

Chemical distinction between igneous and metamorphic orthopyroxenes especially those coexisting with Ca-rich clinopyroxenes: a re-evaluation

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ABSTRACT. A previously suggested simple relationship in a diagram of $(Al_2O_3 \text{ vs. } MgO + FeO + Fe_2O_3)_{\text{opx}}$ for the distinction between igneous and metamorphic orthopyroxenes is shown to be inadequate. A revised diagram is presented and its limitations are discussed. A diagram showing $Fe^{2+}/(Fe^{2+} + Mg) \text{ vs. } 100Ca/(Fe^{2+} + Mg + Ca)$ for orthopyroxenes coexisting with Ca-rich clinopyroxenes proves to be useful for the discrimination of igneous and metamorphic orthopyroxenes and for evaluation of the extent and physical conditions of regional orthopyroxene re-equilibration.

In charnockite migmatite terranes textures of basic rocks (e.g. norites, pyroxene granulites) are often inconclusive for discriminating between an igneous or high-grade metamorphic origin. Bhattacharyya (1971) suggested that such a distinction could be made on the basis of the orthopyroxene composition alone. In a diagram of $MgO + FeO + Fe_2O_3 \text{ vs. } Al_2O_3$ (wt. %) fields for igneous and metamorphic orthopyroxenes are separated by a clearly defined line. Bhattacharyya observed that complications may arise due to host-rock bulk chemistry. He also noted that in thermally and in some regionally metamorphosed rocks, retention of the igneous compositions may be found.

In the past decade a great number of pyroxene analyses have become available. Therefore it was felt necessary to update Bhattacharyya's diagram by supplementing his data with recent data for orthopyroxenes of known origin (excluding volcanic occurrences), because it may present a quick method of elucidating the origin of orthopyroxene-bearing rocks.

Re-evaluation of the diagram shows its limitations and alternatives are explored.

Survey of methods

Most rock-forming pyroxenes may be described in the system $FeO-MgO-CaO-SiO_2$ in which the

ternary system $Mg_2Si_2O_6-Fe_2Si_2O_6-Ca_2Si_2O_6$ represents a planar cross-section. Tie lines joining coexisting ortho- and clinopyroxenes may intersect with the En-Wo and Fs-Wo sides of the ternary system. Hess (1941), Brown (1957), and Wilson (1960) suggested that the intersection points relate to the origin of coexisting phases. However, O'Hara (1960), Muir and Tilley (1958), and Brown (1961) showed that this graphical method is inadequate.

Kretz (1963) suggested that the distribution coefficient,

$$K_D^{\text{opx-clpx}} = (Fe^{2+}/Mg)_{\text{opx}} / (Fe^{2+}/Mg)_{\text{clpx}}$$

can be used to distinguish coexisting ortho- and clinopyroxenes in igneous from those in metamorphic rocks. A simple relationship between the distribution coefficient and the equilibration temperature was suggested. Kretz observed that K_D may depend on the physical conditions of equilibration, but is not affected by variations of the pyroxene Fe^{2+}/Mg ratio under a given set of equilibrium conditions.

The non-ideal nature of the pyroxene solid solution, in which Fe^{2+} has a preference for the $M2$ sites, may result in a complex interrelation between K_D and the equilibrium temperature. Davidson (1968) showed that with increasing $Fe^{2+}/(Fe^{2+} + Mg)$ (= fe-ratio) the $M2$ sites in orthopyroxene will become saturated and Fe^{2+} will enter the $M1$ sites, resulting in different K_D values for Mg-rich and intermediate to Fe-rich pyroxenes. For coexisting ortho- and clinopyroxenes from granulite-facies rocks Kretz (1981) calculated a linear correlation between K_D and the fe-ratio of orthopyroxene. Increasing Ca contents in orthopyroxene will also result in a saturation of $M2$ sites, even at low fe-ratios, because Ca will enter pyroxene $M2$ sites preferentially ahead of ferrous iron. A similar non-ideal behaviour for Ca-rich clinopyroxenes was used by Fleet (1974a, b) to explain differences

in K_D values for igneous and metamorphic pyroxene pairs.

Dependence of K_D on the Al_2O_3 content, tetrahedral Al and the whole-rock chemistry was noted by Maxey and Vogel (1974) and Lindh (1975). Lindh (1974) showed that the distribution of manganese between coexisting ortho- and clinopyroxenes ($K_{D_{Mn}}^{opx-cpx}$) is similar for igneous and metamorphic rocks.

