CALCULATING PROCEDURE OF END-MEMBERS OF CLINOPYROXENE*, COMPUTER PROGRAM AND ESTIMATION OF FERRIC AND FERROUS IN EPMA ANALYSES

KO IKEDA

Department of Mining and Mineral Engineering, Yamaguchi University, Ube, Japan.

End-members of clinopyroxene have been calculated to satisfy stoichiometry on the basis of experimental results previously reported. Some calculations of the quadrilateral plots and ferric and ferrous estimation are demonstrated for published analyses.

INTRODUCTION

Several methods for the calculation of end-members for clinopyroxene have been developed by many authors (Yagi, 1953, Kushiro, 1962, Yoder and Tilley, 1962 p. 366-7, and Kushiro and Kuno, 1963). But little has been discussed on Cr-bearing clinopyroxenes, although the role of chromium is very important especially in clinopyroxenes from ultrabasic and basic rocks. In view of structures clinopyroxene is expressed as $X Y Z_2 O_6$, where X cations are in 8-fold coordination sites, M_2 , Y are those in 6-fold coordination sites, M_1 and Z are those in 4-fold coordination sites, T. It has been generally considered that cations in M_2 and M_1 are disordered in their distribution. However, little study has been made on this problem, owing to experimental difficulty, with the exception of detecting Fe^{2+} ions by Moessbauer spectroscopy. Nevertheless disorder between M_2 and M_1 would be not so great (Bancroft et al., 1967). In contrast, determination of cation distributions between T and M_1 has been

recently achieved, especially by means of the Moessbauer spectroscopy. By this method Ohashi and Hariya (1970) reported that clinopyroxene $CaFeAlSiO_6$ has disorder of Al^{3+} ions and Fe^{3+} ions between T and M_1 . The same conclusion was reached by Ikeda (1972) using the wavelength shift of $Al-K\alpha$ fluorescent X-ray radiation. Temperature dependence of the occupation of Fe^{3+} ions in both tetrahedral and octahedral sites was not studied, but it is known that Fe^{3+} ions are more concentrated in octahedral sites at high pressure in clinopyroxene $CaFeAlSiO_6$ and $(95)CaMgSi_2O_6(5)CaFeAlSiO_6$ (Ohashi and Hariya, 1973). On the other hand Dickey et al. (1971) studied phase equilibria of the join $CaMgSi_2O_6$ - $CaCrAlSiO_6$ and found the formation of diopside solid solutions with up to 15 wt percent of $CaCrAlSiO_6$. Crystal-field spectra suggesting order-disorder transformation of Al^{3+} -ions and Cr^{3+} ions between T and M_1 have been partly demonstrated by Ikeda (1976). Recent study shows that Cr^{3+} ions in tetrahedral sites begin to move to

* In this paper clinopyroxenes have more CaO than Al_2O_3 in molecular proportions.
(Manuscript received January, 1979)

octahedral sites abruptly, when specimens reach the temperature at 1150°C by raising the temperature. This order-disorder relation also will probably occur between Cr^{3+} ions and Fe^{3+} ions in CaCrFeSiO_6 molecule (Ikeda, unpublished data). In this paper the author will study the more reasonable algebraical arrangement of end-members of clinopyroxene on the basis of phase equilibria and spectroscopy previously reported, will present a computer program for the calculation of end-members from chemical analyses and will attempt the separation of ferric and ferrous in EPMA analyses of clinopyroxene as an application of the computer program.

TRI-VALENT CATION DISTRIBUTIONS BETWEEN TETRAHEDRAL SITE AND OCTAHEDRAL SITE

Clinopyroxenes generally contain Al^{3+} , Fe^{3+} and Cr^{3+} as trivalent ions forming Tschermak's molecules, although chromium is restricted to clinopyroxenes from ultrabasic and basic rocks. Incorporation of Al^{3+} ions in the tetrahedral site has been regarded as Al-Tschermak's molecule CaAlAlSiO_6 and its solubility in diopside was studied by many authors (Clark et al., 1962, Neufville and Schairer, 1962, Hijikata and Yagi, 1967, Schairer and Yoder, 1970). Huckenholz et al. (1968) investigated the join $\text{CaMgSi}_2\text{O}_6$ - CaFeFeSiO_6 and confirmed the solubility of up to 33 wt percent Fe-Tschermak's molecule CaFeFeSiO_6 in diopside. It has been generally postulated that Cr^{3+} ions take 6-fold coordination, judging from their larger ionic radii (0.615 Å). However, the classic concept of ionic radii has several deficiencies as pointed out by Shannon and Prewitt (1969) and the most important matter is the spin state of

electrons for transitional elements. The numeral of 0.615 Å is the radius of Cr^{3+} ions in the high spin state of octahedral configuration. Although theoretically Cr^{3+} ions in a low spin state are expected in tetrahedral configuration, this state was not observed until recently when a phase equilibrium investigation of the join $\text{CaMgSi}_2\text{O}_6$ - CaCrCrSiO_6 was achieved by Ikeda and Yagi (1977). In that study they found the solubility of Cr-Tschermak's molecule CaCrCrSiO_6 reaches 6.7 wt percent and, moreover, tetrahedral Cr^{3+} ions are in a low spin state, whereas octahedral Cr^{3+} ions are in a high spin state from the crystal-field spectra of the diopside solid solutions of this join. Measurement of magnetic susceptibilities also confirmed this result (Ikeda and Yagi, 1978). Ionic radii of low spin Cr^{3+} ions were determined as 0.47–0.53 Å, decreased as much as 14–24 percent from high spin Cr^{3+} ions by the result of spin transformation.

