable variation, and gradations from a coarse micrognanite to a fine devitrified glass are not uncommon. The groundmass is dense and fine-grained throughout and contains a few phenocrysts of quartz and feldspar.

Mineralogical composition of these rhyolites is similar to that of the granites. Essential minerals are orthoclase, microcline, albite, and quartz. Ferromagnesian minerals are rare, while zircon, apatite, and magnetite are present as accessory minerals scattered throughout the groundmass.

The felsites include various types of rhyolites, trachytes, andesites, and latites. As yet, there has been no systematic regional investigation of the so-called felsites of Missouri.

The granite and granite porphyries are rather coarse-grained rocks and reddish to grayish in color. Although they vary somewhat in grain size they show a great deal of similarity. Most of them are exceptionally high in orthoclase and quartz with a little biotite or hornblende. They are low in calcium plagioclase feldspar and relatively free of ferromagnesian silicates. The soda and potash contents are normal with the potash usually slightly in excess of soda.

Generally the texture approaches porphyritic. When the texture is definitely porphyritic, the rock is classified as a true granite porphyry. Potash feldspar phenocrysts an inch or more in length are not infrequent in these rocks. On the other hand, the rock may also exhibit fine-grained texture.

Small basic dikes are common throughout the area. These dikes cut both the granites and porphyries. They range from diorite and diabase to gabbro in composition.

Robertson and Tolman (1960) show on the Precambrian Map of Missouri five Precambrian groups. These are arranged from older to younger and include: Middlebrook Group, Van East Group, Musco Group, Bevos Group, and basic intrusives. Age relationships of these groups are relative and based on field relationships. Intra-group sequences are not well known. Robertson and Tolman's grouping follows.

Middlebrook Group:

	Sequence Determined	Sequence Undetermined
younger:		
	Pilot Knob felsite	Undifferentiated
	Royal Gorge rhyolite	Marlow Mountain rhyolite
	Oak Mountain felsite	Clark Mountain rhyolite
older:		
		Stegall Mountain rhyolite

As noted, the age relationships here have been determined for only three of the seven rock units. The oldest of the three having known age relationships, is the Oak Mountain felsite, followed by the Royal Gorge rhyolite, and lastly the Pilot Knob felsite. The undetermined sequence lies somewhere within or outside of these known rock sequences.

Van East Group

	Sequence Determined	Sequence Undetermined
younger:		
	Hogan Mountain rhyolite	Unassigned
	Stouts Creek rhyolite	Undifferentiated
		Annapolis rhyolite
older:		
		French Mills felsite

Robertson and Tolman determined only two age relationships in the Van East Group and four were not determined. The Stouts Creek rhyolite is assigned as the older and the Hogan rhyolite the younger. The position of the others is yet to be determined.

No definite age sequence is known for the Musco Group as indicated below.

Musco Group

Sequence Determined	Sequence Undetermined
None	Slabtown granite Stono granite Buford granite porphyry Carver Creek granite porphyry

As in the Musco Group, Robertson and Tolman were not able to assign an age sequence to the Bevos Group.

Bevos Group

Sequence Determined	Sequence Undetermined
None	Mudlick latite Breadtray granite Butler Hill granite Knoblick granite Silvermine granite Graniteville granite Brown Mountain rhyolite

Only two rock units constitute the basic intrusive sequence of Robertson and Tolman. Since these rock units cut the rocks assigned in the other four groups, the basic rocks represent the youngest group of igneous rocks.

Basic Intrusives

Sequence Determined	Sequence Undetermined
None	Undifferentiated Skrainka diabase

With the gap in knowledge of individual age relationships of the various igneous rocks, an attempt was made to determine if K_2O/Na_2O ratios would show a somewhat systematic intragroup relationship and give possible leads to the individual age relationships of the rock units.

LABORATORY INVESTIGATION

Theory of Flame Photometry

The atoms of lithium, sodium, and potassium, according to the "Quantum Theory," consist of electrons existing in definite quantum or energy levels. The quantum can be written in such a way as to show the position of the electrons in these energy levels around the nucleus of the atom.

Lithium = $1s^2\ 2s^1$
Sodium = $1s^2\ 2s^2\ 2p^6\ 3s^1$
Potassium = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

Whole numbers in front of the letters signify main orbits, letters signify energy levels or suborbitals, while the numbers raised to a power show the total number of electrons in the orbital and suborbital positions. Thus lithium in the ground state has two orbitals, two electrons in the 1s suborbital and one electron in the 2s suborbital. Sodium is similar to lithium, except that sodium has one more electron in the 2s suborbital plus seven additional electrons. Six electrons pair off, two in each of the three p suborbitals. Sodium has its last electron in the 3s suborbital. Potassium can be explained similarly with its last electron being in the 4s suborbital energy level. Only these last s orbital electrons will be of importance in this study for they are the valence electrons and are the easiest to excite in the flame photometer.

When the lithium, sodium, and potassium atoms are sprayed into the flame, the energy from the flame must be enough to excite the valence electrons to a higher energy level. When these excited valence electrons fall back into a lower energy level, energy is given off in various wavelengths according to the equation:

$$\Delta E = \frac{hc}{\lambda} \qquad (1)$$

ΔE = energy of the higher level minus energy of lower level

h = Planck's constant

c = speed of light

λ = wavelength of radiation given off

According to the equation, the farther the valence electron drops from its excited position, the more energy is entailed and therefore the shorter (λ) wavelength produced.

Now it may be that when the electron is raised to a definite energy level its fall back to a lower energy level may not be direct but instead may return in a series of steps. Under these circumstances more than one wavelength of radiation is produced. For example, the lithium atom in the ground state would have its $2s^1$ electron raised to the next energy level, the $2p^1$ state. The excited electron will fall back into the $2s^1$ ground state and produce an emitted wavelength of 671 millimicrons, according to equation (1). The electron falls back to a lower energy level because of its attraction to the positive charge of the nucleus of the atom. If the energy is great enough to raise the $2p^1$ electron to the $4d^1$ energy level, it would be possible to have two separate emissions by the falling of the electron from this level to the $2p^1$ level and then to the original $2s^1$ state. This produces a 460 and 671 millimicron wavelength line respectively.

Accordingly, for the sodium atom, the ground state valence electron, which is bound with less magnitude to the positively charged nucleus, can be raised to various levels and produce several different wavelengths. The $3s^1$ ground state electron can be raised to the $4p^1$ energy level; if return to the ground state is direct, an emission of a 330 millimicron wavelength line would be produced. If on the other hand, the $3s^1$ electron was raised to the $4p^1$ state or equivalent, and dropped back into the $3p^1$ state first and then into the $3s^1$ energy level, wavelengths of 819 and 589 millimicrons will be emitted. If the latter value here is subtracted from the former value in the step process, the difference will not be equal to the direct drop from the $4p^1$ to the $3s^1$ energy level, i.e., 330 millimicrons.

The potassium $4s^1$ ground state valence electron, if raised to the $5p^1$ level and returned directly to the $4s^1$ energy state produces a 404 millimicron emission. If raised from the ground state to the high $4d^1$ energy level, the electron could fall first to the $4p^1$ level and produce a 694 emission line and from the $4p^1$ level to the ground state and produce a 766/769 multiplet.

Emission lines which are used here for the quantitative work and not filtered out by special filters on the phototubes, are the lithium 671 millimicron line, the sodium 589 millimicron line, and the potassium 766/769 multiplet. It is not known which multiplet is actually used, possibly both.

The energies in electron volts (1 ev = 23 kilocalories per gram mole) needed for the excitation of the valence electrons from their ground state to the higher energy level necessary to produce the characteristic wavelengths are as follows:

a) for lithium and its 671 millimicron line about 1.85 ev

b) for sodium and its 589 millimicron line about 2.00 ev

c) for potassium and its 766/769 millimicron multiplet about 1.60 ev

The lithium line, as mentioned before, is used as an internal standard. Its emission line is constant because of controlled dilution in sample and standard solutions. It is used as a common denominator over both the sodium and potassium concentrations which represent numerators and change with percent concentrations of sodium and potassium in the samples.

Temperature of the flame is of great importance. Should the flame be too hot and excite the atoms such that their ionization potentials are reached and exceeded, then the ionized atom produces a completely different spectrum. The resulting spectrum resembles the excitation lines emitted by the element of preceding atomic number, and therefore because of the additional positive charge on the nucleus, the emission lines are displaced toward the ultra-violet.

Since concentrated acids are used to dissolve the samples, interference of the acid and acid anions (Dean, J. A., 1960, pp. 165-166, 171-172) may effect the results. Hydrofluoric, sulfuric, and nitric acids can produce errors if the concentration is great enough. It is possible to have as much as 30% error in the potassium analysis if the concentration of acid in the K_2O solution is 1M HCl or H_2SO_4. Also up to 12% and 23% error occurs if the concentration of the acid in the Na_2O solution is 2N H_2SO_4 or 1N HCl. These errors just mentioned occur only if the solution percents of sodium and potassium lie in the ranges of around .001% to .008%. The more concentrated the potassium and sodium, the less seems the chance for any great error. Nitric acid shows the smallest error over a long range concentration in both the sodium and potassium analyses. Only about 7% error occurs in sodium analyses when 3N HNO_3 is present and about 10% error in potassium analyses if 2M HNO_3 constitutes the solution.

