A multivariate statistical analysis of clinopyroxene composition: empirical coordinates for the crystallisation PT-estimations

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Abstract: In spite of several studies attempting to relate the chemical composition of clinopyroxenes to the nature of their host rock or depth of crystallisation, there is no empirical background to enable compilation of both pressure and temperature conditions of CPX crystallisation. On the basis of experimental data and employing multivariate statistics, the empirical PT-space was developed. This PT-space allows distinction of CPXs crystallising from basaltic magmas over a large range of temperature (1100–1300°C) and pressure (0–20 kbar). In low-pressure crystallisation (P<2 kbar), the Ti/Mg ratio in magma can be related to the clinopyroxene composition enabling primitive and evolved basaltic magmas to be distinguished in spite of coincidence in the En–Wo–Fs values of clinopyroxenes. These diagrams are particularly useful in studies of rocks and xenoliths in the oceanic floor environment, since the stratigraphical sequence of samples and crystallisation parameters, including a nature of possible parental magmas, are difficult to establish directly.

Keywords: Clinopyroxene, clinopyroxene composition, crystallisation, multivariate statistics, Principal Component Analysis, PT-estimations.

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The chemical composition of clinopyroxenes (CPX) reflects the nature of their host rock, as well as the depth and temperature of crystallisation. Several graphical methods exist that attempt to relate CPX composition to rock types and crystallisation conditions. This includes the popular En–Wo–Fs diagram, and some binary and ternary correlation diagrams (e.g. Nisbet & Pearce 1977). Multivariate statistical analysis have been used to distinguish the CPXs of garnet, spinel and plagioclase depth facies (Koloskov & Zhavin 1993). The temperature factor is usually not considered in the resulting diagrams. The petrological-statistical approach, presented here, attempts to separate two effects on CPX composition. Firstly, the CPX composition dependence on the crystallisation pressure and temperature is considered. For this purpose, the multivariate analysis of CPXs from a large number of experimental studies of natural terrestrial and lunar systems is carried out. Secondly, the CPXs from the Thverartindur central volcanic complex, southeastern Iceland, which exhibits a large variety of rock types, are used to develop a discriminant diagram enabling distinction between clinopyroxenes crystallising from primitive olivine-tholeiitic and evolved tholeiitic magmas.

The obtained diagrams can be employed to indicate crystallisation temperature and pressure, and as a tool for the assessment of a coexisting liquid composition, particularly the Ti/Mg ratio of magma. These diagrams are particularly useful in studies of rocks and xenoliths in an oceanic-floor environment, since the stratigraphical sequence of samples and nature of possible parental magmas are difficult to establish directly.

Principal component analysis of clinopyroxene composition

Multivariate statistical analysis is a powerful tool for petrological and petrogenetical purposes since petrology and geochemistry deal with multistructural data arrays which do not have simple properties like the common-sense two or three-dimensional space arrangement. One of the best known multivariate methods is principal component analysis (PCA). The geological application of PCA has been described and analysed by many authors (e.g. Till & Colley 1973; Marriot 1974; Le Maitre 1982). Only brief comments will be given here.

PCA is a mathematical technique for reducing a number of original variables into a new set of variables, called principal components which contain a decreasing amount of variance and are uncorrelated with each other. Usually, the first two or three principal components account for a sufficiently high proportion of variance to allow the remaining components to be dismissed. In an idealised case, every component will be interpreted as a process(es).

Geometrically, the derivation of the principal components involves rotation of the original variable axes to positions of maximum variance. The first principal component axis is oriented so as to account for a maximum proportion of the variability in the data; the second axis is in turn orthogonal to the first axis and oriented in a way that it explains as high a proportion as possible of the remaining variability. All the remaining axes are mutually orthogonal and arranged to account for decreasing portions of the variability. In the present case, eight variables were considered, viz. SiO2, TiO2, Al2O3, total FeO, MnO, MgO, CaO, and Na2O, forming an 8-dimensional space and gaining the characteristics of closed data array.

