A Petrological Study on the Basalts of Hyogo Prefecture, Japan

Part I. X-ray Microanalysis of Clinopyroxenes

By

Hajime YOSHIZAWA, Tadao WAKABAYASHI* and **Taiji TAKASE****

Geological and Mineralogical Institute, University of Kyoto

(Received August 30, 1966)

Abstract

X-ray microanalysis has been made quantitatively on the clinopyroxenes from the basalts of the Quarternary Period in Hyogo Pref. to determine their composition of Na_2O, MgO, Al_2O_3, SiO_2, TiO_2, MnO and FeO (or Fe_2O_3) by use of the reference standard of the augite phenocryst in the andesite of Nisekarita, Mt. Zao.   Owing to the similarity in composition between the standard and the unknowns, analysis has been carried out directly comparing the accumulated X-ray counts obtained from the standard and the unknowns.

Oxide totals show good results having errors of only 3% or less and these errors should be attributed mainly to chemical diversity in analyzed grains, discordancy between area bombarded by electron and pyroxene grain to be analyzed, and X-ray source size.

Quantitative results were also calculated into Wo-En-Fs-percent and atomic percent with respect to Ca, Mg and $(Fe^{+2}+Fe^{+3}+Mn)$ atoms and these pyroxenes were determined to be diopside—diopsidic augite.

Although further refinement of analytical techniques is required to decrease errors equivalent to statistical errors, these good results give a promise of satisfactory applications of the microanalyser to routine analysis in mineralogy and petrology.

Introduction

Basalts in the Kinki District of the Quarternary Age have been studied occasionally by the students of Kyoto University, i.e., S. KOKAWA[1], and recently by Y. OCHI[2] of Fukuoka University of Arts and Sciences.

The authors, having participated in the Upper Mantle Project, are now investigating the rocks of this kind from Hyogo Pref., and these results will be reported in succession hereafter.

Generally speaking, the chemical composition of each main constituent mineral

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* Scientific Instrument Division, Shimadzu Seisakusho Ltd., Kyoto
** A graduate of the Geol. and Min. Inst., this Univ.

in a rock must be accurately and precisely determined petrologically.   However, in volcanic rocks such as basalt and andesite, constituent minerals, especially ground-mass minerals, are generally of very fine grain.   Therefore, samples of such a fine grained mineral free from other minerals and convenient for the determination of its chemical composition are very difficult to be acquired.   Such determination under the microscope, i.e., optical determination of these fine-grained minerals, cannot be done with high accuracy.

Accordingly, X-ray microanalysis is required in such a case, because X-ray microanalyser, by applying a finely focused electron beam (approximately 1μ or less) to a particular point of the surface of the specimen whose chemical composition is to be examined, enables qualitative or quantitative analysis non-destructively.

This method is very useful for mineralogy and petrology because of elimination of time-loss, high spatial resolution and unnecessity of tedious mineral separation. If the minerals forming rocks can be analyzed individually with high accuracy by use of microanalyzer, studies of the magmatism and the regional and thermal metamorphism of rocks will be greatly promoted.

There have been made a few reports (3–6) on the quantitative analysis of rock-forming minerals by microanalyzer, but most of them deal with synthetic mine-rals and semi-quantitative analysis.

This paper deals with quantitative analysis of natural clinopyroxenes from the basalts mentioned above making use of the methods of direct comparison with augite phenocryst of already-known composition as the reference standard.

The field survey of this study has been performed by H. YOSHIZAWA and K. ISHIZAKA, the microscopical observation mainly by S. NISHIDE, the analysis of the bulk chemical composition of their rocks by K. NISHIMIYA and X-ray micro-analysis of their minerals by T. WAKABAYASHI assisted by T. TAKASE.   These experiments have been directed by H. YOSHIZAWA.

Standard and unknown specimens

Five unknown specimens of basalt have been used in this study, whose localities are Izoe, Mikata-cho ($\sharp$ 10), Ikeyama, Oya-cho ($\sharp$ 22), Kannabe, Hidaka-cho ($\sharp$ 33), Gembudo, Toyooka-city ($\sharp$ 41′) and Yakuno, Santo-cho ($\sharp$ 51).