Therefore since the analyses for this study never reached concentrations of Na_2O or K_2O below 900 ppm (.09%), there was no known interference of acid anions.

Equipment

Curtin and Company Advanced Flame Photometer as other types, consists essentially of six main parts: the atomizer, the burner, the optical system, the photosensitive detector, and the pressure regulators (circuit diagram Figure 3, p. 20).

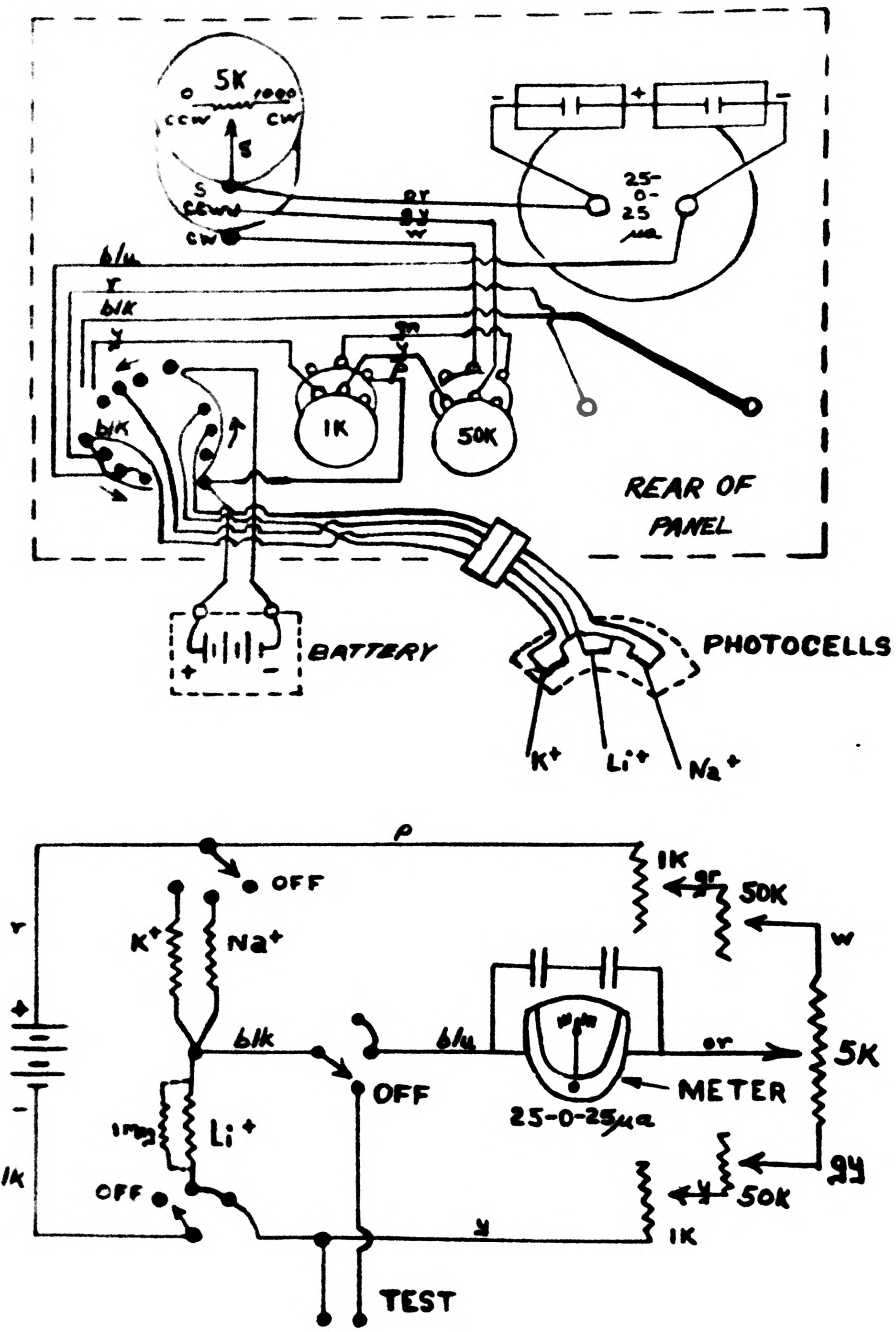

Figure 3
Circuit diagram of Curtin & Co., Advanced Flame Photometer

The atomizer is of the discharge type and is constructed in such a manner that two capillary tubes are oriented so that their bores are perpendicular to each other. One capillary tube leads to the air source and the other is the end of the funnel into which the sample solution is entered. Both capillary bores are rubber corked in a glass chamber which has two openings leading to the burner and the waste bottle.

When the solution is poured at the funnel end, gravity pulls down the liquid which is atomized by an air jet, into a very fine mist and carried into the tube leading to the burner. The excess atomized liquid forms droplets on the side of the glass chamber and leaves the glass chamber through an opening to be collected and discarded. The drain tube must always lead downward since "backup" of the liquid could cause drifting of the needle on the detector. A small hole should be cut on top of the drain tube near the connection of the "U" tube at the bottom of the chamber so as to prohibit a suction of liquid back into the "U" tube.

The burner in the flame photometer is of the Meker type. It produces a flame of about 2000° C with its mixture of propane gas and air. The propane gas is fed into the burner at a regulated .5 - 2 psi and mixed at the burner base with the air and atomized sample with 10 psi pressure.

The maximum intensity of the instrument is obtained when the regulator at the base of the instrument is turned 3/4 of a full turn from the closed position. This regulation gives optimum flame height (6 - 10") and temperature to excite the potassium and sodium atoms to give off their characteristic excitation wavelengths. If the regulator is opened too wide, the flame is unsteady and flickers giving an unsteady source of energy, causing the dial on the indicator to drift excessively.

The entire burner is encircled in a water jacket through which tap water is circulated to keep the phototubes cool. The water absorbs the heat energy from the burner and keeps the phototubes nearly at constant temperature helping to prevent unnecessary instrument drift. Water circulation should be rapid enough so that there is no noticeable warming of the water.

The optical system consists of three photocells connected to the water jacket and pointing into the base of the flame. These photocells have about 1000 times the sensitivity of the older barrier layer cells (Curtin and Co., pamphlet on the Advanced Flame Photometer). Because of the seal of glass covering them, they are unaffected by moisture or oxidation which shortens the life of many barrier layer cells. There are absorption filters on the cells that permit only the 766/769 millimicron wavelengths of potassium, the 589 millimicron wavelength of sodium, and the 670 millimicron wavelength of lithium to pass.

The photocells collect a double beam radiation ratio coming from the potassium or sodium and the lithium internal standard. The primary beam is the numerator of either potassium or sodium while the secondary beam is the common denominator and is produced by a uniform amount of a non-interfering linear ion lithium. The ratio is constant despite flame variation and gives a steady source of radiation to the photocells. Therefore, as the concentration of the potassium atoms increases the ratio of $\frac{\text{potassium concentration}}{\text{lithium concentration}}$ increases, the denominator being constant. Likewise, as the sodium concentration of the sample increases, the $\frac{\text{sodium concentration}}{\text{lithium concentration}}$ increases, again the lithium being constant.

Accuracy depends much upon keeping the water jacket wall next to the burner, between the burner and the pohtocell, clean from any grease or dirt.

Battery power is essential in keeping the photocells in good working order. One 67 1/2 volt Burgess radio battery no. K45 or Eveready no. 457 is used and should be changed after about 6 months of ordinary use for maximum operational efficiency of cells and dial.

In order to achieve a steady emission reading, it is of prime importance to have a flame that is steady and free from flicker. If flicker is present the dial drifts and analysis is impossible.

To insure no flicker, fuel and air pressures must remain constant while the flame photometer is in use. The air regulator follows the air filter in the hook-up line to the photometer and lets 10 psi of air into the base of the burner to mix with the propane. The cutoff gauge for the air is located between the air regulator and the air filter.

Fuel regulation consists of a primary and secondary regulator. The primary regulator is connected to a 100 pound propane tank which lets out 4 psi of gas. The second regulator receives the 4 pound gas pressure and reduces it to between .5 and 2 psi. The gas is mixed with the 10 psi air in the burner base and burned at a steady rate.

Preparation of Stock and Standard Solutions

Stock Solutions. In order to compare the unknown values of K_2O and Na_2O in the samples to known quantities of K_2O and Na_2O, standards were prepared. Two separate stock solutions, one for K_2O and the other for Na_2O, were prepared such that the K_2O and Na_2O concentration was .5 mg/ml or .05%.