The distribution of Ca between coexisting pyroxenes ($K_{D_{Ca}}^{opx-cpx}$) in igneous and metamorphic rocks is similar, although values greater than 0.16 are restricted to igneous occurrences (Lindh, 1975). Lindh also showed that a multivariate statistical approach may discriminate between coexisting pyroxenes which equilibrated at different temperatures, but that certain limitations are involved because temperature and bulk chemical composition are not uncorrelated parameters.

Sophisticated mathematical expression describing the relationship between $K_{D_{(Fe-Mg)}}^{opx-cpx}$ and the equilibration temperature are given by Wood and Banno (1973) and Wells (1977). The accuracy of the geothermometers is claimed to be $\pm 70^\circ C$ within the calibration range. Hewins (1975) concluded that the Wood and Banno pyroxene geothermometer is accurate within $\pm 50^\circ C$, although the influence of Al on the equilibration temperature has not been considered. Wells (1977) claims that his pyroxene geothermometer is valid for pyroxenes containing up to 10 wt. % Al_2O_3 . Recently Turnock and Lindsley (1981) pointed out that the thermodynamic data and phases employed by Wells are erroneous and necessitate a recalibration of his geothermometer. Fleet (1974c) showed that $K_{D_{(Fe-Mg)}}^{opx-cpx}$ is influenced by the cooling rate. He compared extruded and other quickly cooled rocks with plutonic and metamorphic rocks. This effect is probably negligible for comparison of igneous and metamorphic pyroxenes.

Quadrilateral pyroxene phase relations

The pyroxene quadrilateral $Mg_2Si_2O_6$ - $Fe_2Si_2O_6$ - $MgCaSi_2O_6$ - $FeCaSi_2O_6$ (enstatite-ferrosilite-diopside-hedenbergite) is a subsystem of the ternary system enstatite-ferrosilite-wollastonite. Experimentally determined pseudobinary T-X (Wollastonite) sections for fixed fe-ratios describing the relations between coexisting Ca-poor and Ca-rich pyroxenes (Ross *et al.*, 1973; Ross and Huebner, 1975, 1979; Huebner and Turnock, 1980), show that with increasing temperature the amount of Ca in Ca-rich clinopyroxenes will decrease while it increases in Ca-poor pyroxenes. Since pyroxene equilibration temperatures in basic igneous rocks are likely to be higher than in metamorphic rocks

the effect of Ca on $K_{D_{(Fe-Mg)}}^{opx-cpx}$ (Davidson, 1968; Fleet, 1974a, b) will be marked in Ca-rich clinopyroxenes from metamorphic rocks and in Ca-poor pyroxenes from igneous rocks.

Huebner (1980) observed that all orthopyroxenes (fe-ratio 0.08-0.94) with $Wo > 0.5$ mole % from plutonic and high-grade metamorphic rocks typically contain Ca-rich clinopyroxene exsolution lamellae $\parallel 100_{opx}$. Orthopyroxenes devoid of lamellae have $Wo < 0.5$ mole % which may be the upper limit for Ca solubility in orthopyroxene at low temperatures.

Pyroxene data

Published data for orthopyroxenes with or without coexisting Ca-rich clinopyroxene are collected from the literature (see Appendix). Chemical compositions have been obtained by wet-chemical or by electron microprobe analysis. The latter method analyses all iron as FeO. If the original author(s) give(s) no data for the amount of Fe_2O_3 I have calculated its amount from pyroxene stoichiometry accepting that the sum of X, Y cations ($X_{1-p}Y_{1+p}Z_2O_6$) may be 2.00 ± 0.02 (structural formula based on six oxygens). Ferric iron is calculated using the method of Hamm and Vieten (1971),

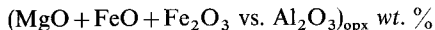
$$M' = \frac{24}{(6 - \frac{1}{2}Fe^{3+})}$$

where $M' = (X + Y + Z)$ based on O = 6.

The amount of Fe_2O_3 is accordingly calculated and the original amount of FeO corrected. In rare cases it was necessary to calculate ferric iron in the coexisting Ca-rich clinopyroxene. Ferric iron was taken into consideration in the calculation of the pyroxene equilibration temperature using pyroxene geothermometry.

Orthopyroxenes with $MnO > 3$ wt. % are excluded because of the effect of Mn on orthopyroxene stability.

References have been checked to ascertain if orthopyroxene is the host phase of inverted pigeonite. In cases of doubt the data are omitted. Inverted pigeonite is not considered in the present paper.



The updated diagram of Bhattacharyya (fig. 1) shows that fields for igneous and metamorphic orthopyroxenes are separated by a 'transition zone' which covers a substantial amount of the data for metamorphic rocks compiled by Bhattacharyya (1971).

