Revision 2

WinPyrox: A Windows program for pyroxene calculation classification and thermobarometry†

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ABSTRACT

A Microsoft® Visual Basic program, called WinPyrox, has been developed to calculate structural formulae of both wet-chemical and microprobe-derived pyroxene analyses. Based on the standard International Mineralogical Association (IMA-88) nomenclature scheme, WinPyrox primarily calculates and classifies pyroxene groups and then determines a specific pyroxene name with its possible modifiers. It is developed to predict cation site-allocations at the different structural positions, including *T*, *M1*, and *M2* sites, as well as to estimate end-members, molar fractions, end-member activities, components and activities, and single-clinopyroxene and two-pyroxene thermobarometers. The program allows the user editing and loading Microsoft® Excel files to calculate electron-microprobe pyroxene analyses for different ferric iron estimation methods and normalization schemes. This software generates and stores all the calculated results in the output of Microsoft® Excel file, which can be displayed and processed by any other software for verification, general data manipulation, and graphing purposes. The compiled program code is distributed as a self-extracting setup file, including a help file, test data files and related graphic files, which are designed to produce a high-quality printout from the Golden Software's Grapher™ software. The self-extracting setup file, which is approximately 11 Mb, may be downloaded from http://code.google.com/p/winpyrox/ or can be obtained from author on request.

Keywords: International Mineralogical Association; pyroxene; classification; modifier; end-member; activity; thermobarometer; normalization; software

INTRODUCTION

Pyroxenes are important rock-forming ferromagnesian silicates in igneous and metamorphic rocks. Although previous studies on pyroxenes were focused on petrographic and petrogenetic aims, today there is a wide range of research providing thermometry, barometry, and fO_2

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conditions. The subcommittee on pyroxenes of the International Mineralogical Association (IMA) published a classification and nomenclature scheme of pyroxene group minerals via its Commission on New Minerals and Mineral Names (CNMMN) (Morimoto 1988). The proposed scheme is similar to that IMA's amphibole classification (e.g., Leake et al. 1997, 2004; Yavuz 1999, 2007). Despite its incomplete and imprecise form (e.g., Rock 1990), the current IMA-88 pyroxene classification scheme allows the derivation of a pyroxene formula from chemical analysis obtained from wet-chemical and electron-microprobe techniques.

Although several computer programs have been published for pyroxene calculation and classification in recent years, restricted attention was given to the estimation of end-members, which play an important role in thermodynamic and thermobarometric estimations. Petrakakis and Dietrich (1985) developed a FORTRAN-77 subroutine, called MINSORT, to calculate, sort, and create data files of microprobe analyses of silicate and oxide minerals. Using the MINSORT program, Dietrich and Petrakasis (1986) proposed a linear algebraic method for the sequence-independent calculation of eleven end-member components of pyroxene (i.e., Jd, Acm, Ur, TiTs, CaTs, FeTs, CrTs, Pm, Fs, En, and Wo; see Table 1) based on microprobe analyses. Lindsley (1986) criticized these eleven independent compositional variables and emphasized that in the absence of knowledge concerning the energetics of exchange reactions, there should be only nine parameters (i.e., Al^{IV}, Al^{VI}, Fe^{3+}, Cr, Ti, Fe^{2+}, Mn, Mg, and Ca). According to Lindsley (1986), a tenth independent parameter in pyroxene exists when tetrahedral Fe^{3+} is required by stoichiometry or Mössbauer analysis. McHone (1987) developed a simple APL program, called PXC, for calculating pyroxene structural formulae and end-members in the sequence proposed by Cawthorn and Collerson (1974), which is modified from Kushiro (1962). Gómez (1990)

presented a compiled program, named PX, for pyroxene calculation, classification, and end-member components based on the procedure given by Cawthorn and Collerson (1974). Rock (1990) introduced a FORTRAN-77 program for pyroxenes, called PXTAB, discussed some poorly described statements in the report, and drew our attention to the lack of defined compositional boundaries for certain rare pyroxene species, further problems related to adjectival modifiers, and some incomplete, inexact and often ambiguous rules in computerization of the IMA-88 nomenclature scheme. Yavuz (2001) developed a QUICKBASIC program, PYROX, providing the IMA-88 pyroxene calculation and classification together with Rock's (1990) suggestions for the Subcommittee on Pyroxenes. Sturm (2002) introduced a Microsoft® Excel spreadsheet which allows the user to calculate structural formulae of pyroxene analyses and to determine pyroxene names according to the IMA-88 pyroxene nomenclature scheme.

A Visual Basic program (i.e., WinPyrox) described in this paper is the revised and enhanced form of the earlier PYROX program (Yavuz 2001) for pyroxene analyses obtained both from wet-chemical and electron-microprobe techniques. WinPyrox is a compiled program that only runs on the Microsoft® Windows platform. The program recalculates multiple pyroxene chemical analyses into their structural formulae, partitions the recalculated anions into the *T*, *M1*, and *M2* sites, classifies and names pyroxene group minerals with modifiers based on the IMA-88 nomenclature scheme, allocates iron from microprobe-derived analysis to Fe^{2+} and Fe^{3+} based on different procedures , estimates end-member components and activities, calculates single-clinopyroxene thermometers and barometers, provides various two-pyroxene thermometers and geobarometers, and plots recalculated analyses on various binary and ternary pyroxene classification and thermobarometer diagrams by using the Golden Software's Grapher™

program. All the calculated pyroxene data can be displayed in a single window and stored in a Microsoft® Excel file (i.e., output.xlsx) for further data manipulation and graphing purposes. WinPyrox is a user-friendly software that allows users to calculate pyroxene analyses assuming different normalization schemes, such as structural formulae with or without a total of four cations and presents a better user interface and interaction with its enhanced functionality and visual effects.

CALCULATION AND CLASSIFICATION PROCEDURE OF PYROXENE

Pyroxene group minerals belong to the chain silicates with a general formula of $M2M1T_2O_6$. They are constructed of single chains of silicon tetrahedral (i.e., *T*) and two octahedral (i.e., *M2* and *M1*) sites. The procedure of ideal site allocation of cations at *T*, *M1*, and *M2* sites can be carried out by the following steps (see Morimoto et al. 1988):

1. Sum *T* to 2.00 using Si^{4+}, then Al^{3+}, then Fe^{3+}.

2. Sum *M1* to 1.00 using any excess Al^{3+} and Fe^{3+} from (1). If there is insufficient Al^{3+} and Fe^{3+} to sum to 1.00, then add Ti^{4+}, Cr^{3+}, V^{3+}, Zr^{4+}, Sc^{3+}, Zn^{2+}, (if exists Ni^{2+}, Co^{2+}), Mg^{2+}, Fe^{2+} and finally, Mn^{2+} until the sum is 1.00.

3. Sum *M2* to 1.00 using any excess Mg^{2+}, Fe^{2+}, Mn^{2+} from (2) and then add Li^{+}, Ca^{2+}, Na^{+}, and K^{+} (if exists). If the sum of *M2* is far from 1.00, then the analysis may be inaccurate.

Pyroxene group minerals are classified based on the occupancy of the *M2* site (Nesse 2004). However, as the allocation of cations in the *T*, *M1*, and *M2* sites is, in part, a function of

temperature, Morimoto et al. (1988) considered *M1* and *M2* sites as a single *M* site in order to avoid the difference between the real and ideal site occupancies. Twenty accepted and widely used pyroxene names by the IMA are listed in Table 1. The definition of pyroxene species in Table 1 is based on thirteen end-members or chemical components, including $Mg_2Si_2O_6$ (Enstatite (En)), $Fe^{2+}{}_2Si_2O_6$ (Ferrosilite (Fs)), $MnMgSi_2O_6$ (Konoite (Ka)), $CaMgSi_2O_6$ (Diopside (Di)), $CaFe^{2+}Si_2O_6$ (Hedenbergite (Hd)), $CaMnSi_2O_6$ (Johannsenite (Jhn)), $CaZnSi_2O_6$ (Petedunnite (Pe)), $CaFe^{3+}AlSiO_6$ (Esseneite (Es)), $NaAlSi_2O_6$ (Jadeite (Jd)), $NaFe^{3+}Si_2O_6$ (Aegirine (Aeg)), $NaCr^{3+}Si_2O_6$ (Kosmochlor (Kos)), $NaSc^{3+}Si_2O_6$ (Jervisite (Je)), and $LiAlSi_2O_6$ (Spodumene (Spd)).

There is a wide variety of solid solutions in the Mg-Fe group pyroxenes and in some of the Ca pyroxenes (e.g., diopside and hedenbergite). These two groups cover the most common rock-forming pyroxenes. For an exact classification, Morimoto et al. (1988) proposed the following characteristics to divide all the pyroxenes into four chemical groups (see Table 2) :

1. Describe the Mg-Fe pyroxenes and Ca pyroxenes as the “Ca-Mg-Fe” or “quadrilateral” pyroxenes.

2. The “Na” pyroxenes show continuous solid-solution with the “quadrilateral", resulting in the Na-Ca pyroxenes.

3. Owing to rare occurrence of some pyroxene minerals (e.g., donpeacorite and kanoite in the Mn-Mg pyroxene group; johannsenite, petedunnite, and esseneite in the Ca pyroxene group; and spodumene in the Li pyroxene group), they are all treated as the “other” pyroxenes.

The 20 mineral names recommended by IMA-88 thus can be divided into four chemical groups for the classification of pyroxenes, including “Ca-Mg-Fe” pyroxenes (i.e., “Quad” with eight names), “Ca-Na" pyroxenes (with two names), “Na" pyroxenes (with two names), and “other” pyroxenes (i.e., “Others”, with eight names). Pyroxene analyses obtained from both wet-chemical and electron-microprobe techniques are initially calculated based on six oxygens and then classified into four groups by using the *Q*-*J* diagram (see Fig. 1), where *Q* = Ca+ Mg+ Fe^{2+} (atoms per formula unit; *apfu*) and *J* = 2Na (*apfu*). The pyroxenes that plot in the “Quad” area of *Q*-*J* diagram are classified on the Wo-En-Fs ternary diagram (see Fig. 2) with normalized Ca-Mg-(Fe_{tot}+Mn) cations. The most common pyroxenes are those of the “Quad”, which is also called as the En ($Mg_2Si_2O_6$)-Fs ($Fe^{2+}{}_2Si_2O_6$)-Di ($CaMgSi_2O_6$)-Hd ($CaFe^{2+}Si_2O_6$) quadrilateral. The pyroxenes that belong to the “Quad” cover clino- and orthopyroxenes with monoclinic and orthorhombic symmetry, respectively. When compared to the clinopyroxenes, the orthopyroxenes are characterized by enstatite and ferrosilite compositional end-members, $(Mg,Fe)_2Si_2O_6$ solid solution series, and low wollastonite components (≤ 5%).

The classification of “Na” and “Ca-Na” pyroxenes are carried out on the Quad-Jd-Ac diagram (see Fig. 3) with the normalized *Q* (Wo+En+Fs), Jd ($NaAlSi_2O_6$), and Ae ($NaFe^{3+}Si_2O_6$) components. In the Quad-Jd-Ac diagram, the division between the “Quad” pyroxenes and the “Ca-Na” pyroxenes is defined at the *Q* = 80, whereas the discrimination between the “Ca-Na” pyroxenes and the “Na” pyroxenes are established at the *Q* = 20. Subdivisions between the “Ca-Na” pyroxenes, including omphacite and aegirine-augite, and “Na” pyroxenes, consisting of jadeite and aegirine, are obtained by applying the 50 % rule (see Fig. 3).

Natural pyroxenes called as the "Others" in the *Q*-*J* classification diagram consist virtually of johannsenite ($CaMnSi_2O_6$), petedunnite ($CaZnSi_2O_6$), and spodumene ($LiAlSi_2O_6$). No specific binary or ternary classification diagram was proposed by the IMA-88 for variety of other pyroxenes. However, Rock (1990) showed that some of Mn-bearing pyroxenes, including johannsenite, kanoite and its dimorph danpeacorite can be classified on the Ca-Mn-Mg ternary diagram. Several pyroxenes with an unusual chemical composition plot outside the area between the $Q+J = 2.0$ and $Q+J = 1.5$ lines in the *Q*-*J* classification diagram, because of some substitutions (e.g., $(R^{+})R^{2+}_{0.5}(R^{4+}_{0.5})2R^{4+}$, $R^{2+}(R^{3+})(R^{3+})R^{4+}$, and $R^{2+}R^{2+}_{0.5}(R^{4+}_{0.5})(R^{3+})R^{4+}$). These types of chemical constituents do not belong to the specific pyroxene groups proposed by Morimoto et al. (1988) and, thus can be divided into two groups, including Ca-rich pyroxenes (e.g., $CaR^{3+}AlSiO_6$ and $CaR^{2+}_{0.5}Ti^{4+}_{0.5}AlSiO_6$) and Na-rich pyroxenes (e.g., $NaR^{2+}_{0.5}Ti^{4+}_{0.5}Si2O_6$). According to Morimoto et al. (1988), these unusual pyroxenes can be classified with the accepted pyroxene names and adjectival modifiers (see Table 3).

The adjectival modifiers, in general, are used to describe the mineral with an uncommon amount of any chemical component. Although the prefix is an essential part of a mineral name, it is not considered in the current IMA-88 pyroxene classification scheme. The modifier generally defines a subsidiary substitution and is optional. All modifiers have an "-ian" or "-oan" ending. The suffix "-ian" is commonly used for the higher valence state (except for lithian) and the suffix of "-oan" is always applied for the lower valence state of element (Nickel and Mandarino 1987). In the current IMA-88 pyroxene nomenclature scheme, there are no rules for the Sc^{3+}-, V^{3+}- and Zr^{4+}-bearing pyroxenes. However, Rock (1990) defined the "scandian",

"vanadoan", and "zirconian" to cover pyroxenes with Sc^{3+}, V^{3+}, or Zr^{4+} > 0.01 *apfu*, respectively (see rows 17 to 19 in Table 3).

PYROXENE THERMOMETERS AND BAROMETERS

Thermometry and barometry, also called thermobarometry, are the estimation of temperature (*T*, ^{o}C) and pressure (*P*, kbar) conditions of metamorphic and igneous rocks based on the presence and compositions of liquid and mineral components. Over the past 40 years, the application of mineral–pair thermobarometers to ultramafic rocks played an important role in understanding the thermal structure and history of the Earth's upper mantle (Taylor 1998). A practical good thermometer is based on chemical reactions with low volume (ΔV_r) and high entropy (ΔS_r) and enthalpy (ΔH_r) (Powell 1985; Ravna and Paquin 2003). These reactions are extremely *T* dependent and show steep slopes in the *P*-*T* diagrams. According to Essene (1982), a good thermometer with $\Delta S_r \geq 4.0$ J/mole.K and $\Delta V_r \geq 0.2$ J/bar is essential for the metamorphic systems, and these limits may also be used for the igneous systems (e.g., Putirka 2008). Similarly, a good geobarometer can be obtained by mineral reactions with high ΔV_r and low to moderate ΔS_r and ΔH_r (Wood and Fraser 1978; Ravna and Paquin 2003). These reactions are substantially dependent on variations in *P* and to a lesser extent on *T,* and thus producing gentle slopes in the *P*-*T* diagrams. Although some thermobarometers are developed from volumetric and calorimetric data, most practical ones are based on the regression analysis obtained from experimental data, where the equilibrium constant (K_{eq}), *P*, and *T* are all known (Putirka 2008).

Davis and Boyd (1966) presented the first two-pyroxene thermometer for the join $Mg_2Si_2O_6$-$CaMgSi_2O_6$ at a pressure of 30 kbar, and numerous pyroxene thermobarometers have been

published since then. The two-pyroxene thermometer, however, received much more attention than the single-pyroxene approach. The lesser amount of both clino- and orthopyroxene phenocrysts in volcanic rocks than in mafic-ultramafic rocks limited the application of two-pyroxene thermobarometers in volcanic systems, and thus thermobarometers were produced based on single-clinopyroxene compositions (e.g., Nimis 1995, 1999; Nimis and Ulmer 1998; Nimis and Taylor 2000) or clinopyroxene-liquid equlibria (e.g., Putirka et al. 1996, 2003; Putirka 2008).

Single-clinopyroxene barometers

Recent studies on clinopyroxenes have shown that crystal-chemical variations, as well as the *P-T* conditions, play an important role in the composition of clinopyroxenes crystallized from magmas (e.g., Dal Negro et al. 1985; Malgarotto et al. 1993; Pasqual et al. 1995; Nazzareni et al. 1998; Bindi et al. 1999; Aydin et al. 2009). Clinopyroxene in basic magmas has received particular interest because its stability is a strong function of pressure. Crystal-structure modeling is an important technique to estimate structural changes in *C2/c* pyroxenes. Dal Negro et al. (1989) showed that the structural parameters of natural pyroxenes can be used as the applicable petrogenetic markers. As the alumina content of parental basalt is a sensitive factor for clinopyroxene, Nimis (1995) proposed a clinopyroxene geobarometer based on the crystal-structure, which is applicable only to *C2/c* clinopyroxenes that crystallized from anhydrous melts of basaltic composition (i.e., $Mg/(Mg+Fe^{2+})_{Cpx}$ = 0.7-0.9), excluding high-alumina basalts (i.e., $Al_2O_3 \geq 18$ wt%), and experimental conditions between 0 and 24 kbar:

$$P N_{95\text{-}BS\text{-}Cpx}\ (\pm 2, \text{kbar}) = 698.443 - 1.15378 * V_{Cell}\ (\text{Å}^3) - 16.1598 * V_{M1}\ (\text{Å}^3) \quad (1)$$

where $P_{N_{95\text{-}BS\text{-}Cpx}}$ denotes the Nimis (1995) geobarometer for basaltic systems and V_{Cell} and V_{M1} are the unit cell volume and *M1*-site volume, respectively.

The V_{Cell} and V_{M1} volumes at room conditions (i.e., P_0 = 1 atm and T_0= 25 ^{o}C) can be either measured by the *X*-ray diffraction analysis or calculated by the following equations using recalculated cations (*apfu*) at different sites:

$$V_{Cell} = 11.864*Fe^{2+}_{M1} + 9.107*Fe^{3+} - 18.375*Al_{M1} + 11.794*Ti - 1.4925*Cr + 439.97*Ca + 419.68*Na + 431.72*Mg_{M2} + 432.56*Fe^{2+}_{M2} + 428.03*Mn - 28.652*(Mg_{M2})^2 - 12.741*(Fe^{2+}_{M2})^2 \quad (2)$$

$$V_{M1} = -0.3085*Al_T + 0.8130*Fe^{2+}_{M1} - 0.4173*Fe^{3+} - 2.029*Al_{M1} - 1.0864*Ti - 0.8001*Cr + 11.931*Ca + 11.288*Na + 11.432*Mg_{M2} + 11.885*Fe^{2+}_{M2} + 12.038*Mn + 2.4335*(Mg_{M2})^2 - 1.1661*(Fe^{2+}_{M2})^2 \quad (3)$$

In the absence of *X*-ray diffraction data, Eq. 4 is useful for the geobarometric condition of clinopyroxenes:

$$P\ (\pm 2, \text{kbar}) = 698.443 + 4.985*Al_T - 26.826*Fe^{2+}_{M1} - 3.764*Fe^{3+} + 53.989*Al_{M1} + 3.948*Ti + 24.651*Cr - 700.431*Ca - 666.629*Na - 682.848*Mg_{M2} - 691.138*Fe^{2+}_{M2} - 688.384*Mn - 6.267*(Mg_{M2})^2 - 4.144*(Fe^{2+}_{M2})^2 \quad (4)$$

In these equations, the elements with no sites show the total amount of that element in the formula (*apfu*).

The Nimis (1995) geobarometer can be used for many natural clinopyroxenes occurring both as phenocrysts and megacrysts or forming well-preserved cumulate pyroxenites. Alternatively, cell volume (V_{Cell}) vs. *M1*-site volume (V_{M1}) plot may also be used to determine the pressure conditions of clinopyroxene during the magma crystallization. According to Putirka (2008), geobarometers based on co-existing clinopyroxene and liquid compositions proposed by

Putirka et al. (1996, 2003) are the highest precision and have the least systematic error for anhydrous and hydrous systems, when compared to the Nimis (1995) model. Nimis and Ulmer (1998) produced a new calibration of the geobarometer, which is valid for only clinopyroxenes with (Ca+Na) > 0.5 (*apfu*), $Mg/(Mg+Fe^{2+}) > 0.7$, and Al_2O_3/SiO_2 (wt%) < 0.375 (i.e., Al_2O_3 < 18 wt%) based on the crystal-structure modeling of Ca-rich clinopyroxenes coexisting with anhydrous, basic, and ultrabasic melts at pressure conditions corresponding Earth's crust and uppermost mantle (i.e., *P* = 0-24 kbar):

$$P\mathrm{NU}_{98\text{-BA-Cpx}}\ (\pm\ 1.75,\ \mathrm{kbar}) = 771.48 - 1.323*V_{Cell}\ (\text{Å}^3) - 16.064*V_{M1}\ (\text{Å}^3) \quad (5)$$

where $P\mathrm{NU}_{98\text{-BA-Cpx}}$ denotes the Nimis and Ulmer (1998) geobarometer and V_{Cell} and V_{M1} show the cell volume and *M1*-site volume, respectively.

In the absence of *X*-ray diffraction data, the pressure value can be estimated from Eq. 6 for the geobarometric formulation of clinopyroxenes (Nimis and Ulmer 1998):

$$\begin{aligned} P\ (\pm\ 1.75,\ \mathrm{kbar}) = {} & 771.48 + 4.956*Al_T - 26.756*Fe^{2+}_{M1} - 5.345*Fe^{3+} + 56.904*Al_{M1} + 1.848*Ti + \\ & 14.827*Cr - 773.74*Ca - 736.57*Na - 754.81*Mg_{M2} - 763.20*Fe^{2+}_{M2} - 759.66*Mn \\ & - 1.185*(Mg_{M2})^2 - 1.876*(Fe^{2+}_{M2})^2 \end{aligned} \quad (6)$$

According to Nimis and Ulmer (1998), the revised clinopyroxene geobarometer has smaller residuals (i.e., $P_{Cal} - P_{Exp}$) and data show similar values for *P* < 10 kbar, but slightly higher values for *P* > 10 kbar, when compared with the earlier version of Nimis (1995) model (i.e., $P_{95\text{-BS-Cpx}}$ in Eq. 1). The V_{Cell} and V_{M1} may not reflect the true unit-cell and site volumes of the clinopyroxenes during the *P-T* conditions of crystallization, and thus needs a correction for

246 thermal expansivity and compressibility. For that reason Eq. 7, which is the corrected
247 clinopyroxene structural geobarometer, is used for anhydrous and hydrous basic magmas:

248 $$P\mathrm{NU}_{98\text{cor-BH-Cpx}}\ (\pm\ 1.70,\ \text{kbar}) = 654.47 - 1.186*\mathrm{V}^{\mathrm{corr}}{}_{Cell}\ (\text{Å}^3) - 9.140*\mathrm{V}^{\mathrm{corr}}{}_{M1}\ (\text{Å}^3) \quad (7)$$

249 where $P_{98\text{cor-BH-Cpx}}$ denotes the corrected Nimis and Ulmer (1998) geobarometer and $\mathrm{V}^{\mathrm{corr}}{}_{Cell}$ and
250 $\mathrm{V}^{\mathrm{corr}}{}_{M1}$ show the corrected cell volume and *M1*-site volume, respectively.

251 Nimis and Ulmer (1998) suggest that this geobarometer is applicable to a wide range of natural
252 clinopyroxenes in basic and ultrabasic rocks, as well as the mantle equilibrium partial-melting
253 residua, if they are unable to re-equilibrate after the melt extraction. The $\mathrm{V}^{\mathrm{corr}}{}_{Cell}$ vs. $\mathrm{V}^{\mathrm{corr}}{}_{M1}$ plot
254 can also be used to understand the pressure conditions of crystallization. The simple
255 geobarometric formula proposed by Nimis and Ulmer (1998) showed that clinopyroxene molar-
256 volume variations and structural balance play a major role in the regulation of
257 clinopyroxene/liquid equilibria at different pressure conditions.