Since KCl and NaCl were used to make the stock solutions, and since K_2O and Na_2O is the .5 mg/ml concentration wanted and not .5 mg/ml KCl and NaCl, a simple equation was set up in order to convert a given weight of KCl or NaCl to equivalent weights of K_2O and Na_2O.

$$2KCl \longrightarrow K_2O \quad \text{and} \quad 2NaCl \longrightarrow Na_2O$$

$$\frac{\text{weight of KCl}}{2(\text{molecular weight of KCl})} = \frac{\text{weight of } K_2O}{\text{molecular weight of } K_2O}$$

$$\frac{\text{weight of NaCl}}{2(\text{molecular weight of NaCl})} = \frac{\text{weight of } Na_2O}{\text{molecular weight of } Na_2O}$$

Calculations showed that dissolving .792 grams of dry KCl in one liter of metal free water, gave an equivalent concentration of .5 mg/ml of K_2O. Likewise, dissolving .943 grams of dry NaCl in one liter of metal free water, an equivalent concentration of .5 mg/ml of Na_2O was obtained.

An internal standard stock solution of $Li_2SO_4 \cdot H_2O$ was prepared in which the lithium concentration was 2000 ppm. In order to obtain this concentration, 18.44 grams of dried $Li_2SO_4 \cdot H_2O$ was dissolved in one liter of metal free water.

Standard Solutions. From the stock solutions, .5 mg/ml (.05%) K_2O and Na_2O, .5 and 1 through 11 percent solutions of K_2O and Na_2O were prepared by diluting 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 110 mililiters respectively of the stock solution and 50 mililiters of stock solution of lithium to one liter with demineralized water. New standards need to be prepared once every 30 days. Accurate results cannot be obtained if the solutions age for several months.

The preparation of a 200 ppm lithium internal standard solution was made for sample solutions by diluting 100 ml of lithium stock solution to one liter with metal free water. The internal standard is used in the secondary diluting of the sample solution after its final digestion and primary dilution.

Sample Preparation

Since the rocks were broken in the field by steel hammers, consideration was given to the possibility of iron contamination. This investigation is not concerned with the total rock analyses, and iron contamination does not interfere chemically with the K_2O, Na_2O determinations. However, if iron contamination were present, it could produce some error in the final results since the analyses are based on weight percents. Iron contamination would, in effect, lower the weight percent values of K_2O and Na_2O.

By scrubbing the rock samples with tap water, and rinsing them with demineralized water, most of the extraneously introduced iron was removed.

Smaller rock samples (15 - 20 grams) were chipped from the larger cleansed samples. Care was taken to pick chips or fragments which were unaltered, free from any introduction of iron contamination, and representative of the specimen.

Representative sampling is one of the most important techniques to be considered in rock analysis. Fortunately, mineral constituents of the rhyolites are of rather uniform distribution throughout the rock. However, as rocks become coarser-grained, heterogeny begins to predominate with respect to the constituent minerals. Granites are therefore more heterogeneous than the rhyolites. Rhyolite examined in almost any thin section appears rather homogeneous throughout. On the other hand, granites and granite porphyries differ widely in the distribution of the coarser-grained constituents. To partly compensate for this difference, larger amounts of granite and granite porphyries were used (70-80 grams), in contrast to smaller amounts of rhyolite (35-40 grams).

Once representative chips were chosen, they were scrubbed free of any possible extraneous contamination, dried, and broken to about 1/8" in size with a steel hammer. These smaller chips were washed and then placed in a diamond mortar and pestle, crushed to about 1/16th inch size, mixed, and then quartered. Two diagonal quarter portions were taken and the remainder discarded. The selected sample was crushed in the mortar and pestle to about 1/32nd inch and quartered twice using the same procedure as above. The selected remaining sample was pulverized in the diamond mortar and pestle and passed through a 250 mesh Swiss bolting cloth. Approximately three grams of sieved sample were saved for use in both the standard method and modified method of analysis.

Sieved powder samples were placed in one dram uncapped glass vials, thoroughly mixed, and left to dry overnight in a closed furnace at 110°C. temperature. The drying eliminates any adsorbed water which could affect the dry weight of the sample.

Analytic Procedure

It was found that in reanalyzing granites and rhyolites with known K_2O and Na_2O values, time could be saved by using a method much faster than the standard overnight digestion of the sample. Using the modified method it was possible to reduce the digesting time to 2 1/2 hours. The K_2O, Na_2O values thus obtained differed in values from the overnight digestion method by as little as .00 and as much as .07. Hence part of this study compared these two methods of procedure.

The two methods used, and a comparison of the results, are presented below. Both methods were applied to each sample analyzed.

Standard Method.

1) After the pulverized samples have dried in the furnace at 110°C. overnight, a .4000 gram sample of rock was weighed and transferred to a platinum crucible of about 100 ml capacity.

2) Ten mls. of concentrated hydrofluoric acid were added and the crucible gently swirled under a hood in order to get the finely powdered rock sample in a more dispersed form.

3) Three mls. of concentrated sulfuric acid were added to the platinum crucible to assist in the dissolving of the sample.[1]

4) The platinum crucible was covered with its platinum top and set on a steam bath overnight.[2]

5) After overnight digestion, the platinum cover was removed and the contents left to dissolve until reduced to about 5 mls.

6) Two mls. of concentrated nitric acid were added and the platinum crucible placed over an electric heater until strong SO_3 fumes evolved.

7) The crucible and its contents were allowed to cool and demineralized water was added to dilute the acidic solution.

8) The solution was transferred to a 400 ml. Vycor beaker and boiled very gently for 10 - 15 minutes.[3]

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[1] If sulfuric acid was added too fast, and the sample not properly swirled, reaction with the rock sample resulted in a violent effervescence and possible loss of sample. Thus sulfuric acid was added slowly.

[2] Overnight the equivalent of ten hours.

[3] Care should be taken to see that all the contents are transferred to the beaker. A rubber policeman should be used to scrub the crucible sides and this aliquot transferred to the beaker. There will usually be a small residue present which will dissolve when gently heated. If boiled too vigorously, a sample portion may be lost and final results inaccurate. Since Vycor beakers contain very small quantities of K_2O and Na_2O, contamination will not be significant when attacked by HF acid.

9) If a small residue still remains after the above, this can be discarded by filtration or retained. Such residues may contain $BaSO_4$, Zr, or even tourmaline. They will not interfere with the K_2O, Na_2O determinations. All of the K_2O and Na_2O equivalents should, at this point, be in solution.

10) The solution is then transferred to a 200 ml. volumetric flask, diluted to volume and mixed well by shaking.[4]

11) The solution is immediately transferred to a polyethelene bottle from which 25 mls. of solution is diluted with 25 mls. of demineralized water and 50 mls. of standard lithium solution in a polyethelene bottle. This solution is now ready for the flame photometer.

Modified Method. To carry out the rock analysis for K_2O and Na_2O in a much more efficient way, timewise, a modified method of digestion was used. In this method the time to digest and analyze the sample was only about 2 1/2 hours, or a saving of 7 1/2 - 8 hours per sample.

The modified method described below is similar to the standard method in many ways. After the addition of 3 ml. of sulfuric acid in step (3) of the standard method, the solution is allowed to remain

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[4] Wash down the sides of the Vycor beaker with a squeeze bottle containing metal free water to obtain all the K_2O and Na_2O. Transfer to the Vycor beaker.

in the steam bath between 1 and 1 1/2 hours then placed on an electric burner for 1/2 hour.

Three mls. of nitric acid were added slowly and the crucible gently swirled.

The contents were transferred to a 400 ml. Vycor beaker and boiled over a bunsen burner slightly more intensely than in the standard method of digestion for 15 - 20 minutes until all was dissolved. While boiling, the beaker was swirled. The residue, which may be present, may contain the same elements as mentioned previously.

Again, careful transfer of the sample from the platinum crucible to the Vycor beaker is of extreme importance. The sides of the crucible must be scrubbed and the residue transferred to the beaker. The very small additions of K_2O and Na_2O from the Vycor beaker will not contaminate the sample solution to such a degree that end results will be materially affected.

After the sample is dissolved, procedures beginning with step (9) of the standard method are used to bring the sample solution to the final analysis with the flame photometer.

RESULTS

Results for the 31 analyzed samples are summarized in Table 1, p. 38. The K_2O, Na_2O content, and K_2O/Na_2O ratio for each sample has been calculated.

Comparison of the standard method and modified method shows very similar results. Differences per sample, between the two methods averages only .03 percent for the Na_2O analyses and averages only .04 percent for the K_2O analyses. Maximum variation between the two methods was only .07 percent.

Middlebrook Group

The K_2O/Na_2O ratios in the Middlebrook Group are considerably higher than the other groups. Since these are the oldest exposed units of the Precambrian rocks, one might expect them to have the lowest values if all five groups were to have been derived from the same magma source. This problem is discussed later.

