Relationship Between Clinopyroxene Composition and the Formation Environment of Volcanic Host Rocks

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This work presents new binary and ternary diagrams based on the chemical composition of volcanic clinopyroxenes that distinguish the tectonic environments in which their host rocks were formed. The present work identifies the following tectonic environments: intraplate calc-alkaline volcanism (IP), alkaline volcanism in a thinned continental crust (CI), alkaline volcanism in islands over an oceanic crust (OI), calc-alkaline volcanism in subduction zones (SU), calc-alkaline volcanism originating in crustal anatexis (AX), and ultrapotassic volcanism (UP). The SU field was subdivided into andesitic (AN) and trachyandesitic (TA) compositions.

Keywords: Clinopyroxenes, Volcanic rocks, Geotectonic environments

Introduction

Clinopyroxene is one of the most widely distributed minerals, which is found as a component of many metamorphic, plutonic and volcanic rocks (in acidic through to basic rocks). Its varying chemical composition in these different host rocks provides a good marker of the environments in which the latter was formed.

Le Bas (1962) was the first to distinguish between the clinopyroxenes of alkaline, peralkaline and non-alkaline rocks in terms of their \( \text{Al}_2\text{O}_3 \), \( \text{SiO}_2 \), Fe, Mg and Ca contents. Later, Nisbet and Pearce (1977) precisely distinguished between ocean floor basalts (OFB), volcanic arc basalts (VAB), within-plate alkaline basalts (WPAB) and within-plate tholeiitic basalts (WPT) though the use of (mainly) a \( \text{TiO}_2 \)-\( \text{MnO} \)-\( \text{N}_2 \) ternary diagram. Leterrier et al. (1982) then described the use of binary diagrams involving Ti, Ca, Al, Cr, Na to establish fields in basaltic rocks from environments defined as alkaline, orogenic and expansion (tholeiites). These same diagrams were valid for use with palaeovolcanic rocks. More recently, Beccaluva et al. (1989) studied the Ti-Si-Na relationship in augitic clinopyroxenes in basalts from ophiolitic complexes of the Phanerozoic age and established fields for MORB, OIB, IAT and boninites (BON) in binary and ternary diagrams. However, all the above rocks were basic (basaltic); no acidic or intermediate rocks were considered in the preparation of any of the above diagrams.

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A great quantity of geochemical data has been obtained over recent decades on clinopyroxenes from areas of current and recent volcanic activity, providing an opportunity to establish relationships between their chemical composition and the tectonic environments in which their host rocks formed. The aim of the present work was to construct binary and ternary diagrams based on the chemical composition of clinopyroxenes from basic, acidic and intermediate volcanic rocks of different types - something that till now has only been done for basic rocks.

Methodology
The results of 165 electronic microprobe analyses of clinopyroxenes from acidic, basic and intermediate volcanic rocks (basanites, basalts, trachybasalts, trachyandesites, basaltic andesites, andesites, phonolites, trachytes, dacites and rhiolites) were examined and projected in binary and ternary diagrams. All the data used in this work were taken from published papers, authored or coauthored by this author since 1984 (Araña et al., 1983 and 1984; Viramonte et al., 1984; Aparicio et al., 1991; Aparicio and García, 1995; Aparicio et al., 1997; Solana, 1998; Aparicio and García, 2008; Aparicio and Frazetta, 2008; and Aparicio and García, 2009). The electronic microprobe analyses cited in these works were all performed under the same conditions at the Electron Microscope Laboratory of the Complutense University, Madrid, using a Jeol-Jxa-8900 apparatus with EPMA, employing a WDS set at 15 kv and 20 nA. Only clinopyroxenes in volcanic rocks of the Cenozoic age (Miocene-present) from areas of current or recent volcanic activity and which had not been altered by later processes were taken into account. The TAS classification and diagram were used for the classification of the host rock and provided the nomenclature used (Le Maitre, 1984). The host rock content margins for SiO$_2$ and alkalis were understood to be those represented in the latter diagram.

