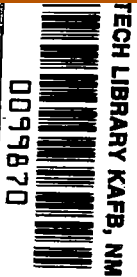NASA CONTRACTOR
REPORT

NASA CR-310

NASA CR-3

THE DISTINCTION OF ROCK TYPES ON THE BASIS OF THEIR MASS SPECTRA, WITH SPECIAL REFERENCE TO LUNAR-SURFACE APPLICATIONS

by Werner G. Deuser

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1965
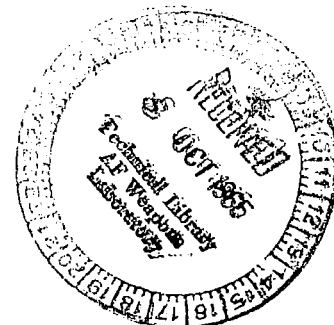
NASA CR-310

THE DISTINCTION OF ROCK TYPES ON THE BASIS OF THEIR

MASS SPECTRA, WITH SPECIAL REFERENCE

TO LUNAR-SURFACE APPLICATIONS

By Werner G. Deuser

ABSTRACT

It is shown that the rock types most commonly expected to be encountered on the lunar surface can for the most part be readily distinguished, chemically, by plotting their relative concentrations of Fe, Mg and Al on a ternary variation diagram. The necessary data for characterizing an unknown as to rock type can be quite easily extracted from complete or partial mass spectra such as may be obtained by means of a robot mass spectrometer on the lunar surface. For most compositions, determination of only two nuclide or element ratios will characterize the sample. For others, the determination of one additional ratio or comparison with a few standard spectra previously obtained in the laboratory may be necessary to classify the unknown in terms of the chemistry of terrestrial or meteoritic equivalents. No quantitative assay of element concentrations is necessary for such a first classification.

ACKNOWLEDGMENTS

THE DISTINCTION OF ROCK TYPES ON THE BASIS OF THEIR MASS SPECTRA, WITH SPECIAL REFERENCE TO LUNAR-SURFACE APPLICATIONS

Introduction

Rocks are usually classified on the basis of their mineral content which may be either that obtained by inspection and counting (mode) or that calculated from a chemical analysis in terms of normal mineral "molecules" (norm). It is the objective of this paper to describe a method for a fast and reasonably unambiguous distinction of some rock types on the basis of data obtained from a remote robot analysis as may be required in future lunar and planetary surface experiments. This method employs a minimum number of elements, does not require the cumbersome calculation of a norm, and is especially suited to the interpretation of data obtained from a mass spectrometric analysis.

Today's most widely accepted theories on the chemical composition of the lunar surface variously hold that it consists of rocks comparable in composition, if not necessarily in texture, to granites, basalts, tektites, and various classes of stone meteorites. (See e. g. O'Keefe (1960), Miyamoto (1960), O'Keefe and Cameron (1962), Fielder (1963), Urey (1965).) The present study, therefore, was confined to an attempt to distinguish between these types of rock only. Terrestrial rocks of the intermediate and ultrabasic types have not been considered here but a similar system for distinguishing between them can probably be devised.

Basic Assumptions

In the following discussion two assumptions are made: (1) The elements present in the sample are ionized in proportions bearing a known relationship to their relative proportions in the sample, and (2) the isotopic compositions of the elements on the lunar surface are similar to their isotopic compositions in the earth's crust and the meteorites.

Assumption (1) can be satisfied by proper choice of the ion source and analysis of a few samples of known composition. Assumption (2) appears quite safe, certainly as a first approximation, in view of the gross isotopic similarities between terrestrial and meteoritic samples. The results of this study are not affected by small fluctuations in the isotopic compositions such as are generated by normal terrestrial geochemical processes.

Choice of Elements

The choice of elements best suited to the distinction of the various rock types is dictated by two requirements: (1) They must, either separately or in combination with others, be specific of the rock types, with the smallest possible overlap of concentration ranges between rock types, and (2) they must

be easily and unequivocally identified and measured in a complete or partial mass spectrum of a rock.

Compilations of chemical analyses for the various rock types were drawn from the following sources: granites - Clarke (1924), Nockolds (1954), Tuttle and Bowen (1958), basalts - Clarke (1924), Tilley (1960), Yoder and Tilley (1962), Muir, Tilley and Scoon (1964), tektites - Taylor (1962), Chao (1963), Schnetzler and Pinson (1963), Schnetzler and Pinson (1964), chondrites - Urey and Craig (1953), Wiik (1956), Mason (1962), Craig (1964), achondrites - Urey and Craig (1953), Wiik (1956).