Within the Middlebrook Group, (Figure 4, p. 32) the lowest K_2O/Na_2O is found in the Oak Mountain felsite, the oldest rock unit. Increasing K_2O/Na_2O ratios indicate a near straight line relationship exists between the next three units, Annapolis rhyolite, Clark Mountain rhyolite, and Stegall Mountain rhyolite. The remaining four rock units of this group, the Royal Gorge rhyolite, Pilot Knob

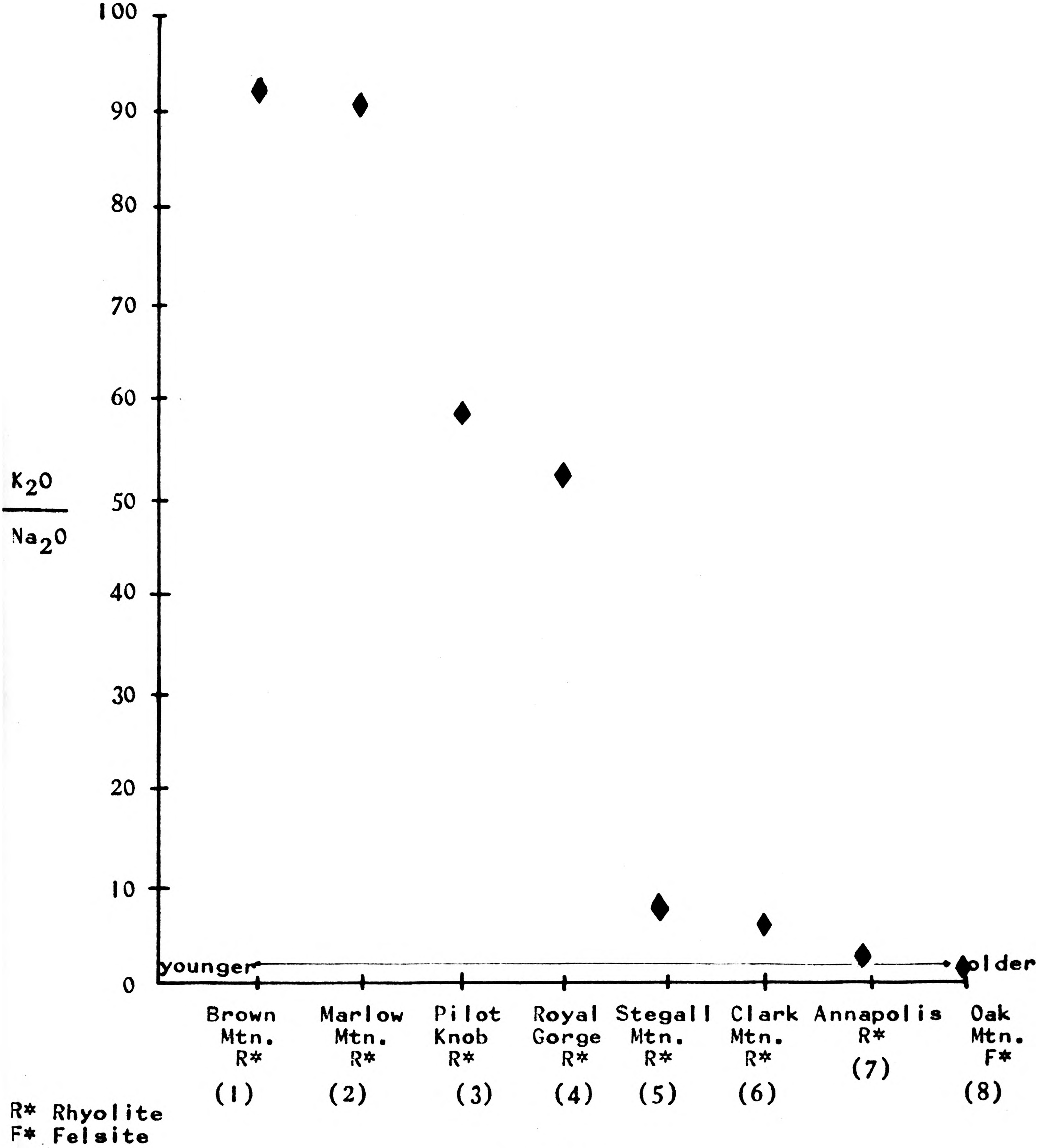

Figure 4
K_2O/Na_2O relationships of Middlebrook Group

rhyolite, Marlow Mountain rhyolite, and Brown Mountain rhyolite form an irregular pattern. This irregular pattern shows a large variation in the K_2O/Na_2O ratios and also high values for K_2O and Na_2O. The suggested sequence, based on the K_2O/Na_2O ratio, is:

younger: Brown Mountain rhyolite
Marlow Mountain rhyolite
Pilot Knob felsite
Royal Gorge rhyolite
Stegall Mountain rhyolite
Clark Mountain rhyolite
older: Annapolis rhyolite
Oak Mountain felsite

Van East Group

Rock units of the Van East Group (Figure 5, p. 34), show a similar near straight line relationship, except for the Oak Mountain felsite and Annapolis rhyolite. Actually the latter two units belong in the Middlebrook Group. They are shown in the Van East Group only to indicate a possible gradation of the Van East Group into the Middlebrook Group. However, this gradation is not thought to actually occur since there exists a long hiatus between the Middlebrook Group extrusion and the Van East Group volcanism.

There is a relative enrichment in the K_2O/Na_2O ratio which assumes a nearly straight line relationship between the seven rock units of the Van East Group (Figure 5, p. 34). If this is indicative of decreasing age then the following applies:

younger: Hogan Mountain rhyolite
Undifferentiated U-22
Stouts Creek rhyolite
Undifferentiated type "B"
Undifferentiated type "A"
French Mills felsite
older: Undifferentiated type "C"