These basalts consist of olivine and plagioclase as phenocrysts, and of olivine, clinopyroxene and plagioclase in groundmass, occasionally accompanied by biotite, anorthoclase and glass as mesostases.   No orthopyroxene is observed in these specimens.   The optical micrographs of these basalts are shown in Fig. 1.
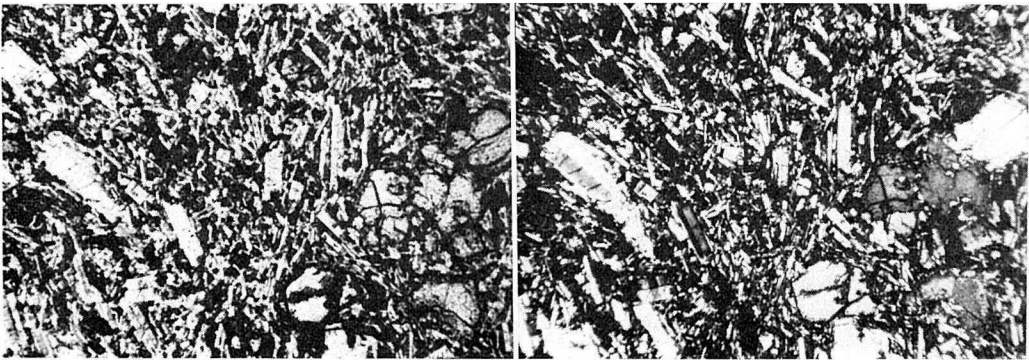
For the microanalysis of these groundmass clinopyroxenes, it is convenient to use as reference standard a pyroxene resembling the pyroxenes to be analyzed as
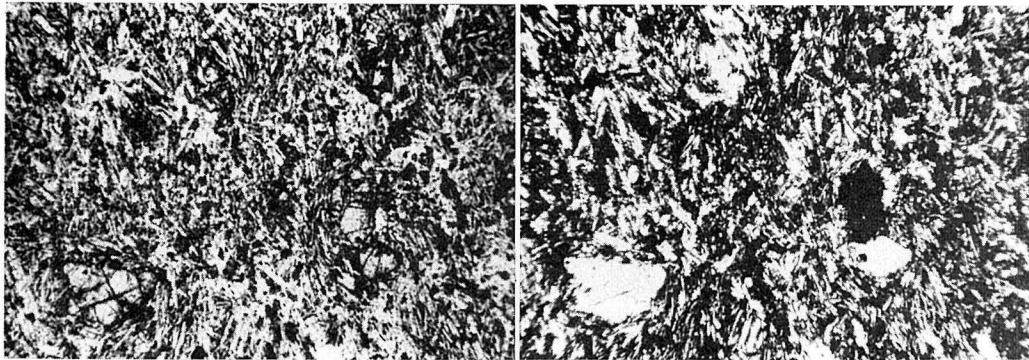
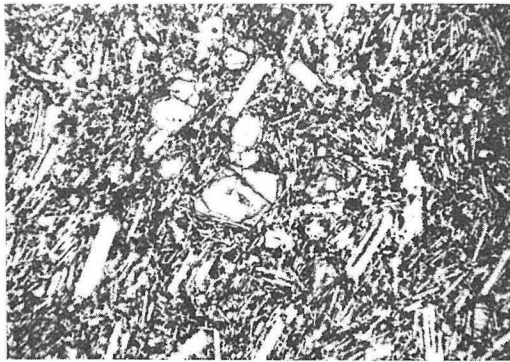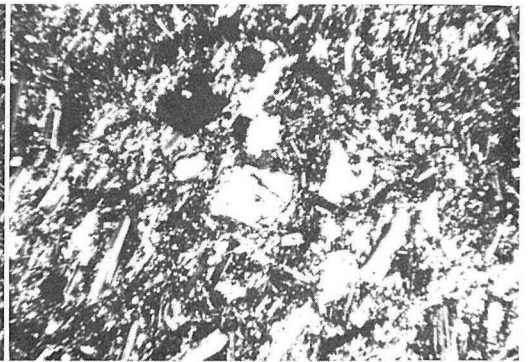Fig. 1.   Microphotograph of the Basalts ($\times$31ca.)
Phenocryst ···olivine (mainly) and plagioclase.
Groundmass···olivine, clinopyroxene, plagioclase, biotite, alkali-feldspar,
            magnetite and glass.