Inspection of all these chemical analyses soon revealed that no single element would satisfy requirement (1) because substantial overlaps occur between the concentration ranges of all major, minor, and trace elements of the different rock types under consideration.

The data most easily obtained from mass spectra are nuclide or element ratios rather than abundances of individual nuclides or elements. Therefore, a variety of plots of two elements, e.g., Fe vs. Si or Mg vs. Si etc., were investigated with respect to requirement (1). (See also discussion by Wyllie in Kendall et al., 1964.) While such plots, called variation diagrams, represent a considerable improvement over single elements, they still are very limited in their ability to distinguish rock types on the basis of nuclide or element ratios only.

The next step is a simultaneous plot of three elements. An example of this type is shown in Figure 1 which shows average compositions of the rock types considered in terms of Fe, Mg and Si. The positions of the points in such a diagram can be arrived at in two different ways. The percentages of the three components as obtained from the total chemical analysis (in this case atom percent) are recalculated to yield percentages of the sum of the three components only and then plotted. The ternary coordinates of each point add up to 100. Alternatively the atomic ratios of any two pairs of the three components are calculated and the proportions of the components of each pair corresponding to their ratio are plotted on the side of the triangular diagram bounded by the two. Mathematically expressed, for components A and B:

$$\frac{A}{B} = R$$

$$B \text{ (in } \% \text{ on side } \overline{AB}) = \frac{100}{1 + R}$$

The points thus determined on two sides of the diagram are connected by straight lines with their opposite apexes. The point of intersection of the two lines is the point characterizing the sample in terms of the three components. The line derived from the remaining pair of components will necessarily also pass through this point. The obvious advantage of this latter method is the fact that knowledge of the concentrations of the three

G   AVERAGE GRANITE
T   AVERAGE TEKTITE
B   AVERAGE BASALT
BTA AVERAGE BASALTIC TYPE ACHONDRITE
C   AVERAGE CHONDRITE
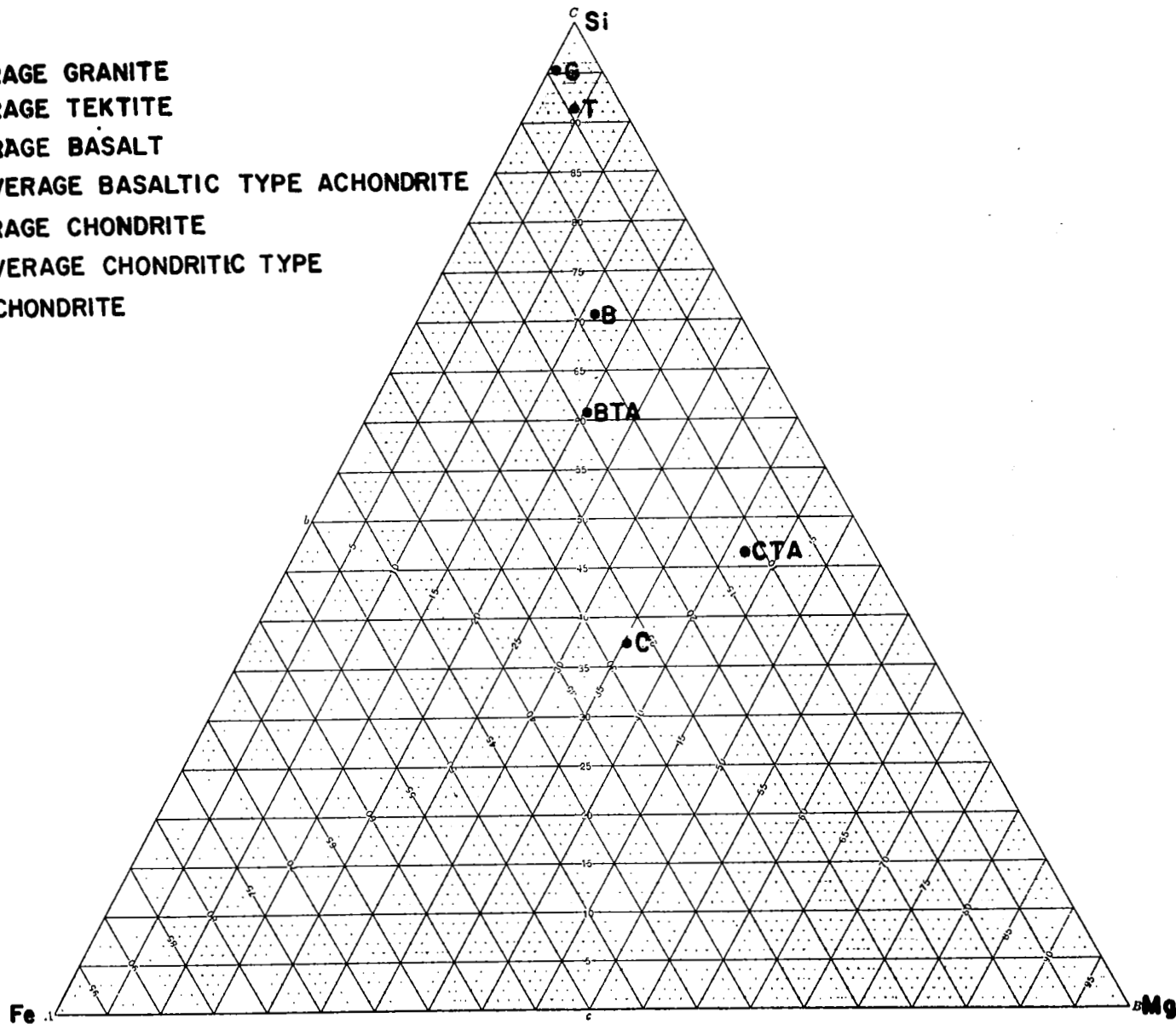CTA AVERAGE CHONDRITIC TYPE
     ACHONDRITE