The amount of Al_2O_3 in orthopyroxene is very often related to the bulk chemical composition (melt or whole-rock) (e.g. Howie, 1965; Binns, 1965; Davidson and Mathison, 1974; Larsen and Draisin,

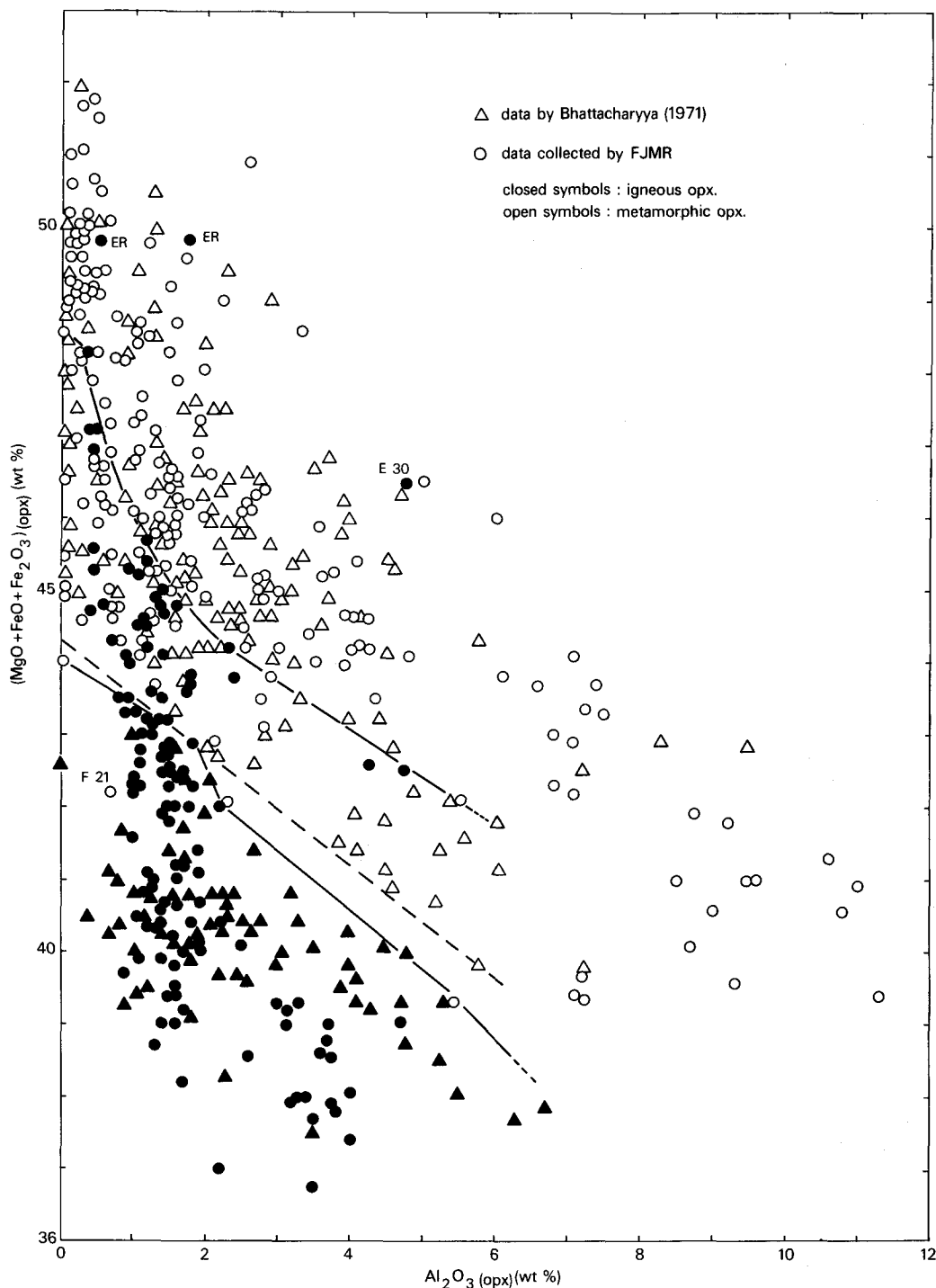


FIG. 1. (MgO+FeO+Fe₂O₃ vs. Al₂O₃)_{opx} (wt. %) for orthopyroxenes from igneous and metamorphic origin (cf. Appendix) showing a 'transition zone' (solid lines) between fields for the two modes of orthopyroxene formation. The original demarcation line of Bhattacharyya (1971) is dashed. F21—ferrohypersthene, metamorphic Iron Formations (Davidson and Mathison, 1974); E30—eulite, hypersthene-granite resulting from magmatic differentiation (Larsen and Draisin, 1950); ER—eulite, Layered Intrusion of Bjerkreim-Sokndal (Rietmeijer and Champness, 1982). Orthopyroxene no. 15 (Deer *et al.*, 1978, table 4) contains 13.9 wt. % Al₂O₃ and is not included in the figure.