Eigenvectors can be calculated either from a variance-covariance matrix or a correlation matrix. The choice of input matrix is highly dependent on the original data and petrologic task. Le Maitre (1982) discussed the choice of matrix type. Although the original data were measured on the same scale (wt.%), it is considered reasonable to use the correlation matrix for extracting the eigenvectors. This approach gives the same weight to every element in the CPX composition. Using the correlation matrix, the weight of the elements is standardised into the range -1 ... 1. Thus, each element acts in a correlative relation to each other and an influence arising from differences in the magnitude of the total weight percentages can be neglected. In order to avoid the constant-sum problem the log-ratio transformation has applied. This procedure has described by Aitchison (1986).
Table 1. Normalised principal component loadings and total cumulative variance (%) for the first three PC as calculated from the clinopyroxene compositional matrix. For calculation procedure see text.

<table>
<thead>
<tr>
<th>Variable</th>
<th>1st PC</th>
<th>2nd PC</th>
<th>3rd PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.843</td>
<td>-0.510</td>
<td>0.029</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-0.354</td>
<td>0.738</td>
<td>-0.406</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-0.764</td>
<td>-0.438</td>
<td>-0.142</td>
</tr>
<tr>
<td>tot FeO</td>
<td>0.653</td>
<td>0.445</td>
<td>-0.008</td>
</tr>
<tr>
<td>MnO</td>
<td>-0.098</td>
<td>0.326</td>
<td>0.922</td>
</tr>
<tr>
<td>MgO</td>
<td>0.584</td>
<td>-0.712</td>
<td>0.212</td>
</tr>
<tr>
<td>CaO</td>
<td>0.814</td>
<td>-0.230</td>
<td>-0.259</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-0.842</td>
<td>-0.211</td>
<td>-0.228</td>
</tr>
<tr>
<td>Tot. cum. var.</td>
<td>67</td>
<td>83</td>
<td>91</td>
</tr>
</tbody>
</table>

Empirical relationship between PT and clinopyroxene composition as derived from experimental data

Several studies have used clinopyroxene compositions as geothermometers and geobarometers. Pyroxene pairs have frequently been used for geothermometry (e.g. Lindsley & Dixon 1976; Wells 1977; Nickel et al. 1985). Fe-Mg exchange reactions between mineral pairs have been used in geothermometry for garnet lherzolite assemblages (Finnerty & Boyd 1984; Carswell & Gibb 1987). Geobarometers involve multimineral assemblages (Mukhopadhyay et al. 1992) or need mineral components as enstatite, diopside and an aluminous phase (Wood 1974). Both geothermometers and geobarometers are based on thermodynamics of the coexisting minerals and have been calibrated either from the experimental data set of oversimplified systems (MAS, CMAS, SMAC) or have completely empirical calibrations and corrections. No geothermobarometers are known to the author over the whole petrogenetically reasonable PT-range. Here, an attempt is made to derive empirical vector-space, compiling both P and T and which is based only on single clinopyroxene compositions. For this purpose, a large data set of 338 experimental clinopyroxene analyses was collected from the literature and from the experimental data base INFOREX encompassing temperatures between 1000 and 1470 °C and pressures from 1 atm to 34 kbar. Natural lunar basalts (Nielsen et al. 1988), MORBs (Walker et al. 1979; Grove & Bryan 1983; Tormey et al. 1987; Longhi & Pan 1988) and island-arc rocks varying in their starting compositions from andesitic (Grove & Juster 1989; Baker & Eggler 1987) to high-Mg basalts (Elton & Scarfe 1984; Falloon & Green 1987; Tormey et al. 1987) have been included. High-Al (Grove et al. 1982; Bartels et al. 1991) and alkali basalts (Sack et al. 1987) were also included. Run-duration ranges between 4 and 600 hours; oxygen buffers were mainly quartz-fayalite-magnetite, iron-wustite, wustite-magnetite, nickel-Ni oxide or were not specified. Iron, graphite and molybdenum capsules, and in few cases platinum loops were used as containers in experiments.