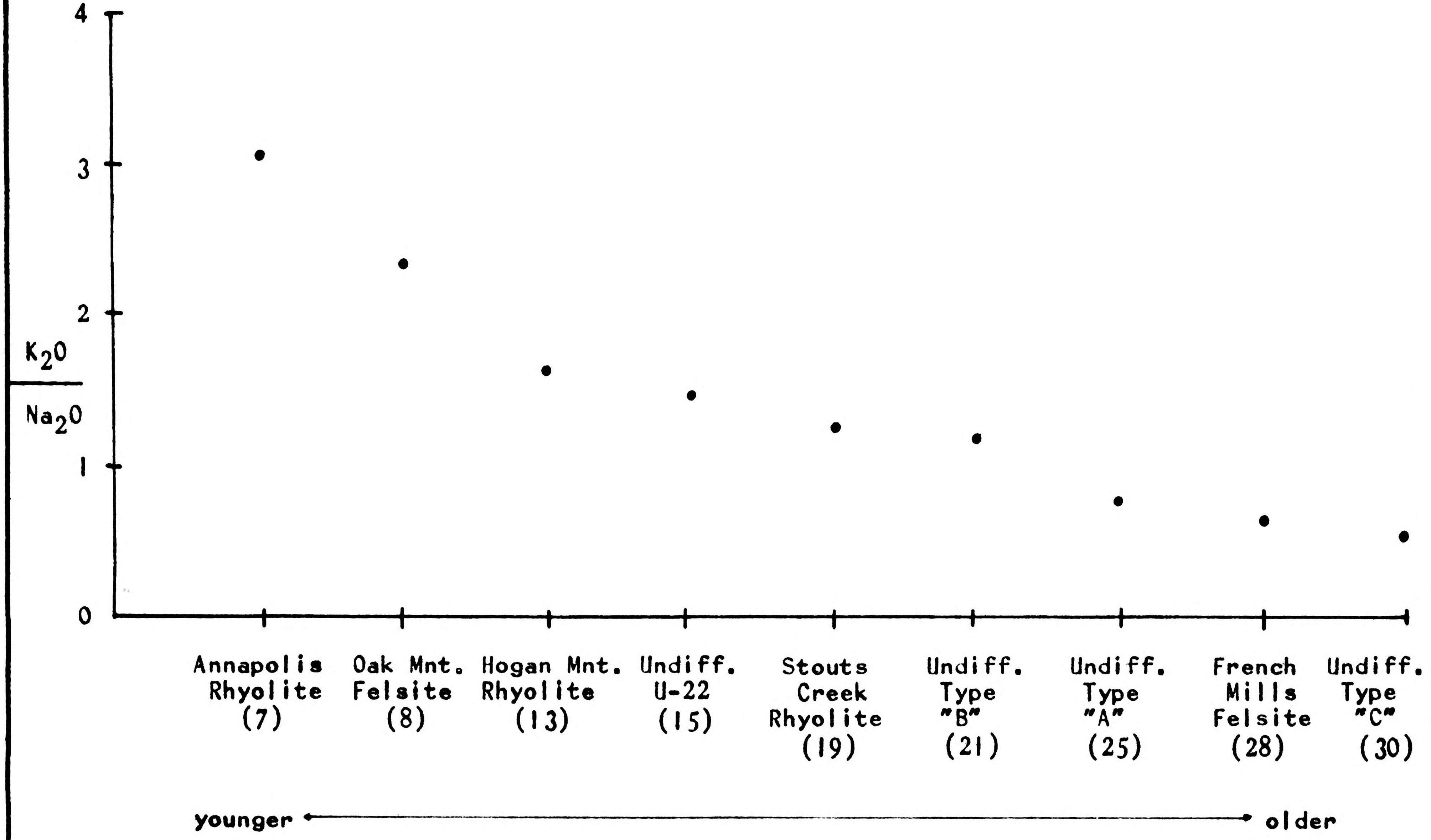

Figure 5
K_2O/Na_2O relationships of Van East Group

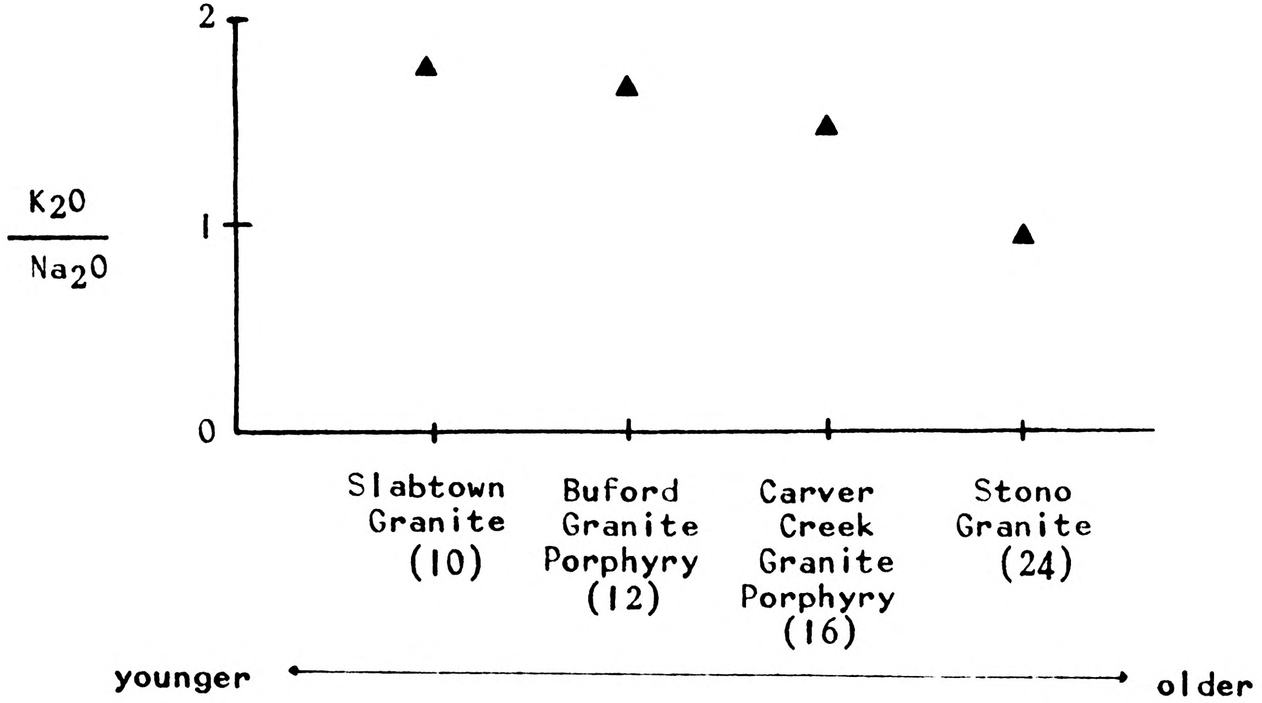

Figure 6
K_2O/Na_2O relationships of Musco Group

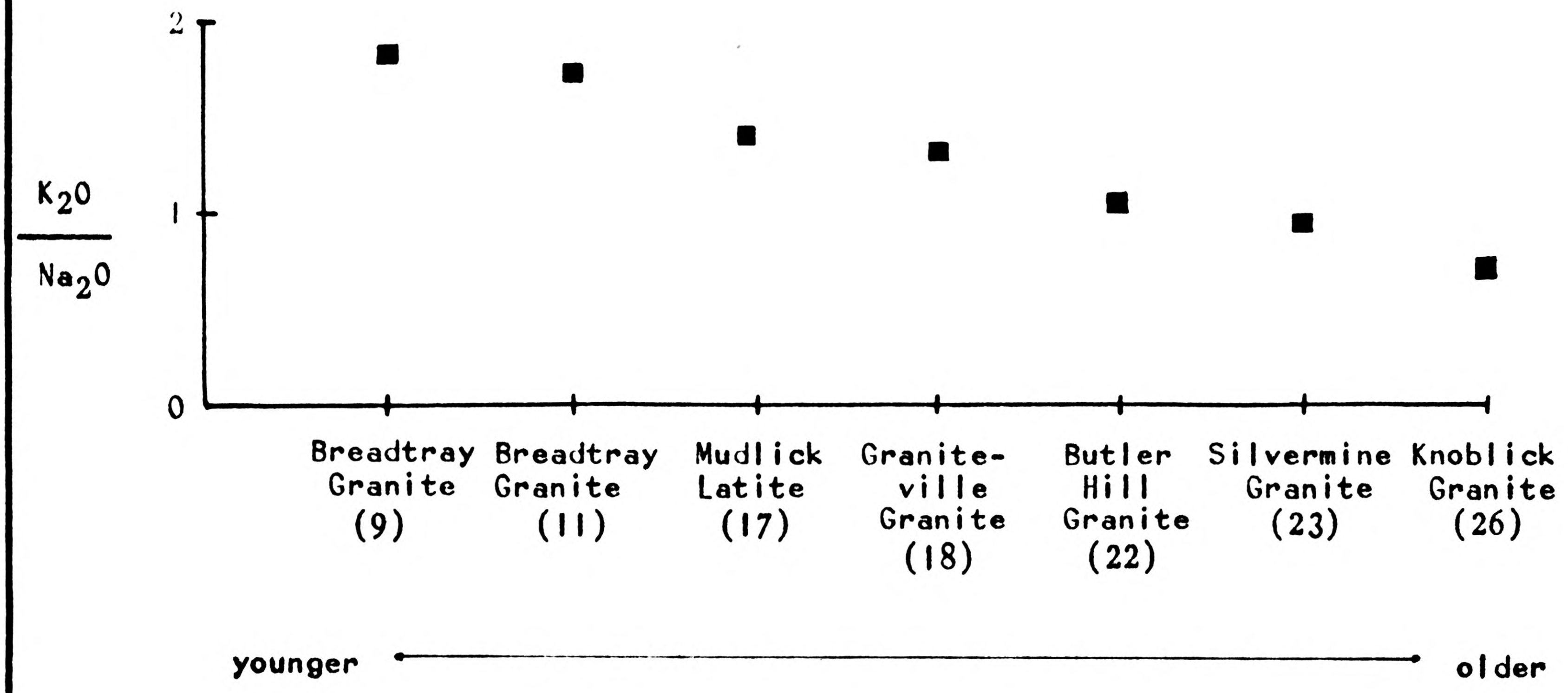

Figure 7
K_2O/Na_2O relationships of Bevos Group

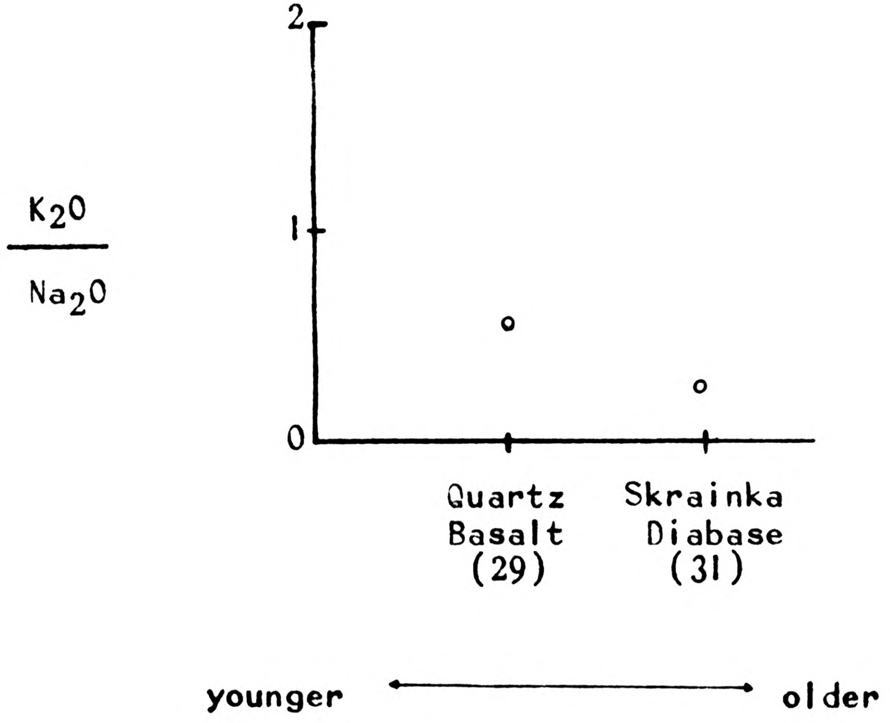

Figure 8

K_2O/Na_2O relationships of Basic Intrusives

Table I
Sample Locations, And Analytical Results For Precambrian Igneous Rocks, St. Francois Mountains, Missouri