1950) and coexisting or coprecipitating phases (e.g. Akella and Boyd, 1973; Windley and Smith, 1974; Fujii, 1976; Sachtleben and Seck, 1981) (cf. data points F21, E30 and ER in fig. 1).

The effect of (high) temperature and total pressure on the Al_2O_3 content has been demonstrated by various authors (e.g. Emslie, 1975; Medaris, 1972). Obata (1976) and Wilson (1976) showed that parameters determining the Al_2O_3 content in orthopyroxenes can be in a complex interrelationship.

It seems thus hardly surprising that in fig. 1. fields for the two modes of orthopyroxene formation overlap.

The Mecklenburg Gabbro-Metagabbro Complex consists of unaffected gabbro and partly to completely recrystallized gabbro. The recrystallization process involved continuous rehomogenization of mafic phases (Hermes, 1970). However, in the original diagram all orthopyroxenes plot in the field for metamorphic orthopyroxenes. In the re-

vised diagram they all are within the 'transition zone' (fig. 2). This example shows the restricted usefulness of the diagram.

$\text{CaSiO}_3(\text{opx})$ vs. $fe\text{-ratio}(\text{opx})$

Orthopyroxene NOT coexisting with Ca-rich clinopyroxene (fig. 3). Metamorphic orthopyroxenes are typically low in wollastonite. For ultramafic and mafic rocks ($fe\text{-ratio} < 0.3$) an isolated field can be outlined within which the wollastonite content is highly variable.

In the Namakkal granulites Madras, India [NMI] (Murthy, 1975), the Amaravathi charnockites Andhra Pradesh, India [AAPI] (Ramaswamy and Murthy, 1973) and a contact metamorphic Iron Formation Montana, USA [CMIF] (Vaniman *et al.*, 1980) some orthopyroxenes have a high wollastonite content (fig. 3). It may indicate un- or incompletely re-equilibrated igneous orthopyroxenes, or the absence of a Ca-buffer, e.g. Ca-rich clinopyroxene.

Orthopyroxene coexisting with Ca-rich clinopyroxene (fig. 4). In the diagram a single line separates fields for igneous and metamorphic orthopyroxenes. Between $fe\text{-ratio}$ 0.2–c. 0.5 the line is well defined but towards higher $fe\text{-ratios}$ the demarcation line becomes the upper limit of CaSiO_3 in Fe-rich metamorphic orthopyroxenes, because no data for Fe-rich igneous pyroxenes are available. Fe-rich igneous rocks are commonly associated with anorthosite masses in Precambrian terranes (cf. Smith, 1974; Malm and Ormaasen, 1978; Rietmeijer, 1979). Subsidiary re-equilibration and recrystallization are commonly extensive in these rocks.

Experimental data on the orthopyroxene-clinopyroxene solvus and on the maximum Ca content in orthopyroxene at low to intermediate pressures (Turnock and Lindsley, 1981; Lindsley 1980; Lindsley *et al.*, 1974; Ross and Huebner, 1979) are rather close to the demarcation line (fig. 5).

Coexisting pyroxenes of the present study show a distinct boundary between igneous and metamorphic origins at 875 °C using the two-pyroxene geothermometer of Wood and Banno (1973), cf. Appendix (Note: the geothermometer of Wells (1977) would produce temperatures c. 70 °C higher, cf. d'Arco and Maury, 1981). The calculated temperatures are in fair agreement with experimental data (fig. 5) suggesting that the demarcation line delineates the maximum solubility of Ca in orthopyroxene at 875 °C. An inventory study by Hewins (1975) showed that pyroxene equilibration temperatures in the hornblende-granulite subfacies are c. 780–860 °C and somewhat higher in the pyroxene-granulite subfacies.