The first step in the PCA was to determine a set of eigenvectors on which loadings the empirical temperature and pressure fields were normalised. Normalised principal component loadings are shown in Table 1. According to the criterion described above, two eigenvectors derived from correlation matrix are calculated as:

\[ X_{PT} = 0.446\text{SiO}_2 + 0.187\text{TiO}_2 - 0.404\text{Al}_2\text{O}_3 + 0.346\text{FeO(tot)} - 0.052\text{MnO} + 0.309\text{MgO} + 0.431\text{CaO} - 0.446\text{Na}_2\text{O} \]
\[ Y_{PT} = -0.369\text{SiO}_2 + 0.535\text{TiO}_2 - 0.317\text{Al}_2\text{O}_3 + 0.323\text{FeO(tot)} + 0.235\text{MnO} - 0.516\text{MgO} - 0.167\text{CaO} - 0.153\text{Na}_2\text{O} \]

where \( X_{PT} \) and \( Y_{PT} \) are the scores of the first and second eigenvectors, respectively. The original data were clustered into the simplified composition-pressure groups in order to establish the PT-fields. In Fig. 1, the temperature and pressure data distribution of experimental CPX are shown; the temperature data have been ranked by interval of 25–50° while six pressure intervals have been considered. It can be noted that there is good correspondence of run temperature and pressure with eigenvector scores, with exception detected only for andesitic compositions. Therefore, the use of present plot to estimate clinopyroxene crystallisation temperature and pressure, being in equilibrium with andesitic magma, may be inadequate.

At temperatures below and slightly above 1100°C, the long run
long duration can result in a shift of eigenvector scores. Long-duration assemblages usually contain oxides (magnetite/ilmenite), and therefore it can be assumed that later Fe-Ti oxide saturation may also modify the CPX composition, which was originally in equilibrium with the liquid, and drive the CPX eigenvector scores to the right (arrow in Fig. 1). In other words, the magnetite and/or ilmenite precipitation may have a drastic influence on the elemental relationships in CPXs.

**Thverartindur clinopyroxenes in the empirical PT-space**
The plutonic part of the Tertiary Thverartindur central volcanic complex, SE Iceland, is composed of several multiple composite intrusions ranging from ultramafic to acid compositions. The basaltic suite of intrusives has both primitive and evolved basaltic compositions which represent different magmas and products of magma mixing. The geology of the Thverartindur complex is treated by Bromann & Soesoo (1994) and Soesoo (1995a, 1995b).
Thverartindur CPXs occupy the low pressure field (P<2 kbar) in the temperature interval of 1100–1150°C (Fig. 2). These conditions can be realised above a depth of 5 km, which is consistent with the general geology and erosional history of the complexes. Some CPXs from the olivine-tholeitic unit fall inside the 2 kbar field, which can be explained either by uncertainties arising from the empirical nature of PT-space or by a relictic nature of CPX crystallisation at greater depth. The CPXs from the ultramafic pyroxene xenolith tend to plot on or close to the 2 kbar pressure field. This is not surprising since an ultramafic xenolith may be carried from the floor or wall of a deeper magma chamber.

Some scattering of CPX analyses in PT-space is likely related to ilmenite-magnetite saturation. CPXs from the quartz-tholeitic gabbros have roughly twice the scatter of the olivine-tholeitic samples, which corresponds well with the high oxide abundances, and iron-rich chemical composition of the rock. Thus, the amplitude of Fe-Ti enrichment in magma can be mirrored in the clinopyroxene composition, i.e., the mutual relationships of major and minor elements in CPX appear related to magma composition. It is necessary to mention that the Thverartindur “olivine- and quartz-tholeitic CPXs” are nondistinctive in the En-Wo-Fs diagram, but display different zoning and trace element distribution patterns (Soesoo 1995a).

**Clinopyroxenes from MORBs and other volcanics in the empirical PT-space**

Clinopyroxene compositions from different types of oceanic and continental environments can be calculated in PT-space, and compared with other kinds of PT-estimation.

Three groups of ultramafic xenoliths collected from alkali basalts in the island of Hierro, Canary Islands (Neumann 1991) show pressure dependence, while the corresponding temperature is 1150–1200°C (Fig. 3). Generally, this temperature range is systematically higher than those estimated using other geothermometers (see Neumann 1991). The closest temperature values for the Cr-diopside series were obtained using Al solubility in OPX (Sachtelen & Seck 1981), but for the Hierro Al-augite series, the best agreement is with the geothermometer of Lindsay & Anderson (1983). Higher temperature estimations are not surprising, since exsolution modifies the original pyroxenes. The CPXs from the Cr-diopside series plot mainly in the 2–5 kbar field, while Al-augite series pyroxenes plot in the higher pressure field up to 6–10 kbar (Fig. 3). Pyroxenes from a third type of xenolith – gabbroic with estimated equilibrium temperatures of 1020–1190°C (Neumann 1991) – give a different pressure; 2 kbar and 6–9 kbar (not shown).