Sample number	Sample location	Sample name	Samples Na_2O content *S (%)	M*	Samples K_2O content *S (%)	M*	Total K_2O,Na_2O (%)	$\frac{K_2O}{Na_2O}$
1	NW1/4 SW1/4 SE1/4 Sec. 7, T33N R5E Ironton, Mo. Quad.	Brown Mountain Rhyolite	.11	.14	11.00	10.97	11.11	91.58
2	NW1/4 SW1/4 NE1/4 Sec. 10, T32N R5E Coldwater, Mo. Quad.	Marlow Mountain Rhyolite	.09	.11	8.96	8.94	9.05	90.50
3	NW1/4 NW1/4 SW1/4 Sec. 29, T34N R4E Ironton, Mo. Quad.	Pilot Knob Rhyolite	.17	.20	10.78	10.73	10.94	59.80
4	NE1/4 NE1/4 SE1/4 Sec. 20, T33N R4E Ironton, Mo. Quad.	Royal Gorge Rhyolite	.16	.16	8.44	8.48	8.62	52.88
5	NW1/4 SW1/4 SW1/4 Sec. 19, T28N R3W Cardareva, Mo. Quad.	Stegall Mountain Rhyolite	.95	.98	8.61	8.57	9.56	8.86
6	SW1/4 NW1/4 NW1/4 Sec. 18, T29N R4E Piedmont, Mo. Quad.	Clark Mountain Rhyolite	1.47	1.47	9.58	9.55	11.04	6.51
7	SW1/4 SE1/4 SW1/4 Sec. 14, T31N R3E Des Arc, Mo. Quad.	Annapolis Rhyolite	2.27	2.29	6.99	6.95	9.25	3.06
8	NW1/4 NW1/4 NW1/4 Sec. 9, T34N R4E Ironton, Mo. Quad.	Oak Mountain Felsite	2.57	2.59	5.98	5.96	8.55	2.31
9	NW1/4 SW1/4 SE1/4 Sec. 26, T35N R4E Ironton, Mo. Quad.	Breadtray Granite	3.19	3.22	5.77	5.82	9.00	1.81
10	SE1/4 NW1/4 SW1/4 Sec. 35, T34N R6E Fredericktown, Mo. Quad.	Slabtown Granite	3.91	3.95	4.24	4.20	3.15	1.74
11	NW1/4 SW1/4 SW1/4 Sec. 25, T35N R4E Ironton, Mo. Quad.	Breadtray Granite	3.15	3.17	5.34	5.41	8.54	1.70
12	NE1/4 NE1/4 SW1/4 Sec. 14, T35N R3E Ironton, Mo. Quad.	Buford Granite Porphyry	3.28	3.25	5.48	5.52	8.76	1.69
13	SW1/4 SE1/4 SW1/4 Sec. 26, T33N R2E Edgehill, Mo. Quad.	Hogan Mountain Rhyolite	3.20	3.22	5.37	5.39	8.59	1.68
14	SW1/4 NW1/4 NE1/4 Sec. 25, T35N R4E Ironton, Mo. Quad.	Stouts Creek Felsite	3.16	3.12	5.16	5.13	8.31	1.65
15	NW1/4 NW1/4 SE1/4 Sec. 13, T35N R2E Edgehill, Mo. Quad.	Undifferentiated U-22	4.00	4.03	4.20	4.21	.22	1.50
16	SE1/4 NE1/4 SE1/4 Sec. 28, T33N R3E Ironton, Mo. Quad.	Carver Creek Granite Porphyry	3.70	3.67	5.28	5.31	8.98	1.44
17	SW1/4 SE1/4 SE1/4 Sec. 14, T29N R3E Piedmont, Mo. Quad.	Mudlick Latite	3.22	3.23	4.40	4.38	7.62	1.36
18	NE1/4 SE1/4 NW1/4 Sec. 14, T34N R3E Ironton, Mo. Quad.	Graniteville Granite	3.90	3.97	5.25	5.30	9.21	1.34
19	NE1/4 NW1/4 SE1/4 Sec. 3, T33N R4E Ironton, Mo. Quad.	Stouts Creek Rhyolite	3.62	3.66	4.59	4.66	8.27	1.27
20	SE1/4 NW1/4 NE1/4 Sec. 1, T33N R5E Fredericktown, Mo. Quad.	Silvermine-Butler Hill Granite	4.14	4.18	5.17	5.12	9.31	1.24
21	SE1/4 SE1/4 NE1/4 Sec. 8, T34N R6E Fredericktown, Mo. Quad.	Undifferentiated Type "B" from Knoblick Mountain	3.81	3.78	4.65	4.60	8.42	1.22
22	NE1/4 NW1/4 SW1/4 Sec. 5, T34N R6E Fredericktown, Mo. Quad.	Butler Hill Granite	3.89	3.87	4.22	4.24	8.11	1.09
23	NE1/4 NE1/4 NW1/4 Sec. 13, T33N R5E Fredericktown, Mo. Quad.	Silvermine Granite	4.21	4.19	4.02	4.06	8.24	.96
24	NE1/4 NW1/4 NE1/4 Sec. 25, T35N R4E Ironton, Mo. Quad.	Stono Granite	4.03	4.06	3.73	3.78	7.80	.93
25	SE1/4 SE1/4 NE1/4 Sec. 8, T34N R6E Fredericktown, Mo. Quad.	Van East Undifferentiated Type "A"	5.22	5.20	3.87	3.91	9.10	.75
26	SW1/4 NW1/4 SW1/4 Sec. 4, T34N R6E Fredericktown, Mo. Quad.	Knoblick Granite	4.48	4.53	3.19	3.14	7.67	.70
27	NW1/4 NW1/4 NE1/4 Sec. 4, T33N R5E Fredericktown, Mo. Quad.	Silvermine-Breadtray Granite	4.58	4.57	3.16	3.15	7.73	.69
28	NW1/4 SW1/4 SE1/4 Sec. 22, T32N R5E Coldwater, Mo. Quad.	French Mills Felsite	5.03	4.98	3.15	3.12	8.14	.63
29	SW1/4 SW1/4 NE1/4 Sec. 2, T33N R5E Fredericktown, Mo. Quad.	Quartz Basalt	3.11	3.14	1.80	1.82	4.93	.58
30	SE1/4 SE1/4 NE1/4 Sec. 8, T34N R6E Fredericktown, Mo. Quad.	Van East Undifferentiated Type "C"	4.24	4.23	2.25	2.20	6.46	.53
31	NE1/4 NW1/4 NW1/4 Sec. 10, T33N R6E Fredericktown, Mo. Quad.	Skrainka Diabase	3.13	3.11	.74	.77	3.88	.24
S M	Standard Method of Analysis Modified Method of Analysis	Average difference	.03		.04			

Musco Group

Rock units of the Musco Group consist of granite and granite porphyry types. Their relative age relationships have not previously been determined. Units in this group also show a nearly straight line relationship (Figure 6, p. 35). Based on K_2O/Na_2O values, i.e., the oldest unit with the lowest K_2O/Na_2O ratio, and the youngest unit with the greatest K_2O/Na_2O ratio, the following sequence is suggested:

younger:	Slabtown granite
	Buford granite porphyry
	Carver Creek granite porphyry
older:	Stono granite

Bevos Group

The six rock units of the Bevos Group consist of granite and one latite (Figure 7, p. 36). To date these units have not been arranged in a specific sequence. Based on the idea that the oldest unit has the lowest K_2O/Na_2O ratio and the youngest the highest K_2O/Na_2O ratio, the following sequence is suggested:

younger:	Breadtray granite
	Mudlick latite
	Graniteville granite
	Butler Hill granite
	Silvermine granite
older:	Knoblick granite

Basic Intrusives

The two basic rock units, Skrainka diabase and quartz basalt, are relatively low in K_2O/Na_2O ratios (Figure 8, p. 37). They have the lowest K_2O/Na_2O ratio of all five groups as would be expected for basic rocks. Quartz basalt has a higher K_2O/Na_2O ratio than the Skrainka diabase suggesting then the quartz basalt is younger of the two and the Skrainka diabase the older.

SUMMARY AND CONCLUSIONS

The Middlebrook Group appears to be much older, 300 million years based on absolute dating, than the other exposed Precambrian igneous rocks of Missouri, (Hayes, 1962, personal communication). Because of this much older age of the Middlebrook Group and because of its markedly different K_2O/Na_2O values, it is thought to have originated from a different magma than the other four groups of Precambrian rocks.

The similar K_2O/Na_2O ratios (Figures 5, 6, and 7, pages 34, 35, and 36, respectively), and similar Na_2O and K_2O content (Figures 9, 10, and 11, pages 42, 43, and 44) for the Van East, Musco, and Bevos Groups, suggest that these groups are differentiates of the same parent magma, or at least closely related in time and space.

Figure 12, page 45, is a composite of Figures 5, 6, and 7, pages 34, 35, and 36, and shows more clearly the chemical similarities of these groups. The K_2O/Na_2O is lowest in the Van East Group, slightly higher in the Musco Group, and greatest in the Bevos Group. This suggests that the Van East Group was formed first, the Musco Group next, and the Bevos Group last in a differentiating magma. This agrees with the assigned chronology based on field relationships, as outlined by Robertson and Tolman (1961).