Clinopyroxene composition formulae were produced by taking six oxygens into account, using the PTOXY (Ferric) program (Nasir, 1994). Clinopyroxene microprobe analysis data were taken for alkaline and calc-alkaline volcanic host rocks from well-studied areas. Alkaline volcanism was represented by areas of the Iberian Peninsula and the Canary Islands, this included the basic volcanism of the Spanish southeast (Cartagena Sector) (Aparicio and García, 2009), with its Pliocene basalts and basanites (Bellon et al., 1983). This area is located in a zone where the continental crust is some 22 km thick (De Larouziere et al., 1988) undergoing a rifting process. Data were also used for alkaline rocks of the Olot area (Northeast Iberian peninsula), which is home to basanitic rocks (Araña et al., 1983) of about 0.1-2.5 Ma. This area lies on a continental crust some 30 km thick (Gallart et al., 1980) in an area of still-active rifting. Further data were used for alkaline rocks of the Columbretes Islands (Aparicio and García, 1995) in the Western Mediterranean, which lie on an area of thinned continental crust some 15 km thick (Martín and Surinach, 1988). These islands are home to basanitic rocks approximately 0.1-0.3 Ma., and phonolitic rocks approximately 0.3 Ma. Finally, clinopyroxene data for basanitic and basaltic host rocks from the historic volcanoes of Tenerife (Solana, 1998) were used. In this area, the oceanic-type crust (Araña and Ortiz, 1991) is approximately 13 km thick (Ortiz et al., 1986).
Clinopyroxene data for calc-alkaline rocks from two areas of the Western Mediterranean, two areas of the Andes (Argentina) (Araña et al., 1984; and Viramonte et al., 1984), and an area of the Antarctic Peninsula (Aparicio et al., 1997) were also used. One of these Mediterranean areas was the Acolian Islands, which were located in a zone of active subduction (Barberi et al., 1994). The composition of their rocks ranged from trachyandesites to rhyolites and trachytes, all of historic age (Aparicio and Frazetta, 2008). The other Mediterranean area was the Island of Alboran, located in a sector of thinned continental crust approximately 17 km thick (Hatzfeld and Boloix, 1978) and is home to basaltic andesitic rocks approximately 7-25 Ma. (Bellon and Brousse, 1977; and Aparicio et al., 1991). These rocks and those of the Spanish southeast are reported to have formed under calc-alkaline anatexic conditions (Munksgaard, 1984; Zeck, 1992; Cesare et al., 1997; and Zeck et al., 1998).

Clinopyroxene data were also taken for calc-alkaline Andean rocks originating in areas of subduction between the Nazca and American plates. These areas, Arizaro and Archibarca, were the sites of recent volcanism (Viramonte et al., 1984). Arizaro is home to basaltic andesites, while Archibarca contains basalts, basaltic andesites, andesites, dacites and trachytes. Finally, clinopyroxene data were taken for calc-alkaline rocks from an area of active subduction between the Drake and Shetland Plates (Antarctic Peninsula). The volcanism of Deception Island was represented by a series of rocks that varied in composition from trachyte and dacite to andesite, basaltic andesite and basalt (Aparicio et al., 1997). The crust in this area is approximately 32 km thick (Guterch et al., 1985).

Results and Discussion

The environments in which the present host rocks formed were either intraplate calc-alkaline volcanism (IP), alkaline volcanism in a thinned continental crust (CI), alkaline volcanism in islands over an oceanic crust (OI), calc-alkaline volcanism associated with subduction (SU), calc-alkaline volcanism related to crustal anatexic processes (AX), or ultrapotassic volcanism (UP). These environments were clearly distinguished on the basis of the composition of the clinopyroxenes of these host rocks contained. In general, no differences were seen between the projections for the clinopyroxenes of the basic, acidic or intermediate host rocks. The division between the clinopyroxenes of alkaline and calc-alkaline rocks, however, was always clear. Nearly, all the binary diagrams support this separation, as reported by Le Bas (1962).

The Si-Fe binary diagram (Figure 1) defines the AX, SU and CI fields. The OI and IP fields, however, remained somewhat indeterminate. In general, however, the separation of the alkaline (alk) and calc-alkaline (cal) fields was quite clear. The Mg-Ti binary diagram (Figure 2) shows the same fields, although the CI and OI fields were superimposed and the IP fields well separated. In the Mg-Al binary diagram (Figure 3), the IP and OI fields show some overlapping. In the SU field, an appreciable separation was seen between trachyandesite (TA) and andesitic (AN) host rocks.
Figure 1: Si-Fe Diagram for the Clinopyroxenes of Volcanic Rocks from Different Structural Backgrounds

Note: The diagram shows the separation between the clinopyroxenes of the alkaline (alk) and calc-alkaline (cal) series and defines the following formation environments: intraplate calc-alkaline volcanism (IP), alkaline volcanism in a thinned continental crust (Cl), alkaline volcanism in islands over an oceanic crust (OI), calc-alkaline volcanism associated with subduction (SU), calc-alkaline volcanism related to crustal anatexic processes (AX), or ultrapotassic volcanism (UP). Symbols: IP = + (Cartagena, southeast Iberian Peninsula); X = Olot area, northeast Iberian Peninsula; OI = ▲ (Canary Islands); Cl = □ (Columbretes Islands, western Mediterranean); SU = ■ (Acician Islands, Mediterranean zone); ♦ (Deception Island, Antarctic); O = Andes, Arizaro sector; ● = Andes, Archibarca sector; Y = Andes, Mendoza sector; UP = o (lamproites of the Spanish southeast); AX = * (anatexic rocks of Alboran western Mediterranean sector).