258 This approach for clinopyroxenes was later extended by Nimis (1999) for a wide range of
259 magmatic compositions, including basic to acidic and from tholeiitic subalkaline (i.e., Eq. 8, *P* =
260 0-18 kbar) to be mildly alkaline (i.e., Eq. 9, *P* = 0-24 kbar) magmas, as well as the shoshonitic
261 series:

262 $$P\mathrm{N}_{99\text{-TH-Cpx}}\ (\pm\ 1.00,\ \text{kbar}) = 537.003 - 1.017*\mathrm{V}^{P,T}{}_{Cell} - 5.663*\mathrm{V}^{P,T}{}_{M1} - 2.722*mg \quad (8)$$

263 $$P\mathrm{N}_{99\text{-MA-Cpx}}\ (\pm\ 1.10,\ \text{kbar}) = 621.151 - 1.220*\mathrm{V}^{P,T}{}_{Cell} - 4.620*\mathrm{V}^{P,T}{}_{M1} - 7.773*mg \quad (9)$$

264 where $P\mathrm{N}_{99\text{-TH-Cpx}}$ and $P\mathrm{N}_{99\text{-MA-Cpx}}$ denote the Nimis (1999) geobarometers. In these equations
265 (i.e., Eq. 8 and Eq. 9), the $mg = \mathrm{Mg}/(\mathrm{Mg}+\mathrm{Fe}^{2+})^{\mathrm{Cpx}}$ and $\mathrm{V}^{P,T}{}_{Cell}$ and $\mathrm{V}^{P,T}{}_{M1}$ show volumes corrected

for thermal expansivity and compressibility at valid *P*-*T* conditions. The *mg* term, which is not considered in previous (e.g., Nimis 1995; Nimis and Ulmer 1998) models should be required, especially for clinopyroxenes coexisting with the fractionated melts. Ignoring this term in equations 8 and 9 may result in lower pressure estimation for iron-rich clinopyroxenes (Nimis 1999). At higher pressures, the *TH*-formulation in Eq. 8 may give lower pressure values than the *MA*-formulation in Eq. 9. Accordingly, pressures exceeding 15 kbar estimated by using the *TH*-formulation should be regarded with caution. The Nimis (1999) model can be applied to basic through intermediate-acid magmatic rocks. According to Nimis (1999), an attempt to extend this approach to clinopyroxenes from calc-alkaline melts for the *MA*- and *TH*-formulations, either in combination or separately, may give unsatisfactory results, and they must be used with caution.

Nimis and Taylor (2000) used the CMS (CaO-MgO-SiO_2) and CMAS-Cr (CaO-MgO-Al_2O_3-SiO_2) systems at 850-1500 ^{o}C and 0-60 kbar experimental conditions to calibrate a Cr-in-Cpx barometer and enstatite-in-Cpx thermometer for Cr-diopsides from garnet peridotites. The Cr-in-Cpx barometer is based on the Cr exchange between clinopyroxene and garnet and, thus can be used as an alternative to the Al-in-Opx barometer to determine the pressure conditions of equilibration of natural garnet lherzolites. It is formulated as a function of *T* (K) and clinopyroxene composition:

$$P\mathrm{NT}_{00\text{-}\mathrm{Cpx}}(\mathrm{kbar}) = \frac{T(^{o}\mathrm{K})}{126.9} * \ln\left[a_{\mathrm{CaCrTs}}^{\mathrm{Cpx}}\right] + 15.483 * \ln\left(\frac{\mathrm{Cr}\#^{\mathrm{Cpx}}}{T(^{o}\mathrm{K})}\right) + \frac{T(^{o}\mathrm{K})}{71.38} + 107.8 \qquad (10)$$

where $a^{\mathrm{Cpx}}_{\mathrm{CaCrTs}}$ = Cr-0.81*Cr#*(Na+K) and Cr# = (Cr/(Cr+Al).

Putirka (2008) recalibrated using experiment conditions from 0.001 to 80 kbar and proposed three new barometers for clinopyroxene composition (i.e., Eq. 32a in Putirka 2008) and pyroxene-liquid components (i.e., Eq. 32b and 32c in Putirka 2008) based on the Nimis (1995) model. The current WinPyrox program allows the user to estimate the *P*-*T* conditions only for clinopyroxene-orthopyroxene analyses, but not pyroxene-liquid components. Geobarometer proposed by Putirka (2008) for clinopyroxene composition is calculated by WinPyrox program as follows:

$$P\mathrm{P}_{\text{08-Cpx (Eq. 32a)}}(\text{kbar}) = 3205 + 0.384*T(\text{K}) - 518*\ln(T(\text{K})) - 5.62*(X_{\text{Mg}}^{\text{Cpx}}) + 83.2*(X_{\text{Na}}^{\text{Cpx}}) + 68.2*(X_{\text{DiHd}}^{\text{Cpx}}) + 2.52*\ln(X_{\text{Al}^{\text{VI}}}^{\text{Cpx}}) - 51.1*(X_{\text{DiHd}}^{\text{Cpx}})^2 + 34.8*(X_{\text{EnFs}}^{\text{Cpx}})^2 \quad (11)$$

where $X_{\text{DiHd}}^{\text{Cpx}} = \text{Ca - CaTs - CaTi - CrCaTs}$ and $X_{EnFs}^{\text{Cpx}} = ((\text{Fe}_{\text{tot}} + \text{Mg}) - (\text{Ca - CaTi - CaTs - CrCaTs}))/2$. Although Eq. 11, improves the precision of the Nimis (1995) model (i.e., Eq. 1), it still contains systematic errors due to the hydrous experiments (Putirka 2008).

Single-clinopyroxene thermometers

Compared to the two-pyroxene thermometer formulations, studies on single-pyroxene thermometers, either in clinopyroxene or orthopyroxene, are scarce. Bertrand and Mercier (1985/1986) provided a reliable method to estimate an equilibrium temperature for natural lherzolites. They gave a simplified thermometer based only on the clinopyroxene solvus, which is calibrated for potential applications in a single clinopyroxene phase, provided that the clinopyroxene was once in equilibrium with the orthopyroxene (e.g., xenocrysts, intensely altered lherzolites):

$$T\mathrm{BM}_{85/86\text{-Cpx}}\ (^{\circ}\mathrm{K}) = \frac{33696 + 454.5 * P\ (\mathrm{GPa})}{17.61 - 8.314 * \ln\left(\frac{1 - X_{Ca}^{M2}}{0.95}\right) - 12.13 * (X_{Ca}^{M2})^2} \quad (12)$$

Pyroxene thermometry is a powerful tool for the estimation of the equilibration temperature of natural lherzolites. Temperature calculation methods for single-pyroxene, either in clino- or orthopyroxene, are commonly based on Ca-Mg equilibria. Taking into account that $a^{\mathrm{Cpx}}_{\mathrm{en}}$ is close to unity in natural peridotitic rocks, Nimis and Taylor (2000) formulated Brey and Köhler's (1990) two-pyroxene thermometry as a single-clinopyroxene thermometer:

$$T\mathrm{NT}_{00\text{-Cpx}}(^{\circ}\mathrm{K}) = \frac{23166 + 39.28{*}P\ (\mathrm{kbar})}{13.25 + 15.35{*}\mathrm{Ti} + 4.5{*}\mathrm{Fe} - 1.55{*}(\mathrm{Al} + \mathrm{Cr} - \mathrm{Na} - \mathrm{K}) + (\ln a_{\mathrm{en}}^{\mathrm{Cpx}})^2} \quad (13)$$

where all cations in (*apfu*) and $a^{\mathrm{Cpx}}_{\mathrm{en}}$ = (1-Ca-Na-K)*(1-0.5*(Al+Cr+Na+K)). The enstatite-in-Cpx thermometer (Eq. 13) and Cr-in-Cpx barometer (Eq. 10), can be used to estimate the *P-T* conditions of equilibration of Cr-diopside alone, and thus allowing application to partly altered xenoliths, inclusions in diamonds, and loose grains from sediments. This thermobarometer is a powerful tool in diamond exploration.

Using Nimis and Taylor's (2000) activity model, Putirka (2008) produced a new and more precise thermometer:

$$T\mathrm{P}_{08\text{-Cpx}}(^{\circ}\mathrm{K}) = \frac{93100 + 544{*}P(\mathrm{kbar})}{61.1 + 36.6{*}(X_{\mathrm{Ti}}^{\mathrm{Cpx}}) + 10.9{*}(X_{\mathrm{Fe}}^{\mathrm{Cpx}}) - 0.95{*}(X_{\mathrm{Al_{tot}}}^{\mathrm{Cpx}} + X_{\mathrm{Cr}}^{\mathrm{Cpx}} - X_{\mathrm{Na}}^{\mathrm{Cpx}} - X_{\mathrm{K}}^{\mathrm{Cpx}}) + 0.395{*}\left[\ln(a_{\mathrm{En}}^{\mathrm{Cpx}})\right]^2} \quad (14)$$

where $a_{\mathrm{En}}^{\mathrm{Cpx}} = (1 - X_{\mathrm{Ca}}^{\mathrm{Cpx}} - X_{\mathrm{Na}}^{\mathrm{Cpx}} - X_{\mathrm{K}}^{\mathrm{Cpx}}){*}(1 - 0.5{*}(X_{\mathrm{Al_{tot}}}^{\mathrm{Cpx}} + X_{\mathrm{Cr}}^{\mathrm{Cpx}} + X_{\mathrm{Na}}^{\mathrm{Cpx}} + X_{\mathrm{K}}^{\mathrm{Cpx}}))$.

An application of intracrystalline Fe^{2+}-Mg partitioning in clinopyroxene can be used to estimate the closure or equilibration (i.e., quench) temperatures based on the exchange

reaction between the *M2* and *M1* sites. However, the Fe-Mg ordering in clinopyroxene is dependent not only on temperature, but also on the intracrystalline polyhedral configuration. Dal Negro et al. (1982) showed that the *M2* site configuration is mainly controlled by the Ca and Na cations, whereas the *M1* site configuration is intensely affected by the R^{3+} trivalent cations, including Al^{VI}, Fe^{3+}, and Cr^{3+}, as well as Ti^{4+}. Based on data for Ca-rich clinopyroxenes from McCallister et al. (1976), the following equation was proposed by Dal Negro et al. (1982) to determine the temperature of intracrystalline equilibrium:

$$T\mathrm{DN}_{82\text{-Cpx}}(^{o}\mathrm{K}) = \left[1000 * \frac{5.465*(\mathrm{R}^{3+}) + 7.324*\mathrm{Ca}^{''} - 3.039}{-\ln K_D + 4.032*(\mathrm{R}^{3+}) + 5.383*\mathrm{Ca}^{''} - 3.767}\right] \quad (15)$$

where $Ca^{''}$ = (Ca+Na+Mn), R^{3+} = (Al^{VI}+Fe^{3+}+Cr+Ti^{4+}), and K_D = (Fe_{M1}*Mg_{M2})/(Fe_{M2}*Mg_{M1}). An application of Eq. 15 to basaltic pyroxenes, in some cases, may give poor results (Molin and Zanazzi 1991).Assuming $-\ln K_D$ = -1.75+4449.5*1/*T*, Molin and Zanazzi (1991) revised Eq. 15 and proposed a similar expression for the closure temperature of a typical augitic composition:

$$T\mathrm{MZ}_{91\text{-Cpx}}(^{o}\mathrm{K}) = \left[1000 * \frac{1.188*\left[5.465*(\mathrm{R}^{3+}) + 7.324*\mathrm{Ca}^{''} - 3.039\right]}{-\ln K_D + 4.032*(\mathrm{R}^{3+}) + 5.383*\mathrm{Ca}^{''} - 3.767}\right] \quad (16)$$

This thermometer yields reliable results only for augites of comparable chemical composition, as the equilibrium temperature is dependent primarily on the site configuration, which is controlled to the content of Ca and trivalent cations in the *M2* and *M1* sites. Both Dal Negro et al. (1982) and Molin and Zanazzi (1991) methods are therefore, capable of giving useful information on the cooling history of magmatic rocks containing only clinopyroxene.

Two-pyroxene thermometers

342 The mutual solubility of clinopyroxene coexisting with orthopyroxene established that the
343 relationship between the enstatite and diopside components is temperature controlled, and
344 thus can be used as a thermometer (Ravna and Paquin 2003 and references therein). The two-
345 pyroxene solvus in the simple CMS system is controlled by the following Ca-Mg exchange in the
346 *M2* site reaction.

347
$$\begin{array}{lll} CaMgSi_2O_6 + Mg_2Si_2O_6 & \Leftrightarrow & Mg_2Si_2O_6 + CaMgSi_2O_6 \\ \text{Di-in-Opx} \quad \text{En-in-Cpx} & \Leftrightarrow & \text{En-in-Opx} \quad \text{Di-in-Cpx} \end{array} \qquad (17)$$

348 Over twenty different calibrations of two-pyroxene thermometers were proposed and most of
349 the widely used ones are incorporated into the WinPyrox software. Davis and Boyd (1966)
350 studied the phase relations for the join $Mg_2Si_2O_6$-$CaMgSi_2O_6$ at a pressure of 30 kb with its
351 application to Fe- and Al-poor pyroxenes from kimberlites and introduced the concept of the
352 two-pyroxene thermometer. Since then, numerous two-pyroxene thermometers, commonly
353 based on the enstatite-diopside partitioning, have been published to estimate the equilibration
354 temperature of magmatic rocks (e.g., Wood and Banno 1973; Wells 1977; Nickel and Brey 1984;
355 Nickel et al. 1985; Bertrand and Mercier 1985/1986; Carlson and Lindsley 1988; Sen and Jones
356 1989; Brey and Köhler 1990; Taylor 1998; Putirka, 2008).

357 Because of the potential usefulness of Davis and Boyd's (1966) thermometer, Wood and
358 Banno (1973) attempted to apply the same simple approach to the iron-bearing compositions
359 and obtained the following expression for equilibration temperature (*T*, °K):

360
$$T\text{WB}_{73\text{-Opx-Cpx}}(^{\circ}\text{K}) = \frac{-10202}{\ln\left(\frac{a^{\text{Cpx}}_{Mg_2Si_2O_6}}{a^{\text{Opx}}_{Mg_2Si_2O_6}}\right) - 7.65*X^{\text{Opx}}_{\text{Fe}} + 3.88*(X^{\text{Opx}}_{\text{Fe}})^2 - 4.6} \qquad (18)$$

where $a_{Mg_2Si_2O_6} = \left(\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+} + Fe^{2+} + Mn^{2+} + Na^{+}} \right)_{M2} * \left(\frac{Mg^{2+}}{Fe^{3+} + Fe^{2+} + Al^{3+} + Ti^{4+} + Cr^{3+} + Mg^{2+}} \right)_{M1}$ and $X_{Fe}^{Opx} = \left(\frac{Fe^{2+}}{Fe^{2+} + Mg^{2+}} \right)$. In Eq. 18, the activity of the enstatite component in both the clino- and orthopyroxene is calculated using the same formula. In most cases, the model reproduces calculated temperatures within 70 °C. In calculating temperature from microprobe analyses, Wood and Banno (1973) did not consider the possible ferric iron contents in the pyroxenes, and thus all iron is assumed as Fe^{2+}. However, if Fe^{3+} content is taken into account, then the calculated equilibration temperature from Eq. 18 is increased due to the decreased X^{Opx}_{Fe} value. Compared to the optical or *X*-ray diffraction analyses, the Wood and Banno (1973) model gives inconsistent values, particularly at low temperatures with experimental data obtained by microprobe techniques.

Wells (1977) applied simple mixing models to two-pyroxene solid solutions and obtained a semi-empirical equation for the diopside-enstatite miscibility gap for a temperature range of 800 °C to 1700 °C by using the Wood and Bano's (1973) activity formula:

$$T\mathrm{W}_{77\text{-Opx-Cpx}}(^{o}\mathrm{K}) = \frac{7341}{3.355 + 2.44 * X_{Fe}^{Opx} - \ln K} \quad (19)$$

where $K = \frac{a^{Cpx}_{Mg_2Si_2O_6}}{a^{Opx}_{Mg_2Si_2O_6}}$ and $X_{Fe}^{Opx} = \left(\frac{Fe^{2+}}{Fe^{2+} + Mg^{2+}} \right)$. The Wells (1977) model reproduces most of the experimental data within 70 °C and thus is applicable to aluminous pyroxenes in the CMAS system. The Wells (1977) thermometer is similar to the Wood and Banno (1973) model, but deviates significantly for naturally equilibrated Mg-rich, two-pyroxenes due to the large

inaccuracies in the thermometer of Wood and Banno (1973) for Mg-rich compositions. At higher temperatures, the Wells (1977) model gives low temperature values as it inconsiderate both an observed non-ideality and pressure-dependency situations.

The Nickel and Brey (1984) model yields two equilibration temperatures for subsolidus orthopyroxene and clinopyroxene in the CMS system over a large range of temperature (i.e., 850 ^{o}C to 1500 ^{o}C) and pressure (i.e., 2 kbar to 60 kbar) conditions:

$$T\mathrm{NB(A)}_{84\text{-Opx-Cpx}}(^{o}\mathrm{K}) = \frac{(-7 - P\ (kbar)*0.06188 + 34*(X_{\mathrm{Di}}^{\mathrm{Opx}})^2 - (21.905 - P\ (kbar)*0.05229*(X_{\mathrm{Di}}^{\mathrm{Cpx}})^2)}{(0.0083143*\ln K_D(\mathrm{A}) + 0.004431*(X_{\mathrm{Di}}^{\mathrm{Cpx}})^2 - 0.00397)} \quad (20)$$

$$T\mathrm{NB(B)}_{84\text{-Opx-Cpx}}(^{o}\mathrm{K}) = \frac{(12.909 + P\ (kbar)*0.1633 + 34*(X_{\mathrm{En}}^{\mathrm{Opx}})^2 - (21.905 - P\ (kbar)*0.05229*(X_{En}^{\mathrm{Cpx}})^2)}{(0.0083143*\ln K_D(\mathrm{B}) + 0.004431*(X_{\mathrm{En}}^{\mathrm{Cpx}})^2 + 0.0085)} \quad (21)$$

where $K_D(\mathrm{A}) = \frac{X_{\mathrm{En}}^{\mathrm{Cpx}}}{X_{\mathrm{En}}^{\mathrm{Opx}}}$ and $K_D(\mathrm{B}) = \frac{X_{\mathrm{Di}}^{\mathrm{Cpx}}}{X_{\mathrm{Di}}^{\mathrm{Opx}}}$. The model is qualitatively in agreement with observed stability regions for iron-free and low-calcium pyroxenes, including pigeonite. However, this model predicts that pigeonite is not stable at high pressures. According to Nickel and Brey (1984), application of these equations to the experimental data showed that the reproduction of temperatures obtained by the Eq. 20 is better than the Eq. 21, because of the K_D (B) is very sensitive to small changes in $X^{\mathrm{Opx}}_{\mathrm{Di}}$. Accordingly, Eq. 21 gives larger deviations (i.e., over- or underestimations), especially at temperatures < 1000 ^{o}C, and hence is not useful for thermometric studies at relatively low temperatures. These formulations, however, should not be applied directly to pyroxene analyses from more complex systems (i.e., CMAS).

Nickel et al. (1985) proposed a thermometer for coexisting ortho- and clinopyroxene in the CMAS system at 1000 ^{o}C - 1670 ^{o}C and 30 kbar - 50 kbar conditions:

$$T\mathrm{N}_{85\text{-Opx-Cpx}}(^{\circ}\mathrm{C}) = 1616.67 + 287.935*\ln K_D + 2.933*P\ (\mathrm{kbar}) \quad (22)$$

where $K_D = \left(\frac{(1 - \frac{\mathrm{Al}}{2})*(1 - \mathrm{Ca})^{\mathrm{Cpx}})}{(1 - \frac{\mathrm{Al}}{2})*(1 - \mathrm{Ca})^{\mathrm{Opx}})} \right)$ and all cations are in (*apfu*). Although this simple empirical thermometer is valid for CMS and CMAS systems in the *P-T* range of the experiments and gives an idea of formation conditions, it should not be used for natural rocks (e.g., Nickel et al. 1985).

Bertrand and Mercier (1985/1986) provided a reliable method to calculate the equilibration temperature of natural lherzolite based on coexisting ortho- and clinopyroxene, the latter represented as calcic diopside, in the simple (i.e., CMS, MAS) and more complex (i.e., CMAS, CFMS, CFMAS where F = FeO) systems. The proposed two-pyroxene thermometer is given by:

$$T\mathrm{BM}_{85/86\text{-Opx-Cpx}}(^{\circ}\mathrm{K}) = \frac{(36273 + 399*P\ (\mathrm{GPa}))}{\left[19.31 - 8.314*\ln K - 12.15*(\mathrm{Ca}^{*}_{\mathrm{Cpx}})^2\right]} \quad (23)$$

where $K = \frac{1 - \mathrm{Ca}^{*}_{\mathrm{Cpx}}}{1 - \mathrm{Ca}^{*}_{\mathrm{Opx}}}$, $\mathrm{Ca}^{*}_{\mathrm{Cpx}} = \frac{X^{\mathrm{M2}}_{\mathrm{Ca}}}{1 - X^{\mathrm{M2}}_{\mathrm{Na}}} + \left(-0.77 + 10^{-3}*T\right)*\left[\frac{\mathrm{Fe}}{\mathrm{Fe} + \mathrm{Mg}}\right]$, and $\mathrm{Ca}^{*}_{\mathrm{Opx}} = \frac{X^{\mathrm{M2}}_{\mathrm{Ca}}}{1 - X^{\mathrm{M2}}_{\mathrm{Na}}}$

According to Bertrand and Mercier (1985/1986), the advantage of this thermometer is that it is tested against the natural pyroxene analyses from reequlibration experiments in the range of 950 °C-1500 °C and 30 to 44 kbar, and thus can be applied to realistic equilibrium conditions.

Carlson and Lindsley (1988) studied the thermochemistry of pyroxenes on the join $Mg_2Si_2O_6$-$CaMgSi_2O_6$ and proposed two-pyroxene thermometers based on experiments ranging in

temperature from 850 °C to 1500 °C and pressure from 1 bar to 60 kbar. The temperatures of equilibration are obtained by the thermodynamic formulations A and B (see Carlson and Lindsley 1988) and given in the following equations:

$$T\mathrm{CL(A)}_{88\text{-Opx-Cpx}}(^{o}\mathrm{C}) = -273.15 + \frac{4.261 + 0.059*P + W_{G1}^{\mathrm{Cpx}}*(X_2^{\mathrm{Cpx}})^2*(1 - 2*X_1^{\mathrm{Cpx}}) + 2*W_{G2}^{\mathrm{Cpx}}*(X_1^{\mathrm{Cpx}})*(X_2^{\mathrm{Cpx}})^2 - W_G^{\mathrm{Oen}}*(X_2^{\mathrm{Oen}})^2}{0.002721 - 0.0083143*\ln\left(\frac{X_1^{\mathrm{Cpx}}}{X_1^{\mathrm{Oen}}}\right)} \quad (24)$$

$$T\mathrm{CL(B)}_{88\text{-Opx-Cpx}}(^{o}\mathrm{C}) = -273.15 + \frac{-35.92 - 1.753*P + W_{G2}^{\mathrm{Cpx}}*(X_1^{\mathrm{Cpx}})^2*(1 - 2*X_2^{\mathrm{Cpx}}) + 2*W_{G1}^{\mathrm{Cpx}}*(X_2^{\mathrm{Cpx}})*(X_1^{\mathrm{Cpx}})^2 - W_G^{\mathrm{Oen}}*(X_1^{\mathrm{Oen}})^2}{0.002721 - 0.0083143*\ln\left(\frac{X_2^{\mathrm{Cpx}}}{X_2^{\mathrm{Oen}}}\right)} \quad (25)$$

where W^{Cpx}_{G1} = 26.23 - 0.02229**P* (kbar), W^{Cpx}_{G2} = 32.44 - 0.08646**P* (kbar), W^{Oen}_{G} = 28.60-1.749**P* (kbar), and X_i^{Cpx} refers to the mole fraction of component *i* (i.e., X_1^{Cpx} = enstatite and X_2^{Cpx} = diopside) in clinopyroxene. The advantage of these thermometers is their application to the wide range of temperature and pressure conditions of rocks containing two pyroxenes.

Sen and Jones (1989) carried out pyroxene equilibration experiments in the multivariate systems (CMS and CMAS) at 925 °C to 1150 °C and 10 kbar to 15 kbar conditions and proposed two thermometric equations :

$$T\mathrm{SJ}(1)_{89\text{-Opx-Cpx}}(^{o}\mathrm{K}) = \frac{4900}{[1.807 - \ln K_D(1)]} \quad (26)$$

$$T\mathrm{SJ}(2)_{89\text{-Opx-Cpx}}(^{o}\mathrm{K}) = \frac{7045}{[2.47 - \ln K_D(2)]} \quad (27)$$

where $K_D\,(1) = \frac{[X_{\mathrm{En}}]^{\mathrm{Cpx}}}{[X_{\mathrm{En}}]^{\mathrm{Opx}}}$ and $K_D\,(2) = \frac{[X_{\mathrm{Di}}]^{\mathrm{Opx}}}{[X_{\mathrm{Di}}]^{\mathrm{Cpx}}}$.

Compared to Sen and Jones (1989) models, the previous Wells (1977) and Nickel et al. (1985) thermometers give consistently higher temperatures. According to Sen and Jones (1989), thermometer of Bertrand and Mercier (1985/1986) gives a temperature range that is the closest to the Eq. 26 and Eq. 27. These thermometers are found to be useful in estimating temperatures of natural spinel peridotites to within ± 50 ^{o}C.