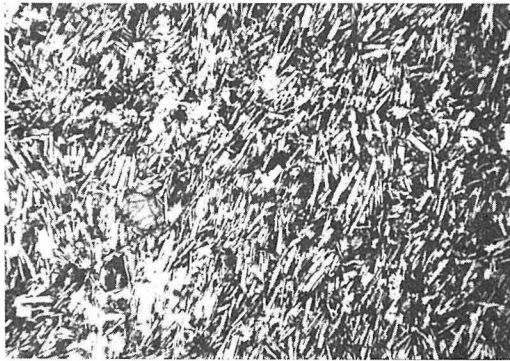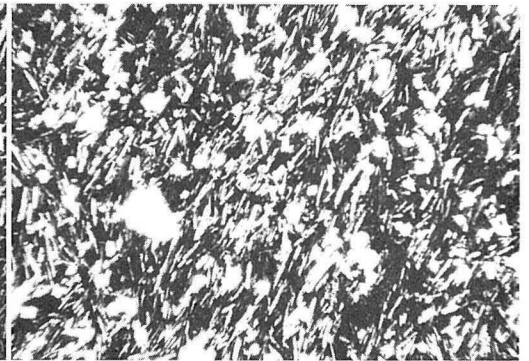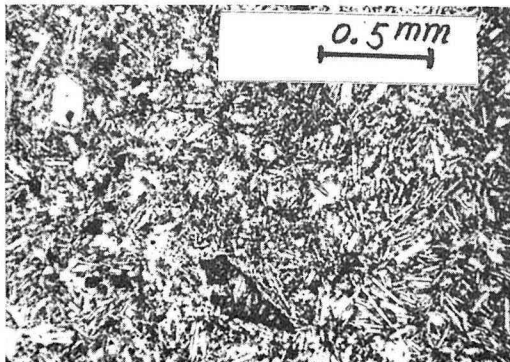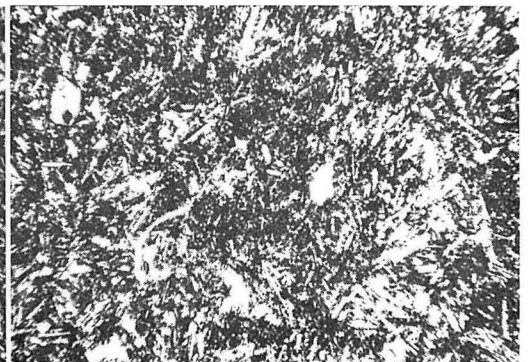♯ 33   Opened   Crossed

♯ 41′   Opened   Crossed

0.5 mm

♯ 55   Opened   Crossed

Table 1. Gravimetric analysis of the standard pyroxene*

SiO_2	50.04
TiO_2	1.07
Al_2O_3	3.19
Fe_2O_3	2.92
FeO	9.95
MnO	0.31
MgO	14.30
CaO	17.95
Na_2O	0.44
K_2O	0.06
$H_2O(+)$	undetermined
$H_2O(-)$	0.22
Total	100.45

closely as possible in its composition in order to be able to ignore the absorption of the X-rays by their specimens, fluorescence excitation by the line radiation and by the continuous X-ray and also the atomic number effect by the specimens.

The clinopyroxene used as the standard is the augite phenocryst in an orthopyroxene-bearing augite andesite from Nisekarita, Mt. Zao, Yamagata Pref., kindly given to the authors by T. TIBA, K. AOKI and H. ŌNUKI.

The composition of the standard shown in Table I was determined chemically by these three scholars. The quantitative microanalysis of this standard will be discussed by one of the authors (T. WAKABAYASHI) in near future.

Experimental Procedures

Each basalt specimen was broken into fragments of appropriate size and embedded in black bakelite of one inch diameter together with the standard pyroxene grain.

Polishing was done, by using, in order, 180–, 320–, 400– and 600 grid carborundum on rotating adhesive-paper laps with water, and then 5–, 0.3– and 0.05 microns alumina on rotating soft cloth laps with water.