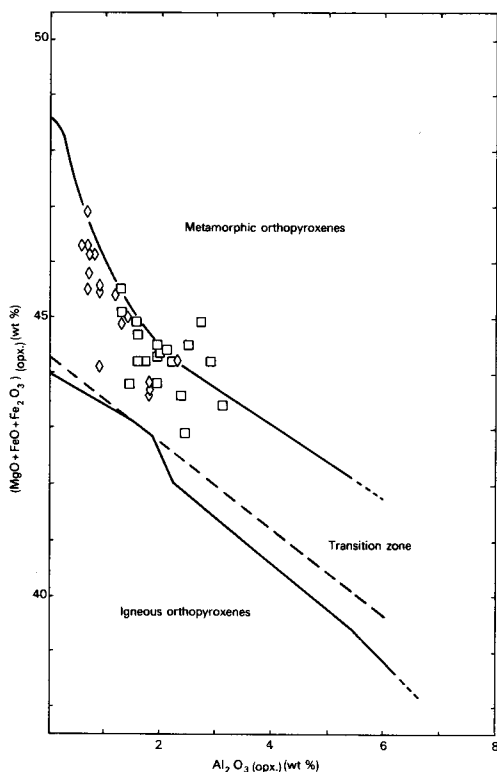


Fig. 2. $(\text{MgO} + \text{FeO} + \text{Fe}_2\text{O}_3)_{\text{opx}}$ vs. $\text{Al}_2\text{O}_3_{\text{opx}}$ (wt. %) for orthopyroxenes from the Mecklenburg Gabbro-Metagabbro Complex (Hermes, 1970; diamonds) and pyroxene-granulites of Swat Kohistan (Jan and Howie, 1980; squares).

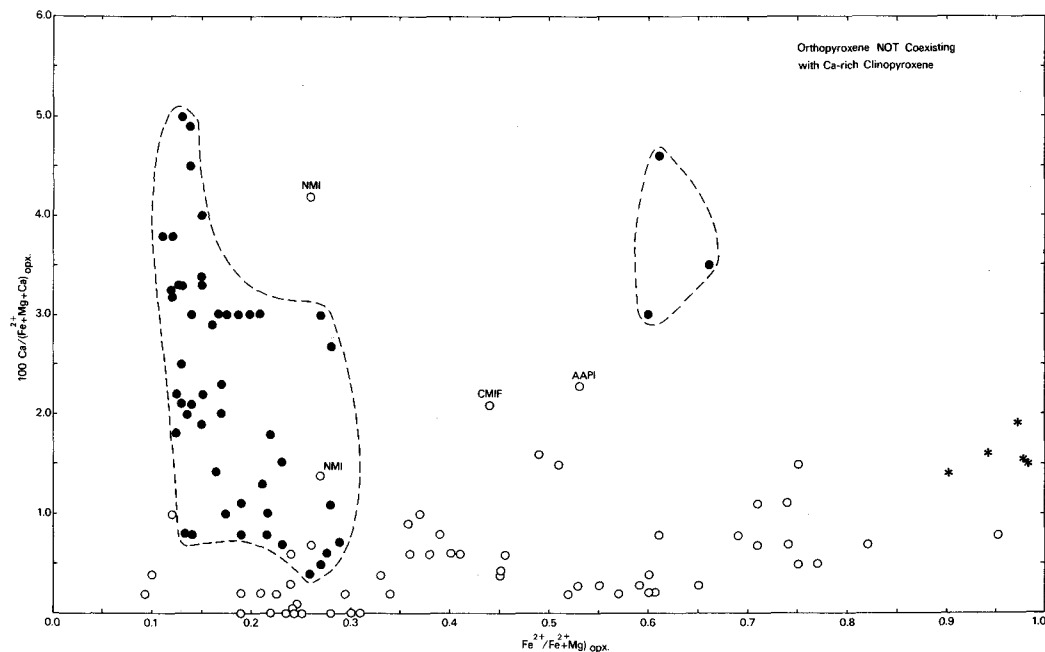


Fig. 3. $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ vs. $100\text{Ca}/(\text{Fe}^{2+} + \text{Mg} + \text{Ca})$ (= wollastonite) for orthopyroxenes *not* coexisting with Ca-rich clinopyroxene of igneous (dots) and metamorphic (circles) rocks. For igneous orthopyroxenes two fields are indicated, viz. for (ultra-)mafic rocks and at higher fe-ratios for the Beaver Bay Intrusion (Nakamura and Konda, 1974). Asterisks: metamorphic orthopyroxenes from the reaction fayalite + quartz in the mangerite-charnockite intrusives in the Lofoten-Vesterålen area (Malm and Ormaasen, 1978). NMI: Namakkal granulites, Madras, India (Murthy, 1975); AAPI: Amaravathi charnockites, Andhra Pradesh, India (Ramaswamy and Murthy, 1973); CMIF: contact metamorphic Iron Formations, Montana USA (Vaniman *et al.*, 1980).

In fig. 4 all orthopyroxene coexisting with Ca-rich clinopyroxene from the Namakkal granulites (Murthy, 1975) and the Amaravathi charnockites (Ramaswamy and Murthy, 1973) would plot in the field for metamorphic orthopyroxenes. It may support the earlier suggestion that only orthopyroxenes coexisting with Ca-rich clinopyroxene are suitable for distinction between modes of formation.

