

Origin and significance of spinel and garnet pyroxenites in the shallow lithospheric mantle: Ultramafic massifs in orogenic belts in Western Europe and NW Africa

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Abstract

Anhydrous spinel and garnet pyroxenites form a small (<10%) but integral part of the shallow sub-continental lithospheric mantle. They occur as layers or dykes within tectonically-emplaced ultramafic massifs and display lithologies that range from orthopyroxenite through websterites to clinopyroxenite, with or without olivine. The ultramafic massifs in orogenic belts of western Europe and Morocco contain many different varieties of mantle pyroxenites that show a wide range of major and trace element compositions. Their bulk compositions tend to vary between at least three end-members: two of these are similar to the constituent clinopyroxene and orthopyroxene, while the third component has concentrations of MgO, CaO, Al₂O₃, TiO₂ and Na₂O that are close to basaltic levels and may indicate the former presence of trapped basaltic melt. These pyroxenites are probably cumulates in the broadest sense. Nevertheless, some pyroxenites from Beni Bousera and Ronda have whole rock compositions that are similar to that of bulk oceanic crust. Most mantle pyroxenites have LREE-depleted whole-rock REE patterns, although with lower absolute concentrations than MORB or bulk oceanic crust, and most lack Eu anomalies. Trace element patterns in clinopyroxenes from pyroxenites are also usually LREE-depleted. Most clinopyroxenes show depletions in Zr, Hf and Sr, although those from the Cabo Ortegal complex (NW Spain) display LREE-enrichment and significant Sr peaks, attributed to the influence of subduction-related fluids or melts. $\delta^{18}\text{O}$ values for clinopyroxenes from mantle pyroxenites in ultramafic massifs tend to be in the range 5.0–5.8‰, i.e. typical mantle values. Rare garnet pyroxenite layers from a few massifs show higher values that reflect recycling of a crustal component. Similarly, most Sr, Nd and Pb isotopic ratios from pyroxenites fall in the depleted mantle field, although with a slightly wider range of values than is typical for shallow sub-continental mantle peridotites from Europe.

Most mantle pyroxenites are best explained as products of crystal accumulation of mantle-derived magmas, together with variable amounts of trapped interstitial magma. Others may be the products of interaction between magma and peridotite or older pyroxenite wall-rock. Only samples from a few massifs (e.g. garnet pyroxenites from Beni Bousera and Ronda) display strong evidence of being related to recycled oceanic crust or melts of oceanic crust. Even fewer mantle pyroxenites show good evidence for derivation either by incipient melting of the host peridotite or by metamorphic segregation. Pyroxenites are low-MgO, high CaO, high Al₂O₃ lithologies that provide a well-documented example of enrichment of the lithospheric mantle. If such material were recycled into the asthenosphere, mantle pyroxenites might melt preferentially to the host peridotite. However, the precise role of mantle pyroxenites in magmagenesis could be difficult to track, as many of their isotope and trace element compositions (e.g. Sm/Nd ratios) are often similar to those of their host mantle peridotites.

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1. Introduction

In those parts of the shallow sub-continental lithospheric mantle for which petrological evidence is available, various types of pyroxenite form the second most common ultramafic rock-type after the spinel lherzolite–harzburgite series. Judging from their abundances in ultramafic massifs and shallow mantle xenolith suites, pyroxenites form <10% of the directly sampled upper mantle. Pyroxenites in the upper mantle have been implicated in the petrogenesis of MORB (Hirschmann and Stolper, 1996), OIB (Hirschmann et al., 2003; Sobolev et al., 2005), ferropicrites (Tuff et al., 2005) and in the source of some island arc magmas (Schiano et al., 2000) and it is therefore pertinent to re-examine their nature and origin. This synthesis builds on the earlier work of Irving (1980) who reviewed the origin of mantle pyroxenite xenoliths and Spray (1989) who discussed upper mantle segregation processes in orogenic peridotites. Bodinier and Godard (2003) also discussed variations in pyroxenites in a wide range of tectonic settings. This paper reviews the nature and origin of anhydrous pyroxenite layers in ultramafic massifs (also known as “orogenic peridotites” or “Alpine peridotites”) in Western Europe and Morocco, using data from numerous detailed studies of field relations, petrology and geochemistry.

