

The Recalculation of Pyroxene End-Member Parameters and the Estimation of Ferrous and Ferric Iron Content from Electron Microprobe Analyses

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Abstract

Calculation schemes of end-member proportions of pyroxenes presented previously have required the knowledge of Fe_2O_3 content. Most mineral analyses currently being presented are electron microprobe analyses, in which ferrous and ferric iron content are not determined separately.

An alternative scheme is suggested here which minimizes the significance of Fe_2O_3 contents and allows for a more rigorous comparison of end-member concentrations, especially between minerals where Fe_2O_3 content is determined and those where it is not available.

Examination of 344 clinopyroxene analyses with Fe_2O_3 content quoted suggests that for certain parageneses the sum of cations based on 6 oxygens approaches the ideal value of 4.00. However, for sub-calcic and jadeitic pyroxenes, deviations from ideality become significant. Hence, calculation of ferric and ferrous iron proportions, on the assumption that the sum of cations equals 4.00, is not valid for these particular pyroxenes.

Introduction

The composition of clinopyroxenes has been used extensively in estimating physical conditions of crystallization of magmas and metamorphic rocks. For these predictions various pyroxene end-member parameters, most notably jadeite and Ca-tschermak's molecule, have been used.

For the most effective use, a recalculation scheme should be applicable to all types of clinopyroxenes, and the diagnostic parameters should be subject to the minimum uncertainties and errors possible. The order of recalculation of end-members is purely arbitrary. Different procedures will usually give different results, but none can be said to be incorrect relative to any other. Choice of method is therefore a matter of convenience, but preference should be given to those which make best use of available data.

Previous Pyroxene Recalculation Schemes

Calculation schemes for pyroxene end-members have been suggested by Banno (1959), Kushiro (1962), Yoder and Tilley (1962), White (1964), and Essene and Fyfe (1967). All these methods have their relative merits. However, all (except Essene and Fyfe, 1967) have a major disadvantage

in that acmite— $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ —is the first end-member to be calculated. With electron microprobe data Fe_2O_3 content is not determined. Hence, no estimate of acmite content is possible. Even with wet chemical analyses there is always the possibility that there has been secondary oxidation (or reduction) of the mineral and that the determined Fe_2O_3 content does not reflect the original oxidation state of the primary pyroxene.

The possible error from this unknown Fe_2O_3 content may be propagated throughout the calculation of all subsequent end-members. Hence, two similar pyroxenes, one with known Fe_2O_3 and one with unknown Fe_2O_3 content, may recalculate to give significantly different end-member proportions and their similarity may be obscured. For example, a pyroxene with 1.59 percent Fe_2O_3 , 0.62 percent Na_2O , and 1.02 percent Al_2O_3 would recalculate as containing acmite and Ca-tschermak's molecule with no jadeite. If the weight percent Fe_2O_3 was not known, but total iron concentration was given as FeO, the same mineral would recalculate with jadeite but neither acmite nor Ca-tschermak's molecule.

Essene and Fyfe (1967) re-examined the problem of calculating pyroxene end-members with specific reference to eclogites and glaucophane schist

facies minerals in which the jadeite component is of prime importance. They suggested the equation:

$$\text{jadeite} = \text{Al}^{\text{VI}} - \text{Al}^{\text{IV}}$$

(where $\text{Si} + \text{Al}^{\text{IV}} = 2$, based on 6 oxygens). This effectively calculates Ca-tschermak's molecule first; it being equivalent to the Al^{IV} content, which assumes that all Al^{IV} is combined within the formula $\text{CaAl}^{\text{VI}}\text{Al}^{\text{IV}}\text{SiO}_6$. Some clinopyroxenes contain insufficient total Al to make the tetrahedral occupancy equal to 2.0, and hence there is no Al^{VI} available to produce Ca-tschermak's molecule. This is an extreme case, but the possibility of Al^{VI} being less than Al^{IV} , thus making the value for jadeite negative in the above equation, is fairly common (e.g., the omphacite in Deer, Howie, and Zussman, 1962, Table 23, No. 11). The method of Essene and Fyfe (1967) ignores TiO_2 and K_2O content. While these components may be depleted in high pressure pyroxenes, this omission may not always be justified, especially as low-pressure titanaugites contain in excess of 4 percent TiO_2 . This calculation is therefore, at best, very restricted in its applicability.