Chen et al. (1992) have studied ultramafic xenoliths from Hualalai volcano, Hawaii. These xenoliths are cumulates from Hawaiian alkaline magma. The depth estimations range from 8 to 30 km i.e. 3–10 kbar (Roedder 1965; Chen et al. 1992). In Fig. 3 the dunite, wehrlite and Ol-pyroxenite xenoliths fall mostly in the field of 6–10 kbar being consistent with the estimations of Chen et al. (1992). The equilibration temperatures estimated by olivine-spinel and pyroxene geothermometers range from 1000 to 1200°C. This temperature is in good agreement with those in the PT-space diagram.

The magmas reaching the surface in the Southwest Indian Ridge are generated over a wide range of depths; 15–60 km (Meyer et al. 1989). The cumulate gabbros, diabases, norites to andesites from this area plot on an elongated field of moderate to low pressure. Relying upon the PT-space diagram it is suggested that CPXs of these rock formations have crystallised at low (<2 kbar) to moderate (2–5 kbar) pressure with prevalence of lower values (Fig. 3).

The gabbros of the Atlantis II Fracture Zone on the Southwest Indian Ridge (Ozava et al. 1991) exhibit low-pressure features; only a few olivine-tholeitic samples plot close to the 2 kbar pressure boundary. More evolved gabbros (oxide-bearing gabbros) from the same location plot in the low-pressure field and show less than 1100°C for crystallisation temperature (Fig. 3).

The gabbroic rocks from the Mid-Cayman Rise Spreading Centre, reported by Elthon (1987), show evidence of low and moderate pressure CPX crystallisation in the PT-space (Fig. 3). Based on the higher Mg-number and Al, Cr and Ti oxide contents in CPXs, Elthon (1987) has discussed the low-pressure nature of some of these rocks and suggested a crystallisation range of 5–10 kbar. One group of CPXs plot on the field similar to the low-pressure CPXs of the Thverartindur complex, whereas another group, emphasised by Elthon (1987) as belonging to a higher pressure regime, plot in the field of 6–10 kbar (Fig. 3).

Xenoliths with high-pressure assemblages, such as eclogites in kimberlite pipes and low- and high-Cr eclogites (E in Fig. 3; Sobolev 1974; Vladimirov et al. 1976; Koloskov & Zharinov 1993) fall in the PT-space diagram in the pressure field higher than 16 kbar. The Iherzolites in basanites (L in Fig. 3; Francis 1976, 1978) occupy the field of 6–10 kbar, while the Iherzolites from alkali basalts in Primorje (P in Fig. 3; Denisov 1974) fall on the boundary between the 6–10 kbar field and the 11–15 kbar field. Spinel-pyroxenites (A in Fig. 3) from Victoria (Griffin et al. 1984) and plagioclase-olivine inclusions (PO in Fig. 3; Aoki 1964; Volynets et al. 1978) exhibit temperatures below 1300°C and pressures around 10 kbar.
Distinguishing between the clinopyroxenes crystallising from primitive and evolved magmas

Analysing the CPX chemistry related to the different original liquid compositions and pressure applied, it appears that the CPXs sustain direct information about parental liquid composition only below a pressure of 2–3 kbar.

In order to specify the internal relationship of major and minor constituents of CPXs at low pressure and to quantify the chemical imprints related to original magmas, principal component analysis was employed. The raw data matrix includes only the Thverartindur CPX analyses because: (1) insufficient low pressure experimental analyses were carried out under uniform conditions among the basaltic systems and also the compositional differences caused by run durations and different oxygen buffers may affect the small-scale data array (i.e. low-pressure basalts), (2) there are some difficulties in correlating CPX analyses with the starting liquid composition, and (3) the Thverartindur central volcanic complex is a well-investigated rock formation with a large number of natural low pressure CPX analyses available.