Taking into account the Ca- and Na-partitioning between orthopyroxene and clinopyroxene, Brey and Köhler (1990) formulated two-pyroxene thermometers based on reversed experiments, which can be applied both to the CMS and the CMAS systems:

$$T\mathrm{BK}_{\text{90-Ca-in-Opx-Cpx}}(^{o}\mathrm{K}) = \frac{23664 + (24.9 + 126.3{*}X_{\mathrm{Fe}}^{\mathrm{Cpx}}){*}P(\mathrm{kbar})}{13.38 + (\ln K_D^{*})^2 + 11.59{*}X_{\mathrm{Fe}}^{\mathrm{Opx}}} \quad (28)$$

$$T\mathrm{BK}_{\text{90-Na-in-Opx-Cpx}}(^{o}\mathrm{K}) = \frac{35000 + 61.5{*}P\ (\mathrm{kbar})}{(\ln D_{\mathrm{Na}})^2 + 19.8} \quad (29)$$

where $K_D^{*} = \frac{(1 - \mathrm{Ca}^{*})^{\mathrm{Cpx}}}{(1 - \mathrm{Ca}^{*})^{\mathrm{Opx}}}$, $\mathrm{Ca}^{*} = \frac{\mathrm{Ca}^{M2}}{(1 - \mathrm{Na}^{M2})}$, $X_{\mathrm{Fe}}^{\text{Cpx or Opx}} = \frac{\mathrm{Fe}^{2+}}{\mathrm{Fe}^{2+} + \mathrm{Mg}}$, and $D_{\mathrm{Na}} = \frac{\mathrm{Na}^{\mathrm{Opx}}}{\mathrm{Na}^{\mathrm{Cpx}}}$.

Considering the suggestion that Ca-in-orthopyroxene, which is in equilibrium with clinopyroxene can be used as a thermometer by Sachtleben and Seck (1981), Brey and Köhler (1990) fitted the reversed experiments in the CMS system, given by Nickel and Brey (1984), as a function of *P* and reciprocal *T* and derived an equation for temperature that may be calculated from the Ca content (*apfu*) of orthopyroxene:

$$T\mathrm{BK}_{\text{90-Ca-in-Opx}}(^{o}\mathrm{K}) = \frac{6425 + 26.4{*}P\ (\mathrm{kbar})}{-\ln \mathrm{Ca}^{\mathrm{Opx}} + 1.843} \quad (30)$$

Equation 30 can be applied both to the CMS and the natural systems, but is not as good as the Ca-in-Opx-Cpx thermometer (i.e., Eq. 28). In natural systems, the Ca content in orthopyroxene is lowered in the presence of Al and a variable amount of Na in the *M2* site. In this case, the Ca-in-Opx thermometer may be used to understand the closure temperature of the Ca-Mg exchange. However, the Ca-in-Opx thermometer (i.e., Eq. 30) may provide a potential alternative to the solvus two-pyroxene thermometers, especially for ultramafic rocks. Among two-pyroxene thermometers, the Brey and Köhler (1990) models (e.g., Eq. 28) have been used widely in mantle systems. The Bertrand and Mercier (1985/1986) model, which is fundamental to Brey and Köhler's (1990) Ca-in-Opx-Cpx thermometer, somewhat underestimates the temperatures, possibly because of the Fe correction of Ca in clinopyroxene and the narrow temperature calibration range (e.g., 800 ^{o}C – 1000 ^{o}C) of the experiments. Brey and Köhler's (1990) formulation showed that if a correction factor of -0.77 in Ca^{*}_{Cpx} (see Eq. 23) is replaced by -0.97, the Bertrand and Mercier (1985/1986) model reproduces results obtained with their thermometer for natural rocks and can be be applied to equilibration temperatures > 750 ^{o}C.

Taylor (1998) carried out an experimental study of upper mantle peridotites, produced a new two-pyroxene thermometer, discussed some of the existing thermobarometers in terms of which thermobarometers are the most applicable to fertile lherzolite and websterite, and proposed modifications or new calibrations for inadequate geobarometers. The Taylor (1998) thermometer is a modified form of the Brey and Köhler (1990) model, which is based on mineral chemical data from a series of high *P*-*T*, fO_2-controlled, fluid-saturated experiments in the range of *P* = 1.0 to 3.5 GPa and *T* = 1050 to 1260 ^{o}C:

$$T\mathrm{T}_{98\text{-Opx-Cpx}}(^{\circ}\mathrm{K}) = \frac{24787 + 678*P\ (\mathrm{GPa})}{15.67 + 14.37*\mathrm{Ti}^{Cpx} + 3.69*\mathrm{Fe}^{\mathrm{Cpx}} - 3.25*X_{\mathrm{ts}} + (\ln K_d)^2} \quad (31)$$

where $X_{\mathrm{ts}} = (\mathrm{Al+Cr-Na})^{\mathrm{Cpx}}$, $\ln K_d = \ln\left[a(\mathrm{En})^{\mathrm{Cpx}}\right] - \ln\left[a(\mathrm{En})^{\mathrm{Opx}}\right]$,

$a(\mathrm{En})^{\mathrm{Cpx\ or\ Opx}} = (1 - \mathrm{Ca} - \mathrm{Na})*(1 - \mathrm{Al}^{\mathrm{VI}} - \mathrm{Cr} - \mathrm{Ti})*\left(1 - \frac{\mathrm{Al}^{\mathrm{IV}}}{2}\right)^2$, $\mathrm{Al}^{\mathrm{IV}} = \left(\frac{\mathrm{Al}}{2} + \frac{\mathrm{Cr}}{2} + \mathrm{Ti} - \frac{\mathrm{Na}}{2}\right)^{\text{for Cpx and Opx}}$,

$\mathrm{Al}^{\mathrm{VI}} = \left(\frac{\mathrm{Al}}{2} - \frac{\mathrm{Cr}}{2} - \mathrm{Ti} + \frac{\mathrm{Na}}{2}\right)^{\text{for Cpx and Opx}}$, and all in cations (*apfu*).

This model is applicable to a wide range of fertile peridotite compositions, including spinel, garnet and pyroxene, with a high *P* range (i.e., 1.0 to 3.5 GPa). Taylor (1998) also established that the Brey and Köhler (1990) formulations (e.g., Eq. 28 and Eq. 29), which are accepted as a standard model in mantle studies, tend to overestimate the *T* of fertile peridotite compositions.

Putirka (2008) introduced two two-pyroxene thermometers, one for mafic systems (i.e., $\mathrm{Mg\#}^{\mathrm{Cpx}} > 0.75$) and the other only for experiments with high Mg# compositions ($\mathrm{Mg\#}^{\mathrm{Cpx}} > 0.75$) based on the partitioning of enstatite+ferrosilite between ortho- and clinopyroxene by using a new global regression model:

$$T\mathrm{P}(1)_{\text{08-Opx-Cpx}} = \frac{10000}{11.2 - 1.96*\ln\left(\frac{X^{\mathrm{Cpx}}_{\mathrm{EnFs}}}{X^{\mathrm{Opx}}_{\mathrm{EnFs}}}\right) - 3.3*(X^{\mathrm{Cpx}}_{\mathrm{Ca}}) - 25.8*(X^{\mathrm{Cpx}}_{\mathrm{CrCaTs}}) + 33.2*(X^{\mathrm{Opx}}_{\mathrm{Mn}}) - 23.6*(X^{\mathrm{Opx}}_{\mathrm{Na}}) - 2.08*(X^{\mathrm{Opx}}_{\mathrm{En}}) - 8.33*(X^{\mathrm{Opx}}_{\mathrm{Di}}) - 0.05*P\ (\mathrm{kbar})} \quad (32)$$

$$T\mathrm{P}(2)_{\text{08-Opx-Cpx}} = \frac{10000}{13.4 - 3.4*\ln\left(\frac{X^{\mathrm{Cpx}}_{\mathrm{EnFs}}}{X^{\mathrm{Opx}}_{\mathrm{EnFs}}}\right) + 5.59*(X^{\mathrm{Cpx}}_{\mathrm{Mg}}) - 8.8*(Mg\ \#^{\mathrm{Cpx}}) + 23.85*(X^{\mathrm{Opx}}_{\mathrm{Mn}}) + 6.48*(X^{\mathrm{Opx}}_{\mathrm{FmAl_2SiO_6}}) - 2.38*(X^{\mathrm{Cpx}}_{\mathrm{Di}}) - 0.044*P\ (\mathrm{kbar})} \quad (33)$$

where $X_{En}^{Opx} = \left[\frac{X_{Mg}^{Opx}}{X_{Mg}^{Opx} + X_{Fe}^{Opx} + X_{Mn}^{Opx}}\right] * (X_{Fm_2Si_2O_6}^{Opx})$ and $X_{Di}^{Opx} = \left[\frac{X_{Mg}^{Opx}}{X_{Mg}^{Opx} + X_{Fe}^{Opx} + X_{Mn}^{Opx}}\right] * (X_{CaFmSi_2O_6}^{Opx})$

In these equations, the $X^{Cpx}{}_{EnFs}$, $X^{Opx}{}_{EnFs}$, $X^{Cpx}{}_{Di}$, $X^{Opx}{}_{Di}$, $X^{Opx}{}_{En}$, and $X^{Opx}{}_{FmAl2SiO6}$ show the components of clino- and orthopyroxene given by formulations in the "Two-pyroxene.xls" Excel spreadsheet developed by Putirka (2008). Two-pyroxene thermometers (i.e., Eq. 32 and Eq. 33) and the other most commonly used formulations can be calculated and compared in an Excel workbook (i.e., "Two-pyroxene.xls") published by Putirka (2008).

According to Nimis and Grütter (2010), the Taylor (1989) model for two-pyroxene and the Nimis and Taylor (2000) model for single-clinopyroxene thermometers give the most reliable temperatures in variety of simple and natural peridotitic systems. However, the temperature estimation methods based on two-pyroxene thermometers for garnet peridotites and pyroxenites show that the models are not internally consistent and in some cases the difference between formulations exceeds 200 ^{o}C in a well-equilibrated mantle xenoliths (e.g., Nimis and Grütter 2010). In order to improve the internal consistency between two-pyroxene and Ca-in-Opx models of Brey and Köhler (1990) for temperatures of mantle-derived rocks, Nimis and Grütter (2010) proposed the following empirical correction:

$$T\mathrm{NT}_{10\text{-Ca-in-Opx}}(^{o}\mathrm{C}) = -628.7 + 2.0690 * T\mathrm{BKN}_{90\text{-Ca-in-Opx}} - 4.530 * 10^{-4} * (T\mathrm{BKN}_{90\text{-Ca-in-Opx}})^2 \quad (34)$$

where TBKN$_{90\text{-Ca-in-Opx}}$ is the Ca-in-Opx thermometer (i.e., Eq. 30) of Brey and Köhler (1990).

Two-pyroxene barometers

Mercier et al. (1984) proposed two empirical *P* formulations to estimate the equilibrium conditions of ophiolitic lherzolites:

503 $$P\mathrm{M}(1)_{84\text{-Opx-Cpx}}(\mathrm{GPa}) = \frac{1.279}{(K_f + 0.0006) - 2.29} \quad (35)$$

504 $$P\mathrm{M}(2)_{84\text{-Opx-Cpx}}(\mathrm{GPa}) = \frac{1.073}{(K_f + 0.028) - 1.65} \quad (36)$$

505 where $K_f = \frac{\left[\mathrm{Ca}^*\right]_{\mathrm{Opx}}}{\left\{1-\left[\mathrm{Ca}^*\right]_{\mathrm{Cpx}}\right\}}$. In this equation, the $[\mathrm{Ca}^*]_{\mathrm{Opx}}$ and $[\mathrm{Ca}^*]_{\mathrm{Cpx}}$ are the Ca (*apfu*) contents

506 of ortho- and clinopyroxene, respectively. Equation 35 is used for all available CMS and CMAS

507 systems, whereas Eq. 36 is considered when discarding the questionable data points in the data

508 set used for calibration at or below 0.5 GPa.

509 Putirka (2008), with a similar limitation on high Mg# composition (i.e., Mg# > 0.75),

510 calibrated Mercier et al.'s (1984) *P* model by applying a new global regression approach:

511 $$P\mathrm{P}(1)_{08\text{-Opx-Cpx}}(\mathrm{kbar}) = -279.8 + 293*(X_{\mathrm{Al^{VI}}}^{\mathrm{Opx}}) + 455*(X_{\mathrm{Na}}^{\mathrm{Opx}}) + 229*(X_{\mathrm{Cr}}^{\mathrm{Opx}}) + 519*(X_{\mathrm{Fm_2Si_2O_6}}^{\mathrm{Opx}}) - 563*(X_{\mathrm{En}}^{\mathrm{Opx}}) + 371*(X_{\mathrm{Di}}^{\mathrm{Opx}}) + 327*(a_{\mathrm{En}}^{\mathrm{Opx}}) + \frac{1.19}{K_f} \quad (37)$$

512 $$P\mathrm{P}(2)_{08\text{-Opx-Cpx}}(\mathrm{kbar}) = -94.25 + 0.045*T(^{\circ}\mathrm{C}) + 187.7*(X_{\mathrm{Al^{VI}}}^{\mathrm{Opx}}) + 246.8*(X_{\mathrm{Fm_2Si_2O_6}}^{\mathrm{Opx}}) - 212.5*(X_{\mathrm{En}}^{\mathrm{Opx}}) + 127.5*(a_{\mathrm{En}}^{\mathrm{Opx}}) - \frac{1.66}{K_f} - 69.4*(X_{\mathrm{EnFs}}^{\mathrm{Cpx}}) - 133.9*(a_{Di}^{\mathrm{Cpx}}) \quad (38)$$

513 where $X_{\mathrm{En}}^{\mathrm{Opx}} = (X_{\mathrm{Fm_2Si_2O_6}}^{\mathrm{Opx}})*\left(\frac{X_{\mathrm{Mg}}^{\mathrm{Opx}}}{\left[X_{\mathrm{Mg}}^{\mathrm{Opx}} + X_{\mathrm{Mn}}^{\mathrm{Opx}} + X_{\mathrm{Fe}}^{\mathrm{Opx}}\right]}\right)$, $X_{\mathrm{Di}}^{\mathrm{Opx}} = (X_{\mathrm{CaFmSi_2O_6}}^{\mathrm{Opx}})*\left(\frac{X_{\mathrm{Mg}}^{\mathrm{Opx}}}{\left[X_{\mathrm{Mg}}^{\mathrm{Opx}} + X_{\mathrm{Mn}}^{\mathrm{Opx}} + X_{\mathrm{Fe}}^{\mathrm{Opx}}\right]}\right)$,

514 $a_{\mathrm{En}}^{\mathrm{Opx}} = \left(\frac{0.5*X_{\mathrm{Mg}}^{\mathrm{Opx}}}{X_{\mathrm{Ca}}^{\mathrm{Opx}} + 0.5*X_{\mathrm{Mg}}^{\mathrm{Opx}} + 0.5*X_{\mathrm{Fe^{2+}}}^{\mathrm{Opx}} + X_{\mathrm{Mn}}^{\mathrm{Opx}} + X_{\mathrm{Na}}^{\mathrm{Opx}}}\right)*\left(\frac{0.5*X_{\mathrm{Mg}}^{\mathrm{Opx}}}{0.5*X_{\mathrm{Fe^{2+}}}^{\mathrm{Opx}} + 0.5*X_{\mathrm{Fe^{3+}}}^{\mathrm{Opx}} + X_{\mathrm{Al^{VI}}}^{\mathrm{Opx}} + X_{\mathrm{Ti}}^{\mathrm{Opx}} + X_{\mathrm{Cr}}^{\mathrm{Opx}} + 0.5*X_{\mathrm{Mg}}^{\mathrm{Opx}}}\right)$,

515 and $a_{\mathrm{Di}}^{\mathrm{Cpx}} = \frac{(X_{\mathrm{Ca}}^{\mathrm{Cpx}})}{(X_{\mathrm{Ca}}^{\mathrm{Cpx}} + 0.5*X_{\mathrm{Mg}}^{\mathrm{Cpx}} + 0.5*X_{\mathrm{Fe^{2+}}}^{\mathrm{Cpx}} + X_{\mathrm{Mn}}^{\mathrm{Cpx}} + X_{\mathrm{Na}}^{\mathrm{Cpx}})}$. In these equations, the K_f ratio

(see Eq. 35 and Eq. 36) is the same as in Mercier et al. (1984) and $X_{\text{element}}^{\text{Pyx}}$ refers to the cations (*apfu*). In contrast to *T*-independent Eq. 37, the temperature-dependent pressure formulation recovers *P* to ± 2.8 kbar and thus the precision is increased when *T* is used as an input in Eq. 38 (Putirka 2008).

DESCRIPTION OF PROGRAM

WinPyrox is a compiled program developed for running in the Microsoft® Windows platform. The program is designed to calculate and classify electron-microprobe and wet-chemical pyroxene analyses. WinPyrox also calculates the most widely used single-clinopyroxene and two-pyroxene thermobarometers, which allows the user to make an extensive comparison of different calibrations using their own pyroxene analyses. The program comes up with a self-extracting setup file (≈ 11 Mb), which is created by the Inno Setup Compiler (i.e., version 5.5.2) developed by Jordan Russell (http://www.jrsoftware.org/isdl.php). The program runs as a single executable file, WinPyrox.exe (4.6 Mb), provided that the Microsoft® Visual Studio package is installed. However, with the help of necessary .ocx and .dll support files in the self-extracting setup file, the users of this program can execute WinPyrox without requiring the Microsoft® Visual Studio package. Upon successful installation of the WinPyrox program, the start-up screen with various pull-down menus and shortcuts appears. Execution of WinPyrox may also be started by clicking the program icon from *All Programs* options.

Data entry

The users of this program can edit pyroxene analyses obtained from wet-chemical or electron-microprobe techniques by clicking the *New* icon on the tool bar, by selecting *New File*

from the pull-down menu of *File* option or pressing the *Ctrl + N* keys. The standard 19 variables are defined by the program for calculation and classification of pyroxene analysis in the following order:

Sample No, SiO_2, TiO_2, Al_2O_3, V_2O_3, Cr_2O_3, Fe_2O_3, FeO, MnO, NiO, CoO, ZnO, MgO, CaO, Na_2O, K_2O, ZrO_2, Sc_2O_3, and Li_2O.

In data entry section, the program thus permits the user to enter a total of 40 variables, including oxides (wt%) both for clino- and orthopyroxenes, *P* (kbar), and *T* (^oC). *P-T* values entered by users are used by the program for estimation of thermobarometric conditions. Pyroxene analyses typed in Excel files with the extension of ".xls" and ".xlsx" in the above order, can be loaded into the program's data entry section by clicking the *Open Excel File* option from the pull-down menu of *File*. For example, two representative pyroxene Excel data files (WinPyrox_Rock and WinPyrox_Putirka) in the folder (C:\Program Files\WinPyrox\Open Excel Files) can be used for this purpose by the user. However, using the copy-paste options, one can incorporate pyroxene data from a Microsoft® Excel spreadsheet into the data entry section of the program more quickly. By selecting the *Edit Excel File* option from the pull-down menu of *File*, pyroxene analyses can be typed in a blank Excel file (i.e., WinPyrox) in the (C:\Program Files\WinPyrox\Edit Excel File) folder, stored in a different file name with the extension of ".xls" or ".xlsx", and then loaded into the program's data entry section by clicking the *Open Excel File* option from the pull-down menu of *File* for further calculation. Once the pyroxene analyses in an Excel file are displayed on the screen by using the *Open Excel File* option, they can be stored with the extension of ".pyx" by clicking the *Save As* option from the pull-down menu of *File*.

Additional information about data entry or similar topics can be accessed by pressing the F1 function key to display the WinPyrox.hlp file on the screen. For example, by selecting the *Data Entry* section from the index of WinPyrox.chm file, it displays the necessary documents concerning the pyroxene *Data Entry* section on the screen.

Normalization

WinPyrox calculates pyroxene analyses with cations estimated based on 6 oxygens in the formula. Once the program is executed, the program begins with to calculate pyroxene data based on the structural formulae with a total of 4 cations. However, by clicking *structural formulae* option from the pull-down menu of *Normalization*, the program allows the user two types of the cation normalization schemes, such as i) *structural formulae with a total of 4 cations* and ii) *structural formulae without a total of 4 cations*. In most of the pyroxene chemical studies, cations are used with normalization to a total of 4, whereas some authors (e.g., Putirka 2008) prefer to use cations without normalization to 4, especially for thermobarometric estimations. WinPyrox, providing these two options in the *Normalization* menu, thus enables the user the opportunity to calculate pyroxene analyses for different total cation procedures.

Ferric iron estimation

Pyroxene analyses with measured Fe_2O_3 (wt%) and FeO (wt%) contents (e.g., wet-chemical) are calculated by program as Fe^{+3} (*apfu*) and Fe^{2+} (*apfu*) separately. If pyroxene analyses are given as Fe_2O_3 (wt%) = 0 and FeO (wt%) > 0, then the program assumes FeO (wt%) content as FeO_{total} (wt%) and estimates the ferric and ferrous iron stoichiometrically. The ferric iron estimation (Fe^{3+}, *apfu*) from a total iron content (FeO_{total}, wt%) of electron-microprobe

pyroxene analysis is carried out by different empirical equations in WinPyrox (e.g., Droop 1987; Papike et al. 1974). The program begins with to estimate the Fe^{3+} content based on method proposed by Droop (1987) as follows:

$$Fe^{3+} = 12 * \left(1 - \frac{4}{S}\right) \quad (39)$$

where *S* shows the observed cation total per 6 oxygens calculated assuming all iron to be ferrous iron. However, WinPyrox also allows the user to select the second procedure proposed by Papike et al. (1974) from the pull-down menu of *the Ferric iron estimation* options in estimating the Fe^{3+} content from a total iron content of pyroxene analysis.

$$Fe^{3+} = Al^{IV} + Na - Al^{VI} - Cr - 2 * Ti \quad (40)$$

In most case, an empirical ferric iron content estimation of electron-microprobe pyroxene analysis between the Droop (1987) and Papike et al. (1974) models can be represented by the following equation:

$$Fe^{3+}_{D87} = \frac{3}{2} * Fe^{3+}_{P74} \quad (41)$$

where Fe^{3+}_{D87} and Fe^{3+}_{P74} denotes the Fe^{3+} contents by Droop (1987) and Papike et al. (1974), respectively. Ferric iron estimation based on the Droop (1987) method produces the maximum Fe^{3+} content, whereas Papike et al.'s (1974) approach gives the minimum Fe^{3+} content. Alternatively, an average Fe^{3+} content based on the Droop (1987) and Papike et al. (1974) formulations can be estimated as follows:

$$Fe^{3+}_{TS} = \frac{(Fe^{3+}_{D87} + Fe^{3+}_{P74})}{2} \quad (42)$$

where TS denotes this study. WinPyrox allows the user to estimate an average Fe^{3+} content of electron-microprobe pyroxene analyses by selecting "Fe3+ estimation (This study)" from the pull-down menu of *Ferric iron estimation* option.

WORKED EXAMPLES

The following examples show how WinPyrox can be used for a variety of calculations and classifications of pyroxenes. Table 4 lists the specific calculation steps in the *Calculation Screen* of the program. Validity of program outputs has been tested for numerous data sets, and results are given in Tables 5–8.

Classification of pyroxenes

Once the pyroxene analyses are processed by clicking the *Calculate* icon (i.e., ∑) in the *Data Entry Section* of the program (Fig. 4a), all estimation parameters both for clinopyroxene and orthopyroxene are displayed in columns 1-130 and 131-211 (see Table 4) of the *Calculation Screen* (Fig. 4b), respectively. Pressing the *Ctrl + F* keys or clicking the *Open File to Calculate* option from the *Calculate* menu also executes the data processing for a selected data file with the extension of ".pyx". Representative pyroxene analyses with their estimations based on six oxygen by the program are given in Table 5.

WinPyrox distributes the recalculated cations into the *T*, *M1*, and *M2* sites (see rows 3 and 15 in Table 4). The program first calculates the structural formulae (see rows 19-36 in Table 5) and then defines pyroxene groups (row 39 in Table 5) in the *Q* vs. *J* classification diagram (see Fig. 1) taking into account the *Q* and *J* values (rows 37 and 38 in Table 5). Following the group name separation, WinPyrox specifies pyroxene names (see row 40 in Table 5) with possible

619 adjectival modifiers (see row 41 in Table 5). The IMA-88 list comprises fifteen adjectival
620 modifiers (see rows 1 to 15 in Table 3), but exclude some of the elements, including V^{3+}, Zr^{4+},
621 and Sc^{3+}. WinPyrox considers these elements and determines adjectival modifiers as vanadoan,
622 zirconian, and scandian, respectively (see rows 17 to 19 in Table 3). The software also identifies
623 the cobaltian adjectival modifier provided that the $Co^{2+} > 0.01$ (see row 16 in Table 3).
624 WinPyrox classifies all IMA-88 proposed pyroxene groups with their mineral subdivisions (see
625 Table 2).