Alternative Recalculation Scheme

The method presented here is somewhat similar to that of Kushiro (1962) except that jadeite is calculated before acmite, and the theoretical end-member $\text{CaFe}^{\text{3+}}\text{Al}^{\text{IV}}\text{SiO}_6$ is not calculated. The procedure is as follows:

(1) $\text{Na} (+\text{K})$ goes into jadeite ($\text{NaAl}^{\text{VI}}\text{Si}_2\text{O}_6$). If $\text{Na} + \text{K}$ is greater than Al, the excess alkali produces acmite. (This is fairly rare, and significant concentrations of acmite are rarely formed.)

(2) If $\text{Na} + \text{K}$ is greater than Al, then $\text{Fe}^{\text{3+}} (+\text{Cr})$, if unknown, is assumed to equal the excess of alkali over Al to satisfy the acmite formula ($\text{Na}(\text{K})$,

$\text{Fe}^{\text{3+}}(\text{Cr})$, Si_2O_6). If $\text{Fe}^{\text{3+}} + \text{Cr}$ is known and is insufficient to satisfy this formula, $\text{Fe}^{\text{2+}}$ to the required extent is incorporated. (This is an exceedingly rare occurrence.)

(3) If $\text{Fe}^{\text{3+}} + \text{Cr}$ is known and in excess of alkali in acmite, Ca-ferritschermak's molecule— $\text{Ca}(\text{Fe}^{\text{3+}}, \text{Cr})_2\text{SiO}_6$ —is produced. Segnit (1953) has argued that this analogue of Ca-tschermak's molecule with Al in both octahedral and tetrahedral lattice sites replaced by $\text{Fe}^{\text{3+}}$ is feasible. We have combined Cr with $\text{Fe}^{\text{3+}}$. Cr may be treated separately and a Ca-chromium-tschermak's molecule ($\text{CaCr}_2\text{SiO}_6$) calculated, if Cr contents are significant.

(4) Ca-Ti-tschermak's molecule ($\text{CaTiAl}_2\text{O}_6$) is produced from all available Ti. Ti shows a pronounced preference for octahedral rather than tetrahedral coordination, and so this end-member is calculated rather than a pyroxene of type $\text{'XY'Ti}_2\text{O}_6$.

(5) The amount of Al used in jadeite and Ca-Ti-tschermak's molecule is deducted from total Al content and this is calculated as Ca-tschermak's molecule. This may conceivably be negative, usually if acmite has been calculated and/or Ca-Ti-tschermak's molecule is large. However, the sum of all tschermak's molecules, i.e. those with less than 2 Si per unit formula, is never negative.

(6) Ca in Ca-tschermak's molecule, in Ca-ferritschermak's molecule, and in Ca-Ti-tschermak's molecule is deducted from total Ca and the remainder calculated as wollastonite.

(7) $\text{Mg} (+\text{Ni})$ is calculated as enstatite.

(8) $\text{Fe}^{\text{2+}} (+\text{Mn})$ —less an amount appropriate to satisfy the ferric iron content of acmite if this end-member is formed and if Fe_2O_3 is unknown or insufficient—is calculated as ferrosilite.

In this way (see worked example in Table 1) all 12 major oxides may be recalculated into pyroxene

TABLE 1. Worked Example of Pyroxene Recalculation Scheme

		Si	Al	Ti	$\text{Fe}^{\text{3+}}$	Cr	$\text{Fe}^{\text{2+}}$	Mn	Mg	Ni	Ca	Na	K	mole percent of end-members
		1.895	0.177	0.010	0.072	0.030	0.107	0.004	0.980	0.002	0.641	0.067	0.003	
					0.102		0.111		0.982			0.070		
Pyroxene end-members	Amount produced													
Jadeite	0.0700	1.755	0.107										0.000	7.1
Acmite	0.0000													0.0
Ca-ferritschermak	0.0510	1.704			0.000						0.590			5.2
Ca-Ti-tschermak	0.0100		0.087	0.000							0.580			1.0
Ca-tschermak	0.0435	1.6605	0.000								0.5365			4.4
Wollastonite	0.2683	1.124									0.000			27.1
Enstatite	0.4910	0.142							0.000					49.6
Ferrosilite	0.0555	0.031					0.000							5.6