Incorporation of Cr^{3+} ions has been generally accepted in the form of CrAl-Tschermak's molecule CaCrAlSiO_6 as well as $\text{NaCrSi}_2\text{O}_6$ molecule in which Cr^{3+} ions always share 6-fold coordination sites on the basis of classic ionic radii. However, CaCrAlSiO_6 molecules in diopside have disorder between Cr^{3+} and Al^{3+} ions in the distribution between tetrahedral and octahedral site similar to the situation in CrFe-Tschermak's molecules CaCrFeSiO_6 as mentioned in the preceding section. Tetrahedral low spin Cr^{3+} ions favour a low temperature environment at constant pressure, thus no tetrahedral low spin Cr^{3+} ions have been found hitherto in naturally occurring diopsides, since natural Cr-diopsides probably form at high temperatures (Ikeda and Yagi, 1977). Accordingly, all of the Cr^{3+} ions of CaCrAlSiO_6

Fig. 1 Tetrahedral representation of the relationship between pure clinopyroxene and Tschermak's molecules.

in diopside solid solution would share 6-fold coordination sites, if the main formational condition is high temperature. However, the occupancy of Cr^{3+} ions may be variable depending on the temperature and pressure of formation as partly reported by Ikeda (1976). Among Tschermak's molecules shown in Fig. 1 only three kinds of molecule, CaAlAlSiO_6 , CaFeFeSiO_6 and CaCrCrSiO_6 may be unit Tschermak's molecules and the other kinds may be intermixtures of these three unit molecules. Therefore, these three kinds of molecule have been selected as representatives of many Tschermak's molecules.

END-MEMBERS OF CLINOPYROXENE

Trivalent ions, Cr^{3+} , Fe^{3+} and Al^{3+} ions form not only Tschermak's molecules but also Na-bearing molecules, $\text{NaCrSi}_2\text{O}_6$, $\text{NaFeSi}_2\text{O}_6$ and $\text{NaAlSi}_2\text{O}_6$ molecules dissolving in clinopyroxenes. In this paper following 13 end-members have been selected to characterize pyroxenes:

$\text{NaCrSi}_2\text{O}_6$ (KO) $\text{NaFeSi}_2\text{O}_6$ (AC)
 $\text{NaAlSi}_2\text{O}_6$ (JD) $\text{CaTiAl}_2\text{O}_6$ (TIPX)
 CaAlAlSiO_6 (ALTS) CaFeFeSiO_6 (FETS)
 CaCrCrSiO_6 (CRTS) $\text{CaMnSi}_2\text{O}_6$ (JOHN)

$\text{CaFeSi}_2\text{O}_6$ (HD) $\text{CaMgSi}_2\text{O}_6$ (DI)
 $\text{MgMgSi}_2\text{O}_6$ (EN) $\text{CaCaSi}_2\text{O}_6$ (WO)
 $\text{FeFeSi}_2\text{O}_6$ (FS)

Minor components such as CoO , NiO and V_2O_5 etc. are ignored here. $\text{H}_2\text{O}+$ is also omitted due to the lack of precise knowledge of its role, but this is probably due to the presence of amphibole phase in lattice order. Since the character of K, whose ionic radius may be too large for the clinopyroxene structure, is not clearly known (Boyd, 1969, p. 57), and since K_2O generally is minor in clinopyroxenes, it is also neglected here. The position of Ti^{4+} has been argued by several authors (Barth, 1931, Yagi and Onuma, 1967, etc.). In present study the molecule $\text{CaTiAl}_2\text{O}_6$ was conventionally adopted instead of the molecule $\text{CaMgTi}_2\text{O}_6$. Since it is hardly possible at present to know the precise amount of Al^{3+} , Fe^{3+} and Cr^{3+} ions sharing both tetrahedral and octahedral sites, $\text{NaCrSi}_2\text{O}_6$ molecule is calculated first in the present method. Kushiro's method (1962) for the order of calculation for the molecules of $\text{NaFeSi}_2\text{O}_6$ and $\text{NaAlSi}_2\text{O}_6$ was followed. After oxide components were recalculated to molecular proportions, end-members are calculated in the following procedure:

Cr_2O_3 is allotted to $(1/2) \text{Na}_2\text{O} \cdot \text{Cr}_2\text{O}_3 \cdot 4\text{SiO}_2$ with Na_2O and SiO_2 . If Na_2O is not sufficient, remaining Cr_2O_3 is allotted to $\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot \text{SiO}_2$ with CaO and SiO_2 .

Fe_2O_3 is allotted to $(1/2) \text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$. If Na_2O is deficient, remaining Fe_2O_3 is allotted to $\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{SiO}_2$ with CaO and SiO_2 .

Al_2O_3 is allotted to $(1/2) \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$. If Na_2O is deficient, remaining Al_2O_3 is allotted to $\text{CaO} \cdot \text{TiO}_2 \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$.

TiO_2 is allotted to $\text{CaO} \cdot \text{TiO}_2 \cdot \text{Al}_2\text{O}_3$ with

CaO and Al_2O_3 .

MnO is allotted to CaO.MnO.2SiO_2 with CaO and SiO_2 .

FeO is allotted to CaO.FeO.2SiO_2 with CaO and SiO_2 . If FeO remains, FeO.FeO.2SiO_2 is calculated. (In the case of FeO.FeO.2SiO_2 , CaO. MgO.2SiO_2 should not be calculated.)

CaO remaining is allotted to CaO.MgO.2SiO_2 with MgO and SiO_2 . If CaO remains, CaO.CaO.2SiO_2 is calculated. (In this case FeO.FeO.2SiO_2 should not be calculated. The case of CaO. CaO.2SiO_2 is rare except for clinopyroxenes from peralkaline rocks.)

MgO remaining is finally used to form MgO.MgO.2SiO_2 with remaining SiO_2 .

Residual SiO_2 is finally calculated.