The time required for polishing totaled more than 100 minutes. The reason for polishing with such particular care is to avoid errors arising from irregularities on the specimen surface. Of course, the microanalyzer employed, having a high take-off angle of 52.5°, is far less sensitive to inaccuracies due to surface irregularities than the microanalyzer with a smaller X-ray take-off angle, but errors may still result if the irregularities are strongly pronounced, especially in the case of weak radiation such as $NaK\alpha$.

The specimens were throughly cleaned and freed of abrasive particles and dirts by using a rotating soft cloth, with slight nap, wet with water, and then dried with air. Then, to give the electrical and thermal conductivity, coating is made on the standard and the unknown specimens simultaneously and at the same distance from the source by vacuum evaporation, covering with carbon layer of about 200Å thickness.

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* Data of the chemical composition of this Zao's pyroxene, having not yet been published, were adopted here by courtesy of T. TIBA, K. AOKI and H. ŌNUKI.

For mounting these specimens brass specimen holder is used, which is designed so that the polished surface of the specimens may be mounted in the proper orientation.

The microanalyzer employed in this study, having three spectrometers of a type having directly readable wavelength with the X-ray take-off angle shown above, permits three elements to be analyzed simultaneously.

The selection of spectrometer were made as follows: for $FeK\alpha$, $MnK\alpha$ and $TiK\alpha$, 4 inch radius LiF spectrometer and "Exatron" counter using Kr gas and 0.01 inch Be window were employed; for $CaK\alpha$ and $SiK\alpha$, 4 inch radius ADP spectrometer and "Exatron" counter using Ne gas and 0.01 inch Be window were employed; for $AlK\alpha$, $MgK\alpha$ and $NaK\alpha$, 4 inch potassium acid phthalate crystal and flow proportional counter with an ultrathin nitrocellulose window using an argon-methane $(P-10)$ flow gas were employed.

Spectrometers were aligned carefully for the analysis of the appropriate elements for pyroxenes, in the combinations as shown next: (a) $FeK\alpha$, $CaK\alpha$ and $MgK\alpha$, (b) $MnK\alpha$ and $NaK\alpha$, (c) $TiK\alpha$ and $AlK\alpha$: the elements forming each group were analyzed simultaneously before changing into a new setting for the monochromator.

For analyzing these elements, the effect of wave-length shift in the characteristic X-ray lines was left out of consideration because of similarity of the composition.

The excitation condition was decided considering the X-ray yield and resolution: A high accelerating voltage brings a greater X-ray yield, but gives a lower resolution, so that the excitation condition must be decided according to the purpose of analysis.   For this analysis, an accelerating voltage of 20 KV, together with a specimen current of 0.08 μA, was used considering the excitation voltage of 7.1 KeV for $FeK\alpha$ and the minimum size of incident electron beam of about 0.5μ.

Since all the specimens were coated with carbon layer it was difficult to decide their pyroxenes with the reflection microscope of this apparatus.   Consequently, X-ray scanning pictures were taken for each element, by which the existing positions of pyroxene on the graticule of oscilloscope were decided.   Incident electron beam upon these specimens was deflected electrically so as to strike pyroxene.

Ten of the pyroxenes were selected for each basalt specimen and each generating X-ray quanta was accumulated in 20 seconds by using scalers so as to yield a small enough statistical error.   The analysis spots for Fe, Ca and Mg did not correspond to the spots for Mn and Si, and also Ti, Al and Na.   For the analysis of the standard pyroxene, ten spots were also selected; in this case, endeavor was made to avoid the inclusions of hypersthene.

Results and Discussions

Fig. 2 shows X-ray scanning pictures of ♯ 33 basalt specimen, as an example, taken for each element in order to decide minerals composing basalt: The scanning picture of the specimen current, also, is shown in Fig. 2.