Sample used is augite analysis from Deer, Howie and Zussman, 1962, Vol. 2, Table 17, No. 1, starting with cation proportions.

end-members, such that the effect of unknown Fe_2O_3 content is minimal. Increasing the oxidation ratio in any analysis in this recalculation scheme has the effect of increasing Ca-ferritschermak's molecule while decreasing ferrosilite. It has generally no effect on the jadeite or Ca-tschermak's molecule component. Furthermore, these latter two parameters are subject *only* to analytical error in Na_2O , TiO_2 and Al_2O_3 . Indeed, only these 3 oxides need be analyzed to obtain the ratio of jadeite to Ca-tschermak's molecule. In the scheme of Essene and Fyfe (1967), the Si content is required and, because it is often close to 2.0, the relative error in Al^{IV} ($= 2 - \text{Si}$) may be extremely large.

This scheme is used in a re-examination of clinopyroxenes from eclogites, granulite facies terrains, and garnet lherzolites, and a more definitive classification will be presented elsewhere (Cawthorn and Collerson, in preparation).

Oxidation Ratio of Clinopyroxenes

An attempt to calculate the ferrous: ferric iron ratios of pyroxenes was presented by Mysen and Heier (1972). They demonstrated that manipulation of the oxidation ratio for a particular analysis, such that the sum of the cations was equal to 4.000 (calculated to 6 oxygens), produced a ferrous: ferric iron ratio comparable to that of a clinopyroxene analyzed by classical methods.

In principle, this is an excellent technique for estimating oxidation ratios, provided that the only error in the analysis is in the unknown Fe_2O_3 content, and provided that the stoichiometry of the clinopyroxene is such that the sum of the cations equals 4.000. These requirements, however, are very reminiscent of the assumption that for a chemical analysis to be good, it must total 100.000 percent.

We have examined 344 clinopyroxene analyses from a wide range of environments in which the Fe_2O_3 content has been quoted. Screening for "good" analyses is a purely subjective process and has not been considered. The data are divided into five groups of analyses: (A) lunar pyroxenes, 54 analyses; (B) eclogitic pyroxenes, 91 analyses; (C) low-pressure igneous pyroxenes, 111 analyses; (D) high-pressure igneous pyroxenes, 37 analyses; (E) granulite facies pyroxenes, 51 analyses. The sources of all the analyses are given in the Appendix.

The cation proportions have been recalculated and the sum of the cations presented on histograms (Fig.

1). The range of cation sums is from 3.92 to 4.04, which is equivalent to 98–101 percent occupancy of the available octahedral and tetrahedral lattice sites. Groups A, C, D, and E have average cation sums close to 4.0, while for eclogitic pyroxenes, there is a much larger spread and the average is significantly less than 4.0.

In an attempt to discover the reason for this difference we have plotted oxide concentrations and end-member parameters against the sum of cations. Generally, little correlation was observed except for Al_2O_3 and Na_2O , which show a similar variation (that for Al_2O_3 being shown in Figure 2), and except for CaO. Figure 3 shows the cation concentration of Ca against the sum of cations. As Ca and Al