Granulites from Swat Kohistan were previously regarded as slightly or non-metamorphosed igneous rocks. Jan and Howie (1980) observed that the petrology and mineralogy suggest recrystallization under granulite-facies conditions. In the revised diagram (fig. 2) 80% of the orthopyroxenes lies inside the 'transition zone' thus leaving any conclusion on their origin uncertain. In the diagram $\text{Wo}_{(\text{opx})}$ vs. $\text{fe-ratio}_{(\text{opx})}$ (fig. 5) the data plot in the fields for igneous and metamorphic orthopyroxenes which is to be expected for a suite of recrystallized igneous rocks in granulite-facies conditions.

In the revised diagram (fig. 2) orthopyroxenes

from the Mecklenburg Gabbro-Metagabbro Complex provide no clue to the origin of the rocks. However, in fig. 4 the unaffected gabbro plot in the field for igneous orthopyroxenes and the intermediate and completely recrystallized gabbros plot progressively towards and into the field for metamorphic orthopyroxenes.

The examples show that compositions of igneous orthopyroxenes may shift into the field for metamorphic orthopyroxenes as the result of re-equilibration/recrystallization under low-granulite to high-amphibolite facies conditions.

Regional re-equilibration: orthopyroxene trends

Metamorphic orthopyroxenes from the Hudson Highlands, the Adirondack Province, the Belcher-town, and the Cordtland Complexes (Jaffe *et al.*, 1975) show a good linear trend in the diagram $\text{Wo}_{(\text{opx})}$ vs. $\text{fe-ratio}_{(\text{opx})}$ (figs. 4 and 5). Deviating samples (447, T52, T65) are ultramafic rocks which are believed to represent the original igneous conditions. Granulite-facies regional metamorphic

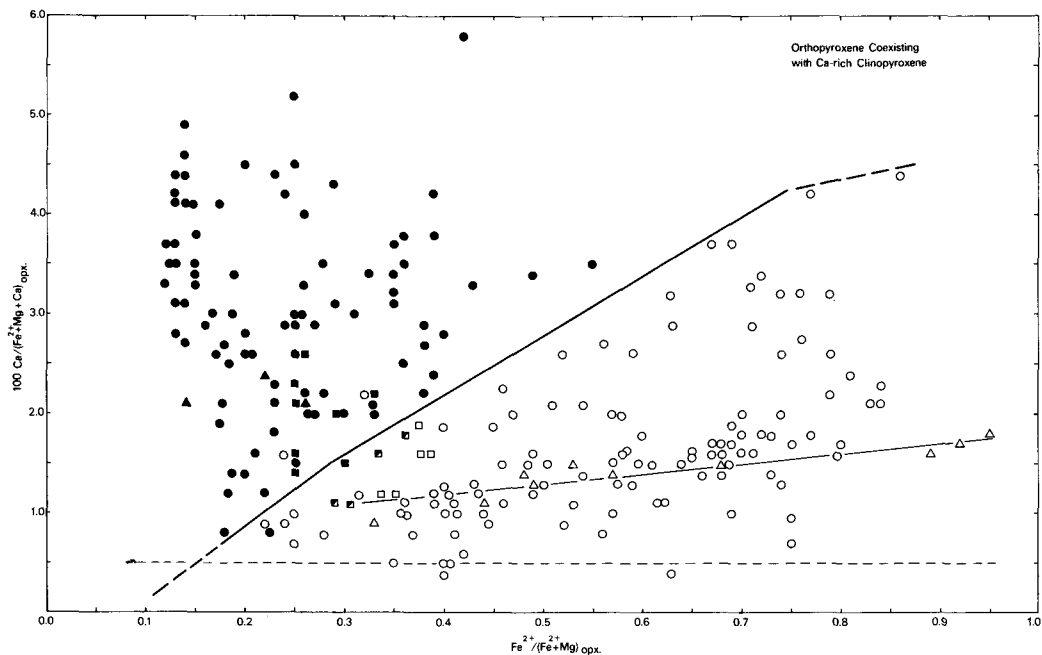


FIG. 4. $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ vs. $100\text{Ca}/(\text{Fe}^{2+} + \text{Mg} + \text{Ca})$ (= wollastonite) for orthopyroxenes coexisting with Ca-rich clinopyroxene of igneous (closed symbols) and metamorphic (open symbols) rocks. Triangles: orthopyroxenes from the Hudson Highlands, Adirondack Province, Belchertown and Cordtland Complexes (Jaffe *et al.*, 1975); squares: orthopyroxenes from the Mecklenburg Gabbro-Metagabbro Complex (Hermes, 1970) (half-filled squares indicate the intermediate gabbros). Maximum solubility of Ca at low temperatures (dashed line) after Huebner (1980). Enstatite data are omitted because of its restricted terrestrial occurrence (cf. Deer *et al.*, 1978).

conditions in the Adirondack Province are estimated at 9–12 kbar/800 °C or 7–9.5 kbar/600 °C (Jaffe *et al.*, 1978).