Fig. 1 - Ternary Variation Diagram   Fe-Mg-Si (Atom%)

components is not required but that it is only necessary to determine the ratios of any two pairs to arrive at the proper point in the diagram. As a mass spectrometer gives atomic ratios and not weight ratios all diagrams shown here are plotted in terms of atom percent.

A variety of ternary combinations of major and minor elements were plotted using the compilations of chemical analyses referred to above, and each plot was evaluated in terms of requirements (1) and (2). The combination Fe-Mg-Al had to be given the highest rating. The concentration ranges in weight percent and the atomic ratio ranges for these elements in each of the rock types considered are shown in Tables 1 and 2.

The three elements Fe, Mg and Al also meet requirement (2) remarkably well, better in fact than most others. This is shown in Table 3 which lists their isotopes and also those of silicon together with each isotope's major sources of interference in the mass spectrum. Below each isotope's mass its natural abundance in percent is given. It can be seen from this table that none of the major isotopes of these elements has a natural isobar and also that corrections for interferences, at least to the extent required for the present purpose, should be relatively easy for Fe and Al. The determination of ^{24}Mg, however, can be complicated by comparable amounts of titanium in the sample as titanium's doubly charged major isotope ^{48}Ti also gives a mass line at the ^{24}Mg position. But even if there is much Ti, Mg may still be determined by use of the ^{26}Mg isotope.

Table 3 also shows that silicon does not meet requirement (2) satisfactorily as it is interfered with by iron and nickel, both abundant elements, especially in meteoritic material.

It is apparent that in many cases, i.e. whenever titanium is not very abundant in the sample, consideration of only the three isotopes ^{24}Mg, ^{56}Fe and ^{27}Al is sufficient to obtain good estimates of the relative proportions of these three elements.

The situation is much improved and simplified if an ion source is used which produces only singly charged ions. In that case, all interferences by multiply charged ions as discussed above are eliminated and more general use can be made of ^{24}Mg and the isotopes of silicon and many other elements. In the following discussion, however, the possibility of such interferences is taken into account.