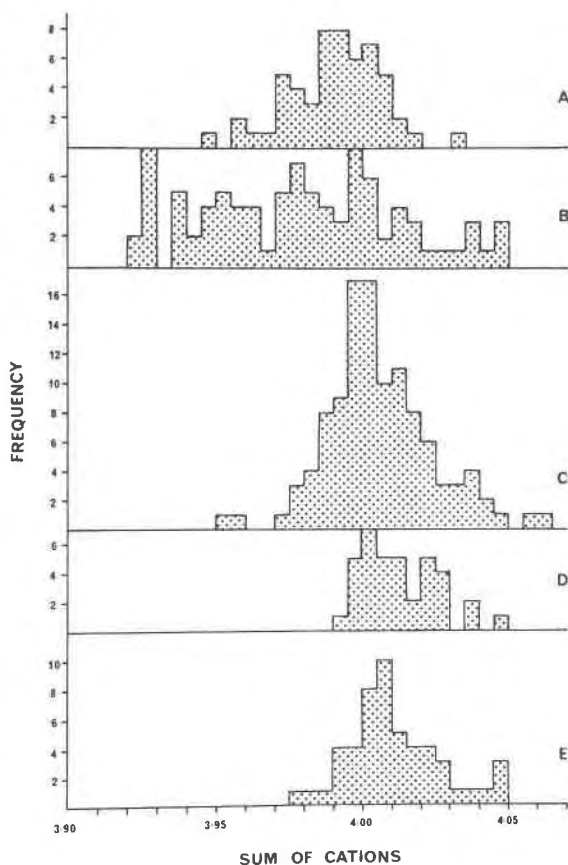


FIG. 1. Histogram of sum of cations of clinopyroxenes from the five different groups calculated to 6.00 oxygens. Class interval is 0.005 units. (A) lunar pyroxenes, average cation content = 3.9870, standard deviation = 0.0184; (B) eclogites (3.9747 ± 0.0336); (C) low-pressure igneous (4.0046 ± 0.0215); (D) high-pressure igneous (4.0082 ± 0.0155); (E) granulite facies (4.0096 ± 0.0233). Average cation content for all pyroxenes = 3.9953; for all pyroxenes with less than 20 percent jadeite (268 analyses) = 4.0028.

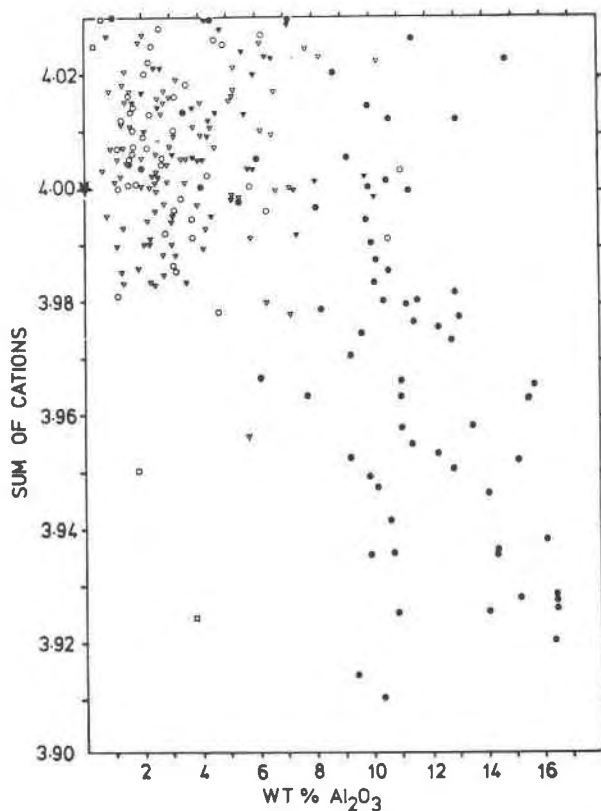


FIG. 2. Plot of Al_2O_3 (wt percent) against sum of cations of clinopyroxenes. All analyses except lunar pyroxenes are presented. Most lunar pyroxenes contain 2–3 percent Al_2O_3 , very few contain over 4 percent. Note increasing scatter of points at high Al_2O_3 contents. Legend: ●—eclogitic pyroxene; ○—granulite facies; ■—lunar; □—sub-calcic augites; ▲—high-pressure igneous; △—low-pressure igneous; ★—diopside (ideal formula).

show opposite trends with changing sum of cations, it appears that Ca-tschermak's molecule concentration does not correlate with the deviation from the ideal total cation concentration of 4.0. This is supported by the data for the high-pressure igneous pyroxenes which contain the largest proportion of Ca-tschermak's molecule, but have an average sum of cations very close to 4.0.