In general, basalt is composed of olivine, pyroxenes, plagioclase and magnetite (or ilmenite).   Having a distinctive feature of being rich in MgO and CaO together
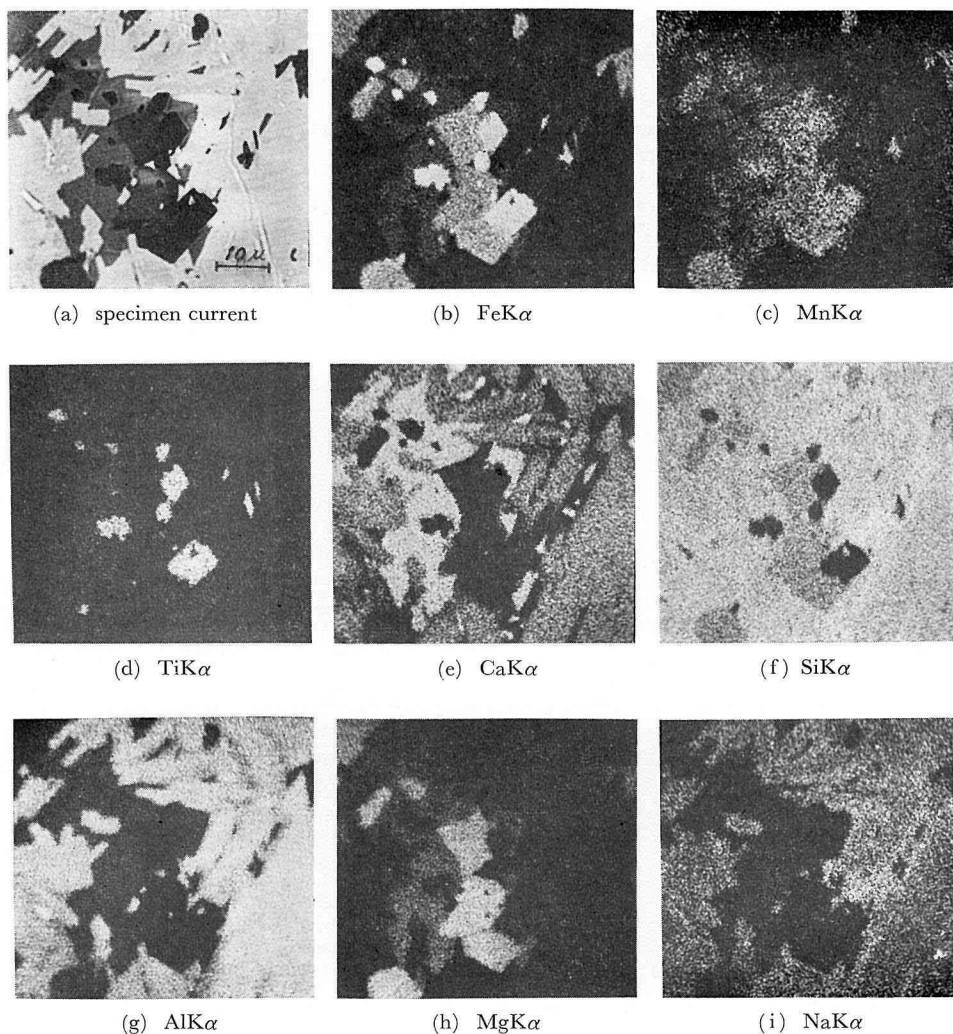

(a) specimen current   (b) FeKα (c) MnKα

(d) TiKα (e) CaKα (f) SiKα

(g) AlKα (h) MgKα (i) NaKα

Fig. 2.   X-ray scanning picture of ♯33 basalt for FeKα, MnKα, TiKα, CaKα, SiKα, AlKα, MgKα and NaKα radiations.   Specimen current scanning picture is also shown as (a).

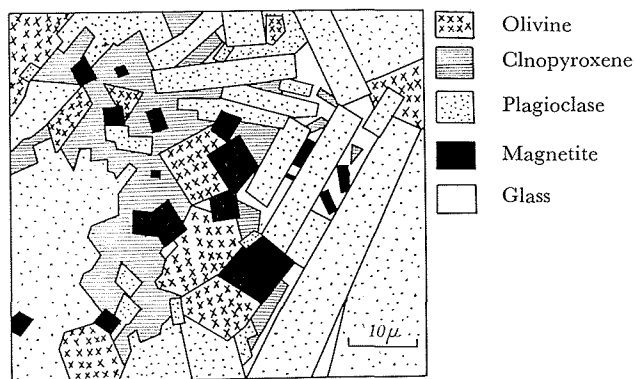| | Olivine |
	Clnopyroxene
	Plagioclase
	Magnetite
	Glass

Fig. 3.   Schematic Illustration for the distribution of minerals
in the basalt (♯33)

Table II.   X-ray microanalyses of clinopyroxenes from the basalts.   Total (I) and Total (II)
correspond to total Fe calculated respectively as FeO and Fe_2O_3.