4

Table 1

Concentration Ranges (wt. %)

	Fe		Mg		Al	
Basalts	4.8	- 10.2	3.1	- 7.0	5.8	- 10.0
Granites	0.53	- 5.9	0	- 0.35	5.1	- 7.8
Tektites	0.98	- 5.15	0.23	- 3.0	4.1	- 9.3
Chondrites (all classes)	13.6	- 36.7	10.2	- 17.3	0.34	- 2.8
Basaltic Type Achondrites	2.3	- 17.0	1.9	- 10.6	0.92	- 14.4
Chondritic Type Achondrites	1.6	- 18.8	14.0	- 24.5	0.1	- 1.5

Table 2

Atomic Ratio Ranges

	$\dfrac{Fe}{Mg}$			$\dfrac{Fe}{Al}$			$\dfrac{Mg}{Al}$		
Basalts	0.41	-	1.40	0.27	-	0.67	0.41	-	1.18
Granites	2.02	-	> 100	0.04	-	0.55	0.00	-	0.06
Tektites	0.38	-	3.50	0.11	-	0.42	0.06	-	0.47
Chondrites	0.35	-	1.56	4.4	-	45.	5.3	-	36.
Basaltic Type Achondrites	0.21	-	1.78	0.09	-	8.5	0.16	-	8.5
Chondritic Type Achondrites	0.03	-	0.47	2.4	-	> 100	12.	-	> 100

Table 3

Isotopes of Mg, Al, Si, and Fe and their main interferences ($>1\%$ of mass to be determined) in the mass spectrum of rocks with an assumed resolution of 100.

Element	At. Wt. of Isotope (% Nat'l Abund.)	Natural Isobar	Interferences	Easily Corrected?
Mg	24 (78.8)	none	$^{48}Ti^{++}$, $(^{12}C_2)^+$	in many cases
	25 (10.1)	none	$^{50}Ti^{++}$, $^{50}Cr^{++}$	?
	26 (11.1)	none	$^{52}Cr^{++}$, $(^{25}MgH)^+$, $(CN)^+$	yes
Al	27 (100)	none	$^{54}Cr^{++}$, $^{54}Fe^{++}$, $(^{26}MgH)^+$	yes
Si	28 (92.17)	none	$^{56}Fe^{++}$, $^{84}Kr^{+++}$, $(CO)^+$, N_2^+	difficult
	29 (4.71)	none	$^{58}Fe^{++}$, $^{58}Ni^{++}$, $(^{28}Si\,H)^+$	no
	30 (3.12)	none	$^{60}Ni^{++}$, $(^{29}Si\,H)^+$, $(NO)^+$	no
Fe	54 (5.9)	^{54}Cr	$^{54}Cr^+$, $(^{53}CrH)^+$, $(^{27}Al_2)^+$	?
	56 (91.6)	none	$(^{55}MnH)^+$, $(^{28}Si_2)^+$, $(^{40}Ca^{16}O)^+$	yes
	57 (2.20)	none	$(^{56}FeH)^+$, $(^{28}Si^{29}Si)^+$, $(^{55}MnH_2)^+$, $(^{41}K^{16}O)^+$	?
	58 (0.33)	^{58}Ni	$^{58}Ni^+$, $(^{57}FeH)^+$, $(^{56}FeH_2)^+$, $(^{28}Si^{30}Si)^+$, $(^{42}Ca^{16}O)^+$, $(^{39}KF)^+$	no

The Fe-Mg-Al Variation Diagram

From the data of Table 2 the variation fields shown in Figure 2 were computed. The size, shape and location of each of these fields is determined by three pairs of straight lines, fanning out from each corner of the diagram and reaching the opposite side at, respectively, the maximum and minimum atomic ratios in the rock type of the two elements named on that side. Each straight line leaving an apex and crossing the diagram is the locus of all points having the same atomic ratio of the two elements on the side opposite the apex.

Figure 2 shows the variation fields of granites, tektites, basalts (alkaline olivine-basalts and tholeiites), basaltic type achondrites, chondrites (all classes) and chondritic type achondrites. The terms basaltic and chondritic type achondrites are used as defined by Urey and Craig (1953). The fields shown include all the chemical analyses listed in the compilations consulted, with two exceptions: (1) Only about 90% of the basaltic type achondrites are included in that field. The remaining analyses (3 out of 25) have a great spread and fall far outside the field. Inclusion of these analyses would have enlarged the field of the basaltic type achondrites by more than a factor of 3 which seemed unwarranted in view of the apparent 0.12 probability of obtaining a point outside the field shown in the figure. (2) For the same reason one chondrite analysis out of more than 100 was excluded. All individual analyses consulted in this work are plotted in Figure 2. It will merely be mentioned here that the division of the chondrites into two distinct groups, the Urey-Craig high- and low-iron chondrites, can be clearly seen on this plot. Similarly, the basaltic type achondrites appear to be composed of two groups which by analogy may be called high- and low-magnesium groups with respect to iron and aluminum.