Though this procedure can be done by hand as illustrated in Table 1, the process was put

into a computer program to apply this method to EPMA analyses. The present method is applied only to clinopyroxenes having more CaO than Al_2O_3 in molecular proportion. Caution should be paid on this point and readers must check the residual amount of each oxide component after computation. If residues are not zero except for SiO_2 , especially on Al_2O_3 , another procedure should be used.

RESIDUAL SiO_2

Excess or deficiency of SiO_2 after the above calculation is called *residual SiO_2* with plus or minus sign for each calculation and the ratio of residual SiO_2 versus original SiO_2 as expressed in percentage affords the measure of correctness of the end-members used in this study. Though the precise amount of cations, Al^{3+} , Fe^{3+}

Table 1. Calculating procedure of end-members for clinopyroxene.

IK-1 CR-DIOPSIDE IN WEHLITE FROM RED HILLS NEW ZEALAND (WET)

COMPO- SITION	WEIGHT PERCENT	MOLE PROP.	KO	AC	JD	TIPX	ALTS	FETS	CRTS	JOHN	HD	DI	EN	WO	FS	RESIDUAL SiO ₂ %		
SiO ₂	52.33	871	16 855				26 829	10 819	2 817	4 813	70 743	632 111	88 423			+2.64		
TiO ₂	0.34	4				4 0												
Al ₂ O ₃	3.03	30				4 26	26 0											
Fe ₂ O ₃	1.58	10						10 0										
Cr ₂ O ₃	0.90	6	4 2						2 0									
FeO	2.49	35									35 0							
MnO	0.15	2								2 0								
NiO	0.05	1																
MgO	16.30	404										316 88	88 0					
CaO	22.15	395				4 391	26 365	10 355	2 353	2 351	35 316	316 0						
Na ₂ O	0.26	4	4 0															
K ₂ O	0.02	-																
H ₂ O+	0.43	24																
H ₂ O-	0.03	2																
TOTAL	100.06	1788	8	-	-	4	26	10	2	2	35	316	44	-	-	447		
			1.79	-	-	0.89	5.82	2.24	0.45	0.45	7.83	70.69	9.84	-	-	100.00		
AC + KO			JD + TIPX + ALTS				DI		HD	EN	TOTAL		DI		HD	WO	TOTAL	
1.79			6.71				80.00		8.86	11.14	100.00							

and Cr^{3+} ions between tetrahedral site and octahedral site is rarely determinable for very complex clinopyroxene solid solutions at present, if the end-members are properly chosen and there are no analytical errors, the residual SiO_2 percent will be expected to become zero, when analyzed specimens are fresh and pure, neglecting the effect of minor components omitted here. Distribution of the values of residual SiO_2 percent obtained from 59 specimens of clinopyroxene from intrusives and nodules cited is given in Fig. 2. When specimens have anomalously high content of H_2O , the deviation of residual SiO_2 becomes very great and is located in the negative area far from zero. However, the values of residual SiO_2 percent deviate around zero and as a consequence it is confirmed that the values come toward zero statistically as previously expected. The deviation will be ± 3 percent for good analyses. I expect that the same conclusion will be reached for clinopyroxenes of different origins.

Fig. 2 Distribution of the frequency of residual SiO_2 percent calculated on 59 specimens of clinopyroxene from intrusives and nodules including megacrysts cited.

GEOMETRY OF QUADRILATERAL DIAGRAM

In order to plot the ratio of quadrilateral end-members, DI, HD, EN and FS, one generally first calculates the amount of triangular end-members, WO, EN and FS. However, this convention is inconvenient for the present method, because one cannot directly find the location of specimens in the quadrilateral. This time the author has developed a method of direct plotting on the quadrilateral diagram to divide the quadrilateral into two triangular parts, DI-HD-EN and FS-EN-HD, or EN-DI-FS and HD-FS-DI. Whichever way one may choose, the same location in the quadrilateral is obtained (Fig. 3). The diagonal HD-EN or DI-FS is not a meaningful boundary, but is only placed for the convenience of plotting. The former set of triangles may be more convenient than the latter for mineralogical and petrological purpose. Then, the former set has been adopted in this study. For clinopyroxenes from peralkaline rocks the extra triangle of

Fig. 3 Figures illustrating triangular method of quadrilateral plotting. An example is shown for the clinopyroxene of IK-1.

WO-DI-HD is additionally required, because some incorporation of $\text{CaCaSi}_2\text{O}_6$ molecules is often noticed after end-member calculation, for instance Tyler and King (1967).

DIAGRAM FOR AC-MOLECULE VERSUS Al-BEARING MOLECULES; Na-Al END-MEMBER DIAGRAM

Quadrilateral plots only cover the relationship among five end-members (including $\text{CaCaSi}_2\text{O}_6$ molecule) out of 13. It is, then, necessary to express the relationship among the rest of 8 end-members to grasp the compositional characters of specimens. For this purpose AC-(JD+TIPX+ALTS) diagram, named Na-Al end-member diagram, has been devised in this study. Since the trend between $\text{NaFeSi}_2\text{O}_6$ molecule and quadrilateral end-members is well-known, one can express the systematic relationship among 4 mole-

cules out of 8 as a function of $\text{NaFeSi}_2\text{O}_6$ molecule. They are $\text{NaFeSi}_2\text{O}_6$, $\text{NaAlSi}_2\text{O}_6$, $\text{CaTiAl}_2\text{O}_6$ and CaAlAlSiO_6 containing either Na or Al, or both. The remaining molecules, NaCrSiO_6 , CaFeFeSiO_6 , CaCrCrSiO_6 and $\text{CaMnSi}_2\text{O}_6$ cannot be shown in this diagram and have been disregarded, because they are of minor importance in amount generally. Total amount of $\text{NaAlSi}_2\text{O}_6$, $\text{CaTiAl}_2\text{O}_6$ and CaAlAlSiO_6 is taken in abscissa and the amount of $\text{NaFeSi}_2\text{O}_6$ in ordinate (Fig. 4). In this diagram compositions of clinopyroxenes from intrusives and nodules, including megacrysts, are plotted. The horizontal bars indicate the amount of $\text{NaAlSi}_2\text{O}_6$ molecule. Clinopyroxenes from intrusives (closed circles) have little acmite molecules, whereas those from nodules (open circles) have generally considerable amount of acmite molecules with higher content of Al-bearing molecules. Megacrysts have anomalously high content

Fig. 4 Na-Al end-member diagram.