Figure 2: Mg-Ti Diagram for the Clinopyroxenes of Rocks from Different Structural Environments Showing the Cl and OI Fields Overlapping

Note: The separation of the clinopyroxenes of the alkaline and calc-alkaline fields is quite clear.
Figure 3: Mg-Al Diagram Showing Separation of the Different Structural Environments

Note: The SU field is divided on the basis of the trachyandesitic (TA) or andesitic (AN) composition of the host rocks.

The \((\text{TiO}_2 \times 10)\)-FeO-(\(\text{Na}_2\text{O} \times 10\)) projection (Figure 4) provides good definition of different fields. The SU field was again divided into the AN and TA compositions. The IP and CI fields appeared superimposed, while the OI field lay at the vertex \((\text{TiO}_2 \times 10)\).

Figure 4: \((\text{TiO}_2 \times 10)\)-FeO-(\(\text{Na}_2\text{O} \times 10\)) Diagram Showing the SU Field Divided on the Basis of the Trachyandesitic (TA) or Andesitic (AN) Composition of the Host Rocks

Note: The CI and IP fields overlap, although the basaltic compositions of the IP field fall to the right.
The \((\text{Al}/5)-\text{Ti}\)-(\text{Mg}/20)\) diagram (Figure 5) also provides good separation between the fields, with the AX subfield more clearly visible within the calc-alkaline field. The separation between the TA and AN compositions in the SU field was also clear.

**Figure 5: The \((\text{Al}/5)-\text{Ti}\)-(\text{Mg}/20)\) Diagram Distinguishing the CI, OI, IP and AX Fields**

The \((\text{Mn} \times 10)-(\text{Fe}/10)-\text{Ti}\) diagram (Figure 6) perfectly distinguishes between the alkaline (alk) and calc-alkaline (cal) fields and between the SU, \((\text{IP} + \text{CI})\) and OI fields.

**Figure 6: The \((\text{Mn} \times 10)-(\text{Fe}/10)-\text{Ti}\) Diagram Separating the Clinopyroxene Fields of the Alkaline (alk) and Calc-Alkaline (cal) Series**

*Note: The AX, SU and OI fields are outlined.*

The \((\text{TiO}_2 \times 1)-(\text{CaO}-(\text{FeO} \times 2))\) diagram (Figure 7) also distinguishes well between different fields, although the distinction between the OI and IP fields was relatively poor. This
diagram also resolves the projection of the clinopyroxene from the lamproitic host rocks of southeastern Spain with a well-defined UP field, irrespective of whether their origin was mantleic (López and Rodríguez, 1980) or crustal anatexic (Aparicio and García, 2008).

Figure 7: The (TiO$_2$ * 10)-CaO-(FeO * 2) Diagram Showing the Fields Established Above

Note: Notice that the large ultrapotassic (UP) sector is occupied by the clinopyroxenes found in the lamproitic host rock of the Spanish southeast. No overlap with other clinopyroxenes occurs.

The (SiO$_2$/10)-(TiO$_2$ * 10)-(Al$_2$O$_3$ * 2) diagram (Figure 8) also distinguishes different fields, although the IP and OI fields were smaller. A comparison with the MnO-TiO$_2$-Na$_2$O

Figure 8: The (SiO$_2$/10)-(TiO$_2$ * 10)-(Al$_2$O$_3$ * 2) Diagram Again Defining the Fields Established Above

Note: The AX, SU and OI fields are outlined.
The diagram of Nisbett and Pearce (1977) (Figure 9) shows that some of the fields defined by these authors superimpose those of the present work. For example, the latter authors’ field C (assigned to within-plate alkaline rock [WPA]) superimposes the OI, IP and CI fields of the present work. Similarly, the D and E fields (assigned to VAB + WP) occupy the area largely covered by SU in the present work.

**Figure 9: Comparison of the Nisbett and Pearce (1977) Diagram and the MnO-TiO-Na₂O Diagram of the Present Work**

![Diagram showing the comparison of two different volcanic diagrams.]

**Note:** The coincidence of field C (within-plate alkaline [WPA] rocks) and the present OI, CI and IP fields is complete, as is that between the E and D fields (largely including volcanic arc basalts) and the present SU field.

The present results provide just a taste of what clinopyroxene analysis could provide in terms of identifying the formation environments of their host rocks. New data will allow the updating and amplification of the diagrams presented in this work.

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**References**


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