The two groups of clinopyroxenes which have lowest sum of cations are the eclogites and lunar pyroxenes, both of which are comparatively low in Ca. It appears that a decrease in the sum of cations below 4.0 may occur for clinopyroxenes with less than about 0.7 cations of Ca per unit formula (Fig. 3).

Comparison of the jadeite content with total cations (Fig. 4) suggests that at high jadeite con-

centrations significant variations from ideality occur. For analyses with less than 20 percent jadeite, average cation content appears to be about 4.0, whereas at higher jadeite contents, cation deficiencies become more pronounced.

The causes of deviations from ideality in the pyroxene structure are unknown. However, there are several possible explanations. Essene and Fyfe (1967) mention two pyroxene species which have site deficiencies, namely $\text{Al}_{1.33}\text{Si}_2\text{O}_6$ and $\text{Ca}_{0.5}\text{AlSi}_2\text{O}_6$, with 3.33 and 3.5 cations per unit formula. The presence of either of these theoretical end-members in the structure could explain the tendency for sub-calcic pyroxenes to show the deviations from ideality. The presence of the second species (Eskola's "pseudojadeite" molecule), because of its similarity to jadeite, could explain why jadeite-rich pyroxenes tend to be cation deficient. If 5 percent of this pseudojadeite species were present in an otherwise perfectly stoichiometric pyroxene, the cation content

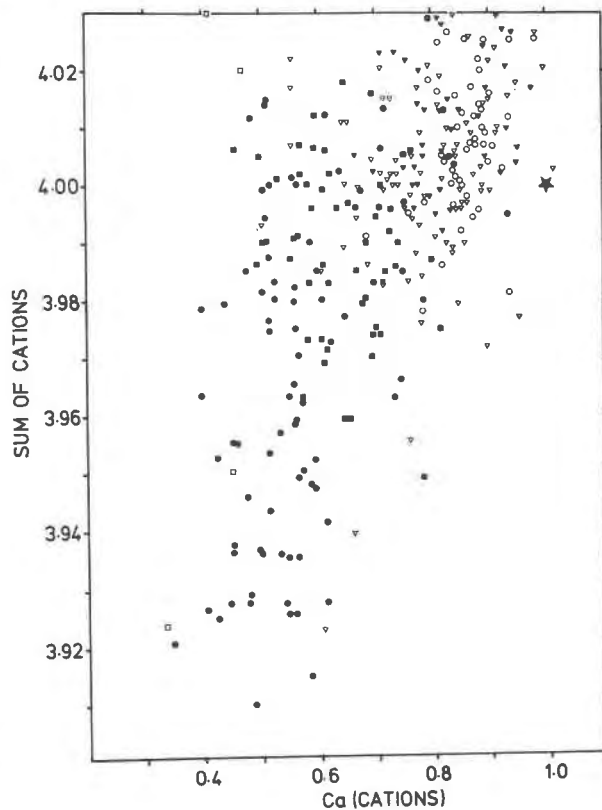


FIG. 3. Plot of Ca (cation proportion to 6 oxygens) against sum of cations of clinopyroxenes. All analyses are plotted. Note the tendency for cation deficiencies at low Ca content. Legend as for Figure 2.

per 6 oxygen anions would be 3.975—the observed value for eclogitic pyroxenes. Alternatively, solubility of kyanite— Al_2SiO_5 —in high pressure pyroxenes might explain the deficiency. Kyanite contains 3.6 cations per 6 oxygen anions. Sobolev, Kuznetsova, and Zyuzin (1968) and O'Hara and Yoder (1967) have argued that kyanite, or its chemical equivalent, may show limited solubility in the pyroxene structure.

The average cation content of groups A, C, D, and E and 15 low-jadeite eclogitic clinopyroxenes, *i.e.*, excluding eclogitic pyroxenes with high jadeite contents, is 4.0028 (for 268 analyses). We suggest, therefore, that for clinopyroxenes containing less than 20 percent jadeite or which are not subcalcic, the assumption that the sum of the cations is 4.00 may be justified.