Table 2. Computer program for the calculation of end-members of clinopyroxene.

C CALCULATION OF END-MEMBERS FOR CLINOPYROXENES		CARD BLOCK I (EPMA)	
DIMENSION P(15),Q(17),R(15),S(17),T(17),U(17),V(5),	1		
W(14),A(17,17),	2		
1C(20)	3		
C READING DATA	4	C KO	87
READ(5,100)(P(1),I=2,15)	5	IF(A(6,3)-A(12,3))1,1,2	88
100 FORMAT(14(A4,1X))	6	1 A(12,4)=A(12,3)-A(6,3)	89
READ(5,101)(Q(J),J=1,17)	7	A(6,4)=A(6,3)-A(6,3)	90
101 FORMAT(17A4)	8	A(2,4)=A(2,3)-4.0*A(6,3)	91
999 READ(5,102)(C(J),J=1,20)	9	A(16,4)=ABS((A(2,3)-A(2,4)))/2.0	92
102 FORMAT(20A4)	10	GO TO 10	93
READ(5,103)(R(I),I=2,15)	11	2 A(12,4)=A(12,3)-A(12,3)	94
103 FORMAT(14F5.2)	12	A(6,4)=A(6,3)-A(12,3)	95
C CHECKING DATA	13	A(2,4)=A(2,3)-4.0*A(12,3)	96
R(16)=R(2)+R(3)+R(4)+R(5)+R(6)+R(7)+R(8)+R(9)+R(10)	14	A(16,4)=ABS((A(2,3)-A(2,4)))/2.0	97
+R(11)+R(12)+R(13)+R(14)+R(15)	15	GO TO 13	98
IF(R(16)-200.0)333,666,666	16	C AC	99
333 DO 500 I=1,17	17	10 IF(A(5,3)-A(12,4))3,3,4	100
A(I,J)=0.0	18	3 A(12,5)=A(12,4)-A(5,3)	101
DO 600 J=1,17	19	A(5,5)=A(5,3)-A(5,3)	102
A(I,J)=0.0	20	A(2,5)=A(2,4)-4.0*A(5,3)	103
600 CONTINUE	21	A(16,5)=ABS((A(2,4)-A(2,5)))/2.0	104
500 CONTINUE	22	GO TO 11	105
C TRANSFORMATION OF DIMENSIONS	23	4 A(12,5)=A(12,4)-A(12,4)	106
A(16,2)=R(16)	24	A(5,5)=A(5,3)-A(12,4)	107
A(1,1)=Q(1)	25	A(2,5)=A(2,4)-4.0*A(12,4)	108
A(1,2)=Q(2)	26	A(16,5)=ABS((A(2,4)-A(2,5)))/2.0	109
A(1,3)=Q(3)	27	GO TO 12	110
A(1,4)=Q(4)	28	C JD	111
A(1,5)=Q(5)	29	11 A(12,6)=A(12,5)-A(12,5)	112
A(1,6)=Q(6)	30	A(4,6)=A(4,3)-A(12,5)	113
A(1,7)=Q(7)	31	A(2,6)=A(2,5)-4.0*A(12,5)	114
A(1,8)=Q(8)	32	A(16,6)=ABS((A(2,5)-A(2,6)))/2.0	115
A(1,9)=Q(9)	33	C TIPX	116
A(1,10)=Q(10)	34	A(11,7)=A(11,3)-A(3,3)	117
A(1,11)=Q(11)	35	A(3,7)=A(3,3)-A(3,3)	118
A(1,12)=Q(12)	36	A(4,7)=A(4,6)-A(3,3)	119
A(1,13)=Q(13)	37	A(16,7)=ABS(A(3,3))	120
A(1,14)=Q(14)	38	C ALTS	121
A(1,15)=Q(15)	39	A(11,8)=A(11,7)-A(4,7)	122
A(1,16)=Q(16)	40	A(4,8)=A(4,7)-A(4,7)	123
A(1,17)=Q(17)	41	A(2,8)=A(2,6)-A(4,7)	124
A(2,1)=P(2)	42	A(16,8)=ABS(A(2,6)-A(2,8))	125
A(3,1)=P(3)	43	C JOHN	126
A(4,1)=P(4)	44	A(11,11)=A(11,8)-A(8,3)	127
A(5,1)=P(5)	45	A(8,11)=A(8,3)-A(8,3)	128
A(6,1)=P(6)	46	A(2,11)=A(2,8)-2.0*A(8,3)	129
A(7,1)=P(7)	47	A(16,11)=ABS(A(8,3))	130
A(8,1)=P(8)	48	GO TO 16	131
A(9,1)=P(9)	49	C TIPX	132
A(10,1)=P(10)	50	12 A(11,7)=A(11,3)-A(3,3)	133
A(11,1)=P(11)	51	A(3,7)=A(3,3)-A(3,3)	134
A(12,1)=P(12)	52	A(4,7)=A(4,3)-A(3,3)	135
A(13,1)=P(13)	53	A(16,7)=ABS(A(3,3))	136
A(14,1)=P(14)	54	C ALTS	137
A(15,1)=P(15)	55	A(11,8)=A(11,7)-A(4,7)	138
A(2,2)=R(2)	56	A(4,8)=A(4,7)-A(4,7)	139
A(3,2)=R(3)	57	A(2,8)=A(2,5)-A(4,7)	140
A(4,2)=R(4)	58	A(16,8)=ABS(A(2,5)-A(2,8))	141
A(5,2)=R(5)	59	C FETS	142
A(6,2)=R(6)	60	A(11,9)=A(11,8)-A(5,5)	143
A(7,2)=R(7)	61	A(5,9)=A(5,5)-A(5,5)	144
A(8,2)=R(8)	62	A(2,9)=A(2,8)-A(5,5)	145
A(9,2)=R(9)	63	A(16,9)=ABS(A(2,8)-A(2,9))	146
A(10,2)=R(10)	64	C JOHN	147
A(11,2)=R(11)	65	A(11,11)=A(11,9)-A(8,3)	148
A(12,2)=R(12)	66	A(8,11)=A(8,3)-A(8,3)	149
A(13,2)=R(13)	67	A(2,11)=A(2,9)-2.0*A(8,3)	150
A(14,2)=R(14)	68	A(16,11)=ABS(A(8,3))	151
A(15,2)=R(15)	69	GO TO 16	152
C CALCULATION OF MOLECULAR PROPORTION	70	C TIPX	153
A(2,3)=A(2,2)/60.09*1000.0	71	13 A(11,7)=A(11,3)-A(3,3)	154
A(3,3)=A(3,2)/79.90*1000.0	72	A(3,7)=A(3,3)-A(3,3)	155
A(4,3)=A(4,2)/101.96*1000.0	73	A(4,7)=A(4,3)-A(3,3)	156
A(5,3)=A(5,2)/159.69*1000.0	74	A(16,7)=ABS(A(3,3))	157
A(6,3)=A(6,2)/151.99*1000.0	75	C ALTS	158
A(7,3)=A(7,2)/71.85*1000.0	76	A(11,8)=A(11,7)-A(4,7)	159
A(8,3)=A(8,2)/70.94*1000.0	77	A(4,8)=A(4,7)-A(4,7)	160
A(9,3)=A(9,2)/74.71*1000.0	78	A(2,8)=A(2,4)-A(4,7)	161
A(10,3)=A(10,2)/40.31*1000.0	79	A(16,8)=ABS(A(2,4)-A(2,8))	162
A(11,3)=A(11,2)/56.08*1000.0	80	C FETS	163
A(12,3)=A(12,2)/61.98*1000.0	81	A(11,9)=A(11,8)-A(5,3)	164
A(13,3)=A(13,2)/94.20*1000.0	82	A(5,9)=A(5,3)-A(5,3)	165
A(14,3)=A(14,2)/18.02*1000.0	83	A(2,9)=A(2,8)-A(5,3)	166
A(15,3)=A(15,2)/18.02*1000.0	84	A(16,9)=ABS(A(5,3))	167
A(16,3)=A(2,3)+A(3,3)+A(4,3)+A(5,3)+A(6,3)+A(7,3)	85	C CRTS	168
+A(8,3)+A(9,3)+A(10,3)+A(11,3)+A(12,3)+A(13,3)+A(14,3)+A(15,3)	86	A(11,10)=A(11,9)-A(6,4)	169
		A(6,10)=A(6,4)-A(6,4)	170
		A(2,10)=A(2,9)-A(6,4)	171
		A(16,10)=ABS(A(2,9)-A(2,10))	172
		C JOHN	173
		A(11,11)=A(11,10)-A(8,3)	174