626 The program, cannot distinguish enstatite/ferrosilite from clinoenstatite/clinoferrosilite and
627 produces two names, such as enstatite/clinoenstatite (e.g., see the sample S1 in row 40 in Table
628 5) and ferrosilite/clinoferrosislite because the identification of the orthorhombic and
629 monoclinic varieties are insensitive to chemical parameters and are commonly identified by
630 their optical properties. There is no distinctive classification procedure for all the other
631 pyroxene group minerals in the IMA-88 nomenclature scheme. WinPyrox, thus names other
632 pyroxene group minerals (see Table 2) based on the criteria given by Rock (1990) such as
633 donpeacorite/kanoite (rare Mn-Mg pyroxene), johannsenite-petedunnite-esseneite (rare Ca
634 pyroxene), spodumene (rare Li-Al pyroxene), kosmochlor (rare-Na-Cr^{3+} pyroxene), and jervisite
635 (rare-Na pyroxene) (e.g., see rows 39 and 40 in Table 5).

636 WinPyrox allows the user to produce eighteen pyroxene-related plots in the pull-down menu
637 of *Graph*, which are grouped as i) *Classification Diagrams* (including six diagrams), ii) *Graphical*
638 *Two-Pyroxene Thermometry* (including four diagrams), and iii) *Miscellaneous Plots* (including
639 eight diagrams). For example, by clicking the *Classification Diagram* option and selecting Wo-

En-Fs and Q-Jd-Ae ternary diagrams from the pull-down menu of *Graph* in the *Calculation Screen*, the program enables the user to display each sample in the specific IMA pyroxene classification plots (Morimoto et al. 1988) (see Fig.2a and Fig. 3a) and on plots suggested by Rock (1990) for the Subcommittee on Pyroxenes (see Fig. 2b and Fig. 3b), provided that the Golden Software's Grapher^{TM} is installed on the computer. Clinopyroxenes, in the four component system (i.e., $CaMgSi_2O_6$-$CaFeSi_2O_6$-$Mg_2Si_2O_6$-$Fe_2Si_2O_6$), can be classified on Poldervaart and Hess's (1951) ternary $CaSiO_3$ (wollastonite)-$MgSiO_3$ (clinoenstatite)-$FeSiO_3$ (clinoferrosilite) diagram (Fig. 5a). Pyroxenes within different compositions may be displayed on the Papike et al.'s (1974) ternary Ti-Na-Al^{IV} diagram (Fig. 5b) with variable solid solution components. All pyroxene analyses belonging to Ca-Mg-Fe, Ca-Na, and Na groups are automatically selected and plotted in each classification diagram by WinPyrox.

End-members, molar fractions and end-member activities

A number of calculation schemes has been proposed for the estimation of pyroxene end-member components (e.g., Yoder and Tilley 1962; Cawthorn and Collerson 1974; Dietrich and Petrakakis 1986; Harlow 1997). Although the order of recalculation of end-members is arbitrary, a scheme of end-member calculation should contain a minimum of uncertainties and errors. However, most calculation schemes are sequential and lead to an overestimation of the component that is calculated first.

The calculation procedure for pyroxene end-members by Yoder and Tilley (1962) starts with acmite, and thus may cause an overestimation of the acmite and the Ca-Tschermak's component when compared to the jadeite and ferri-Tschermak's components (e.g., see rows

58-62 in Table 5). On the other hand, the end-member calculation scheme proposed by Cawthorn and Collerson (1974) starts with jadeite and in this case, the jadeite and ferri-Tschermak's components may show higher values than the acmite and Ca-Tschermak's component (e.g., see rows 63-71 in Table 5). The end-member method based on a linear algebraic model by Dietrich and Petrakakis (1986) calculates 11 linearly independent components, including jadeite (Jd), acmite (Acm), Ureyite (Ur), Ti-Tschermakite (TiTs), Ca-Tschermakite (CaTs), Fe-Tschermakite (FeTs), Cr-Tschermakite (CrTs), pyroxmangite (Pm), ferrosilite (Fs), enstatite (En), and wollastonite (Wo). In these methods (e.g., Yoder and Tilley 1962; Cawthorn and Collerson 1974; Dietrich and Petrakakis 1986), acmite or jadeite is calculated first and may give an overestimation of that component. One attempt to solve this problem was proposed by Harlow (1997) that starts with the Ca-Tschermak's component (see rows 72-79 in Table 5). Except for the Dietrich and Petrakakis (1986) model, WinPyrox estimates all these end-member components (see rows 42-79 in Table 5) in the *Calculation Screen* window for pyroxenes (columns from 48 to 78). The program also gives end-members (e.g., Wo-En-Fs, Q-Jd-Aeg, Wo-Hyp-Jd, and Aug-Jd-Aeg in %) using the simple formula compiled by Soto and Soto (1995) in columns of 48-59 (see rows 42-57 in Table 5).

Estimation of molar fractions at different sites (e.g., $X^{Fe2+}{}_{M1}$, $X^{Fe2+}{}_{M1}$), end-members and their activities (e.g., a_{En}, a_{Di}) from microanalysis of rock-forming minerals are important parameters. These parameters are used in thermometric formulations for estimating the *P-T* conditions of magmatic and metamorphic rocks. WinPyrox calculates seven molar fractions (see rows 86-92 in Table 5) and seven end-member activities (see rows 93-99 in Table 5) of pyroxenes taking into account the formulations compiled by Soto and Soto (1995; see references therein). The

683 program calculates molar fractions and end-member activities of clinopyroxenes in the
684 *Calculation Screen* window between the column numbers of 85-91 and 96-102, respectively.
685 End-member activities such as a_{En} and a_{Di} given in the *Calculation Screen* window, at columns
686 111-112 and 185-186 for clino- and orthopyroxenes, respectively, are estimations following
687 Wood and Banno (1973), which are used in some of the two-pyroxene thermometers (e.g.,
688 Wood and Banno 1973; Carlson and Lindsley 1988; Sen and Jones 1989).

689 **Thermobarometry**

690 The main aim of this study is to recalculate and classify pyroxene analyses according to the
691 current IMA-88 nomenclature scheme, as well as enable the user to estimate widely used
692 pyroxene thermobarometers. The current program ignores in estimation of clino- and
693 orthopyroxene-liquid thermobarometers (e.g., Putirka et al. 1996; Putirka 1999; Putirka et al.
694 2003), but performs calculations for thirty five single-clinopyroxene, two-pyroxene, and Ca-in-
695 orthopyroxene thermobarometers. In order to test the program output, twenty four pyroxene
696 analyses were used from Putirka's (2008) Excel spreadsheet (i.e., Two-pyroxene *P-T*) and
697 selected clino- and orthopyroxenes are given in Table 6 and Table 7, respectively, with their
698 calculation/classification parameters and thermobarometers. In both Nimis' (1995, 1999) and
699 Putirka et al.'s (1996, 2003) models, clinopyroxene components are estimated based on the
700 numbers of cations on 6 six oxygen basis. In contrast to the Putirka et al.'s (1996, 2003)
701 models, the Nimis' (1995, 1999) model assumes cation fractions normalized to 4. Taking into
702 account Putirka's (2008) approach, pyroxene analyses in Table 6 and Table 7 are calculated
703 using the WinPyrox program by clicking *structural formulae* option from the pull-down menu of
704 *Normalization* and selecting *structural formulae without a total of 4 cations* option. Single-

clinopyroxene barometers in Table 6 (rows 42-48) are obtained by using the different calibrations proposed by Nimis (1995; see Eq. 1), Nimis and Ulmer (1998; see Eq. 5 and Eq. 7), Nimis (1999; see Eqs. 8 and 9), Nimis and Taylor (2000; see Eq. 10), and Putirka (2008; see Eq. 11).

Nimis (2000) presented an Excel spreadsheet (i.e., CpxBar) for quantitative pressure estimations of magmatic systems using clinopyroxene compositions. The spreadsheet considers cation fractions that are normalized to 4 and presents four different pressure (kbar) calibrations for: i) anhydrous melts from basalt to low alkali nephelinites (i.e., *P*BA; see Eq. 5), ii) hydrous melts from basalt to low alkali nephelinites (i.e., *P*BH; see Eq. 7), iii) the tholeiitic series from basalt to dacite (i.e., *P*TH; see Eq. 8), and iv) the mildly alkaline series from basalt to dacite (i.e., *P*MA; see Eq. 9) which requires *T* (^{o}C) as an input value. Using Putirka's (2008) clinopyroxene data for different normalization and ferric iron estimation methods, the comparison of CpxBar (see rows 2-5 in Table 8) those with the WinPyrox's outputs (see rows 6-21 in Table 8) are given in Table 8. This table shows that for the selected clinopyroxene data set there is no distinctive *P* (kbar) variation between normalization procedures and ferric iron estimation methods. Correlation coefficients (*r*) for pressures from CpxBar vs. WinPyrox range from 0.99 to 0. 86 (see Fig. 6).

Clinopyroxene barometers for magmatic rocks based on the crystal-structure modeling (e.g., Nimis 1995, 1999; Nimis and Ulmer 1998) can be plotted in several V_{Cell} vs. V_{M1} diagrams. These plots are displayed by WinPyrox from the pull-down menu of *Graph* in the *Calculation Screen*. The user, for example, can display six different barometer plots for clinopyroxenes based on the

empirical expressions by clicking first *Miscellaneous Plots* and then selecting one of six Vcell-VM1 diagrams. The Al^{VI}/Al^{IV} ratio in clinopyroxenes from a variety of petrological environments increases with increasing pressure values (Bondi et al. 2002). Accordingly, aluminium content in the Al^{VI} vs. Al^{IV} diagram (after Aoki and Shiba 1973) can be used to estimate qualitatively the pressure condition of crystallization. WinPyrox allows the user to display this plot from the pull-down menu of *Graph* in the *Calculation Screen* by clicking first *Miscellaneous Plots* and then selecting the Al(VI)-Al(IV) Diagram option.

Following Putirka's (2008) approach, including ferric iron estimation based on Papike et al. (1974) and total cations without normalization to 4, a comparison of two-pyroxene thermobarometry is given in Table 7 (see rows 42-64 and 67-86). Except for a few data points in some of the two-pyroxene thermometers, all lie in a straight line with the high correlation coefficients ($r \geq 0.96$). This is evidence of the good relationship between the Putirka's (2008) model and WinPyrox's outputs. Using different ferric iron estimation methods (e.g., Papike et al. 1974; Droop 1987) and normalization procedures (e.g., cations total to 4 and without normalization to 4) by WinPyrox program for Putirka's (2008) model together with selected pyroxene data display a slight difference, but not an important variation in P (kbar) and T (^{o}C) values. In this study, a calibrated and improved formulation of the Nimis (1995) model proposed by Putirka (2008; i.e., Eq. 32a) is also tested against Nimis (1995), Nimis and Ulmer (1998), and Nimis (1999) models. High correlation coefficients between $PN_{95\text{-}BS\text{-}Cpx}$ and $PP_{08\text{-}Cpx(Eq.\ 32a)}$ and $PNU_{98\text{-}BA\text{-}Cpx}$ and $PP_{08\text{-}Cpx(Eq.\ 32a)}$ ($r = 0.94$) decrease to $r = 0.59$ for the $PNU_{98\text{-}Cor\text{-}BH\text{-}Cpx}$ vs. $PP_{08\text{-}Cpx(Eq.\ 32a)}$ relationship . Although Putirka's (2008; see Eq. 11) model improves the precision of Nimis (1995) model and yields a high correlation coefficient ($r = 0.94$) through the

Nimis and Ulmer (1998; see Eq. 5) method for anhydrous melts from basalt to low-alkali nephelinites, it still preserves the systematic error with respect to hydrous experiments. The low correlation coefficient (i.e., r = 0.59) between the Putirka (2008; i.e., Eq. 32a) and Nimis and Ulmer (1998; see Eq. 7) models for hydrous melts from basalt to low-alkali nephelinites, thus is consistent with the anhydrous to hydrous components.

Graphical two-pyroxene thermometry

Lindsley and Andersen (1983) and Lindsley (1983) proposed graphical, two-pyroxene thermometers based on experimentally determined Ca-Mg-Fe pyroxene phase relations at 800 ^{o}C-1200 ^{o}C and 1 atm to 15 kbar for the Di-En and Hd-Fs joins. The diagrams should be applied to nearly pure quadrilateral pyroxenes (e.g.,Wo+En+Fs > 98%). The graphical two-pyroxene thermometers are commonly used for the augite-orthopyroxene, augite-pigeonite, and pigeonite-orthopyroxene pairs. The graphical two-pyroxene thermometers also give a minimum T (^{o}C) for the formation of single pyroxenes. From the pull-down menu of *Graphical pyroxene thermometry* in the *Data Entry Screen* of WinPyrox, the program allows the user to select an option of clinopyroxene components for augite and pigeonite. Clinopyroxene components in the Di-Hd-En-Fs quadrilateral can also be displayed by selecting options of Wo-En-Fs end-members from the pull-down menu of *Graphical pyroxene thermometry* in the *Data Entry Screen*. If any of these options from the menu of *Graphical pyroxene thermometry* is not selected by the user, the program automatically calculates the clinopyroxene components based on the augite option according to the estimation procedures proposed by Lindsley (1983). WinPyrox, thus allows the user to display graphical two-pyroxene thermometers from

the pull-down menu of *Graph* in the *Calculation Screen* by clicking first *Graphical Two-Pyroxene Thermometry* and then selecting one of four Di-Hd-En-Fs Quadrilateral diagrams.

SUMMARY AND AVAILABILITY OF THE PROGRAM

WinPyrox is a user-friendly package for pyroxene analyses, which is developed for personal computers running in the Windows operating system. The program calculates structural formulae of multiple clino- and orthopyroxene analyses, obtained both from wet-chemical and electron-microprobe techniques, using different normalization and ferric iron estimation methods. Calculation and classification of each pyroxene analysis are carried out according to the IMA-88 nomenclature. The program generates two main windows. The first window (i.e., *Data Entry Screen*) appears on the screen with several pull-down menus and equivalent shortcuts. By selecting options or clicking buttons on the start-up screen, the user can enter/load pyroxene analyses into the data entry section and make necessary arrangements for a desired calculation scheme. The second window (i.e., *Calculation Screen*) allows the user to display the structural formulae in the *T*, *M1*, and *M2* sites with pyroxene classification parameters, including groups, names and modifiers. In the *Calculation Screen*, the program also gives end-member calculations, Fe^{2+}-Mg partitioning, molar fractions, end-member activities, component activities, and single-clinopyroxene and two-pyroxene thermobarometers. All the estimated pyroxene data in the *Calculation Screen* can be sent to a Microsoft® Excel file (i.e., output.xlsx) and then this file can be used for further data manipulation and graphing purposes.

When compared to the earlier published DOS-based PYROX (Yavuz 2001) program, the present software has additional features, including a better graphical user interface and

interaction for the visual programming environment. WinPyrox classifies recalculated pyroxene analyses in six binary and ternary pyroxene classification diagrams, which can be viewed and printed by the commercial program, Grapher™, available from Golden software. These plots appear on the screen by clicking *Classification Diagrams* option from the pull-down menu of *Graph* in the *Calculation Screen*. The program also allows the user to display four quadrilateral graphical two-pyroxene thermometers and eight binary barometer diagrams based on clinopyroxene data, by clicking *Graphical Two-Pyroxene Thermometry* and *Miscellaneous Plots* options from the pull-down menu of *Graph*, respectively.

WinPyrox is a compiled program that consists of a self-extracting setup file. If the Microsoft® Visual Studio package is not installed on the computer, all the necessary support files used by program are added to the installation file. The program and its associated files are installed into the directory of ''C:\Program Files\WinPyrox'' during the installation process. The self-extracting setup file is approximately 11 Mb and may be downloaded from http://code.google.com/p/winpyrox/ or can be obtained from author on request.

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Figure List

Figure 1. The *Q-J* diagram used for classification of pyroxenes (after Morimoto et al. 1988). Data used in this figure are taken from Rock (1990).

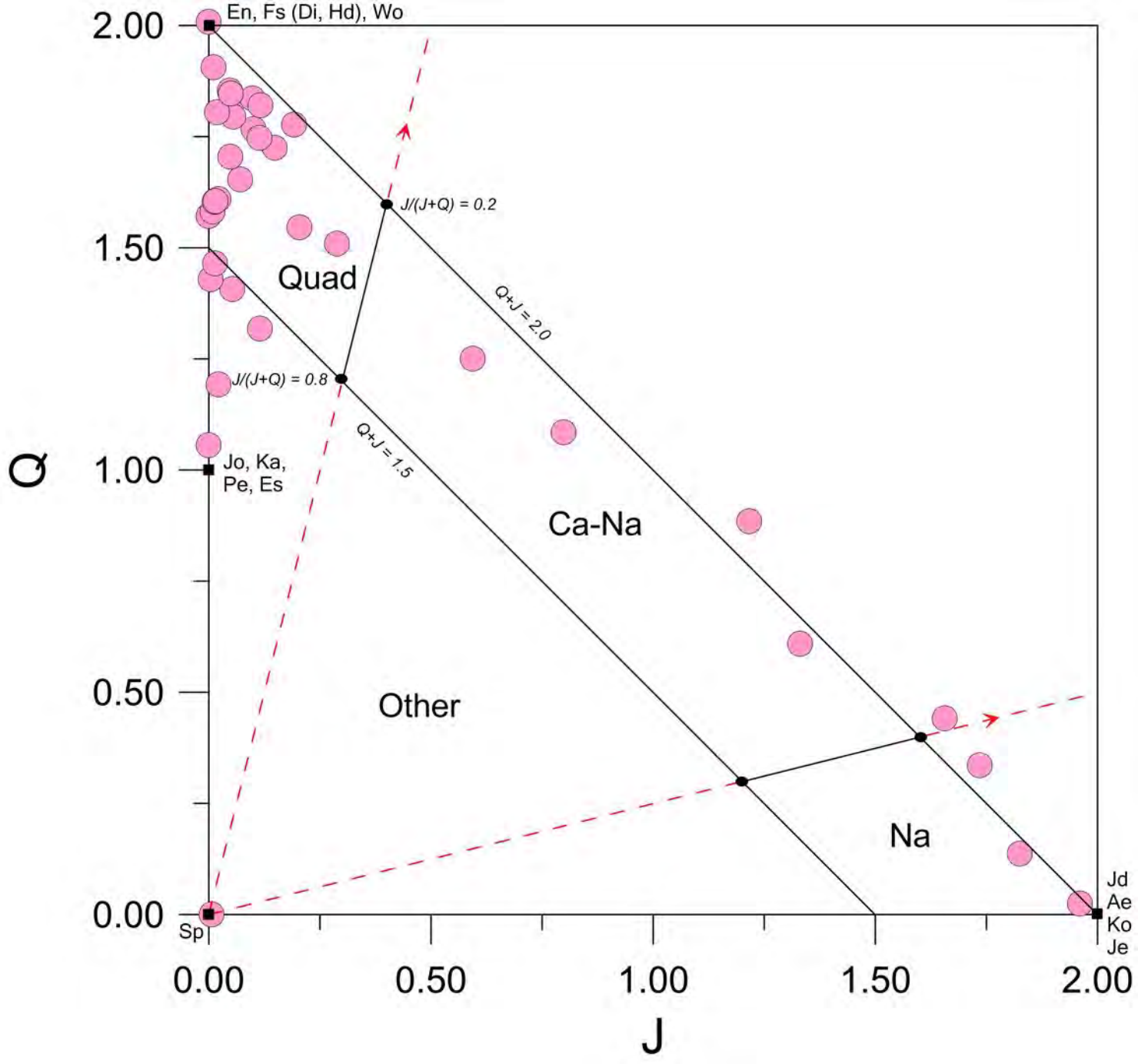
Figure 2. (a) Plot of Ca-Mg-Fe pyroxenes in the Wo-En-Fs ternary diagram (after Morimoto et al. 1988). (b) Classification of Ca-Mg-Fe pyroxenes in the Wo-En-Fs ternary diagram (after Rock 1990). Data used in these figures are taken from Rock (1990).

Figure 3. (a) Plot of Ca-Na and Na pyroxenes in the Q-Jd-Ae ternary diagram [after Morimoto et al. 1988). (b) Classification of Ca-Na and Na pyroxenes in the Q-Jd-Ae ternary diagram (after Rock 1990). Data used in these figures are taken from Rock (1990).

Figure 4. (a) Screenshot of the WinPyrox *Data Entry Screen* showing data edits of pyroxene analyses. (b) *Calculation Screen* window for WinPyrox program displaying results of estimated pyroxene analyses.

Figure 5. (a) Classification of clinopyroxenes in the system $CaMgSi_2O_6$-$CaFeSi_2O_6$-$Mg_2Si_2O_6$-$Fe_2Si_2O_6$ (after Poldervaart and Hess 1951). (b) Plot of clinopyroxenes in the Ti–Na–Al^{IV} (*apfu*) ternary diagram (after Papike et al. 1974). Data used in these figures are taken from Putirka (2008).

Figure 6. Comparison of single-clinopyroxe barometers (kbar) of (a) BA = anhydrous melts from basalt through trachybasalt, basanite, tephrite to low-alkali nephelinites (after Nimis and Ulmer 1998), (b) BH = hydrous melts from basalt through trachybasalt, basanite, tephrite to low-alkali nephelinites (after Nimis and Ulmer 1998), (c) TH = tholeiitic series from basalt to dacite (after Nimis 1999), (d) MA = mildly alkaline series from alkali basalt to trachyandesite, including mildly alkaline and transitional melts of the shoshonitic series (after Nimis 1999). Data used in these figures are taken from Putirka (2008).