The overlaps or approaches between different fields will be dealt with in the following discussion on how this diagram may be used for the interpretation of a mass spectrum of an unknown rock.

Application of the Diagram

A first inspection of the spectrum and brief comparison with reference spectra will show whether or not the unknown sample is a silicate rock which may be compared to common terrestrial rocks, tektites or stony meteorites. Next a semi-quantitative check of the Mg/Ti ratio using the isotopes ^{26}Mg and ^{47}Ti will help to decide whether or not a considerable correction for ^{48}Ti at the ^{24}Mg position is required. If this is not the case the isotopic ternary system ^{56}Fe - ^{24}Mg - ^{27}Al shown in Figure 3 may be used. Figure 3 is based on the same data as Figure 2 and exhibits essentially the same features in slightly distorted form. It may be used as a short-cut whenever the atomic ratios of these three isotopes can be easily ascertained. In this case then it is only necessary to
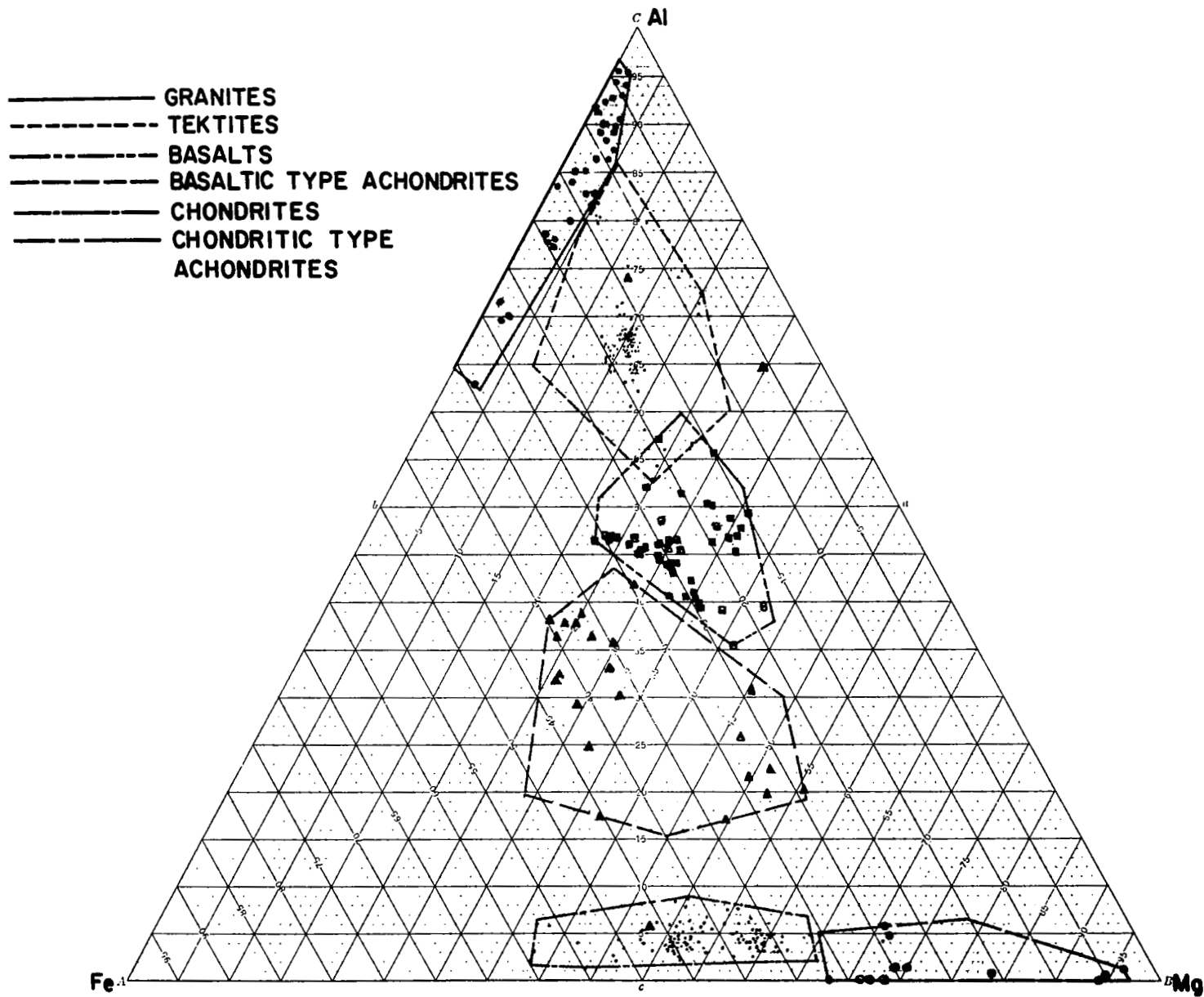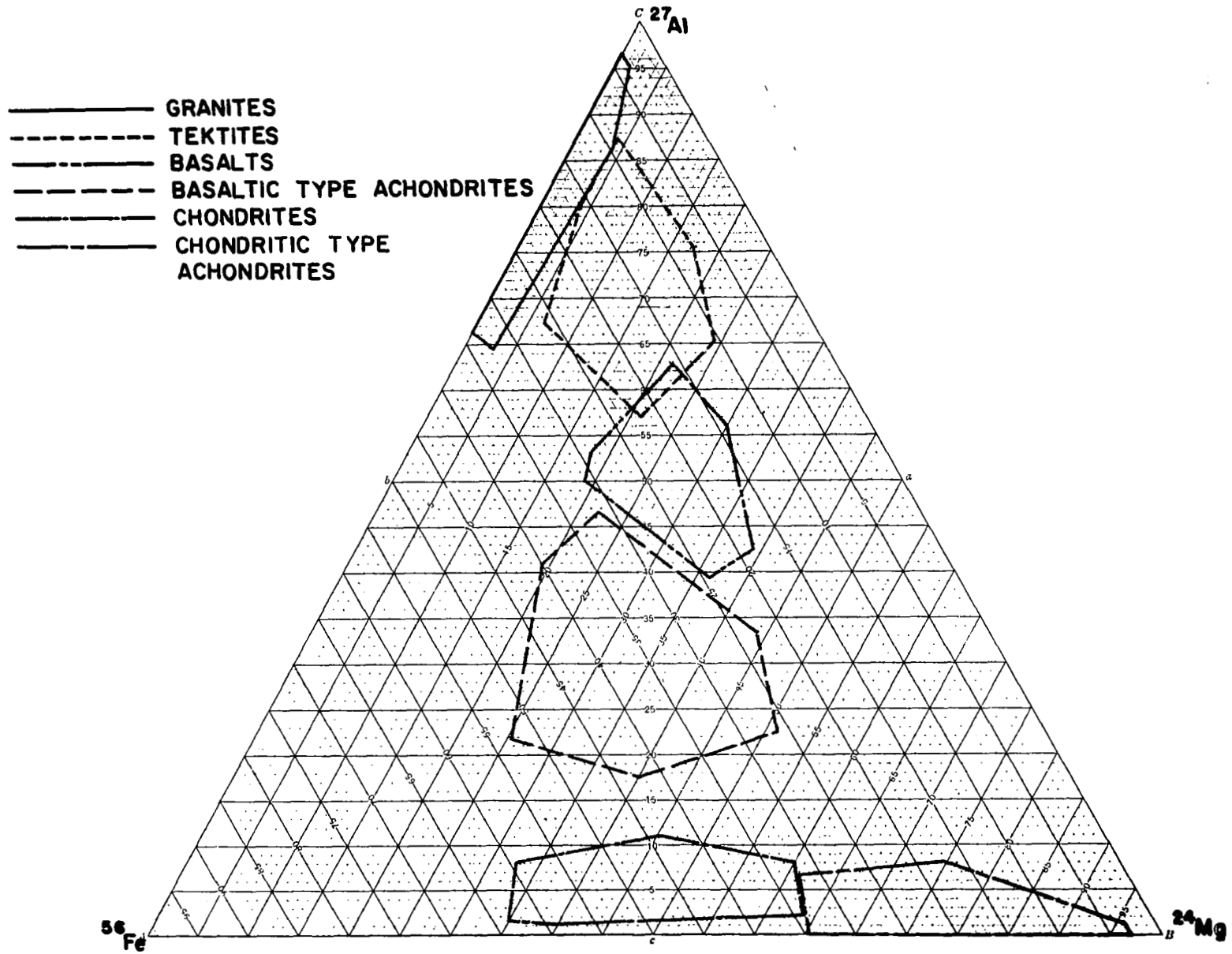
Fig. 2 - Ternary Variation Diagram Fe-Mg-Al (Atom%)

Fig. 3 - Ternary Variation Diagram $^{56}Fe - ^{24}Mg - ^{27}Al$ (Atom%)

measure any two ratios of these three isotopes, plot the points corresponding to these ratios on the appropriate sides of the triangle and connect them with the opposite apex in each case.