From a total of 201 CPX core analyses, 150 were selected which gave the sum of the oxides close to 100% (±1%). Then, the eigenvectors were computed according to the procedure described above, with the only exception that Cr₂O₃ was included. Two eigenvectors, Xₘ and Yₘ, derived from the correlation matrix are:

\[ Xₘ = -0.178SiO₂ + 0.234TiO₂ + 0.211Al₂O₃ + 0.307Cr₂O₃ - 0.562FeO(tot) - 0.599MnO + 0.056MgO + 0.373CaO - 0.102Na₂O \]

\[ Yₘ = 0.562SiO₂ + 0.212TiO₂ + 0.259Al₂O₃ + 0.211Cr₂O₃ + 0.027FeO(tot) - 0.172MnO + 0.522MgO - 0.481CaO + 0.05Na₂O \]

Plotting individual CPX analyses from the Thverartindur complex as their Xₘ and Yₘ eigenvector scores, the discriminant line separating CPXs crystallising from a primitive olivine-tholeiitic magma and more evolved quartz-tholeiitic magmas can be drawn (Fig. 4). The line is easily constructed through the coordinates of (–2.25, 4) and (–8.30) in the Xₘ – Yₘ space.

The CPXs from the ultramafic rocks types reveal a different pattern; CPXs from ultramafic xenolith essentially vary along the Yₘ axis, while CPXs from the dike occupy a field close to the separating line (Fig. 4). This feature may indicate a different depth of crystallisation, which could be deeper for ultramafic xenolith. The Ti/Mg ratio of magma, which is an important index of the stage of magma maturity, can be related to CPX composition. In Fig. 4, three Ti/Mg ranges have been suggested, corresponding to olivine-tholeiitic, quartz-tholeiitic, and granitic magmas, respectively. Thus the first examination of magma type may be accomplished on the basis of clinopyroxene compositions. This test is particularly necessary in the case of primitive and evolved basaltic liquids which can generate CPXs indistinguishable in major composition (En–Fs–Wo).

Comparison of CPXs from the Tverartindur complex and other ocean floor formations (Elthon 1987; Meyer et al. 1989; Ozava et al. 1991; Neumann 1991; Chen et al. 1992) has shown that this discriminant diagram is also valid in the case of highly cumulative rocks derived from MORB-type magmas.

Since the PT diagram (Fig. 2) was developed on the basis of eight elements, the best results are indeed obtained when all these elements are measured and their sum falls into the 0–2.0 per cent uncertainty range. The missing element (usually Na, Mn or Cr) can displace the position in these diagrams, especially when the content of each missing element exceeds 1 per cent. Once again, it should be mentioned that the presented diagram is of a statistical nature and plotting a single analysis on the PT-plot does not provide real solutions to unknown parameters.

Summary and conclusions

(1) The clinopyroxene compositions from experimental studies were analysed by principal component analysis and an empirical PT-space was derived. The PT-plot derived permits distinction between CPXs crystallising from basaltic magmas over a large temperature (1100–1300°C) and pressure range (0–20 kbar).

(2) At low pressure (P<2 kbar), a Ti/Mg ratio diagram, based on statistical analysis of 150 CPXs, enables the separation of CPXs crystallised from primitive (olivine-tholeiitic), evolved (quartz-tholeiitic) basaltic and granitic magmas.

(3) These two diagrams show good agreement with basic petrologic investigations procured from the MORB samples and volcanics in different tectonic settings. The diagrams are particularly useful in studies of rocks and xenoliths in the ocean floor environment, since the stratigraphical sequence, nature of parental magma and crystallisation temperature and pressure are difficult to establish directly.

(4) Using chemical analyses of rocks and clinopyroxenes, and by employing the acheived diagrams, it can be concluded that the gabbroic, ultramafic and hybrid rocks of the Thverartindur central volcanic complex on southeastern Iceland, are generated at low pressure (less than 5 km depth) and mostly in a temperature interval of 1100–1150°C, while CPXs from one hybrid rock type are crystallised at below 1100°C.

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References