Intrusive mangeritic to charnockitic rocks in the Lofoten-Vesterålen area (N. Norway) re-equilibrated in the waning stages of the granulite-facies metamorphism during which they were emplaced (Malm and Ormaasen, 1978). Fayalite in these rocks reacted with quartz to form orthoferrosilite. The re-equilibrated igneous and metamorphic orthopyroxenes define a linear trend in the diagram $\text{fe-ratio}_{(\text{opx})}$ vs. $\text{Wo}_{(\text{opx})}$ (fig. 5). Malm and Ormaasen (1978) estimated the physical conditions during re-equilibration at 11 kbar/800 °C or 10 kbar/600 °C.

The Precambrian charnockite migmatite terrain in Rogaland (SW Norway) underwent a period of regional cooling after peak metamorphism of granulite-facies conditions (Kars *et al.*, 1980). Orthopyroxenes from a wide variety of rocks in the migmatite terrain (cf. Hermans *et al.*, 1975; Jacques de Dixmude, 1978) show a fair linear correlation between the fe-ratio and wollastonite content (fig. 5).

The Layered Intrusion of Bjerkreim-Sokndal intruded during and after the peak of metamorphism (Rietmeijer, 1979; Kars *et al.*, 1980). Throughout the intrusion, small sub- to anhedral orthopyroxene crystals may occur next to large crystals of Ca-poor pyroxene. The latter are of igneous origin (Rietmeijer, 1979). Rare crystals of epitaxially related ortho- and Ca-rich clinopyroxene are also present. They are of igneous origin. Bulk compositions for both types of orthopyroxene plot on the linear trend defined by orthopyroxenes from the Rogaland migmatite terrane suggesting that they re-equilibrated towards prevailing regional metamorphic conditions. The observation that the lines for the three areas almost coincide may suggest that re-equilibration in the areas took place under comparable conditions. It may be essentially a slow-cooling feature because the original and re-equilibrated/recrystallized mineral assemblages are rather similar.

The relative positions of the lines and the projected orthopyroxene limbs of the OPX-CPX solvus (fig. 5) support the lower temperature estimate of 600 °C. Also compositions of the coexisting