The recalculation scheme of ferrous and ferric iron contents to produce a sum of cations equal to 4.00 is given by Mysen and Heier (1972) and Hamm and Vieten (1971). However, because of the scatter of points in Figure 1, we suggest this is not a precise method, but may be used to give only very approximate contents. A quick approximation for this calculation is that for each 0.01 desired increment in cation content, the Fe_2O_3 concentration must be decreased by 1 percent (for example: if the sum of cations = 3.970, Fe_2O_3 must be decreased by 3 percent to give a total of 4.000 cations; conversely a value of 4.03 requires an increase of 3 percent Fe_2O_3). The average sum of cations of eclogitic pyroxenes is 3.9747. To produce an analysis which recalculates to 4.00 cations requires the reduction of 2.5 percent Fe_2O_3 to FeO. In many cases this produces a negative Fe_2O_3 content in the analysis.

Summary

We do not wish to criticize the previous methods of recalculating pyroxene end-members. We merely wish to present an alternative scheme which we believe can handle the data currently becoming available in a more consistent manner. It is the deficiencies in the data (Fe_2O_3 content not being presented for electron microprobe analyses), not in the previous calculation techniques, which we are trying to overcome. Our technique allows the important end-members of pyroxenes (jadeite and Ca-tschermak's molecule) to be calculated in a way which is independent of oxidation ratio.

The calculation of ferrous and ferric iron contents,

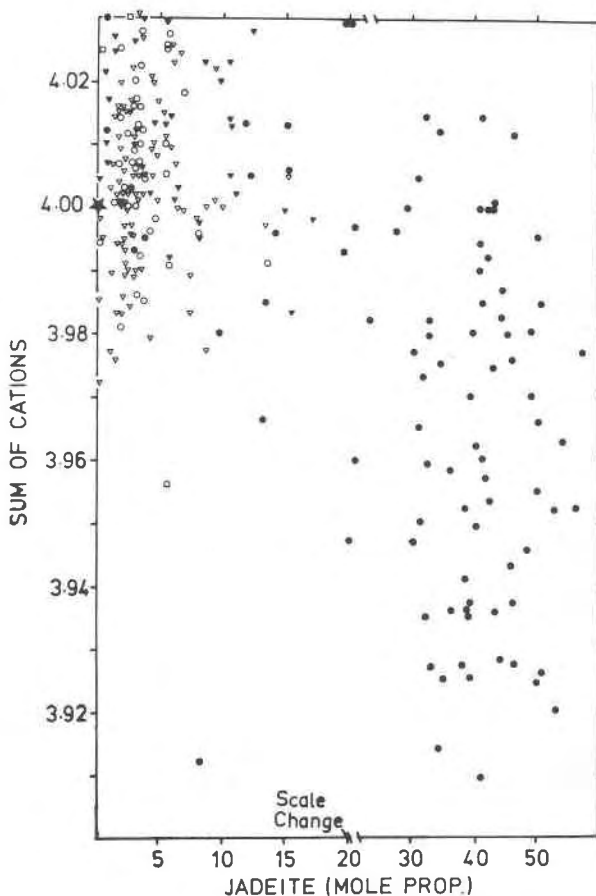


FIG. 4. Plot of molar jadeite content against sum of cations. Lunar analyses, being extremely low in Na_2O , are not plotted. The scale changes on abscissa at jadeite = 20 percent to half scale of low jadeite region of graph. Note the tendency for cation deficiencies at high (greater than 20%) jadeite content. Legend as for Figure 2.

by assuming perfect stoichiometry in the pyroxenes, may be of some value in the absence of an alternative method, but we wish to emphasize that it provides only a very rough approximation.

Appendix: Sources of Clinopyroxene Analyses

Low-Pressure Igneous Clinopyroxenes

Phenocrysts in lavas and in low-pressure intrusive bodies have been sampled. Pyroxenes from alkalic and tholeiitic suites, ranging from basic to highly evolved, are included. Analyses are from: Deer, Howie and Zussman (1962, *Rock-Forming Minerals*, v. 2); Wager and Brown (1967, *Layered Igneous Rocks*); Atkins (1969, *J. Petrol.*); Strong (1973, *J. Petrol.*).