The origin of mantle pyroxenites is controversial. Early work by Dick and Sinton (1979) suggested that they were metamorphic segregations of the host peridotite, formed by dissolution and precipitation of pyroxene during plastic flow. In situ melting was also suggested by Chen et al. (2001) to explain the features of pyroxenite xenoliths from China. In contrast, Wilshire and Shervais (1975), Obata, (1980), Frey (1980), Irving (1980) and Loubet and Allegre (1982) considered that pyroxenites are formed by crystal precipitation from asthenosphere-derived silicate magmas passing through the lithosphere. The mechanism of liquid-crystal separation was considered to be dynamic flow crystallisation or filter-pressing. Conversely, Allegre and Turcotte (1986) suggested that pyroxenites are remnants of subducted oceanic crust, streaked out into thin layers by mantle convection and incorporated into the lithosphere. An alternative hypothesis put forward by Davies et al. (1993) and Pearson et al. (1993) who suggested that some pyroxenites represent high-pressure crystal segregates from magmas derived from melting of subducted ocean crust. Blichert-Toft et al. (1999) considered that they represent the residue from such melting. Garrido and Bodinier (1999) highlighted the importance of melt-rock replacement reactions between older pyroxenites,

peridotites and percolating melts. Several studies (e.g. Loubet and Allegre, 1982; Lenoir et al., 2001) have suggested that mantle pyroxenites have been affected by partial melting after emplacement. Finally, Santos et al. (2002), Brooker et al. (2004) and Berly et al. (2006) have all suggested an arc setting for some pyroxenites.

Fig. 1 shows a cartoon based on the ideas of Irving (1980) and Spray (1989) outlining some of the major processes that have been suggested for the origins of mantle pyroxenites. These include: (a) in-situ partial melting of host peridotite; (b) recycling of oceanic crust; (c) solid-state differentiation and pressure solution creep; (d) flow differentiation by crystallisation within a conduit; (e) movement of melt into the mantle wedge above a subduction zone, (f) interaction between melt and host peridotite. This paper will investigate and test these various hypotheses using a compilation of petrological and whole-rock geochemical data, together with isotope and mineral trace element results, for anhydrous pyroxenites in tectonically emplaced ultramafic massifs.

2. Data sources

The well-studied ultramafic massifs of Europe and northern Africa (Fig. 2) are a major source of geochemical and isotopic data for mantle pyroxenites. In northern Morocco, pyroxenites from the Beni Bousera massif have been analysed by Kornprobst (1969, 1970), Kornprobst et al. (1990), Pearson et al. (1991a,b, 1993), Kumar et al. (1996), Blichert-Toft et al. (1999) and Pearson and Nowell (2004). In SE Spain, pyroxenites within the Ronda massif were investigated by Zindler et al. (1983), Suen and Frey (1987), Reisberg et al. (1991), Davies et al. (1993), Garrido and Bodinier (1999), Garrido et al. (2000) and Sanchez-Rodriguez and Gebauer (2000). Pyroxenites from the Cabo Ortegal massif (NW Spain) have been analysed by Gil Ibarguchi et al. (1990), Girardeau and Gil Ibarguchi (1991), Santos Zalduegui et al. (1996), Santos et al. (2002), Gravestock (1992). The Pyrenees massifs in SW France contain numerous examples of layered pyroxenites that have been studied by Polvé and Allègre (1980), Loubet and Allegre (1982), Hamelin et al. (1984), Bodinier et al. (1987), Fabriès et al. (1991, 1998), Downes et al. (1991), Mukasa et al. (1991) and Henry et al. (1998). Some unpublished whole-rock major element analyses for pyroxenites from the western Pyrenees massifs have been made available by J-P Lorand and additional data for the eastern Pyrenees massifs have been obtained from the PhD thesis of Bodinier (1989). Among the Alpine massifs, pyroxenites from Lanzo were studied by Bodinier (1988), while Balmuccia pyroxenites were