Specimen / Composition	♯10	♯22	♯33	♯41′	♯51	Standard
SiO_2	50.3	50.2	49.2	41.5	50.6	50.04
TiO_2	1.71	1.86	2.79	7.22	2.60	1.07
Al_2O_3	4.54	3.29	4.48	7.72	3.95	3.19
FeO	9.54	9.60	10.1	12.7	9.84	9.95
(Fe_2O_2)	(10.6)	(10.8)	(11.2)	(14.1)	(10.9)	2.92
MnO	0.34	0.29	0.24	0.25	0.33	0.31
MgO	15.0	14.9	13.2	9.71	13.9	14.30
CaO	16.9	20.2	20.9	20.6	18.8	17.95
Na_2O	0.94	0.68	0.87	1.24	0.87	0.44
Total (I)	99.3	101.0	101.8	100.9	100.9	100.17*
Total (II)	100.3	102.2	102.9	102.3	102.0	—
Ca	42.0	46.3	48.3	48.1**	43.8	40.8
Mg	31.3	28.8	25.7	19.0	28.9	27.3
$Fe^{+2}+Fe^{+3}+Mn$	26.7	24.9	26.0	32.9	27.3	31.9
$CaSiO_3$ (wt.%)	38.7	43.1	45.5	47.1**	42.2	38.3
$MgSiO_3$	41.3	38.2	34.5	26.7	37.5	36.7
$FeSiO_3$	20.1	18.7	20.0	26.2	20.3	25.0

Note: 1)   compositions (SiO_2, TiO_2 etc.) are shown in weight precent.
2)   Ca, Mg and ($Fe^{+2}+Fe^{+3}+Mn$) are shown in atomic percent.
3)   * The standard specimen contains 2.92% of Fe_2O_3.
4)   ** ♯41′ is an mixture of mainly clinopyroxene and ilmenite
(this specimen consists of very fine-grained minerals).
5)   The standard was analyzed by T. Tiba, K. Aoki and H. Ōnuki by the gravimetric
method.

with SiO_2, monoclinic pyroxene can be found by searching the grains of high intensity for $MgK\alpha$ and $CaK\alpha$ together with $SiK\alpha$. In a similar way, all minerals composing basalt were found from X-ray scanning pictures as illustrated schematically in Fig. 3.

Table II contains the data of X-ray microanalyses of the monoclinic pyroxenes from each basalt in weight percent, and also the individual atomic percent with respect to Ca, Mg and $(Fe^{+2}+Fe^{+3}+Mn)$ atoms (Fig. 4) and weight percent of each pyroxene molecule.

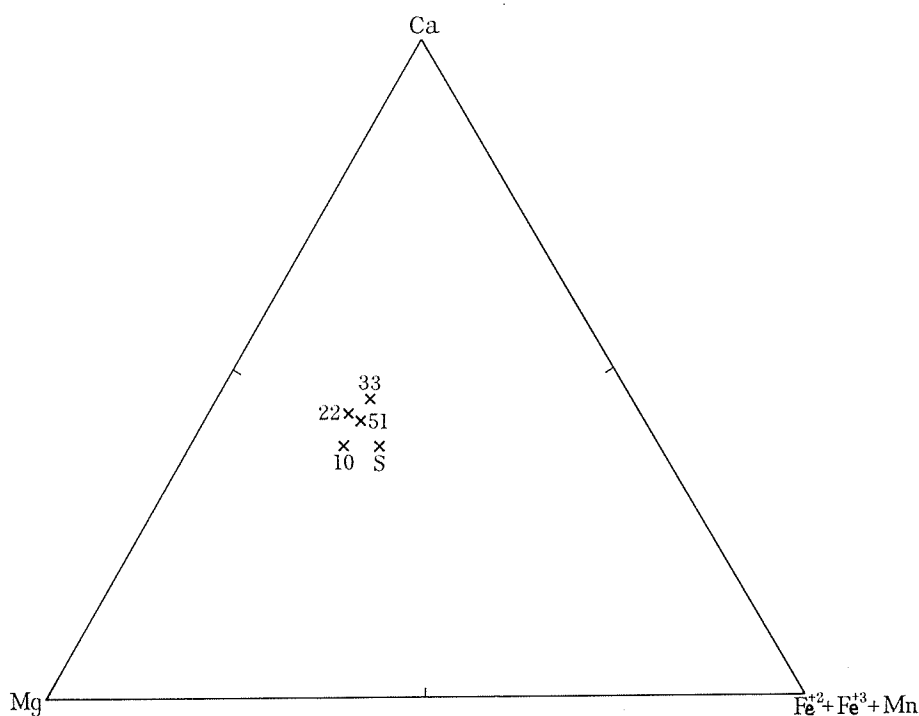Fig. 4. The compositional distribution of the pyroxenes in the $Ca–Mg–(Fe^{+2}+Fe^{+3}+Mn)$ Diagram.