F8.0)]	350	WRITE(6,210)(W(J),J=1,14)	357
WRITE(6,208)(U(J),J=4,17)	351	210 FORMAT(2(4X,F6.2),10X,4(F6.2,2X),4X,4(F6.2,2X),]	358
208 FORMAT(1H ,24Hbbbb-bbbbbbb-bbbbbbb-bb,2H *,]	352	4X,3(F6.2,2X),F6.2/	359
13F7.2,2H *,F8.2)	353	4(////)	360
WRITE(6,209)	354	GO TO 999	361
209 FORMAT(1H0,4X,128HAC+KObbbbbJD+TIPX+ALTSbbbbI]	355	666 STOP	362
bbbbbbHDbbbbbbENbbbb	356	END	
2bbTbTLbbbbbbDIbbbbbbHDbbbbbbWObbbbbTbTL]			
bbbbbbENbbbbbbFSbbbbbb			
3HDbbbbbbTbTLbb)			

of Al-bearing molecules. The presence and absence of jadeite molecule are clearly seen and this diagram can be applied to any other clinopyroxenes from different origins and may serve as a new clinopyroxene classification.

COMPUTER PROGRAM CALCULATING END-MEMBERS PRESENT

Although end-member calculations can be done by hand, a computer program has been developed for ease of calculation (Table 2). This program is more convenient, when EPMA analyses are applied, because one will be able to separate ferric and ferrous from the data of EPMA analyses which do not distinguish ferric and ferrous, i.e., repeated iterations by a computer will reach near zero amount of residual SiO_2 , and the best fit for ferric and ferrous will be obtained after this computer treatment.

Explanation of the program

This program is written in FORTRAN IV for the computer of FACOM 230-28 SYSTEM at Yamaguchi University and can be adapted to other computers with very minor alterations to control cards and READ and WRITE input-code numbers. The card sequence is given in Fig. 5 for wet analytical data: data card I is for oxide components, data card II for end-members including residual SiO_2 percent, data card III for specimen comments and data card IV for chemical compositions. This program is written not in SUBROUTINE but in

CONTROL CARD	\$JEND	
DATA CARD IV]	50.0050,0050,0050.00 0.00,...	
(DUMMY)		
DATA CARD III]	FINAL DATA	
DATA CARD IV		
DATA CARD III		
DATA CARD IV		
DATA CARD III	52.33 0.34 3.03 1.58,.....	
DATA CARD IV (14F5.2)	IK-1 CR-DIOPSIDE RED HILLS..	
DATA CARD III (20A4)	COMPWPCMOLPKO AC JD TIPX.	
DATA CARD II (17A4)	SI02 TI02 AL23 FE23,.....	
DATA CARD I (14(A4,1X))	\$EXEC FTMAIN,RLTB	
CONTROL CARD		
OUT-PUT PROGRAM		
	C OUT-PUT STATEMENTS FOR,...	76
		74
IN-PUT PROGRAM		
	C CALCULATION OF END-MEMBER.	
CONTROL CARD	\$FORTS2 NOSOURCE	
CONTROL CARD	\$JOB IKEDA,ACCT='Y502050L',...	