The basic intrusives, as expected, vary in their K_2O/Na_2O ratio, Na_2O content, K_2O content, and total $K_2O + Na_2O$ content from the other

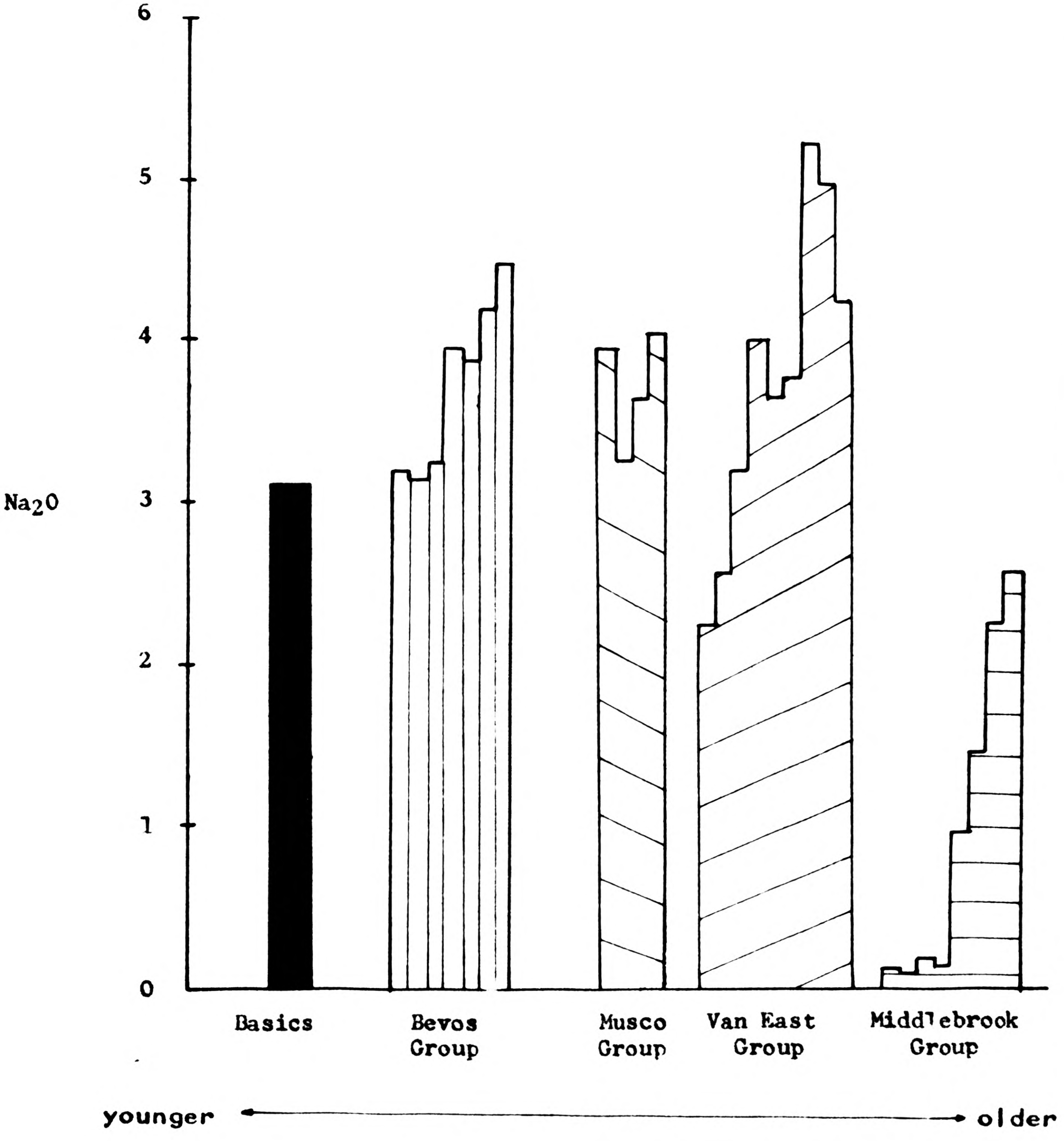

Figure 9

Na$_2$O content of Precambrian rock groups of Southeast, Missouri

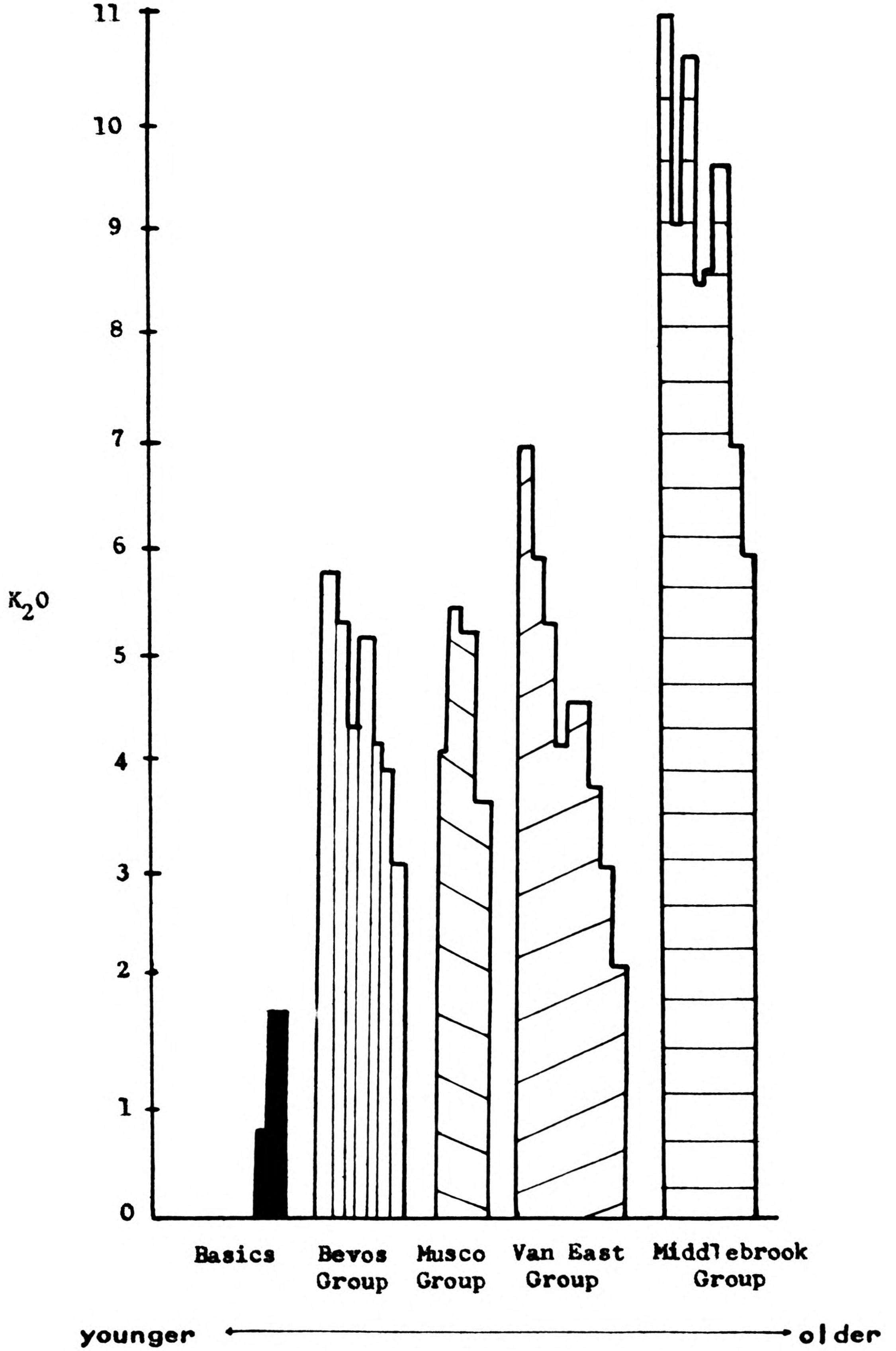

Figure 10

K$_2$O content of Precambrian rock groups of Southeast, Missouri

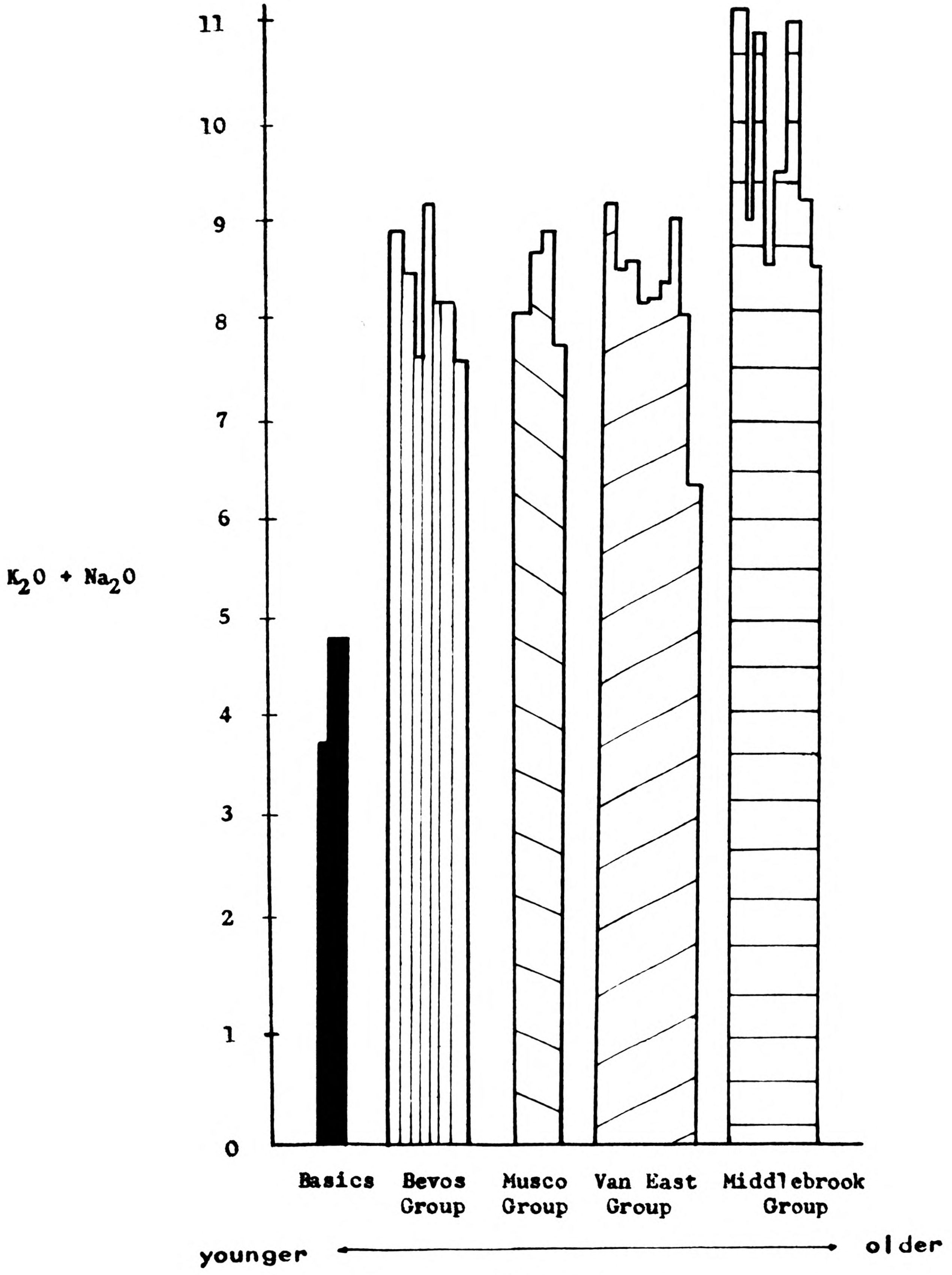

Figure 11

$K_2O + Na_2O$ content of Precambrian rock groups of Southeast, Missouri

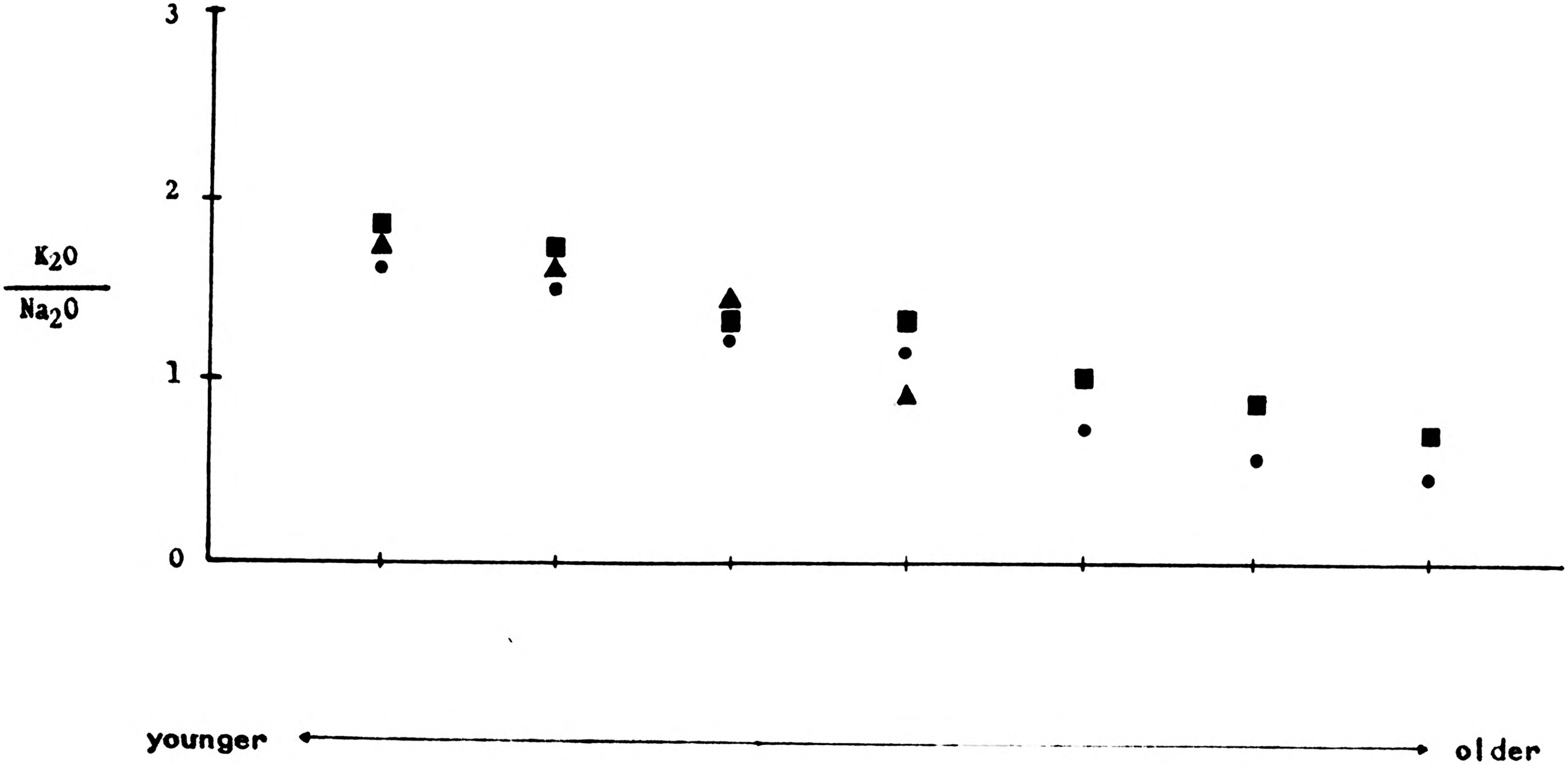

Figure 12
Composite of figures 5, 6, and 7, showing group K_2O/Na_2O relationships

Table II

Suggested Sequence Of Precambrian Rocks, Southeast Missouri, Based On K_2O/Na_2O Values

GROUP NAMES	UNIT NAMES	AGE RELATIONSHIP
Basic Intrusives	Quartz Basalt Skrainka Diabase	Increasing Age ↓
Bevos Group	Breadtray Granite Mudlick Latite Graniteville Granite Butler Hill Granite Silvermine Granite Knoblick Granite	
Musco Group	Slabtown Granite Buford Granite Porphyry Carver Creek Granite Porphyry Stono Granite	
Van East Group	Hogan Mountain Rhyolite Undifferentiated U-22 Stouts Creek Rhyolite Undifferentiated Type "B" Undifferentiated Type "A" French Mills Felsite Undifferentiated Type "C"	
Middlebrook Group	Brown Mountain Rhyolite Marlow Mountain Rhyolite Pilot Knob Rhyolite Royal Gorge Rhyolite Stegall Mountain Rhyolite Clark Mountain Rhyolite Annapolis Rhyolite Oak Mountain Felsite	

groups. This is well illustrated by Figures 8, 9, 10, and 11, pages 37, 42, 43, and 44. These basic rocks have formed, in the opinion of the author, from a different magma source than the other groups. The magma from which these rocks formed was relatively enriched in Na_2O as compared to K_2O.

Table II, page 46, summarizes the suggested age sequence of the Precambrian rocks of Missouri based on the results of this investigation. It must be remembered that the intragroup sequence is based on chemical results only. Current field work now underway, Anderson (1961-1962), may contribute to a better understanding of these relationships.

No previous work had been undertaken in an attempt to obtain chronological age relationships of the Precambrian rock units of Missouri using K_2O/Na_2O ratios.

The more or less regular variations of K_2O/Na_2O ratios is indicative of a differentiating magma. On this basis, the suggestion is made that the chronological sequence can be determined. Results seem to fit this pattern when compared to known sequences.

Additional field and laboratory investigations are necessary before a final solution of the details of the Precambrian stratigraphy of Missouri can be realized.

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