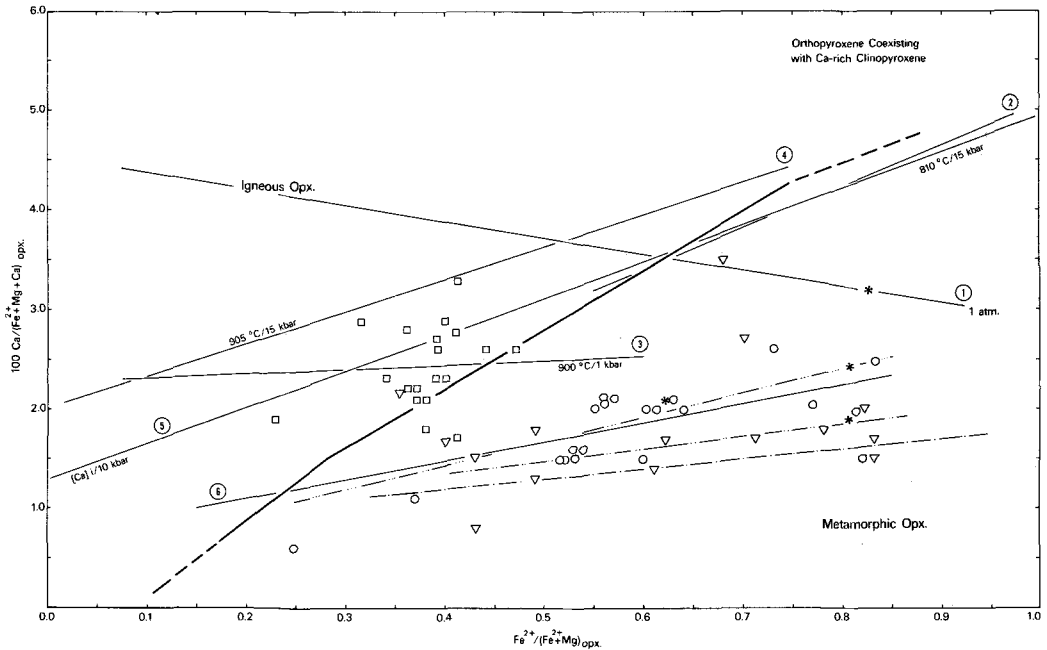


Fig. 5. $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ vs. $100\text{Ca}/(\text{Fe}^{2+} + \text{Mg} + \text{Ca})$ (= wollastonite) showing fields for igneous and metamorphic orthopyroxenes coexisting with Ca-rich clinopyroxene separated by the heavy line. Squares—orthopyroxenes from Swat Kohistan (Jan and Howie, 1980); inverted triangles—orthopyroxenes from mangerite-charnockite intrusives, Lofoten-Vesterålen area (Malm and Ormaasen, 1978); circles—metamorphic orthopyroxenes from charnockite migmatites in Rogaland (Jacques de Dixmude, 1978; Dekker 1978; sample V187/F107-D, Data Base Dept. Petrology, Rijksuniversiteit Utrecht, samples E263/O73); asterisks—orthopyroxene epitaxially related to Ca-CPX from the upper part of the Layered Intrusion of Bjerkreim-Sokndal and the Botnavatnet Igneous Complex (Rietmeijer, 1979). SOLID LINES. 1. Maximum Ca solubility in OPX at its inversion to pigeonite at 1 atm. (Ross and Huebner, 1979); 2. Ditto, c. 10 kbar (cf. Rietmeijer 1979); 3. Orthopyroxene limb of OPX-Ca-CPX solvus at $900^\circ\text{C}/1$ kbar (Turnock and Lindsley, 1981); 4. Ditto, $905^\circ\text{C}/14$ kbar (Lindsley 1980); 5. Ditto, $810^\circ\text{C}/15$ kbar (Lindsley *et al.*, 1974); 6. Maximum amount of wollastonite in metamorphic orthopyroxenes after Howie and Smith (1966). REGIONAL RE-EQUILIBRATION TRENDS: dash-dotted, Adirondack Mountains (Jaffe *et al.*, 1975); dash-double-dotted, Lofoten-Vesterålen (Malm and Ormaasen, 1978); dash-triple-dotted, Rogaland (SW Norway).

Ca-rich clinopyroxenes from the areas coincide in the pyroxene quadrilateral at about 45 mole % CaSiO_3 indicating temperatures of c. 700°C to well below 600°C using the experimental results of Ross and Huebner (1975).

Two data points in fig. 1 (marked ER) are orthopyroxene which forms a partial rim on Ca-rich clinopyroxenes from the upper part of the Layered Intrusion of Bjerkreim-Sokndal. Both pyroxenes are of igneous origin (Rietmeijer and Champness, 1982). In fig. 5 they plot on the trend of regionally re-equilibrated orthopyroxenes from Rogaland. Apparently orthopyroxene re-equilibrated across the orthopyroxene-Ca-rich clinopyroxene interface in response to the regional conditions. Consequently they should be treated as metamorphic orthopyroxenes. The example shows that in the case of slow cooling, igneous

orthopyroxenes may not retain their original composition. The existence of a regional re-equilibration trend may help to recognize this possibility.

Conclusions

In contrast to the results by Bhattacharyya (1971) a diagram showing $(\text{Al}_2\text{O}_3 \text{ vs. } \text{MgO} + \text{FeO} + \text{Fe}_2\text{O}_3)_{\text{OPX}}$ has limited use for the distinction between igneous and metamorphic orthopyroxenes because of the presence of a 'transition zone'. A clear boundary exists in a diagram $\text{Wo}_{(\text{OPX})}$ vs. $\text{fe-ratio}_{(\text{OPX})}$ between fields for igneous and metamorphic orthopyroxenes. The diagram is restricted to orthopyroxenes coexisting with Ca-rich clinopyroxene. Subsolidus reactions in igneous orthopyroxenes may shift their compositions into the metamorphic orthopyroxene field. Thus geological

and petrological constraints must always be considered. The diagram may also be used to evaluate the presence and physical conditions of a regional re-equilibration event.

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APPENDIX

List of references to selected orthopyroxene data used in compilation of figure 1, $(MgO + FeO + Fe_2O_3)_{opx}$ (wt%) vs $(Al_2O_3)_{opx}$ (wt%). (I): igneous orthopyroxenes; (M): metamorphic orthopyroxenes.

The number in parentheses refers to the calculated equilibration temperature for coexisting pyroxenes using the pyroxene geothermometer by Wood and Banno (1973). In rare cases (?) indicates that the temperature could not be calculated because the composition of Ca-rich clinopyroxene is not known. The absence of either a number or a question mark indicates that orthopyroxene does not coexist with Ca-rich clinopyroxene.

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