Fig. 5 Card sequence of the computer program. An example is shown for 3 different analytical data computed in succession.

LOOP, so that a dummy card of specimen comments (data card III) and a dummy card of chemical compositions with total of not less than 200 percent (data card IV) are required to stop the loop of this program (see Fig. 5 and Table 2, line 16). The card I and card II are common to all data and they need not be inserted more than one time. If there are many data to be calculated, the calculation can be repeated

Table 5. An example of the separation of ferric and ferrous.

PIKE (1976) LHERZOLITE A CP-1 99.95							
MOLFEO	RSIO2	FEOWT	FE23WT				
1	4.81	0.07	5.89	38	0.54	2.73	2.93
2	4.69	0.14	5.81	39	0.42	2.80	2.85
3	4.58	0.22	5.73	40	0.31	2.87	2.77
4	4.46	0.29	5.65	41	0.19	2.95	2.69
5	4.35	0.36	5.57	42	0.08	3.02	2.61
6	4.23	0.43	5.49	43	-0.04	3.09	2.53
7	4.12	0.50	5.41	44	-0.15	3.16	2.45
8	4.00	0.57	5.33	45	-0.27	3.23	2.37
9	3.89	0.65	5.25	46	-0.38	3.31	2.29
10	3.77	0.72	5.17	47	-0.50	3.38	2.21
11	3.66	0.79	5.09	48	-0.62	3.45	2.13
12	3.54	0.86	5.01	49	-0.73	3.52	2.06
13	3.42	0.93	4.93	50	-0.85	3.59	1.98
14	3.31	1.01	4.85	51	-0.96	3.66	1.90
15	3.19	1.08	4.77	52	-1.08	3.74	1.82
16	3.08	1.15	4.69	53	-1.19	3.81	1.74
17	2.96	1.22	4.61	54	-1.31	3.88	1.66
18	2.85	1.29	4.53	55	-1.42	3.95	1.58
19	2.73	1.37	4.45	56	-1.54	4.02	1.50
20	2.62	1.44	4.37	57	-1.65	4.10	1.42
21	2.50	1.51	4.29	58	-1.77	4.17	1.34
22	2.39	1.58	4.21	59	-1.89	4.24	1.26
23	2.27	1.65	4.13	60	-2.00	4.31	1.18
24	2.15	1.72	4.05	61	-2.12	4.38	1.10
25	2.04	1.80	3.97	62	-2.23	4.45	1.02
26	1.92	1.87	3.89	63	-2.35	4.53	0.94
27	1.81	1.94	3.81	64	-2.46	4.60	0.86
28	1.69	2.01	3.73	65	-2.58	4.67	0.78
29	1.58	2.08	3.65	66	-2.69	4.74	0.70
30	1.46	2.16	3.57	67	-2.81	4.81	0.62
31	1.35	2.23	3.49	68	-2.92	4.89	0.54
32	1.23	2.30	3.41	69	-3.04	4.96	0.46
33	1.12	2.37	3.33	70	-3.16	5.03	0.38
34	1.00	2.44	3.25	71	-3.27	5.10	0.30
35	0.88	2.51	3.17	72	-3.39	5.17	0.22
36	0.77	2.59	3.09	73	-3.50	5.25	0.14
37	0.65	2.66	3.01	74	-3.62	5.32	0.06

MOLFEO Molecule numbers of FeO. ($\times 1000$)
 RSIO2 Residual SiO₂ percent.
 FEOWT Weight percent of FeO.
 FE23WT Weight percent of Fe₂O₃.

Table 6. Constituent end-members for the EPMA analysis corresponding to Table 5.

PIKE (1976) LHERZOLITE A CP-1															
COMP	WTPC	MOLP	* KO	AC	JD	TIPX	ALTS	FETS	CRTS	JOHN	HD	DI	EN	WO	FS
SI02	52.06	866.	*	862.	0.	0.	0.	840.	825.	812.	812.	726.	273.	-0.	0.
TI02	0.01	0.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
AL23	2.27	22.	*	0.	0.	22.	0.	0.	0.	0.	0.	0.	0.	0.	0.
FE23	2.53	16.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
CR23	2.08	14.	*	13.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
FEO	3.09	43.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
MNO	0.0	0.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
NIO	0.0	0.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
MGO	20.15	500.	*	0.	0.	0.	0.	0.	0.	0.	0.	274.	0.	0.	0.
CAO	17.95	320.	*	0.	0.	320.	298.	282.	269.	269.	226.	0.	0.	0.	0.
NA2O	0.06	1.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
K2O	0.0	0.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
H2O+	0.0	0.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
H2O-	0.0	0.	*	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
TOTL	100.20	1782.	*	2.	0.	0.	22.	16.	13.	0.	43.	226.	137.	0.	0.
-	-	-	*	0.42	0.0	0.0	0.03	4.83	3.45	2.77	0.0	9.37	49.31	29.82	0.0
AC+KO	0.42			55.72	10.59	33.69	100.00								
JD+TIPX+ALTS	4.85							84.03	15.97	0.0		100.00			
DI											0.0				
HD															
EN															
TOTL															
DI															
HD															
EN															
FS															
HD															
TOTL															

In this case quadrilateral plot is done in the triangle DI-HD-EN. Values of RESD except for SiO₂ are meaningless.

have relatively lower precision owing to long analytical time. However, high accuracy will be expected, if energy dispersive techniques are applied hereafter in X-ray analysis.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Prof. K. Yagi for his valuable criticism at the early stage of this work. Thanks are also due to Dr. J.E. Pike of U.S. Geological Survey for the permission of

Table 7. Out-put program block for idealized structural formula to 6 oxygens and an example of the result.