En, Fs (Di, Hd), Wo
2.00
1.50
1.00
0.50
0.00
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Q+J = 2.0
Quad
J/(J+Q) = 0.8
Q+J = 1.5
Jo, Ka,
Pe, Es
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Other
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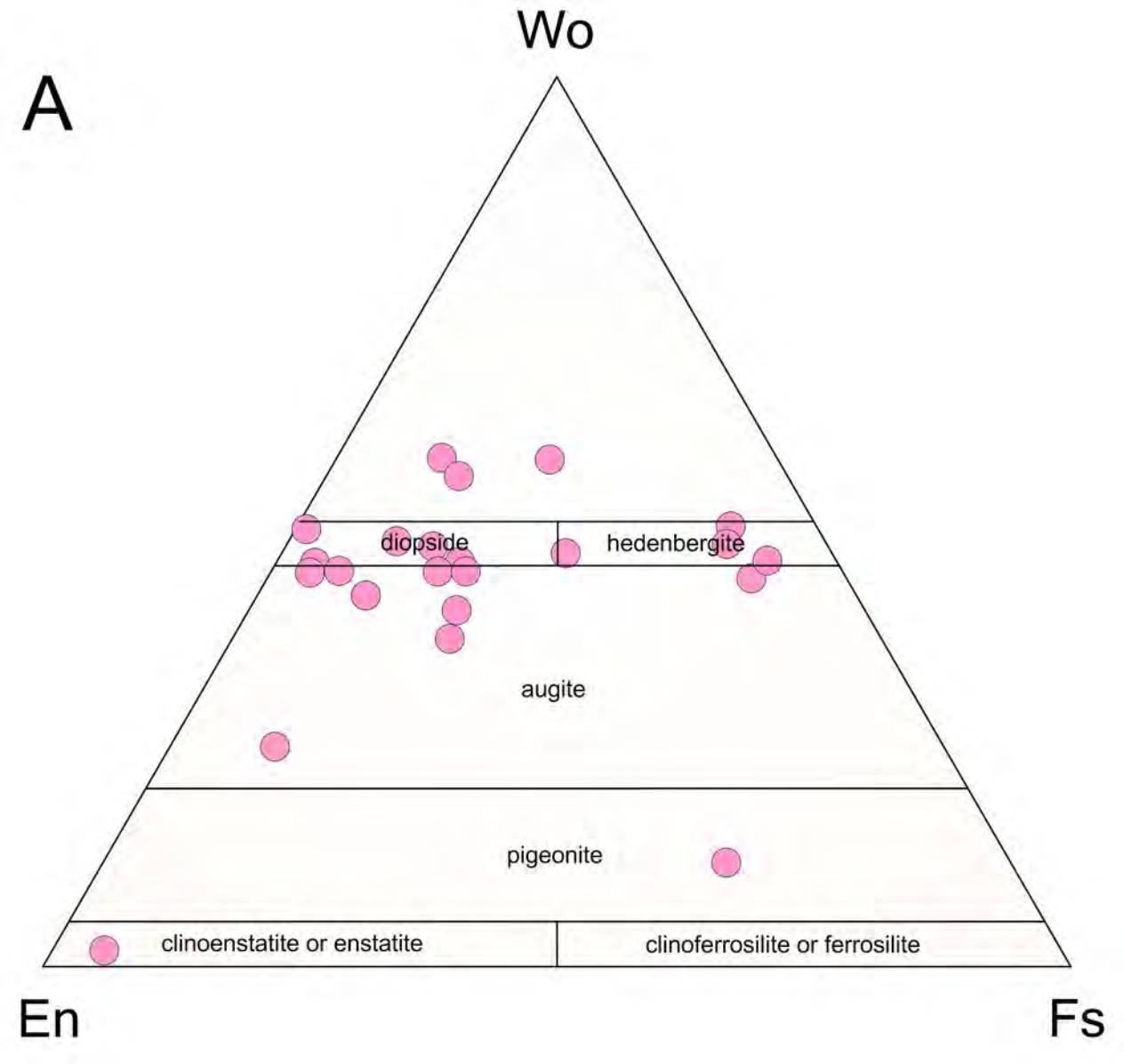
Wo
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En
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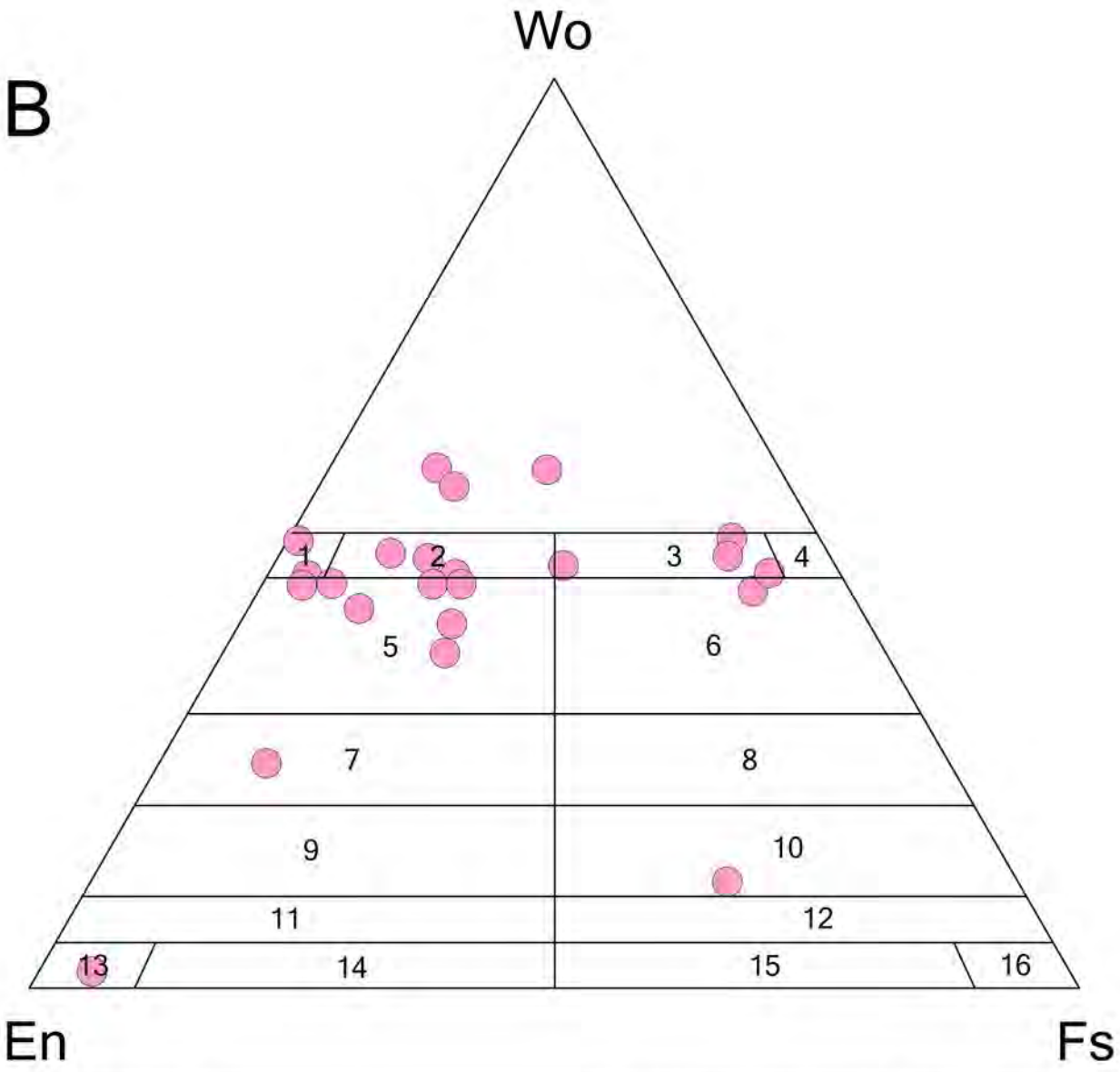
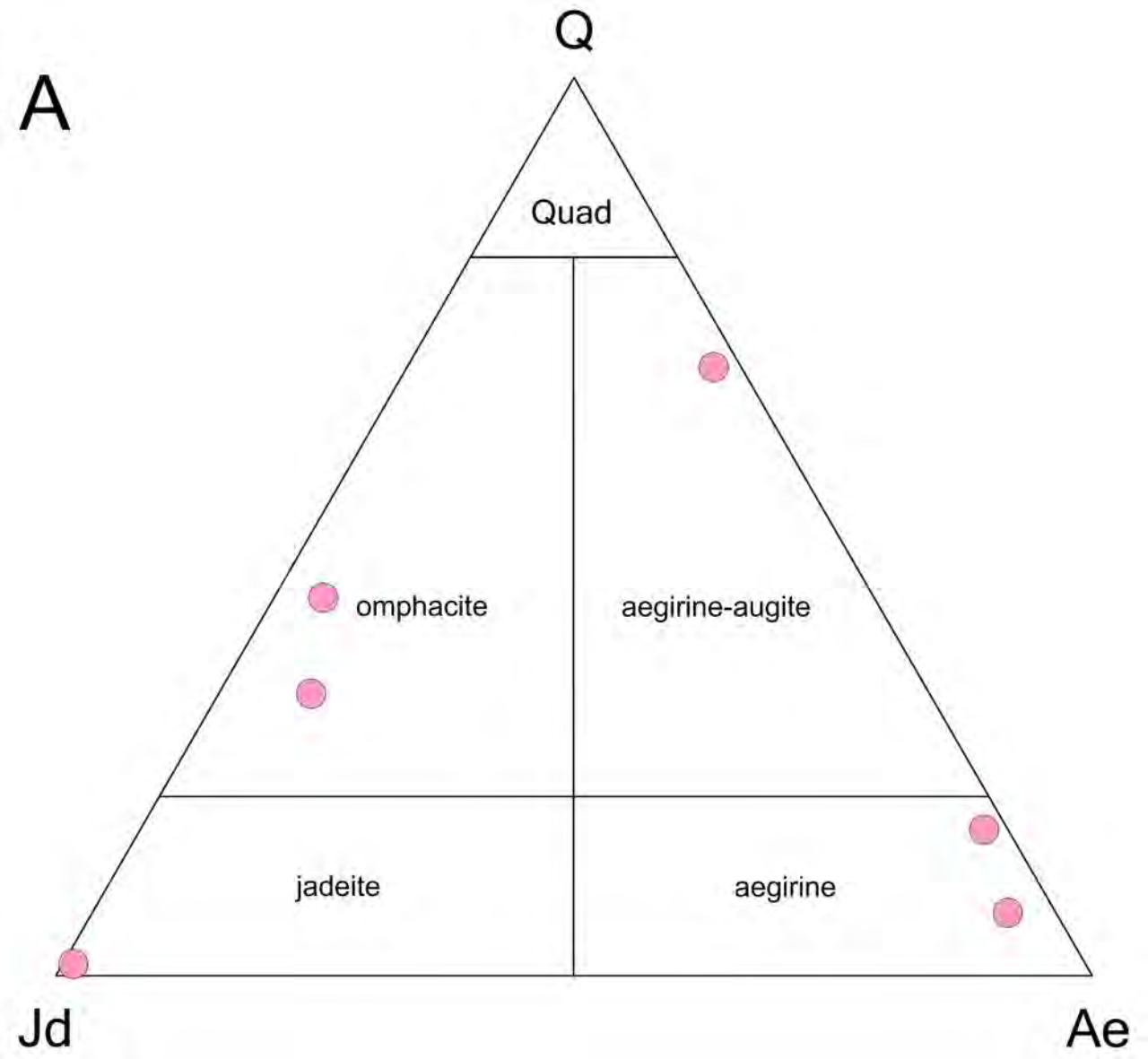


1 = Diopside
2 = Ferroan diopside
3 = Magnesian hedenbergite
4 = Hedenbergite
5 = [Magnesium-rich] Augite
6 = [Iron-rich] Augite
7 = [Subcalcic magnesium-rich] Augite
8 = [Subcalcic iron-rich] Augite
9 = Calcian (magnesium-rich) Pigeonite
10= Calcian (iron-rich) Pigeonite
11= (Magnesium-rich) Pigeonite
12= (Iron-rich) Pigeonite
13= (Clino) Enstatite
14= Ferroan (Clino) Enstatite
15= Magnesian Clino (Ferrosilite)
16= (Clino) Ferrosilite


Q
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Quad
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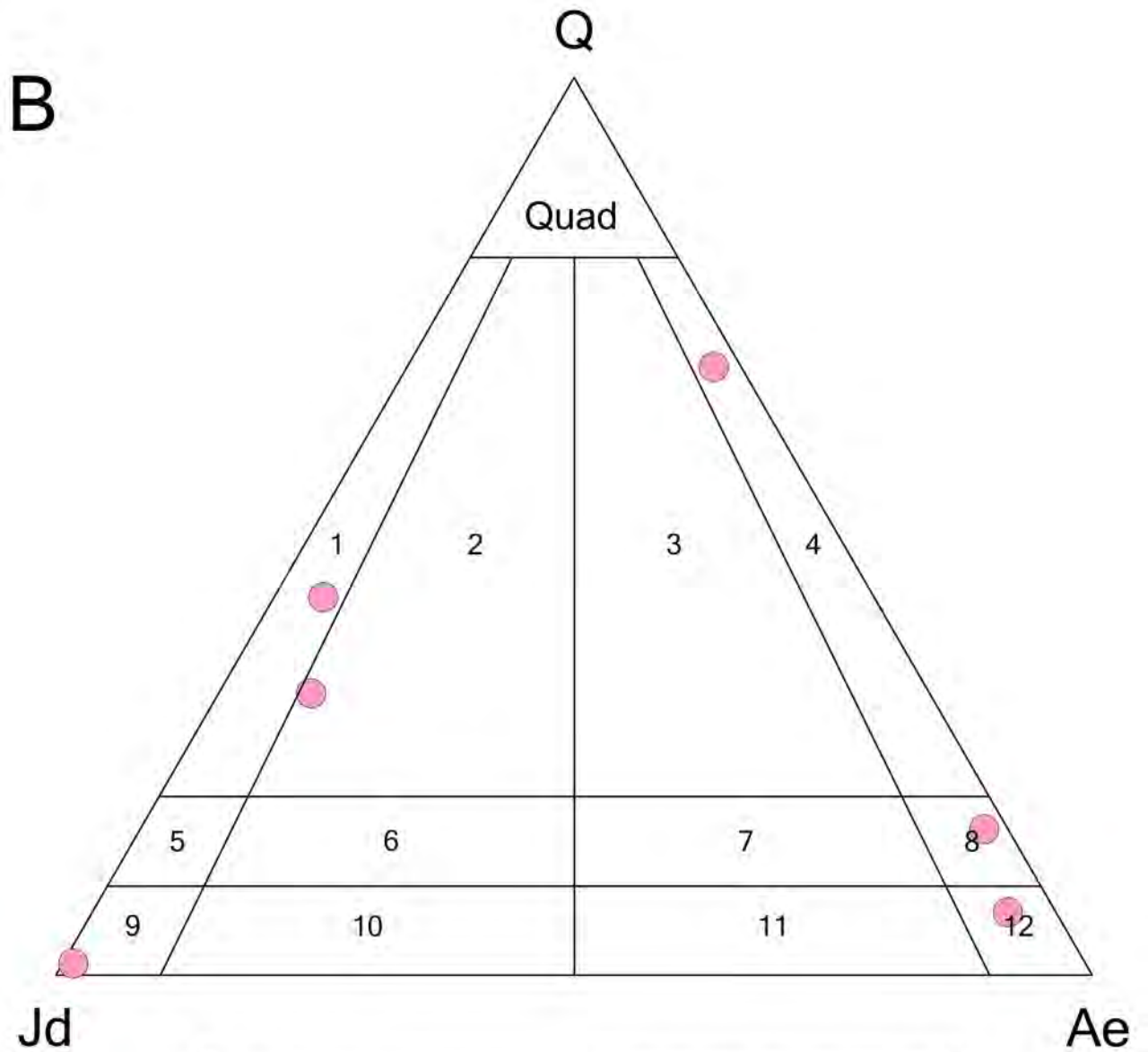
aegirine-augite
jadeite
aegirine
Jd
Ae



1 = Omphacite
2 = Ferrian omphacite
3 = Aluminian aegirine-augite
4 = Aegirine-augite
5 = Calcian jadeite
6 = Calcian ferrian jadeite
7 = Calcian aluminian aegirine
8 = Calcian aegirine
9 = Jadeite
10 = Ferrian jadeite
11 = Aluminian aegirine
12 = Aegirine

WinPyrox

File Edit Normalization Ferric iron estimation Graphical pyroxene thermometry Mg-Fe order-disorder Calculate About Help

A

A Windows Program for Pyroxene Calculation Classification (IMA-1988) and Thermobarometry

Data Entry Screen

Row No	Sample	SiO2 [c]	TiO2 [c]	Al2O3 [c]	V2O3 [c]	Cr2O3 [c]	Fe2O3 [c]	FeO [c]	MnO [c]	NiO [c]	CoO [c]	ZnO [c]	MgO [c]	CaO [c]	Na2O [c]	K2O [c]	ZrO2 [c]	Sc2O3 [c]	Li2O [c]
1	clino1	52.3	0.7	3		0.58		5.1	0.11				16.6	21.5	0.33				
2	clino2	51.7	0.28	8.38		0.05		6.69	0.15				21.4	11.7	0.64				
3	clino3	51.5	0.45	8.1		0.09		6.96	0.17				20.3	12.6	0.56				
4	clino4	51.06	0.62	3.16		0.01		6.18	0.12				15.78	20.82	0.27				
5	clino5	53.32	0.48	2.25		0.12		5.92	0.15				16.91	20.73	0.28				
6	clino6	51.58		7.28		1.2		3.75					19.55	15.94	0.7				
7	clino7	51.12	0.1	8.07		1.16		3.57					17.95	17.26	0.77				
8	clino8	52.5		5.19		1.45		4.12					21.28	15.45					
9	clino9	51.8	0.17	5.1		1.58		4.6	0.19				21.5	14.9	0.21				
10	clino10	51.67	0.16	5.62		1.56		4.45	0.16				21.82	14.34	0.22				
11	clino11	53	0.11	4.5		1.5		5.1	0.2				24.7	10.9	0.16				
12	clino12	51.64	0.38	8.16		0.75		3.97					19.66	14.85	0.66				
13	clino13	51.3	0.19	7.2		0.5		3.9	0.09				17.6	19.1	0.5				
14	clino14	52.4	0.14	6		0.9		4.1	0.08				19.4	17.6	0.49				
15	clino15	52	0.14	9.39		0.09		4.89	0.06				20.8	13.3	0.69				
16	clino16	52.9	0.35	7.4		0.12		5.2	0.17				23.1	11.6	0.55				
17	clino17	51.3	0.53	9.15		0.08		7.15	0.19				20.6	10.8	0.93				
18	clino18	51.5	0.49	8.97		0.08		6.53	0.18				20.09	11.1	0.74				
19	clino19	50.93	0.81	9.02		0.34		5.82					18.51	13.34	1.23				
20	clino20	51.63	0.4	8.59		0.29		6.96					21.39	9.76	0.97				
21	clino21	51.39	0.83	9.38		0.15		7.57					19.55	9.49	1.64				
22	clino22	54.68		2.65		1.76		4.39	0.12				26.41	9.15	0.09				
23	clino23	52.98	0.14	5.04		1.36		3.48	0.11				19.61	17.76	0.23				
24	clino24	53.77	0.11	4.31		1.51		3.6	0.11				20.51	16.95	0.23				
25																			

C:\Program Files\WinPyrox\Putirka_2008.pyx 11:38 28.12.2012 by

WinPyrox

Edit Excel Graph About Help

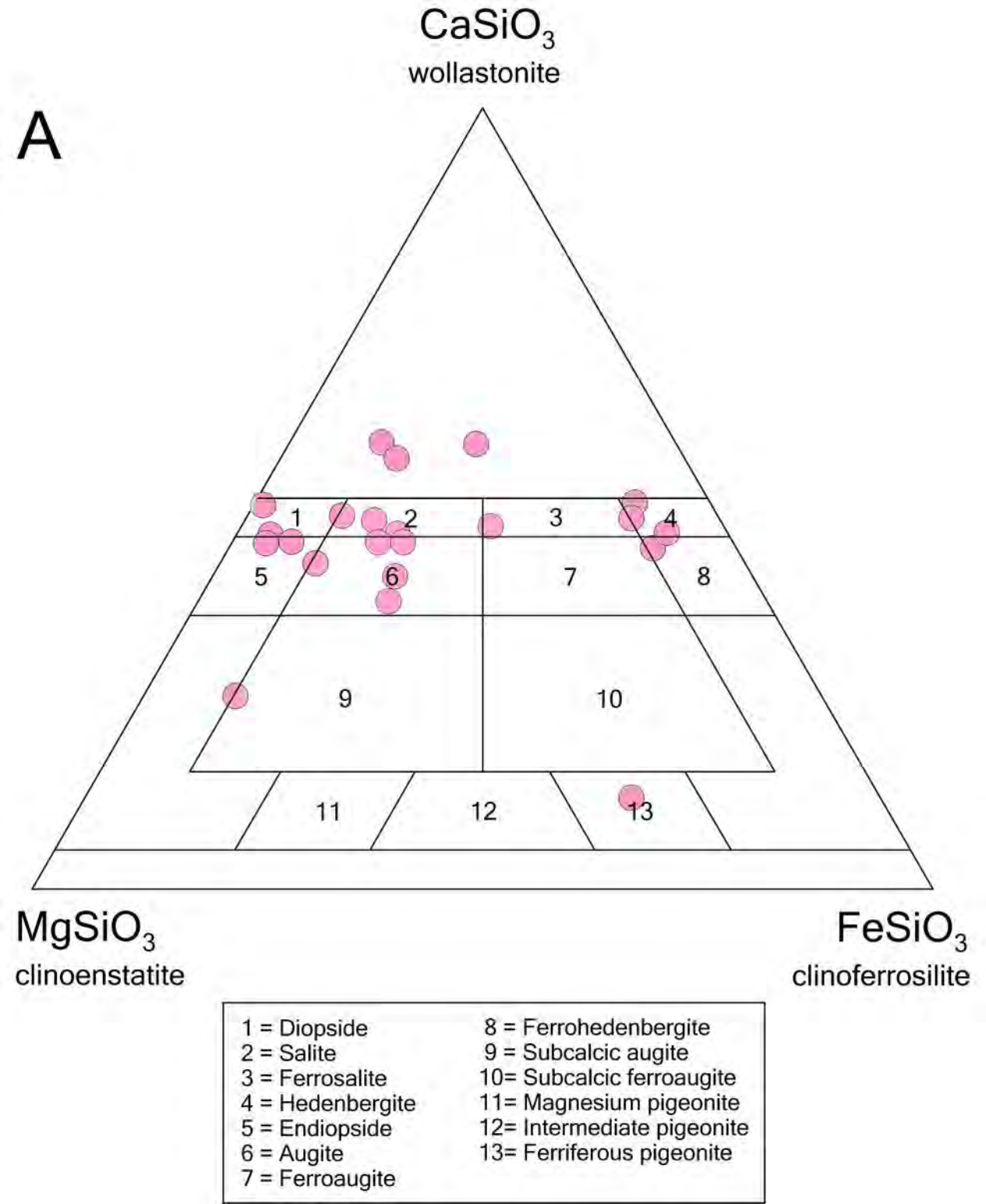
B

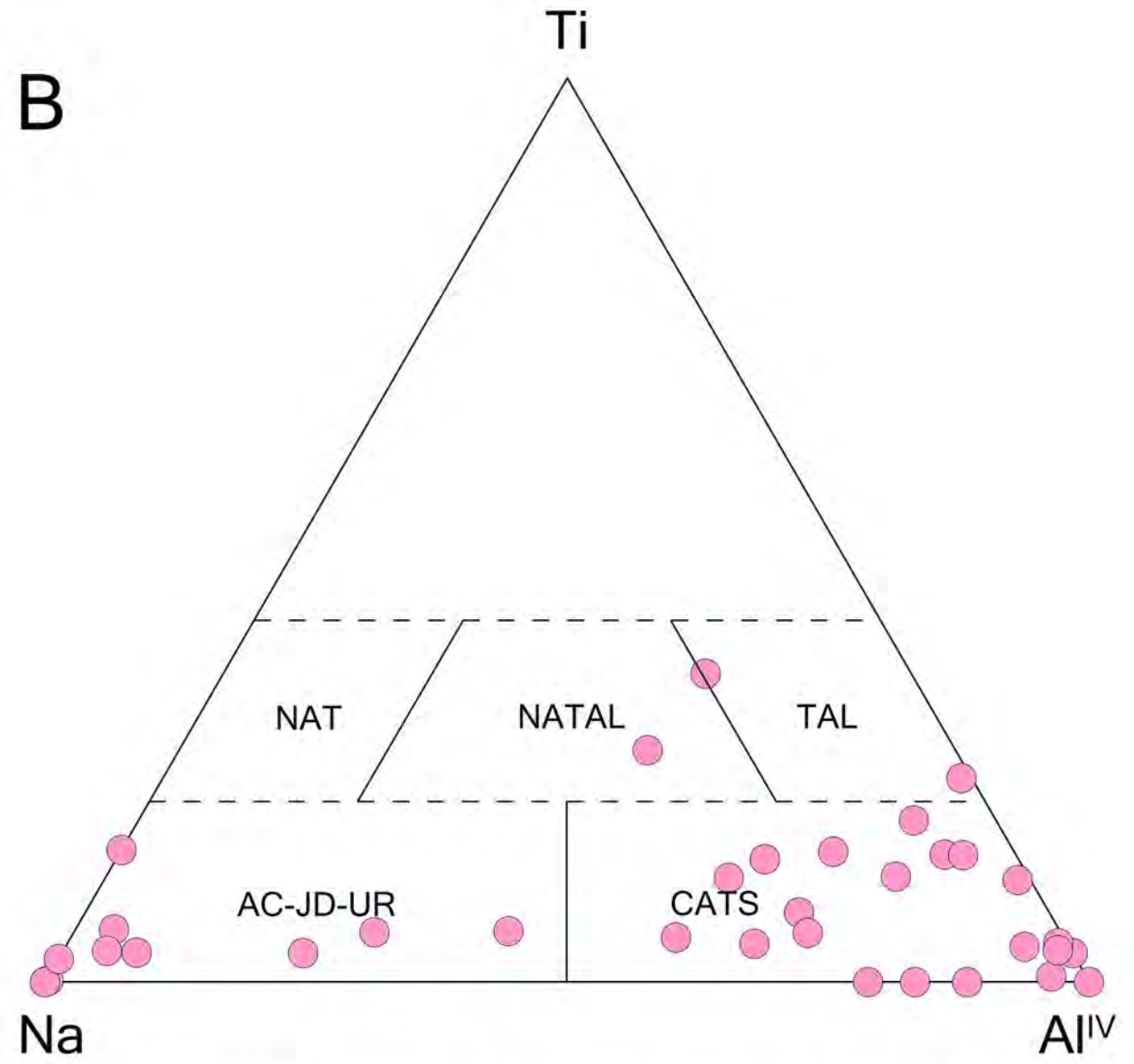
A Windows Program for Pyroxene Calculation Classification (IMA-1988) and Thermobarometry