In the case of a sample having a high titanium content, elemental ratios have to be determined and plotted in an analogous manner on the diagram of Figure 2. The following discussion applies to either case.

If the point of intersection falls within a unique field in the diagram it may quite safely be assumed that the unknown sample has chemical characteristics very similar to those of the rock type of that particular field. Further characterization can, of course, be accomplished by additional evaluation of the mass spectrum and comparison with reference spectra. If the unknown falls into an area which lies within or very near the variation field of 2 rock types it is obviously necessary to examine additional elements in order to attribute the sample to a certain rock type. These cases will be discussed in the following paragraphs.

(a) Granites and tektites. - Relatively few tektite compositions (all of which are North American specimens) fall near the granite field but an additional criterion is needed to distinguish between tektites and granites if an unknown sample falls near the border zone of the two fields. There is a marked difference in alkali content which is roughly twice as high in granites as in tektites. The K/Mg ratio is probably the most specific of all the major element pairs. Moreover, K is another element quite easily measurable in a mass spectrum. Table 4 compares the K and Mg ranges of granites and tektites and shows that the atomic ratio K/Mg varies from 0.33 to 3.5 in tektites and from 7.3 to >100 in granites, making possible their distinction in all cases.

(b) Tektites and basalts. - Only a few extreme compositions of these two rock types overlap on the Fe-Mg-Al plot. If an unknown sample falls into this area of the diagram it can be classified on the basis of an additional rough determination of the Mg/Si ratio. Table 5 compares the ranges of this ratio in basalts and tektites. The highest value of 0.11 for tektites which is closest to the basalt values is from an isolated analysis of a javanite and is certainly not typical for tektites. Thus it appears quite possible always to distinguish between these two rock types.

(c) Basalts and basaltic type achondrites. - As the name implies, the basaltic type achondrites are chemically similar to the basalts and in view of this fact it is remarkable how well the Fe-Mg-Al plot separates these achondrites from the basalts. Any unknown falling close to both fields will have to be dealt with on an individual basis. Na is generally much more abundant in basalts than in the achondrites. Comparison with a basalt standard might also reveal large differences in some other elements which would suggest achondrite material as the basalts exhibit a relatively small spread.

(d) Chondrites and chondritic type achondrites. - The approach in the diagram between these two rock types does not appear critically

Table 4

Comparison of Granites and Tektites

	Weight %				Atomic Ratio
	K		Mg		K/Mg
Granites	3.2 - 6.6		0 - 0.35		7.3 - > 100
Tektites	0.68 - 3.1		0.23 - 3.0		0.33 - 3.5

Table 5

Comparison of Basalts and Tektites

	Weight %				Atomic Ratio
	Si		Mg		Mg/Si
Basalts	21.1 - 26.7		3.1 - 7.0		0.15 - 0.38
Tektites	32.1 - 39.5		0.23 - 3.0		0.01 - 0.11

Table 6

Comparison of Chondrites and Chondritic Type Achondrites

	Weight %				Atomic Ratio
	Si		Fe		Si/Fe
Chondrites	12.2 - 21.5		13.6 - 36.7		0.80 - 3.2
C.T.A.	18.8 - 26.9		1.6 - 18.8		3.2 - 19.

close in view of the implied similarities of the two groups. Only one iso-
lated chondrite analysis falls into the achondrite field. An unknown falling
near both fields can best be classified as one or the other by an additional
determination of the Si/Fe ratio which is lower in chondrites than in the
chondritic type achondrites as is shown in Table 6. It is significant here
that none of the low Si/Fe achondrites fall near the chondrite field on the
Fe-Mg-Al diagram thus making possible an unequivocal distinction. It
might also be mentioned here that it would be straightforward to test
chondrite material for some other elements, such as carbon, if a further
characterization were desired.