C OUT-PUT STATEMENT FOR THE CALCULATION OF IDEAL			
FORMULA TO 6 OXYGENS			
06	1	06	86
06	2	06	87
06	3	06	88
06	4	06	89
06	5	06	90
06	6	06	91
06	7	06	92
06	8	06	93
06	9	06	94
06	10	06	95
06	11	06	96
06	12	06	97
06	13	06	98
06	14	06	99
06	15	06	100
06	16	06	101
06	17	06	102
06	18	06	103
06	19	06	104
06	20	06	105
06	21	06	106
06	22	06	107
06	23	06	108
06	24	06	109
06	25	06	110
06	26	06	111
06	27	06	112
06	28	06	113
06	29	06	114
06	30	06	115
06	31	06	116
06	32	06	117
06	33	06	118
06	34	06	119
06	35	06	120
06	36	06	121
06	37	06	122
06	38	06	123
06	39	06	124
06	40	06	125
06	41	06	126
06	42	06	127
06	43	06	128
06	44	06	129
06	45	06	130
06	46	06	131
06	47	06	132
06	48	06	133
06	49	06	134
06	50	06	135
06	51	06	136
06	52	06	137
06	53	06	138
06	54	06	139
06	55	06	140
06	56	06	141
06	57	06	142
06	58	06	143
06	59	06	144
06	60	06	145
06	61	06	146
06	62	06	147
06	63	06	148
06	64	06	149
06	65	06	150
06	66	06	151
06	67	06	152
06	68	06	153
06	69	06	154
06	70	06	155
06	71	06	156
06	72	06	157
06	73	06	158
06	74	06	159
06	75	06	160
06	76	06	161
06	77	06	162
06	78	06	163
06	79	06	164
06	80	06	165
06	81	06	166
06	82	06	167
06	83	06	168
06	84	06	169
06	85	06	170

```

WRITE(6,206)FNA28,CA28,FMG28,FE28,OM2,CR36DS,] 06 167      8,1X,F5.3,1X,F5.3,1X///// 06 170
FE36DS,AL36DS,TI46,FM                                GO TO 999      06 171
7N26,FE26,FMG26,CA26,OM1,AL34DS,FE34DS,CR34DS,] 06 168      666 STOP      06 172
OTK,SI44,OTET,006                                END      06 173
206 FORMAT(1H,1X,4F6.3,1X,F5.3,1X,8F6.3,1X,]
F5.3,2X,3F6.3,1X,F5.3,F6.3      06 169

```

In this program alphabet "O" is used except in the cases of statement numbers and numerals "2.0" and "6.0".

1X-1 CR-DIOPSIDE IN WEHLITE FROM RED HILLS NEW ZEALAND (WET)

```

LOW TEMPERATURE FORMULA
(NA  CA  MG  FE2  )  (CR  FE3  AL  TI  MN  FE2  MG  CA  )  ((AL  FE3  CR  )  SI  )  0
0.019 0.883 0.098 0.0 1.000 0.023 0.022 0.057 0.010 0.005 0.078 0.807 0.0 1.000 0.076 0.022 0.004 0.102 1.898 2.000 6.000

HIGH TEMPERATURE FORMULA
(NA  CA  MG  FE2  )  (CR  FE3  AL  TI  MN  FE2  MG  CA  )  ((AL  FE3  CR  )  SI  )  0
0.019 0.883 0.098 0.0 1.000 0.026 0.044 0.031 0.010 0.005 0.078 0.807 0.0 1.000 0.102 0.0 0.0 0.102 1.898 2.000 6.000

```

using the EPMA data and for reading the paper in manuscript. A part of the cost of this study was financially aided by the Grant of Scientific Researches from the Ministry of Education of the Japanese Government.

APPENDIX I

Idealized structural formula to 6 oxygens can be obtained, using the in-pur program in Table 2 by attaching the program card block given in Table 7 instead of the out-pur program in Table 2. By this program low temperature formula is first calculated. However, in actual crystals of terrestrial origin Cr^{3+} ions are present in octahedral sites in high spin state because of high temperature of formation. Then, low temperature formula is finally rewritten into high temperature formula as to Cr^{3+} ions. Since temperature dependence of the occupancy of Fe^{3+} ions between tetrahedral site and octahedral site has not been clearly known hitherto, Fe^{3+} ions are regarded in the same way of Cr^{3+} ions in high temperature formula for convenience. This is the problem to be studied in future. A calculated example is shown in addition of the program and it may be more convenient to combine this program to the program in Table 2, if both end-member

data and idealized structural formula are required simultaneously. Though present computer program for the calculation of endmembers has been developed to clinopyroxenes having more CaO than Al_2O_3 in molecules, it will be applicable also to orthopyroxenes and Ca-poor Al-rich clinopyroxenes with minor change of the program.

APPENDIX II

Quadrilateral plotting sheet for present triangular method is added here for the convenient use of readers (Fig. 6). The same idea has been also argued by Banno (1968).