High-Pressure Igneous Clinopyroxenes

Nodules in volcanic rocks, and high-pressure intrusive bodies are included. Analyses are from: Aoki and Kushiro (1968, *Contrib. Mineral. Petrol.*); Kutolin (1970, *Contrib. Mineral. Petrol.*); Ross *et al* (1954, *Am. Mineral.*); Dawson *et al* (1970, *J. Petrol.*); Green (1964, *J. Petrol.*); Conqu  r   (1971, *Contrib. Mineral. Petrol.*); Borisenko (1967, *Mineral. Mag.*).

Lunar Clinopyroxenes

It is assumed that these pyroxenes contain no ferric iron as they were erupted into the reducing atmosphere of the lunar surface. Data are from the *Proceedings of the Apollo II Lunar Science Conference*, Vol. 1. *Geochimica et Cosmochimica Acta, Supplement 1*, Vol. 34, 1970; and *Proceedings of the Second Lunar Science Conference, Supplement 2*, 1971; Brown *et al* (1970); Agrell *et al* (1970); Dense *et al* (1970); Keil *et al* (1970); Weill *et al* (1970); Kushiro *et al* (1970); Hollister *et al* (1970); Newton *et al* (1970); Brown *et al* (1971); Carter *et al* (1971); Reid *et al*, (1973, *Earth Planet. Sci. Lett.*); Boyd (1972, *Carnegie Inst. Year Book*); Gancarz *et al* (1972, *Earth Planet. Sci. Lett.*); Papike *et al* (1972, *Earth Planet. Sci. Lett.*).

Granulite Facies Clinopyroxenes

Analyses of pyroxenes from granulite facies terrains are taken from: Muir and Tilley (1958, *Mineral. Mag.*); Davidson (1968, *Contrib. Mineral. Petrol.*); Binns (1965, *Mineral. Magazine*); Sen and Rege (1966, *Mineral. Mag.*); Sriramadas *et al* (1969, *Proc. Indian Acad. Sci.*); Leelanandam (1967, *Mineral. Mag.*); Lovering and White (1969, *Contrib. Mineral. Petrol.*); Ray and Sen (1970, *Neues Jahrb. Mineral. Abh.*).

Eclogitic Clinopyroxenes

Pyroxenes from all the various types of eclogite parageneses, inclusions in glaucophane schist facies melanges, lenses in migmatite terrains and high-grade metamorphic terrains, and inclusions in basaltic lavas and kimberlites, have been included. Data are taken from: Banno (1967, *Neues Jahrb. Mineral. Monatsh.*); Matthes *et al* (1969, *Neues Jahrb. Mineral. Abh.*); Yoder and Tilley (1962, *J. Petrol.*);

O'Hara (1960, *Mineral. Mag.*); Alderman (1936, *Q. J. Geol. Soc.*); Pinus *et al* (1970, *Pac. Geol.*); Sobolev *et al* (1968, *J. Petrol.*); Bryhni *et al* (1969, *Norsk Geol. Tidsskr.*); Velde *et al* (1970, *Am. Mineral.*); Green and Mysen (1972, *Lithos*); Kozlowski (1958, *Bull. Acad. Pol. Sci.*); Coleman *et al* (1965, *Geol. Soc. Am. Bull.*); Deer, Howie and Zussman (1962, *Rock-Forming Minerals*, Vol. 2); Binns (1967, *J. Petrol.*); Morgan (1970, *J. Petrol.*); Lovering and White (1969, *Contrib. Mineral. Petrol.*); White (1972, *Contrib. Mineral. Petrol.*).

Acknowledgments

We are grateful to Dr. D. F. Strong and W. L. Griffin for criticism of the final manuscript. Computing costs on this study were defrayed by research grants A8694 and A7975 from the National Research Council of Canada.

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Manuscript received, March 4, 1974; accepted for publication, May 29, 1974.