Finally, there remains, of course, the chance that an unknown may
fall outside any of the fields discussed here. Such a case might be rare
achondrite material, perhaps another rock type with terrestrial equivalent
not included here or something quite unlike any material known to us at
present. Iron meteorites would naturally be located at or very near the
Fe corner of the diagram. Stony irons have insignificant amounts of
aluminum and fall on or near the Fe-Mg side of the diagram in the chon-
drite-chondritic type achondrite range. But as far as today's preponderant
theories are concerned, chances for finding any of these materials on the
lunar surface are small.

Conclusions

The ternary variation diagram Fe-Mg-Al has been shown to be most
useful for chemically classifying lunar-surface material in terms of rock
types most commonly thought to occur on the lunar surface. Plotting of
mass spectral data on this diagram provides a simple and fast means for
accomplishing this classification. In many cases determination of only two
nuclide or element ratios is sufficient; quantitative assay of element con-
centrations is unnecessary. In other cases, determination of an additional
element ratio or comparison with a few standard spectra may be required.

References

Chao, E.C.T., The petrographic and chemical characteristics of tektites, in: Tektites, J.A. O'Keefe (ed.), Univ. Chicago Press, pp. 51-94 (1963).

Clarke, F.W., The data of geochemistry, U.S. Geol. Survey Bull. 770, 841 pp (1924).

Craig, H., Petrological and compositional relationships in meteorites, in: Isotopic and Cosmic Chemistry, H.Craig, S.L. Miller, G.J. Wasserburg (eds.), North Holl. Publ. Co., pp 401-451 (1964).

Fielder, G., Nature of the lunar maria, Nature 198, 1256-1260 (1963).

Kendall, B.R.F., L.F. Herzog, P.J. Wyllie, D.S. Edmonds, C. Bauer, Analysis of the lunar surface and atmosphere by mass spectroscopy, NASA-CR-56552, 168 pp (1964).

Mason, B., Meteorites, John Wiley & Sons, Inc., 274 pp (1962).

Miyamoto, S., A geological interpretation of the lunar surface, Planet. Space Sci., 2, 256-260 (1960).

Muir, I.D., C.E. Tilley and J.H. Scoon, Basalts from the northern part of the rift zone of the Mid-Atlantic Ridge, J. Petrol. 5, 409-434 (1964).

Nockolds, S.R., Average chemical composition of some igneous rocks, Geol. Soc. Am. Bull. 65, 1007-1032 (1954).

O'Keefe, J.A., The origin of tektites, in: Space Res. Proc. 1st Int. Space Sci. Symp., H.K. Bijl (ed.) North Holl. Publ. Co., pp. 1080-1105 (1960).

O'Keefe, J.A. and W.S. Cameron, Evidence from the moon's surface features for the production of lunar granites, Icarus 1, 271-285 (1962).

Schnetzler, C.C. and W.H. Pinson, Jr., The chemical composition of tektites, in: Tektites, J.A. O'Keefe (ed.) Univ. Chicago Press, pp 95-129 (1963).

Schnetzler, C.C. and W.H. Pinson, Jr., A report on some recent major element analyses of tektites, Geochim. Cosmochim. Acta 28, 793-806 (1964).

Taylor, S.R., The chemical composition of australites, Geochim. Cosmochim. Acta 26, 685-722 (1962).

Tilley, C.E., Differentiation of Hawaiian basalts: some variants in lava suites of dated Kilauean eruptions, J. Petrol. 1, 47-55 (1960).

Tuttle, O.F. and N. L. Bowen, Origin of granite in the light of experimental studies in the system $Na\ Al\ Si_3O_8$ - $K\ Al\ Si_3O_8$ - SiO_2 - H_2O, Geol. Soc. Am. Memoir 74, 152 pp (1958).

Urey, H.C., Meteorites and the moon, Science 147, 1262-1265 (1965).

Urey, H.C. and H. Craig, The composition of the stone meteorites and the origin of the meteorites, Geochim. Cosmochim. Acta 4, 36-82 (1953).

Wiik, H.B., The chemical composition of some stony meteorites, Geochim. Cosmochim. Acta 9, 279-289 (1956).

Yoder, H.S., Jr. and C.E. Tilley, Origin of basalt magmas: an experimental study of natural and synthetic rock systems, J. Petrol. 3, 342-532 (1962).