Although an important question arises concerning the state of oxidation of iron in pyroxene, it was impossible in this study to divide Fe into FeO and Fe_2O_3 accurately since oxygen was not measured. However, the Total (I) in Table II shows better results compared with Total (II), therefore, it is considered that most of the total Fe in each pyroxene in this study have the divalent form rather than the trivalent form.

Judging from the results obtained by the microanalysis, the pyroxenes from

the basalts (♯ 10, ♯ 22, ♯ 33, and 51), except for one (♯ 41′) are obviously diopside to diopsidic augite, and this fact agrees with the data obtained from the optical microscopical observations which will be discussed in Part II.

As these pyroxenes in question abound in Na_2O and TiO_2 slightly more than common diopside and augite, they distinctly have, in some degree, the molecules of titanaugite and acmite.

As for the accuracy of the analyses, the Total (I) gives the resultant errors of 2% ca; moreover, an error from K_2O is to be expected if K_2O is measured, but it will be trivial. Although there is no doubt that the error of 2% is satisfactory for routine work, the promotion of accuracy can be expected by inspecting the sources of error.

Table III. Errors arised from statistical variation, chemical difference in each analysis point and positional discordancy between area bombarded by electron and pyroxene-grain, calculated by the method of Least Squares.

Com-position	Standard			♯ 10		♯ 22		♯ 33		♯ 41′		♯ 51	
	C_w %	σ_1 %	σ_2 %	C_x %	σ_2 %	C_x %	σ_2 %	C_x %	σ_2 %	C_x %	σ_2 %	C_x %	σ_2 %
SiO_2	50.04	0.12	0.15	50.3	0.45	50.2	0.48	49.2	0.50	41.5	0.41	50.6	0.40
TiO_2	1.07	0.01	0.05	1.71	0.10	1.86	0.15	2.79	0.11	7.22	0.19	2.60	0.38
Al_2O_3	3.19	0.07	0.22	4.54	0.30	3.29	0.32	4.48	0.28	7.72	0.44	3.95	0.34
FeO	12.87*	0.04	0.12	9.54	0.28	9.60	0.27	10.1	0.32	12.7	0.40	9.84	0.51
MnO	0.31	0.00	0.01	0.34	0.00	0.29	0.00	0.24	0.00	0.25	0.01	0.33	0.01
MgO	14.30	0.06	0.13	15.0	0.43	14.9	0.38	13.2	0.25	9.71	0.60	13.9	0.49
CaO	17.95	0.03	0.10	16.9	0.60	20.2	0.59	20.9	0.43	20.6	0.73	18.8	0.60
Na_2O	0.44	0.01	0.03	0.94	0.03	0.68	0.02	0.87	0.02	1.24	0.04	0.87	0.03
Total	100.17	0.34	0.81	99.3	2.19	101.0	2.21	101.8	1.91	100.9	2.82	100.9	2.76

Notes 1) * Contains 2.92% of Fe_2O_3
      2) C_w and C_x represent the compositions by wet chemical analyses and X-ray microanalyses respectively.
      3) σ_1 represnets statistical errors. σ_2 represents errors arised from statistical variation, chemical difference in analysis point and positional discordancy between area bombarded by electron and that of pyroxene-grain. σ_1 and σ_2 are calculated in weight percent.
      4) K_2O was undetermined.