Calculation Screen

	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127
Sample	[PN95-BS	PNU98-BA	PNU98-BH	PN99-TH	PN99-MA	PNT00	'08Eq32a](kl	[TBM85/86	TNT00	TP08Eq32d	TDN82	TMZ91](oC)	[Pyx. Group	Pyx. Name]	[Modifiers]
dino1	1.31	1.22		21.89	24.97	0.35		1156	993	1202	879	900	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino2	15.94	17.62	11.79	18.52	22.93	14.54	15.45	1476	1357	1325	648	875	Ca-Mg-Fe p	AUGITE	Aluminian
dino3	14.81	16.25	15.24	15.57	20.10	17.28	16.18	1461	1333	1313	677	877	Ca-Mg-Fe p	AUGITE	Aluminian
dino4	1.03	0.94	12.95	11.22	15.22		4.39	1161	998	1171	873	899	Ca-Mg-Fe p	AUGITE	Aluminian
dino5	0.90	0.87	11.00	8.85	12.34	20.46	2.91	1193	1052	1179	852	895	Ca-Mg-Fe p	AUGITE	
dino6	13.41	14.51	12.47	9.46	12.10	25.19	17.48	1405	1312	1345	810	890	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino7	13.91	14.87	13.71	9.98	12.17	22.87	16.49	1371	1255	1335	850	896	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino8	9.23	10.20	11.02	8.09	10.40	27.61	11.77	1404	1345	1295	711	879	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino9	9.02	10.01	9.97	7.52	9.76	28.28	12.15	1414	1337	1298	720	880	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino10	10.14	11.28	11.07	8.63	11.03	26.71	11.73	1423	1352	1300	703	879	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino11	10.44	12.18	13.52	11.29	14.83	29.73	11.46	1474	1397	1298	390	865	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino12	15.07	16.34	15.48	11.99	15.16	22.72	17.36	1428	1319	1329	782	887	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino13	10.53	11.15	14.66	10.61	13.19	18.31	9.53	1310	1185	1302	867	899	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino14	9.88	10.61	13.39	9.53	11.84	23.82	10.35	1363	1260	1310	822	891	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino15	17.45	19.09	16.33	12.21	14.99	19.29	21.75	1462	1376	1371	728	881	Ca-Mg-Fe p	AUGITE	Aluminian
dino16	14.98	16.77	18.81	14.58	18.35	19.24	15.15	1481	1386	1342	589	872	Ca-Mg-Fe p	AUGITE	Aluminian
dino17	18.01	19.81	22.40	17.33	21.85	14.95	16.31	1490	1342	1321	655	876	Ca-Mg-Fe p	AUGITE	Aluminian
dino18	17.94	19.69	23.43	17.87	22.82	15.61	16.60	1487	1337	1315	663	877	Ca-Mg-Fe p	AUGITE	Aluminian
dino19	17.45	18.87	23.55	17.42	22.07	18.51	17.31	1448	1280	1307	785	887	Ca-Mg-Fe p	AUGITE	Aluminian
dino20	18.34	20.35	23.32	17.58	22.66	22.82	21.31	1513	1372	1358	576	872	Ca-Mg-Fe p	AUGITE	Aluminian
dino21	20.86	22.86		20.02	25.45	18.95	21.14	1517	1317	1340	678	878	Ca-Mg-Fe p	AUGITE	Aluminian Sodian
dino22	9.76	11.81	18.08	15.39	21.29	37.04	14.12	1501	1407	1295		857	Ca-Mg-Fe p	PIGEONITE	Aluminian Calcian Chromian Ferroan Magnesian
dino23	8.41	9.06	13.01	9.89	13.91	27.00	9.73	1355	1269	1289	806	889	Ca-Mg-Fe p	AUGITE	Aluminian Chromian
dino24	8.06	8.78	9.78	7.16	10.05	30.12	11.17	1379	1295	1290	773	885	Ca-Mg-Fe p	AUGITE	Aluminian Chromian

C:\Program Files\WinPyrox\Putirka_2008.pyx | 6 oxygen | without 4 cations | Papike et al. (1974) | Augite | 11:45 | 28.12.2012


A
CaSiO3
wollastonite
1
2
3
4
5
6
7
8
9
10
11
12
13
MgSiO3
clinoenstatite
FeSiO3
clinoferrosilite
1 = Diopside
2 = Salite
3 = Ferrosalite
4 = Hedenbergite
5 = Endiopside
6 = Augite
7 = Ferroaugite
8 = Ferrohedenbergite
9 = Subcalcic augite
10= Subcalcic ferroaugite
11= Magnesium pigeonite
12= Intermediate pigeonite
13= Ferriferous pigeonite

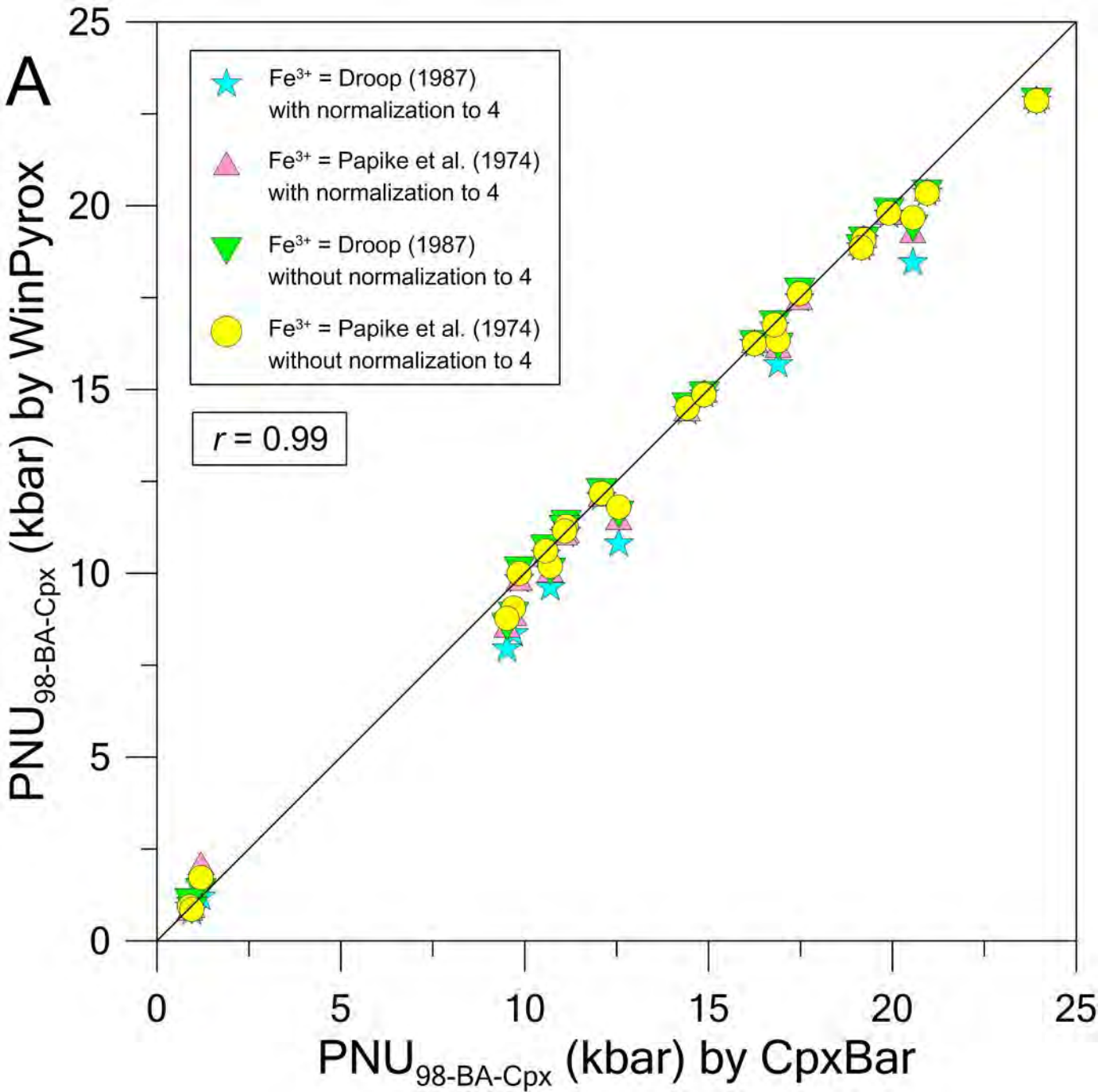


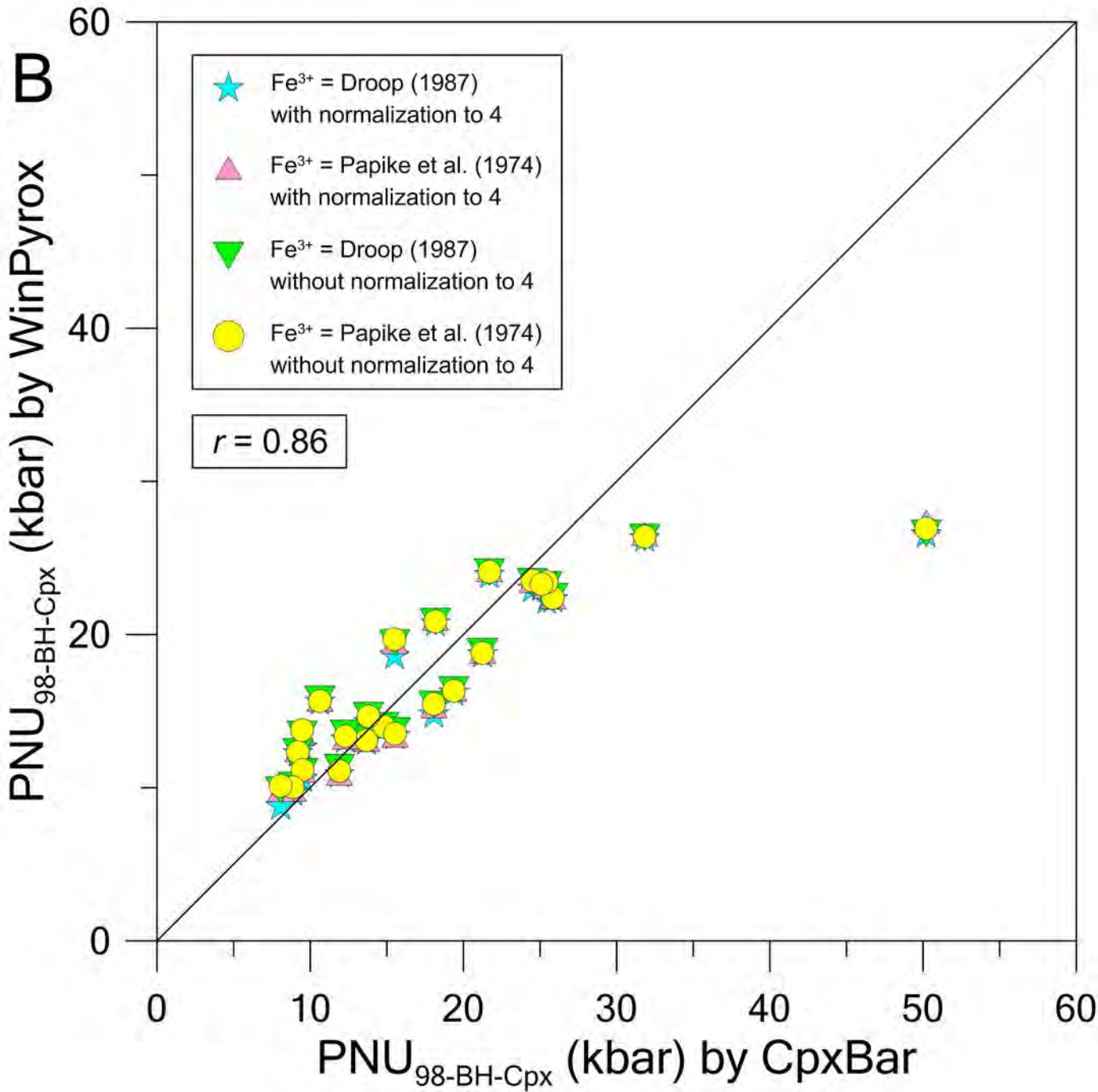
NAT = $NaTi_{0.5}R^{2+}{}_{0.5}Si_2O_6$ NATAL = $NaTiSiAlO_6$

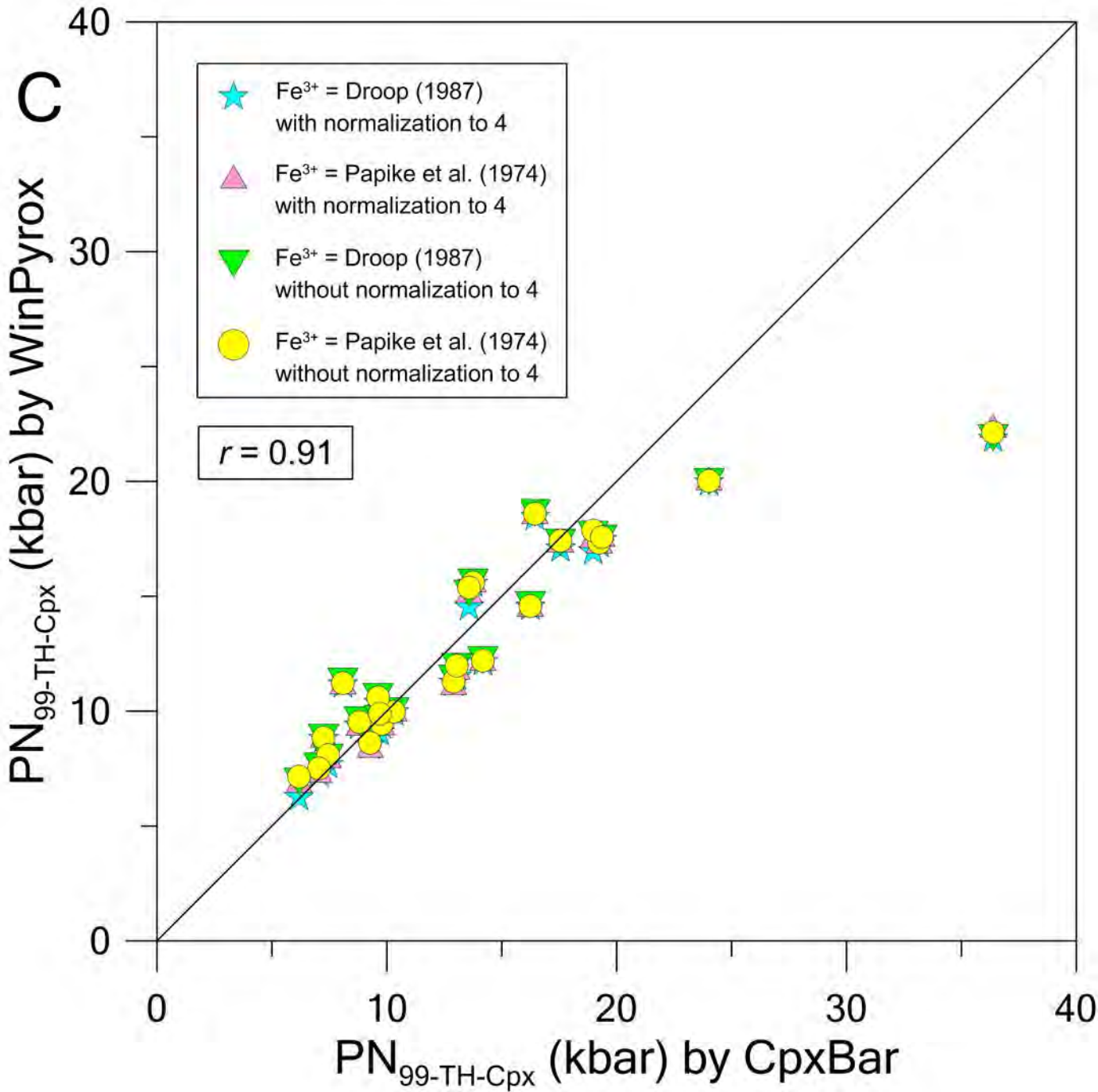
TAL = $CaTiAl_2O_6$ AC = $NaFeSi_2O_6$

JD = $NaAlSi_2O_6$ UR = $NaCrSi_2O_6$

CATS = $CaAlAlSiO_6$ and $CaFeAlSiO_6$


A
Fe3+ = Droop (1987)
with normalization to 4
Fe3+ = Papike et al. (1974)
with normalization to 4
Fe3+ = Droop (1987)
without normalization to 4
Fe3+ = Papike et al. (1974)
without normalization to 4
r = 0.99
PNU98-BA-Cpx (kbar) by WinPyrox
PNU98-BA-Cpx (kbar) by CpxBar
0
5
10
15
20
25


B
Fe3+ = Droop (1987)
with normalization to 4
Fe3+ = Papike et al. (1974)
with normalization to 4
Fe3+ = Droop (1987)
without normalization to 4
Fe3+ = Papike et al. (1974)
without normalization to 4
r = 0.86
PNU98-BH-Cpx (kbar) by WinPyrox
PNU98-BH-Cpx (kbar) by CpxBar
0
10
20
30
40
50
60


C
Fe3+ = Droop (1987)
with normalization to 4
Fe3+ = Papike et al. (1974)
with normalization to 4
Fe3+ = Droop (1987)
without normalization to 4
Fe3+ = Papike et al. (1974)
without normalization to 4
r = 0.91
PN99-TH-Cpx (kbar) by WinPyrox
PN99-TH-Cpx (kbar) by CpxBar
0
10
20
30
40

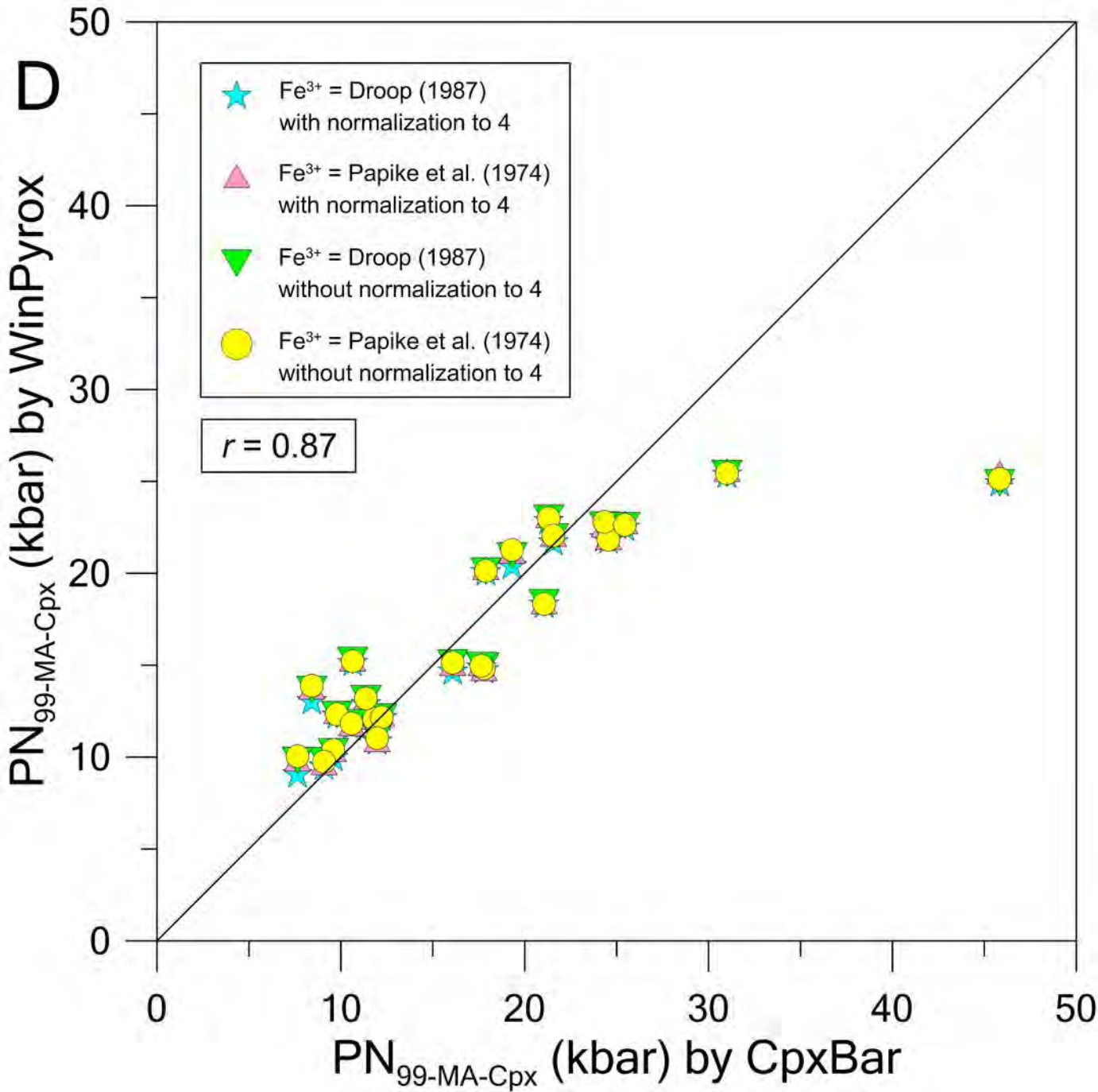

D
Fe3+ = Droop (1987)
with normalization to 4
Fe3+ = Papike et al. (1974)
with normalization to 4
Fe3+ = Droop (1987)
without normalization to 4
Fe3+ = Papike et al. (1974)
without normalization to 4
r = 0.87
PN99-MA-Cpx (kbar) by WinPyrox
PN99-MA-Cpx (kbar) by CpxBar
0
10
20
30
40
50

Table 1. IMA-accepted pyroxene mineral names and their chemical subdivisions (from Morimoto et al. 1988)

	Mineral Names	Composition as End-member	Main Composition as Solid Solution	Space Group
	I. Mg-Fe Pyroxenes			
1	Enstatite (En)[1]	$Mg_2Si_2O_6$	$(Mg, Fe)_2Si_2O_6$	Pbca
2	Ferrosilite (Fs)[2]	$Fe^{2+}{}_2Si_2O_6$		
3	Clinoenstatite		$(Mg, Fe)_2Si_2O_6$	$P2_1/c$
4	Clinoferrosilite			
5	Pigeonite		$(Mg, Fe, Ca)_2Si_2O_6$	$P2_1/c$
	II. Mn-Mg Pyroxenes			
6	Donpeacorite		$(Mn, Mg)MgSi_2O_6$	Pbca
7	Kanoite (Ka)[3]	$MnMgSi_2O_6$	$(Mn, Mg)MgSi_2O_6$	$P2_1/c$
	III. Ca Pyroxenes			
8	Diopside (Di)[4]	$CaMgSi_2O_6$	$Ca(Mg, Fe)Si_2O_6$	C2/c
9	Hedenbergite (Hd)[5]	$CaFe^{2+}Si_2O_6$		
10	Augite		$(Ca, Mg, Fe)_2Si_2O_6$	C2/c
11	Johannsenite (Jo)[6]	$CaMnSi_2O_6$		C2/c
12	Petedunnite (Pe)[7]	$CaZnSi_2O_6$		C2/c
13	Esseneite (Es)[8]	$CaFe^{3+}AlSiO_6$		C2/c
	IV. Ca-Na Pyroxenes			
14	Omphacite		$(Ca,Na)\ (R^{2+}, Al)Si_2O_6$	C2/c, P2/n
15	Aegirine-augite		$(Ca,Na)\ (R^{2+}, Fe^{3+})Si_2O_6$	C2/c
	V. Na Pyroxenes			
16	Jadeite (Jd)[9]	$NaAlSi_2O_6$	$Na(Al, Fe^{3+})Si_2O_6$	C2/c
17	Aegirine (Ae)[10]	$NaFe^{3+}Si_2O_6$		
18	Kosmochlor (Ko)[11]	$NaCr^{3+}Si_2O_6$		C2/c
19	Jervisite (Je)[12]	$NaSc^{3+}Si_2O_6$		C2/c
	VI. Li Pyroxene			
20	Spodumene (Sp)[13]	$LiAlSi_2O_6$		C2/c

Notes : Superscripts (from 1 to 13) in the column of mineral names show end-members.

Table 2. IMA-88 proposed pyroxene groups with their mineral subdivisions (from Morimoto et al. 1988)

Row	*I. Ca-Mg-Fe Pyroxenes (Quadrilateral or Quad)*	*II. Ca-Na Pyroxenes*	*III. Na Pyroxenes*	*IV. Other Pyroxenes*
1	Enstatite (En)[a]	Omphacite (Omp)[a]	Jadeite (Jd)[a]	Donpeacorite (Dpc)[c]
2	Ferrosilite (Fs)[a]	Aegirine-augite (Agt)[b]	Aegirine (Aeg)[a]	Kanoite (Ka)[d]
3	Clinoenstatite (Cen)[a]			Johannsenite (Jhn)[a]
4	Clinoferrosilite (Cfs)[a]			Petedunnite (Pe)[d]
5	Pigeonite (Pgt)[a]			Esseneite (Es)[d]
6	Diopside (Di)[a]			Spodumene (Spd)[a]
7	Hedenbergite (Hd)[a]			Kosmochlor (Kos)[a]
8	Augite (Aug)[a]			Jervisite (Je)[d]

Notes for abbreviations: (a) = from (Whitney and Evans 2010); (b) = from (Siivola and Schmid 2007); (c) = this study; (d) = from (Morimoto et al. 1988).