REFERENCES

- Bancroft, G.M., Maddock, A.G., and Burns, R.G. (1967) Applications of the Mössbauer effect to silicate mineralogy — I. Iron silicates of known crystal structure. *Geochim. Cosmochim. Acta*, **31**, 2219–2246.
- Banno, S. (1968) On the end-member composition of solid solutions. *Jour. Geol. Soc. Japan*, **74**, 521–528 (in Japanese).
- Barth, T.F.W. (1931) Pyroxen von Hiva Oa, Marquesas-Inseln, und die Formel titanhaltiger Augite. *Neues Jahrb. Mineral., Abt. A, Bd.* **64**, 217–224.
- Boyd, F.R. (1969) Electron-probe study of diopside inclusions from kimberlite. *Amer. Jour. Sci., Schairer Vol.*, **267-A**, 50–69.
- Clark, S.P., Jr., Schairer, J.F. and Neufville, J. de. (1962) Phase relations in the system $\text{CaMgSi}_2\text{O}_6\text{-CaAl}_2\text{SiO}_6\text{-SiO}_2$ at low and high pressure.

Fig. 6 Quadrilateral plotting sheet.

- Carnegie Inst. Wash. Yearbook*, **61**, 59–61.
- Dickey, J.S., Jr., Yoder, H.S., Jr., and Schairer, J.F. (1971) Chromium in silicate-oxide systems. *Carnegie Inst. Wash. Yearbook*, **70**, 118–122.
- Hijikata, K., and Yagi, K. (1967) Phase relation of Ca-Tschermak's molecule at high pressures and temperatures. *J. Fac. Sci. Hokkaido Univ. Ser. IV*, **13**, 407–417.
- Huckenholz, H.G., Schairer, J.F., and Yoder, H.S. Jr. (1968) Synthesis and stability of ferri-diospide. *Carnegie Inst. Wash. Yearbook*, **66**, 335–346.
- Ikeda, K. (1972) Study of coordination number of Al^{3+} by wavelength shift of Alka radiation in a clinopyroxene $CaFe^{3+}AlSiO_6$. *Memoir. Facult. Engineer. Yamaguchi Univ.*, **23**, 19–22.
- Ikeda, K. (1973) Chrome-rich clinopyroxene from Red Hills, New Zealand with special reference to the exsolution phenomena. *J. Japan. Assoc. Min. Petr. Econ. Geol.*, **68**, 125–131.
- Ikeda, K. (1976) Experimental study on the phase equilibria in the joins $CaMgSi_2O_6$ - $CaCrCrSiO_6$ and $CaCaSiO_4$ - $CaCrCrO_4$, with special reference to the role of Cr^{3+} ions. *D. Sc. dissertation presented to Hokkaido University*. pp. 124.
- Ikeda, K., and Yagi, K. (1977) Experimental study on the phase equilibria in the join $CaMgSi_2O_6$ - $CaCrCrSiO_6$ with special reference to the blue diopside. *Contrib. Mineral. Petrol.*, **61**, 91–106.
- Ikeda, K., and Yagi, K. (1978) Reply to H.D. Schreiber. *Contrib. Mineral. Petrol.*, **66**, 343–344.
- Kushiro, I. (1962) Clinopyroxene solid solutions. Part I. The $CaAl_2SiO_6$ component. *Japan. Jour. Geol. Geogr.*, **33**, 213–220.
- Kushiro, I., and Kuno, H. (1963) Origin of primary basalt magmas and classification of basaltic rocks. *Jour. Petrol.*, **4**, 75–89.
- Neufville, J. de., and Schairer J.F. (1962) The join Diopside-CaTschermak's molecule at atmospheric pressure. *Carnegie Inst. Wash. Yearbook*, **61**, 56–59.
- Ohashi, H., and Hariya, Y. (1970) Order-disorder of ferric iron and aluminum in Ca-rich clinopyroxene. *Proc. Japan Academy*, **46**, 684–687.
- Ohashi, H., and Hariya, Y. (1973) Order-disorder of ferric iron and aluminum in the system $CaMgSi_2O_6$ - $CaFeAlSiO_6$ at high pressure. *J. Japan. Assoc. Min. Petr. Econ. Geol.*, **68**, 230–233.
- Pike, J.E.N. (1976) Pressures and temperatures calculated from chromium-rich pyroxene compositions of megacrysts and peridotite xenoliths, Black Rock Summit, Nevada. *Amer. Mineral.*, **61**, 725–731.
- Schairer, J.F., and Yoder, H.S. Jr. (1970) Critical planes and flow sheet for portion of the system CaO - MgO - Al_2O_3 - SiO_2 having petrological applications. *Carnegie Inst. Wash. Yearbook*, **68**, 202–214.
- Shannon, R.D., and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. *Acta Cryst.*, **25**, 925–946.
- Tyler, R.C., and King, B.C. (1967) The pyroxenes of the alkaline igneous complexes of eastern Uganda. *Min. Mag.*, **36**, 5–21.
- Yagi, K. (1953) Petrochemical studies on the alkalic rocks of the Morotu district, Sakhalin. *Bull. Geol. Soc. Amer.*, **64**, 769–810.
- Yagi, K., and Onuma, K. (1967) Synthetic study on titan-augites. *Jour. Min. Soc. Japan*, **8**, 149–156.
- Yoder, H.S. Jr., and Tilley, C.E. (1962) Origin of basalt magmas: An experimental study of natural and synthetic rock systems. *Jour. Petrol.*, **3**, 342–532.

電子計算機による単斜輝石端成分の計算と第1鉄第2鉄分離に関する EPMA への応用

池 田 攻

石灰の量がアルミナよりも分子数において多い単斜輝石について、13の端成分を設定し電算機により計算処理した。本法の特徴はチェルマック分子群として $CaAl_2SiO_6$, $CaFeFeSiO_6$, $CaCrCrSiO_6$ の3者をチェルマック分子群の端成分として扱ったことにある。電算機プログラムの若干の改変により、本法の応用として EPMA 分析における Fe^{2+} と Fe^{3+} の分離が可能であり、また理想化学組成における構造式も算出することができる。