Sources of error are considered as follows:

a) Statistical error—Analyses were made under the accelerating voltage of 20KV and the sample current of $0.08\mu A$, and these conditions would yield a small enough statistical error for 20 seconds accumulation of quanta, but statistical error must be considered for the elements of low concentration such as Na, Al, Ti and Mn. Resultant statistical error σ_1 shown in Table III was obtained from the standard pyroxene by measuring ten times at the same spot of one crystal by calcu-

lating by the method of least squares.   As the amount of statistical error is 0.34%
and small enough in comparison with resultant analyzed error of 2–3%, it is con-
sidered that the statistical error does not constitute one of the main source of error.
b)   Compositional diversity between different analyzed grains—Analyses were
made ten times on each different setting of monochromator, that is (a) Fe, Ca, Mg,
(b) Mn, Si, Na and (c) Ti, Al.   Errors arising from the chemical diversity between
different analyzed grains or analyzed points are shown in Table III as σ_2 for each
oxide.   Each σ_2 was obtained from ten different grains or ten different points by
the method of least squares.   As σ_2 contains, moreover, errors arising from dis-
cordance of positions between striking electron beam and pyroxene to be analyzed
as discussed in the following (in c), it has a large value of about 2–3% and it is con-
sidered to be a main source of error: However, even if the error σ_2 is attributed
mainly to the diversity of the chemical composition between each analyzed grain,
it is important that the errors due to the diversity do not exceed 3%.
c)   Positional discordancy between bombared part and pyroxene grain to be
analyzed may bring large errors—For the analysis of pyroxenes, X-ray scanning
pictures were taken for each element as mentioned previously.   However, the size
of each pyroxene grain is small, and is generally several microns or less, so that
the incident beam is apt to strike partially on other minerals at the same time.*
d)   X-ray source size—Accelerated electrons penetrate into specimen surface.
The higher the electron energy is, the deeper electron penetrates into specimen, and
deeper penetration means a larger X-ray source size.   The approximate value of
the depth of analyzed region Zm was expressed by Castaing (7) as follows:

$$Zm = 0.033\,(V^{1.7} - Vk^{1.7})\frac{A}{\rho Z} \text{ microns,}$$

where V and Vk are respectively accelerating voltage and excitation voltage ex-
pressed in kilovolts; A is the mean atomic weight of the bombarded point, Z is its
mean atomic number, and ρ the local density in grams per cubic centimeter.
Then, the diameter of the actual analyzed region is expressed as $\delta = d + Zm$, where
d is the beam size of the incident electron.   In this study accelerating voltage of
20KV yields Zm of 2.5 μ to 3.2 μ for FeKα to NaKα, therefore δ amounts to
about 3 μ.   Of course, the effective X-ray source size may be smaller than δ
due to absorption effect, X-ray source size may cause errors in case of analyzing
pyroxenes smaller than 3 μ in grain size.
e)   Chemical analyses of the standard sample—The standard pyroxene includes

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* The pyroxenes of the basalts (♯41′) are very fine grained ($\leqq 1\mu$) compared with other specimens
   and, moreover, coexist intimately with ilmenite, judging from their microscopical observation.
   Therefore, ♯41′ basalt is considered to show the largest σ_2(2.82).

some impurities of hypersthene and gives the gravimetric chemical analysis error of 0.45% as shown in Table I (the standard specimen). Hence, microprobe analyses give fundamentally at least 0.45% of error.

f) Other sources of error—Many other sources of error are considered such as damage of carbon layer, contamination, finite resolving power of the detector or associated electronics etc., but they are considered to be trivial in this study in comparison with the error sources discussed above, and do not affect seriously the accuracy of microprobe analyses.

In conclusion, it can be said that chemical diversity in analyzed grains, positional discordancy between bombarded part and pyroxene grain to be analyzed and X-ray source size cause most of the analytical errors. The total possible errors amount to about 2–3% in maximum. Hence, since the statistical error is 0.34%, if an ideal analysis is made by avoiding these sources of error, resultant error of microprobe analysis will be lowered to less than 0.34%, i.e. statistical error under the measuring conditions adopted in this study.

Acknowledgements

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