Table 3. Adjectival modifiers for pyroxene group minerals (revised from Morimoto et al. 1988)

Row	Cation	Content (*apfu*)	Name	Applicable to
1	Al^{3+}	> 0.10	Aluminian	All groups, except for jadeite and spodumene
2	Ca^{2+}	> 0.10	Calcian	"Na" and "Other" groups, but excludes those species defined by the abundance of Ca^{2+} (e.g., johannsenite, petedunnite, esseneite)
3	Cr^{3+}	> 0.01	Chromian	All groups, except for kosmochlor
4	Fe^{2+}	> 0.10	Ferroan	All groups, but excludes those species defined by the abundance of Fe^{2+} (e.g., ferrosilite, hedenbergite, pigeonite)
5	Fe^{3+}	> 0.10	Ferrian	All groups, but excludes those species defined by the abundance of Fe^{3+} (e.g., esseneite, aegirine)
6	Li^{+}	> 0.01	Lithian	All groups, but excludes those species defined by the abundance of Li^{+} (e.g., spodumene)
7	Mg^{2+}	> 0.10	Magnesian	All groups, but excludes those species defined by the abundance of Mg (e.g., enstatite, pigeonite, donpeacorite/kanoite, diopside, augite)
8	Mn^{2+}	> 0.10	Manganoan	All groups, but excludes those species defined by the abundance of Mn^{2+} (e.g., donpeacorite/kanoite, johannsenite)
9	Mn^{3+}	> 0.01	Manganian	All groups, but excludes those species defined by the abundance of Mn^{3+}
10	Na^{+}	> 0.10	Sodian	"Ca-Mg-Fe" and "Other" groups, but excludes those species defined by the abundance of Na^{+} (e.g., kosmochlor, jervisite)
11	Ni^{2+}	> 0.01	Nickeloan	All groups
12	Si^{4+}	< 1.75	Subsilicic	All groups, except for esseneite
13	Ti^{3+}	> 0.01	Titanoan	All groups
14	Ti^{4+}	> 0.10	Titanian	All groups
15	Zn^{2+}	> 0.01	Zincian	All groups, except for petedunnite
16	Co^{2+}	>0.01	Cobaltian[(a)]	All groups
17	V^{3+}	> 0.01	Vanadoan[(b)]	All groups
18	Zr^{4+}	> 0.01	Zirconian[(b)]	All groups
19	Sc^{3+}	> 0.01	Scandian[(b)]	All groups, except for jervisite

Notes : (a) = In this study; (b) = Not given in the IMA report (Morimoto et al. 1988), but defined by Rock (1990).

Table 4. Description of column numbers in the *Calculation Screen* window of WinPyrox program

Row		Explanations	Column Numbers in the "*Calculation Screen*" of WinPyrox Program
1	Clinopyroxene	Major oxide (wt%) clinopyroxene analyses	1-19
2		*P* (kbar) and *T* (^{o}C) input for thermobarometry calculations	20-21
3		Recalculated cations in the *T*, *M1*, and *M2* sites	22-47
4		End-member calculations	48-78
5		Fe^{2+}-Mg partitioning	79-84
6		Molar fractions	85-91
7		Parameters used in estimating closure temperature	92-95
8		End-member activities	96-102
9		Components and activities	103-112
10		Single-clinopyroxene barometers	113-119
11		Single-clinopyroxene thermometers	120-124
12		Pyroxene classification parameters (e.g., groups, names, modifiers, and *Q-J*)	125-129
13		Checking of clinopyroxene into the quadrilateral for *P-T* estimations	130
14	Orthopyroxene	Major oxide (wt%) orthopyroxene analyses	131-150
15		Recalculated cations in the *T*, *M1*, and *M2* sites	151-176
16		End-member activities and components	177-186
17		Two-pyroxene barometers	187-190
18		Two-pyroxene thermometers	191-207
19		Single-orthopyroxene thermometers	208-209
20		Checking of orthopyroxene into the quadrilateral for *P-T* estimations	210

Table 5. Selected pyroxene analyses (wt%) with their structural formulae (*apfu*), end-members (%), Fe^{2+}-Mg partitioning (*apfu*), molar farctions, and end-member activities calculated by WinPyrox program. Pyroxene analyses are taken from Rock (1990)

		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16
1	SiO_2	54.01	49.17	37.52	45.9	51.78	53.84	48.82	59.06	50.12	29.51	48.40	50.42	55.12	47.90	56.00	64.89
2	TiO_2	0.03	0.68	5.72	1.4	0.38	3.71	0.43	0.08	1.14	0.99	0.00	0.55	0.00	0.00	0.00	0.00
3	Al_2O_3	3.95	1.42	14.29	5.9	5.14	7.91	2.60	24.62	2.57	17.95	1.20	0.42	0.23	0.00	0.00	26.74
4	V_2O_3	0.00	0.00	0.00	0.00	0.04	0.00	0.03	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	Cr_2O_3	0.57	0.00	0.11	0.00	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	22.6	0.00
6	Fe_2O_3	2.07	1.30	4.43	8.10	1.75	1.11	10.29	0.41	28.74	23.89	3.80	0.00	0.00	0.25	0.40	0.57
7	FeO	1.57	32.93	7.12	7.60	2.14	11.45	9.91	0.18	1.57	0.69	5.70	8.59	0.14	0.98	0.00	0.04
8	MnO	0.00	0.59	0.14	0.35	0.12	0.37	2.93	0.03	0.60	0.11	0.00	0.44	18.48	26.81	0.00	0.01
9	NiO	0.09	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	12.60	0.00	0.00	0.00	0.00	0.00
11	MgO	35.65	8.87	6.72	8.00	16.04	3.01	4.08	0.17	0.59	2.68	2.40	2.80	26.31	0.96	5.40	0.00
12	CaO	0.99	5.25	24.06	20.00	20.32	9.05	16.48	0.35	1.30	23.4	21.30	7.25	0.69	21.62	3.70	0.00
13	Na_2O	0.08	0.30	0.09	1.35	1.06	8.42	3.92	14.95	12.24	0.14	0.70	5.55	0.03	0.00	11.60	0.05
14	K_2O	0.00	0.21	0.00	0.04	0.08	0.14	0.16	0.01	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.16
15	ZrO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.65	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16	Sc_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.48	0.00	0.00	0.00	0.00
17	Li_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.12
18	Total (wt%)	99.01	100.72	100.20	98.64	99.84	99.01	99.84	99.86	99.72	99.36	96.10	94.50	101.00	98.52	99.70	99.58
	Cations based on 6 oxygen																
19	Si	1.855	1.965	1.441	1.788	1.883	2.006	1.907	1.998	1.927	1.188	2.049	1.870	1.972	1.991	2.061	2.063
20	Ti	0.001	0.020	0.165	0.041	0.010	0.104	0.013	0.002	0.033	0.030	0.000	0.015	0.000	0.000	0.000	0.000
21	Al	0.160	0.067	0.647	0.271	0.220	0.347	0.120	0.981	0.117	0.851	0.060	0.018	0.010	0.000	0.000	1.002
22	V	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
23	Cr	0.015	0.000	0.003	0.000	0.027	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.658	0.000
24	Fe^{3+}	0.054	0.039	0.128	0.237	0.048	0.031	0.303	0.010	0.832	0.723	0.121	0.000	0.026	0.008	0.011	0.014
25	Fe^{2+}	0.045	1.101	0.229	0.248	0.065	0.356	0.324	0.005	0.050	0.023	0.202	0.643	0.000	0.034	0.000	0.001
26	Mn	0.000	0.020	0.005	0.012	0.004	0.012	0.097	0.001	0.020	0.004	0.000	0.014	0.560	0.944	0.000	0.000
27	Ni	0.002	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
28	Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.394	0.000	0.000	0.000	0.000	0.000
29	Mg	1.826	0.529	0.385	0.465	0.870	0.167	0.238	0.008	0.034	0.161	0.151	0.155	1.403	0.059	0.296	0.000
30	Ca	0.036	0.225	0.990	0.835	0.792	0.361	0.690	0.013	0.054	1.009	0.966	0.288	0.026	0.963	0.146	0.000
31	Na	0.005	0.023	0.007	0.102	0.075	0.608	0.297	0.981	0.913	0.011	0.057	0.399	0.002	0.000	0.828	0.003
32	K	0.000	0.011	0.000	0.002	0.004	0.007	0.008	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.006
33	Zr	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000	0.000
34	Sc	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.597	0.000	0.000	0.000	0.000
35	Li	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.910
36	Total (*apfu*)	3.999	4.000	4.000	4.001	4.000	3.999	4.002	3.999	4.001	4.000	4.000	3.999	3.999	3.999	4.000	3.999
37	*Q* (*apfu*)	1.907	1.854	1.604	1.547	1.726	0.885	1.251	0.026	0.138	1.193	1.319	1.086	1.430	1.057	0.442	0.001
38	*J* (*apfu*)	0.011	0.047	0.013	0.204	0.149	1.216	0.594	1.961	1.825	0.022	0.115	0.798	0.004	0.000	1.656	0.006
39	Group	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Na	Ca-Na	Na	Na	Rare Ca	Rare Ca	Rare Na	Rare Mn-Mg	Rare Ca	Rare $Na-Cr^{3+}$	Rare Li-Al
40	Name	En or Cen	Pgt	Di	Hd	Aug	Omp	Agt	Jd	Aeg	Es	Pe	Je	Dpc/Ka	Jhn	Kos	Spd
41	Modifiers	Aluminian, chromian	Calcian, ferroan, magnesian	Aluminian, ferroan, ferrian, subsilicic, titanian	Aluminian, ferrian, magnesian, sodian	Aluminian, chromian	Ferroan, magnesian, titanian	Aluminian, ferroan, magnesian		Aluminian, zirconian		Ferroan, ferrian, magnesian	Calcian, ferroan, magnesian			Calcian, magnesian	

42	Wo	1.91	12.13	61.74	53.96	45.86	40.81	55.13	48.14	38.85	84.57	73.22	26.54	1.85	91.14	33.00	0.00
43	En	95.73	28.51	23.99	30.03	50.37	18.89	18.99	32.54	24.53	13.48	11.48	14.26	98.15	5.64	67.00	0.00
44	Fs	2.36	59.36	14.27	16.01	3.77	40.30	25.88	19.32	36.62	1.95	15.30	59.20	0.00	3.22	0.00	100.00
45	*Total* (%)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*
46	Q	99.45	97.55	99.17	88.35	92.03	42.12	67.81	1.33	7.02	98.20	91.99	57.63	99.71	100.00	21.08	14.71
47	Jd	0.12	1.11	0.34	2.32	5.45	53.12	2.65	97.63	4.64	0.09	2.65	0.00	0.00	0.00	0.00	84.14
48	Aeg	0.43	1.34	0.49	9.33	2.52	4.76	29.54	1.04	88.34	1.71	5.36	0.00	0.29	0.00	78.92	1.15
49	*Total* (%)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*57.63*	*100*	*100*	*100*	*100*
50	Wo	1.88	11.65	58.02	48.55	40.90	19.50	41.25	0.64	4.81	80.94	67.24	19.23	1.33	48.14	7.57	0.00
51	Hyp	96.26	85.47	36.22	42.09	48.48	28.92	39.37	0.73	9.33	15.06	24.59	54.14	98.57	51.86	15.37	0.13
52	Jd	1.86	2.88	5.76	9.36	10.62	51.58	19.38	98.63	85.86	4.00	8.17	26.63	0.10	0.00	77.06	99.87
53	*Total* (%)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*
54	Aug	93.28	92.84	78.75	72.29	85.08	53.91	65.49	1.31	7.30	43.89	78.48	100.00	96.50	98.54	95.23	0.05
55	Jd	1.49	3.24	8.67	5.52	10.2	42.30	2.84	97.65	4.63	2.87	7.12	0.00	0.00	0.00	0.00	98.61
56	Aeg	5.23	3.92	12.58	22.19	4.72	3.79	31.67	1.04	88.07	53.24	14.40	0.00	3.50	1.46	4.77	1.34
57	*Total* (%)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*
58	Acm+Jd	0.55	2.32	0.56	8.98	6.81	45.91	23.38	57.6	87.92	1.21	4.85	30.95	0.18	0.00	66.72	0.93
59	Ts	27.92	21.11	77.34	55.88	52.2	25.85	40.15	41.88	5.4	90.38	64.25	18.13	22.64	42.34	8.82	49.57
60	Hd	4.67	76.57	19.37	22.4	5.97	27.51	32.26	0.35	6.68	3.00	17.05	50.92	49.49	57.33	0.00	0.13
61	Di	66.86	0.00	2.73	12.74	35.02	0.73	4.21	0.17	0.00	5.41	13.85	0.00	27.69	0.33	24.46	49.37
62	*Total* (%)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*
63	Jd	0.51	3.46	0.67	10.62	7.87	44.4	25.46	98.32	41.55	1.09	7.68	30.01	0.29	0.00	38.72	1.87
64	Acm	0.00	0.00	0.00	0.00	0.00	19.32	15.46	0.00	36.31	0.00	0.00	28.62	0.00	0.00	38.72	0.00
65	Ca-ferriTs	3.27	1.99	6.56	12.13	3.77	1.12	12.63	0.52	18.75	36.24	8.09	0.00	1.79	0.74	15.65	1.33
66	Ca-Ti-Ts	0.07	2.08	16.5	4.19	1.04	7.51	1.05	0.20	1.49	3.00	0.00	1.15	0.00	0.00	0.00	0.00
67	Ca-Ts	7.26	0.00	15.47	4.34	6.07	0.00	0.00	0.00	0.00	39.09	0.16	0.00	0.53	0.00	0.00	96.70
68	Wo	0.00	9.42	30.17	32.33	34.29	8.73	21.96	0.27	0.00	11.37	60.46	10.25	0.67	90.44	0.00	0.00
69	En	86.63	26.95	19.21	23.74	43.64	6.04	9.92	0.43	0.76	8.05	10.12	5.82	96.74	5.61	6.93	0.00
70	Fs	2.26	56.1	11.42	12.65	3.32	12.88	13.52	0.26	1.14	1.16	13.49	24.15	0.00	3.21	0.00	0.10
71	*Total* (%)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*
72	CaTs	7.16	1.81	33.62	11.64	6.46	0.00	4.60	0.21	6.63	65.34	0.00	1.14	0.49	0.00	0.00	0.00
73	Jd	0.26	1.22	0.40	5.60	4.13	35.65	14.75	97.09	83.07	0.88	2.62	24.74	0.10	0.00	65.18	0.61
74	KJd	0.00	0.56	0.00	0.11	0.21	0.39	0.40	0.04	0.85	0.00	0.00	0.00	0.00	0.00	0.00	1.28
75	CaEs	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	97.85
76	Di	0.00	19.94	51.94	68.42	74.63	42.36	59.35	2.08	0.00	31.61	88.11	33.44	1.68	66.32	22.98	0.00
77	En	90.35	17.73	0.00	0.00	10.77	0.00	0.00	0.00	3.08	0.00	0.00	0.00	69.61	0.00	11.84	0.00
78	Fs	2.23	58.74	14.04	14.23	3.80	21.6	20.9	0.59	6.37	2.17	9.21	40.68	28.12	33.68	0.00	0.26
79	*Total* (%)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*
80	Fe_{M1}	0.004	0.451	0.000	0.210	0.034	0.345	0.313	0.002	0.046	0.018	0.197	0.358	0.000	0.000	0.000	0.000
81	Mg_{M1}	0.908	0.457	0.313	0.453	0.775	0.166	0.237	0.006	0.033	0.160	0.150	0.141	0.992	0.000	0.270	0.000
82	Fe_{M2}	0.041	0.649	0.649	0.038	0.031	0.011	0.011	0.003	0.005	0.005	0.005	0.285	0.285	0.285	0.285	0.990
83	Mg_{M2}	0.917	0.072	0.072	0.012	0.095	0.001	0.001	0.002	0.001	0.001	0.001	0.014	0.411	0.411	0.026	0.026
84	Ca_{M2}	0.036	0.225	0.011	0.835	0.792	0.361	0.402	0.013	0.054	0.015	0.057	0.288	0.026	0.944	0.146	0.000
85	Na_{M2}	0.005	0.034	0.007	0.104	0.078	0.615	0.305	0.981	0.922	0.011	0.057	0.399	0.002	0.000	0.828	1.000
86	X^{3+}_{M1}	0.085	0.471	0.615	0.535	0.189	0.833	0.737	0.992	0.966	0.835	0.716	0.615	0.026	0.413	0.693	1.000
87	X^{Fe2+}_{M1}	0.004	0.451	0.000	0.210	0.034	0.347	0.351	0.002	0.047	0.019	0.373	0.696	0.000	0.000	0.000	0.000
88	X^{Mg}_{M1}	0.911	0.457	0.448	0.453	0.777	0.167	0.265	0.006	0.034	0.165	0.285	0.275	0.974	0.000	0.288	0.000
89	X^{Fe2+}_{M2}	0.041	0.649	0.649	0.038	0.031	0.011	0.011	0.003	0.005	0.005	0.005	0.285	0.222	0.222	0.222	0.491

90	X^{Mg}_{M1}	0.917	0.072	0.072	0.012	0.095	0.001	0.001	0.002	0.001	0.001	0.001	0.014	0.320	0.320	0.020	0.013
91	X^{Ca}_{M2}	0.036	0.225	0.011	0.835	0.792	0.361	0.402	0.013	0.054	0.015	0.057	0.288	0.021	0.735	0.114	0.000
92	X^{Na}_{M2}	0.005	0.034	0.007	0.104	0.078	0.615	0.305	0.981	0.922	0.011	0.057	0.399	0.002	0.000	0.644	0.496
93	a_{En}	0.835	0.033	0.032	0.005	0.074	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.312	0.000	0.006	0.000
94	a_{Di}	0.033	0.104	0.443	0.379	0.617	0.061	0.169	0.000	0.002	0.162	0.269	0.071	0.026	0.000	0.043	0.000
95	a_{Fs}	0.000	0.293	0.000	0.008	0.001	0.004	0.004	0.000	0.000	0.000	0.002	0.198	0.000	0.000	0.000	0.000
96	$a_{Ca\text{-}Ts}$	0.001	0.007	0.001	0.049	0.082	0.125	0.011	0.012	0.002	0.001	0.003	0.000	0.000	0.000	0.000	0.000
97	$a_{Mg\text{-}Ts}$	0.014	0.002	0.006	0.001	0.010	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.013
98	a_{Hd}	0.000	0.102	0.000	0.175	0.027	0.125	0.141	0.000	0.002	0.000	0.021	0.200	0.000	0.000	0.000	0.000
99	a_{Jd}	0.000	0.001	0.001	0.006	0.008	0.214	0.008	0.961	0.040	0.000	0.003	0.000	0.000	0.000	0.000	0.497

Notes : *apfu* = atomic per formula unit; *Q* = Ca+Mg+Fe^{2+} (row 37); *J* = 2Na (row 38); Abbreviation of pyroxene names: En = Enstatite, Cen = Clinoenstatite, Pgt = Pigeonite, Di = Diopside, Hd = Hedenbergite, Aug = Augite, Omp = Omphacite, Agt = Aegirine-Augite, Jd = Jadeite, Aeg = Aegirine, Es = Esseneite, Pe = Petedunnite, Je = Jervisite, Dpc/Ka = Donpeacorite/Kanoite, Jhn = Johannsenite, Kos = Kosmochlor, Spd = Spodumene ; Abbreviation of end-member components : Wo = Wollastonite (rows 42 and 50), En = Enstatite (rows 43 and 68), Fs = Ferrosilite (rows 44 and 69), Q = Quad (row 46), Jd = Jadeite (rows 47, 52, 55and 64), Aeg = Aegirine (rows 48 and 56), Hyp = Hyperstene, Aug = Augite, Acm =Acmite, Ts = Tschermakite, Hd = Hederbergite; Di = Diopside, CaTs = Ca tschermakite, KJd = K-jadeite, CaEs = Ca-Eskola, Ca-ferriTs = Ca-ferritschermakite, Ca-Ti-Ts = Ca-Ti-tschermakite, Ca-Ts = Ca-tschermakite; Formulations for end-members (rows 42-57) from Soto and Soto (1995); End-members (rows 58-62) from Yoder and Tilley (1962); End-members (rows 63-71) from Cawthorn and Collerson (1974); End-members (rows 72-79) from Harlow (1997); Fe^{2+}-Mg partitioning as: Fe_{M1}= Fe^{2+} in *M2* site, Mg_{M1} = Mg in *M1* site, Fe_{M2} = Fe^{2+} in *M2* site, Mg_{M2} = Mg in *M2* site, Ca_{M2} = Ca in *M2* site, and Na_{M2} = Na in *M2* site from Nimis (2000); Molar fractions (rows 86-92) from Soto and Soto (1995; see references therein), $X^{3+}_{M1}=(Al^{VI}+Ti+Cr+Fe^{3+}+Fe^{2+}_{M1})/(Fe^{2+}_{M1}+Mg_{M1}+Al^{VI}+Fe^{3+}+Cr+Ti)$, $X^{Fe2+}_{M1}=Fe^{2+}_{M1}/(Fe^{2+}_{M1}+Mg_{M1}+Al^{VI}+Fe^{3+}+Cr+Ti)$, $X^{Mg}_{M1}=Mg_{M1}/(Fe^{2+}_{M1}+Mg_{M1}+Al^{VI}+Fe^{3+}+Cr+Ti)$, $X^{Fe2+}_{M2}=Fe^{2+}_{M2}/(Fe^{2+}_{M2}+Mg_{M2}+Ca+Mn+Na)$, $X^{Ca}_{M2}=Ca_{M2}/(Fe^{2+}_{M2}+Mg_{M2}+Ca+Mn+Na)$, $X^{Na}_{M2}=Na_{M2}/(Fe^{2+}_{M2}+Mg_{M2}+Ca+Mn+Na)$; End-member activities (rows 93-99) from Soto and Soto (1995; see references therein), $a_{En}=X^{Mg}_{M2}*X^{Mg}_{M1}$, $a_{Di}=X^{Ca}_{M2}*X^{Mg}_{M1}$, $a_{Fs}=X^{Fe2+}_{M2}*X^{Fe2+}_{M1}$, $a_{Ca\text{-}Ts}=X^{Ca}_{M2}*X^{AlVI}_{M1}$, $a_{Mg\text{-}Ts}=X^{Mg}_{M2}*X^{AlVI}_{M1}$, $a_{Hd}=X^{Ca}_{M2}*X^{Fe2+I}_{M1}$, $a_{Jd}=X^{Na}_{M2}*X^{AlVI}_{M1}$.

Table 6. Calculation (total cation fractions without normalization to 4) and classification of clinopyroxenes by WinPyrox program with their calculated components and thermobarometers. Analyses are taken from an Excel spreadsheet (i.e., Two-pyroxene *P*-*T*) developed by (Putirka 2008)

Row		Cpx1 (-)	Cpx4 (Z-342-02)	Cpx7 (A-12)	Cpx13 (B 304)	Cpx19 (1KH-39)	Cpx23 (INT-D5)	Cpx24 (INT-D2)
1	SiO_2	52.30	51.06	51.12	51.3	50.93	52.98	53.77
2	TiO_2	0.70	0.62	0.10	0.19	0.81	0.14	0.11
3	Al_2O_3	3.00	3.16	8.07	7.20	9.02	5.04	4.31
4	Cr_2O_3	0.58	0.01	1.16	0.50	0.34	1.36	1.51
5	FeO_{tot}	5.10	6.18	3.57	3.90	5.82	3.48	3.60
6	MnO	0.11	0.12	0.00	0.09	0.00	0.11	0.11
7	MgO	16.60	15.78	17.95	17.60	18.51	19.61	20.51
8	CaO	21.50	20.82	17.26	19.10	13.34	17.76	16.95
9	Na_2O	0.33	0.27	0.77	0.50	1.23	0.23	0.23
10	Total (wt%)	100.22	98.02	100.00	100.38	100.00	100.71	101.10
	T-site							
11	Si	1.912	1.915	1.836	1.846	1.826	1.890	1.907
12	Al^{IV}	0.088	0.085	0.164	0.154	0.174	0.110	0.093
13	Total (*apfu*)	2.000	2.000	2.000	2.000	2.000	2.000	2.000
	M1-site							
14	Al^{VI}	0.041	0.054	0.178	0.151	0.207	0.102	0.087
15	Fe^{3+}	0.014	0.016	0.001	0.013	0.000	0.000	0.000
16	Ti	0.019	0.017	0.003	0.005	0.022	0.004	0.003
17	Cr	0.017	0.000	0.033	0.014	0.010	0.038	0.042
18	Mg	0.905	0.882	0.786	0.816	0.762	0.856	0.868
19	Fe^{2+}	0.003	0.030	0.000	0.000	0.000	0.000	0.000
20	Total (*apfu*)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	M2-site							
21	Mg	0.000	0.000	0.176	0.128	0.227	0.187	0.217
22	Fe^{2+}	0.117	0.148	0.107	0.105	0.175	0.126	0.133
23	Mn	0.003	0.004	0.000	0.003	0.000	0.003	0.003
24	Ca	0.842	0.836	0.664	0.736	0.512	0.679	0.679
25	Na	0.023	0.020	0.054	0.035	0.085	0.016	0.016
26	Total (*apfu*)	0.986	1.008	1.000	1.006	1.000	1.011	1.013
27	*Q* (*apfu*)	1.867	1.897	1.732	1.785	1.676	1.848	1.862
28	*J* (*apfu*)	0.047	0.039	0.107	0.070	0.171	0.032	0.032
29	Group	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe
30	Name	Aug	Aug	Aug	Aug	Aug	Aug	Aug
	Clinopyroxene components							
31	Jd	0.023	0.020	0.054	0.035	0.085	0.016	0.016
32	CaTs	0.018	0.035	0.125	0.117	0.121	0.086	0.071
33	CaTi	0.035	0.025	0.020	0.019	0.026	0.012	0.011
34	CrCaTs	0.008	0.000	0.016	0.007	0.005	0.019	0.021
35	DiHd	0.781	0.776	0.504	0.594	0.360	0.562	0.541
36	EnFs	0.129	0.150	0.282	0.234	0.402	0.304	0.338
37	Total	0.994	1.006	1.001	1.006	0.999	0.999	0.998
38	En	0.112	0.122	0.254	0.207	0.342	0.270	0.301
39	Di	0.678	0.634	0.453	0.527	0.306	0.500	0.480
40	α_{En}	0.245	0.227	0.247	0.242	0.253	0.291	0.312
41	α_{Di}	0.610	0.602	0.531	0.567	0.434	0.529	0.506
	Single-clinopyroxene barometers (kbar)							
42	$PN_{95\text{-}BS\text{-}Cpx}$ (Eq. 1)	1.77	1.03	13.91	10.53	17.45	8.41	8.06
43	$PNU_{98\text{-}BA\text{-}Cpx}$ (Eq. 5)	1.72	0.94	14.87	11.15	18.87	9.06	8.78
44	$PNU_{98cor\text{-}BH\text{-}Cpx}$ (Eq. 7)	26.94	15.69	14.00	14.66	23.55	13.77	10.14
45	$PN_{99\text{-}TH\text{-}Cpx}$ (Eq. 8)	22.13	11.23	9.98	10.61	17.42	9.89	7.16
46	$PN_{99\text{-}MA\text{-}Cpx}$ (Eq. 9)	25.15	15.24	12.17	13.19	22.07	13.91	10.05
47	$PNT_{00\text{-}Cpx}$ (Eq. 10)	0.35	n.d.	22.87	18.31	18.51	27.00	n.d.
48	$PP_{08\text{-}Cpx}$ (Eq. 11)	n.d.	4.39	16.49	9.53	17.31	9.73	11.17

	Single-clinopyroxene thermometers (^{o}C)								
49	TBM$_{85/86\text{-Cpx}}$	(Eq. 12)	1120	1161	1371	1310	1448	1355	1379
50	TNT$_{00\text{-Cpx}}$	(Eq. 13)	1000	998	1255	1185	1280	1269	1295
51	TP$_{08\text{-Cpx}}$	(Eq. 14)	1207	1171	1335	1302	1307	1289	1290
52	TDN$_{82\text{-Cpx}}$	(Eq. 15)	879	873	850	867	785	806	773
53	TMZ$_{91\text{-Cpx}}$	(Eq. 16)	900	899	896	899	887	889	885

Notes : *apfu* = atomic per formula unit; Fe^{3+} estimation by Papike et al. (1974); Q = Ca+Mg+Fe^{2+} (row 27); J = 2Na (row 28); Aug = Augite (row 30); Estimation method of clinopyroxene components (rows 31-37) from Putirka (2008); En (row 38) = $Fm_2Si_2O_6$*(Mg/(Mg+Fet_{ot}+Mn)); Di (row 39) = $CaFmSi_2O_6$*(Mg/(Mg+Fe_{tot}+Mn)); a_{En} (row 40) = (0.5*Mg/(Ca+0.5*Fe^{2+}+Mn+Na))*(0.5*Mg/(Fe^{3+}+0.5*Fe^{2+}+Al^{VI}+Ti+Cr+0.5*Mg)); a_{Di} (row 41) = Ca/(Ca+0.5*Mg+0.5*Fe^{2+}+Mn+Na); Single-clinopyroxene barometers of PN$_{95\text{-BS-Cpx}}$ (row 42) from Nimis (1995; see Eq. 1 in text), PNU$_{98\text{-BA-Cpx}}$ (row 43) from Nimis and Ulmer (1998; see Eq. 5 in text), PNU$_{98\text{cor-BH-Cpx}}$ (row 44) from Nimis and Ulmer (1998; see Eq. 7 in text), PN$_{99\text{-TH-Cpx}}$ (row 45) from Nimis (1999; see Eq. 8 in text], PN$_{99\text{-MA-Cpx}}$ (row 46) from Nimis (1999; see Eq. 9 in text), PNT$_{00\text{-Cpx}}$ (row 47) from Nimis and Taylor (2000; see Eq. 10 in text), PP$_{08\text{-Cpx}}$ (row 48) from Putirka (2008; see Eq. 11 in text); Single-clinopyroxene thermometrs of TBM$_{85/86\text{-Cpx}}$ (row 49) from Bertrand and Mercier (1985/1986; see Eq. 12 in text), TNT$_{00\text{-Cpx}}$ (row 50) from Nimis and Taylor (2000; see Eq. 13 in text), TP$_{08\text{-Cpx}}$ (row 51) from Putirka (2008; see Eq. 14 in text), TDN$_{82\text{-Cpx}}$ (row 52) from Dal Negro et al. (1982; see Eq. 15 in text), TMZ$_{91\text{-Cpx}}$ (row 53) from Molin and Zanazzi (1991; see Eq. 16 in text); n.d. = not determined.

Table 7. Calculation (total cation fractions without normalization to 4) and classification of orthopyroxenes by WinPyrox program with their calculated components and thermobarometers. Analyses are taken from an Excel spreadsheet (i.e., Two-pyroxene *P-T*) developed by (Putirka 2008)

Row		Opx1 (-)	Opx4 (Z-342-02)	Opx7 (A-12)	Opx13 (B 304)	Opx19 (1KH-39)	Opx23 (INT-D5)	Opx24 (INT-D2)
1	SiO_2	55.00	55.15	54.10	52.90	52.95	58.89	56.66
2	TiO_2	0.34	0.17	0.00	0.09	0.52	0.04	0.05
3	Al_2O_3	1.50	1.19	5.70	6.90	7.43	3.19	3.47
4	Cr_2O_3	0.19	0.15	0.50	0.50	0.16	0.84	0.94
5	FeO_{tot}	11.30	10.21	6.30	6.72	8.01	5.48	5.40
6	MnO	0.24	0.22	0.00	0.12	0.00	0.10	0.12
7	MgO	30.70	29.90	31.50	30.60	28.72	33.72	32.82
8	CaO	0.90	1.66	1.65	1.63	1.93	1.05	1.56
9	Na_2O	0.01	0.03	0.25	0.07	0.27	0.00	0.04
10	Total (wt%)	101.18	98.77	100.00	99.53	99.99	101.31	101.06
	T-site							
11	Si	1.944	1.969	1.875	1.847	1.849	1.934	1.933
12	Al^{IV}	0.056	0.031	0.125	0.153	0.151	0.066	0.067
13	Total (*apfu*)	2.000	2.000	2.000	2.000	2.000	2.000	2.000
	M1-site							
14	Al^{VI}	0.006	0.019	0.108	0.131	0.154	0.061	0.072
15	Fe^{3+}	0.027	0.001	0.020	0.009	0.000	0.000	0.000
16	Ti	0.009	0.005	0.000	0.002	0.014	0.001	0.001
17	Cr	0.005	0.004	0.014	0.014	0.004	0.023	0.025
18	Mg	0.952	0.971	0.858	0.844	0.827	0.915	0.901
19	Fe^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000
20	Total (*apfu*)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	M2-site							
21	Mg	0.665	0.625	0.769	0.748	0.667	0.793	0.768
22	Fe^{2+}	0.306	0.304	0.163	0.187	0.250	0.175	0.184
23	Mn	0.007	0.007	0.000	0.004	0.000	0.003	0.003
24	Ca	0.034	0.063	0.061	0.061	0.072	0.038	0.057
25	Na	0.001	0.002	0.017	0.005	0.018	0.000	0.003
26	Total (*apfu*)	1.014	1.001	1.010	1.005	1.008	1.010	1.015
27	*Q* (*apfu*)	1.958	1.963	1.852	1.841	1.818	1.922	1.910
28	*J* (*apfu*)	0.004	0.004	0.034	0.009	0.037	0.000	0.005
29	Group	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe	Ca-Mg-Fe
30	Name	En	En	En	En	En	En	En
	Orthopyroxene components							
31	$NaAlSi_2O_6$	0.001	0.002	0.017	0.005	0.018	0.000	0.003
32	$FmTiAlSiO_6$	0.009	0.005	0.000	0.002	0.014	0.001	0.001
33	$CrAl_2SiO_6$	0.005	0.004	0.014	0.014	0.004	0.023	0.025
34	$FmAl_2SiO_6$	0.000	0.013	0.078	0.112	0.132	0.039	0.044
35	$CaFmSi_2O_6$	0.034	0.064	0.061	0.061	0.072	0.038	0.057
36	$Fm_2Si_2O_6$	0.958	0.913	0.836	0.808	0.764	0.904	0.877
37	Total	1.003	1.000	1.000	1.000	1.000	1.000	1.000
38	En	0.791	0.764	0.751	0.718	0.654	0.819	0.788
39	Di	0.028	0.053	0.055	0.054	0.062	0.035	0.051
40	a_{En}	0.645	0.637	0.656	0.632	0.555	0.723	0.686
41	a_{Di}	0.034	0.062	0.063	0.064	0.075	0.039	0.058
	Two-pyroxene barometers (kbar)							
42	$PM(1)_{84\text{-}Opx\text{-}Cpx}$ (Eq. 35)	27.49	6.21	36.55	25.46	50.93	n.d.	51.71
43	$PM(2)_{84\text{-}Opx\text{-}Cpx}$ (Eq. 36)	22.40	6.76	28.75	20.95	38.46	54.43	38.98
44	$PP(1)_{08\text{-}Opx\text{-}Cpx}$ (Eq. 37)	2.19	2.38	14.91	10.90	15.34	10.88	10.50
45	$PP(2)_{08\text{-}Opx\text{-}Cpx}$ (Eq. 38)	2.57	3.24	16.18	11.12	17.18	7.83	11.34
	Two-pyroxene and single-orthopyroxene thermometers (^oC) by WinPyrox							
46	$TWB_{73\text{-}Opx\text{-}Cpx}$ (Eq. 18)	1252	1237	1361	1341	1320	1376	1396
47	$TW_{77\text{-}Opx\text{-}Cpx}$ (Eq. 19)	1285	1263	1338	1333	1361	1361	1400
48	$TNB(A1)_{84\text{-}Opx\text{-}Cpx}$ (Eq. 20)	1133	1232	1109	1189	1201	1229	1299

49	TNB(A2)$_{84\text{-Opx-Cpx}}$	(Eq. 20)	937	907	1007	1037	1091	1069	1136
50	TNB(B1)$_{84\text{-Opx-Cpx}}$	(Eq. 21)	1264	1399	1423	1301	1421	1296	1385
51	TNB(B2)$_{84\text{-Opx-Cpx}}$	(Eq. 21)	968	1123	1262	1141	1230	1154	1227
52	TN$_{85\text{-Opx-Cpx}}$	(Eq. 22)	1085	1106	1346	1282	1462	1317	1359
53	TBM$_{85/86\text{-Opx-Cpx}}$	(Eq. 23)	962	986	1285	1217	1375	1280	1320
54	TCL(A)$_{88\text{-Opx-Cpx}}$	(Eq. 24)	1131	1031	938	1049	862	993	1060
55	TCL(B)$_{88\text{-Opx-Cpx}}$	(Eq. 25)	757	938	1321	1221	1448	1064	1165
56	TSJ(1)$_{89\text{-Opx-Cpx}}$	(Eq. 26)	1493	1452	1486	1499	1616	1530	1615
57	TSJ(2)$_{89\text{-Opx-Cpx}}$	(Eq. 27)	1042	1213	1258	1239	1394	1113	1244
58	TBK$_{90\text{-Ca-in-Opx-Cpx}}$	(Eq. 28)	971	999	1265	1189	1286	1255	1275
59	TBK$_{90\text{-Na-in-Opx-Cpx}}$	(Eq. 29)	812	1140	1426	1229	1346	1526	1275
60	TBK$_{90\text{-Ca-in-Opx}}$	(Eq. 30)	1230	1408	1472	1453	1525	1310	1421
61	$TT_{98\text{-Opx-Cpx}}$	(Eq. 31)	960	976	1291	1229	1346	1233	1261
62	TP(1)$_{08\text{-Opx-Cpx}}$	(Eq. 32)	965	1000	1325	1172	1321	1225	1273
63	TP(2)$_{08\text{-Opx-Cpx}}$	(Eq. 33)	957	975	1295	1170	1334	1228	1247
64	TNT$_{10\text{-Ca-in-Opx}}$	(Eq. 34)	953	987	1264	1191	1283	1254	1272
	Input *T-P* values for thermobarometric estimations (from Putirka 2008)								
65	T (^{o}C)		0	950	1325	1215	1300	1270	1300
66	P (kbar)		0.00	1.94	15.00	12.00	15.00	10.00	10.00
	Two-pyroxene and single-orthopyroxene thermometers (^{o}C) with an Excel spreadsheet by Putirka (2008)								
67	TWB$_{73\text{-Opx-Cpx}}$		1247	1237	1361	1341	1329	1394	1425
68	TW$_{77\text{-Opx-Cpx}}$		1277	1263	1338	1333	1363	1371	1414
69	TNB(A1)$_{84\text{-Opx-Cpx}}$		1177	1232	1109	1189	1213	1206	1277
70	TNB(A2)$_{84\text{-Opx-Cpx}}$		936	907	1007	1037	1092	1077	1146
71	TNB(B1)$_{84\text{-Opx-Cpx}}$		1261	1397	1419	1298	1389	1279	1357
72	TNB(B2)$_{84\text{-Opx-Cpx}}$		972	1123	1262	1141	1233	1153	1226
73	TN$_{85\text{-Opx-Cpx}}$		1085	1106	1346	1282	1462	1317	1359
74	TCL(A)$_{88\text{-Opx-Cpx}}$		1086	1031	938	1049	846	1014	1078
75	TCL(B)$_{88\text{-Opx-Cpx}}$		760	938	1321	1221	1452	1068	1172
76	TSJ(1)$_{89\text{-Opx-Cpx}}$		1477	1452	1486	1499	1604	1533	1613
77	TSJ(2)$_{89\text{-Opx-Cpx}}$		1044	1213	1258	1239	1397	1114	1246
78	TBK$_{90\text{-Ca-in-Opx-Cpx}}$		967	1003	1254	1183	1295	1266	1291
79	TBK$_{90\text{-Na-in-Opx-Cpx}}$		812	1140	1426	1229	1346	n.d.	1275
80	TBK$_{90\text{-Ca-in-Opx}}$		957	1135	1198	1180	1252	1037	1148
81	TP(1)$_{08\text{-Opx-Cpx}}$		980	1000	1325	1172	1321	1217	1265
82	TP(2)$_{08\text{-Opx-Cpx}}$		964	975	1295	1170	1337	1240	1265
83	PM(1)$_{84\text{-Opx-Cpx}}$		34.71	9.54	44.93	30.99	60.12	79.36	54.06
84	PM(2)$_{84\text{-Opx-Cpx}}$		27.47	9.28	34.46	24.88	44.44	56.46	40.52
85	PP(1)$_{08\text{-Opx-Cpx}}$		2.2	2.4	14.9	10.9	14.8	10.8	10.3
86	PP(2)$_{08\text{-Opx-Cpx}}$		3.1	3.2	16.2	11.1	16.5	7.1	10.3

Notes : *apfu* = atomic per formula unit; Fe^{3+} estimation by Papike et al. (1974); Q = Ca+Mg+Fe^{2+} (row 27); J = 2Na (row 28); En = Enstatite (row 30); Estimation method of orthopyroxene components (rows 31-37) from Putirka (2008); En (row 38) = $Fm_2Si_2O_6$*(Mg/(Mg+Fet_{ot}+Mn)); Di (row 39) = $CaFmSi_2O_6$*(Mg/(Mg+Fe_{tot}+Mn)); a_{En} (row 40) = (0.5*Mg/(Ca+0.5*Fe^{2+}+Mn+Na))*(0.5*Mg/(Fe^{3+}+0.5*Fe^{2+}+Al^{VI}+Ti+Cr+0.5*Mg)); a_{Di} (row 41) = Ca/(Ca+0.5*Mg+0.5*Fe^{2+}+Mn+Na); Two-clinopyroxene barometers of PM(1)$_{84\text{-Opx-Cpx}}$ (row 42) from Mercier et al. (1984; see Eq. 35 in text), PM(2)$_{84\text{-Opx-Cpx}}$ (row 43) from Mercier et al. (1984; see Eq. 36 in text), PP(1)$_{08\text{-Opx-Cpx}}$ (row 44) from Putirka (2008; see Eq. 37 in text), PP(2)$_{08\text{-Opx-Cpx}}$ (row 45) from Putirka (2008; see Eq. 38 in text); Two-pyroxene thermometers of TWB$_{73\text{-Opx-Cpx}}$ (row 46) from Wood and Banno (1973; see Eq. 18 in text), TW$_{77\text{-Opx-Cpx}}$ (row 47) from Wells (1977; see Eq. 19 in text), TNB(A1)$_{84\text{-Opx-Cpx}}$ (row 48) from Nickel and Brey (1984; using FmO as in Putirka 2008 ; see Eq. 20 in text), TNB(A2)$_{84\text{-Opx-Cpx}}$ (row 49) from Nickel and Brey (1984; using Mg as in Putirka 2008 ; see Eq. 20 in text), TNB(B1)$_{84\text{-Opx-Cpx}}$ (row 50) from Nickel and Brey (1984; using FmO as in Putirka 2008 ; see Eq. 21 in text), TNB(B2)$_{84\text{-Opx-Cpx}}$ (row 51) from Nickel and Brey (1984; using Mg as in Putirka 2008 ; see Eq. 21 in text), TN$_{85\text{-Opx-Cpx}}$ (row 52), from Nickel et al. (1985; see Eq. 22 in text), TBM$_{85/86\text{-Opx-Cpx}}$ (row 53) from Bertrand and Mercier (1985/1986; see Eq. 23 in text), TCL(A)$_{88\text{-Opx-Cpx}}$ (row 54) from Carlson and Lindsley (1988; see Eq. 24 in text), TCL(B)$_{88\text{-Opx-Cpx}}$ (row 55) from Carlson and Lindsley (1988; see Eq. 25 in text), TSJ(1)$_{89\text{-Opx-Cpx}}$ (row 56) from Sen and Jones (1989; see Eq. 26 in text), TSJ(2)$_{89\text{-Opx-Cpx}}$ (row 57) from Sen and Jones (1989; see Eq. 27 in text), TBK$_{90\text{-Ca-in-Opx-Cpx}}$ (row 58) from Brey and Köhler (1990; see Eq. 28 in text), TBK$_{90\text{-Na-in-Opx-Cpx}}$ (row 59) from Brey and Köhler (1990; see Eq. 29 in text), TBK$_{90\text{-Ca-in-Opx}}$ (row 60) from Brey and Köhler (1990; see Eq. 30 in text), $TT_{98\text{-Opx-Cpx}}$ (row 61) from Taylor (1998; see Eq. 31 in text), TP(1)$_{08\text{-Opx-Cpx}}$ (row 62) from Putirka (1998; see Eq. 32 in text), TP(2)$_{08\text{-Opx-Cpx}}$ (row 63) from Putirka (1998; see Eq. 33 in text), TNT$_{10\text{-Ca-in-Opx}}$ (row 64) from Nimis and Grütter (2010; see Eq. 34 in text); Calculation inputs of T (^{o}C) and P (kbar) (rows 65-66) for pyroxene thermobarometry are taken from Putirka (2008); *P-T* values in rows 67-86 are taken from Putirka (2008) for comparison of outputs by WinPyrox (see rows 42-64); n.d. = not determined.

Table 8. Comparison of single-clinopyroxene barometers based on ferric iron estimation methods and normalizations

Row		Cpx1	Cpx4	Cpx7	Cpx13	Cpx19	Cpx23	Cpx24
	Input *T* values for barometric estimations (from Putirka 2008)							
1	*T* (^{o}C)	0	950	1325	1215	1300	1270	1300
	Single-clinopyroxene barometers (kbar) by CpxBar (Nimis 2000)[(a)]							
2	$PNU_{98\text{-}BA\text{-}Cpx}$	*1.20*	*0.89*	*14.87*	*11.08*	*19.15*	*9.69*	*9.52*
3	$PNU_{98cor\text{-}BH\text{-}Cpx}$	*50.21*	*10.64*	*14.79*	*13.82*	*24.52*	*9.48*	*8.08*
4	$PN_{99\text{-}TH\text{-}Cpx}$	*36.39*	*8.09*	*10.32*	*9.62*	*17.55*	*9.69*	*6.17*
5	$PN_{99\text{-}MA\text{-}Cpx}$	*45.85*	*10.65*	*12.23*	*11.37*	*21.56*	*8.43*	*7.65*
	Single-clinopyroxene barometers (kbar) by WinPyrox[(b)]							
6	$PNU_{98\text{-}BA\text{-}Cpx}$	1.20	0.92	14.86	11.07	18.86	8.36	7.95
7	$PNU_{98cor\text{-}BH\text{-}Cpx}$	26.54	15.61	13.95	14.27	22.99	12.60	8.78
8	$PN_{99\text{-}TH\text{-}Cpx}$	21.84	11.17	9.95	10.36	17.07	9.08	6.25
9	$PN_{99\text{-}MA\text{-}Cpx}$	24.89	15.13	12.12	12.88	21.67	13.04	9.07
	Single-clinopyroxene barometers (kbar) by WinPyrox[(c)]							
10	$PNU_{98\text{-}BA\text{-}Cpx}$	2.02	0.78	14.86	10.99	18.87	8.80	8.47
11	$PNU_{98cor\text{-}BH\text{-}Cpx}$	27.15	15.51	13.90	14.31	23.29	13.31	9.60
12	$PN_{99\text{-}TH\text{-}Cpx}$	22.28	11.10	9.92	10.39	17.27	9.58	6.80
13	$PN_{99\text{-}MA\text{-}Cpx}$	25.30	15.11	12.10	12.94	21.89	13.59	9.67
	Single-clinopyroxene barometers (kbar) by WinPyrox[(d)]							
14	$PNU_{98\text{-}BA\text{-}Cpx}$	1.35	1.08	14.87	11.23	18.87	8.87	8.56
15	$PNU_{98cor\text{-}BH\text{-}Cpx}$	26.64	15.82	14.06	14.75	23.47	13.52	9.86
16	$PN_{99\text{-}TH\text{-}Cpx}$	21.91	11.31	10.02	10.66	17.36	9.70	6.96
17	$PN_{99\text{-}MA\text{-}Cpx}$	24.96	15.28	12.20	13.21	22.00	13.69	9.83
	Single-clinopyroxene barometers (kbar) by WinPyrox[(e)]							
18	$PNU_{98\text{-}BA\text{-}Cpx}$	1.72	0.94	14.87	11.15	18.87	9.06	8.78
19	$PNU_{98cor\text{-}BH\text{-}Cpx}$	26.94	15.69	14.00	14.66	23.55	13.77	10.14
20	$PN_{99\text{-}TH\text{-}Cpx}$	22.13	11.23	9.98	10.61	17.42	9.89	7.16
21	$PN_{99\text{-}MA\text{-}Cpx}$	25.15	15.24	12.17	13.19	22.07	13.91	10.05

Notes : (a) = Fe^{3+} estimation by Papike et al. (1974) and cation fractions with normalization to 4 using CpxBar (Nimis 2000); (b) = Fe^{3+} estimation by Droop (1987) and cation fractions with normalization to 4 using WinPyrox; (c) = Fe^{3+} estimation by Papike et al. (1974) and cation fractions with normalization to 4 using WinPyrox; (d) = Fe^{3+} estimation by Droop (1987) and cation fractions without normalization to 4 using WinPyrox; (e) = Fe^{3+} estimation by Papike et al. (1974) and cation fractions without normalization to 4 using WinPyrox.