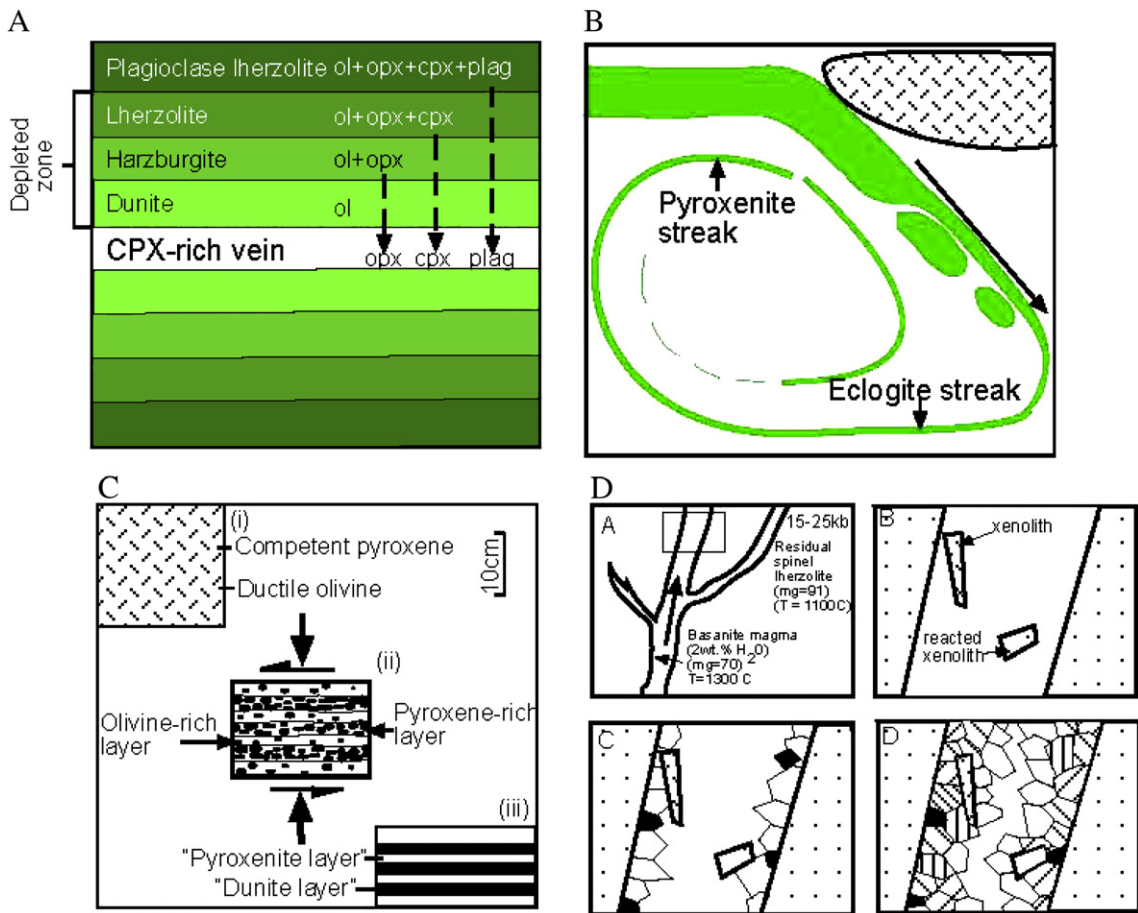


Fig. 1. A cartoon based on those of [Spray \(1989\)](#) and [Irving \(1980\)](#) showing some of the processes that could give rise to mantle pyroxenites. (A) Segregation by in-situ partial melting of host peridotite; (B) Formation by deep recycling of oceanic crust; (C) Segregation by solid-state differentiation and pressure solution creep; (D) Flow differentiation by crystallisation within a conduit.

analysed by [Sinigoi et al. \(1983\)](#), [Shervais and Mukasa \(1991\)](#), [Rivalenti et al. \(1995\)](#), [Voshage et al. \(1988\)](#) and [Mukasa and Shervais \(1999\)](#). Additional data have been obtained from the PhD thesis of [Obermiller \(1994\)](#). Pyroxenites also occur in the Malenco ultramafic complex ([Müntener and Hermann, 1994](#); [Müntener and Hermann, 1996](#)) and in numerous localities in the Eastern Alps ([Melcher et al., 2002](#); [Konzett et al., 2005](#)). Ultramafic massifs in the Bohemian Massif, lower Austria, were emplaced during the Hercynian orogeny and contain garnet pyroxenite layers that have been studied by [Becker \(1996\)](#) and [Becker et al \(2001, 2004\)](#).

In order to supplement the data available in the literature, some additional analyses have been undertaken for this review. Appendix A gives trace element compositional data by LA-ICPMS on clinopyroxenes separated from layered pyroxenites from the Pyrenees (samples from [Downes et al., 1991](#)) and Beni Bousera (samples from [Pearson et al., 1993](#)), analysed at the

University of Utrecht and at the University of London. Appendix B gives new oxygen isotope determinations on separated clinopyroxenes from pyroxenites in ultramafic massifs of the Pyrenees, Alps and Ronda, using a laser fluorination technique at Royal Holloway, University of London, described by [Mattey and Macpherson \(1993\)](#) and [Dobosi et al. \(1998\)](#).

For clarity and simplicity, this survey has not included well-known pyroxenite-bearing ultramafic massifs outside western Europe, such as Zabargad in the Red Sea ([Piccardo et al., 1988](#); [Vannucci et al., 1991](#); [Kurat et al., 1993](#); [Brooker et al., 2004](#)), Tinaquillo in Venezuela ([Seyler and Mattson, 1993](#)) and Horoman in Japan ([Shiotani and Niida, 1997](#); [Takazawa et al., 1999](#); [Saal et al., 2001](#)). The processes and products inferred from the study of these massifs generally do not differ from those in the examples considered here and the conclusions of this review would not be substantially modified by their inclusion.

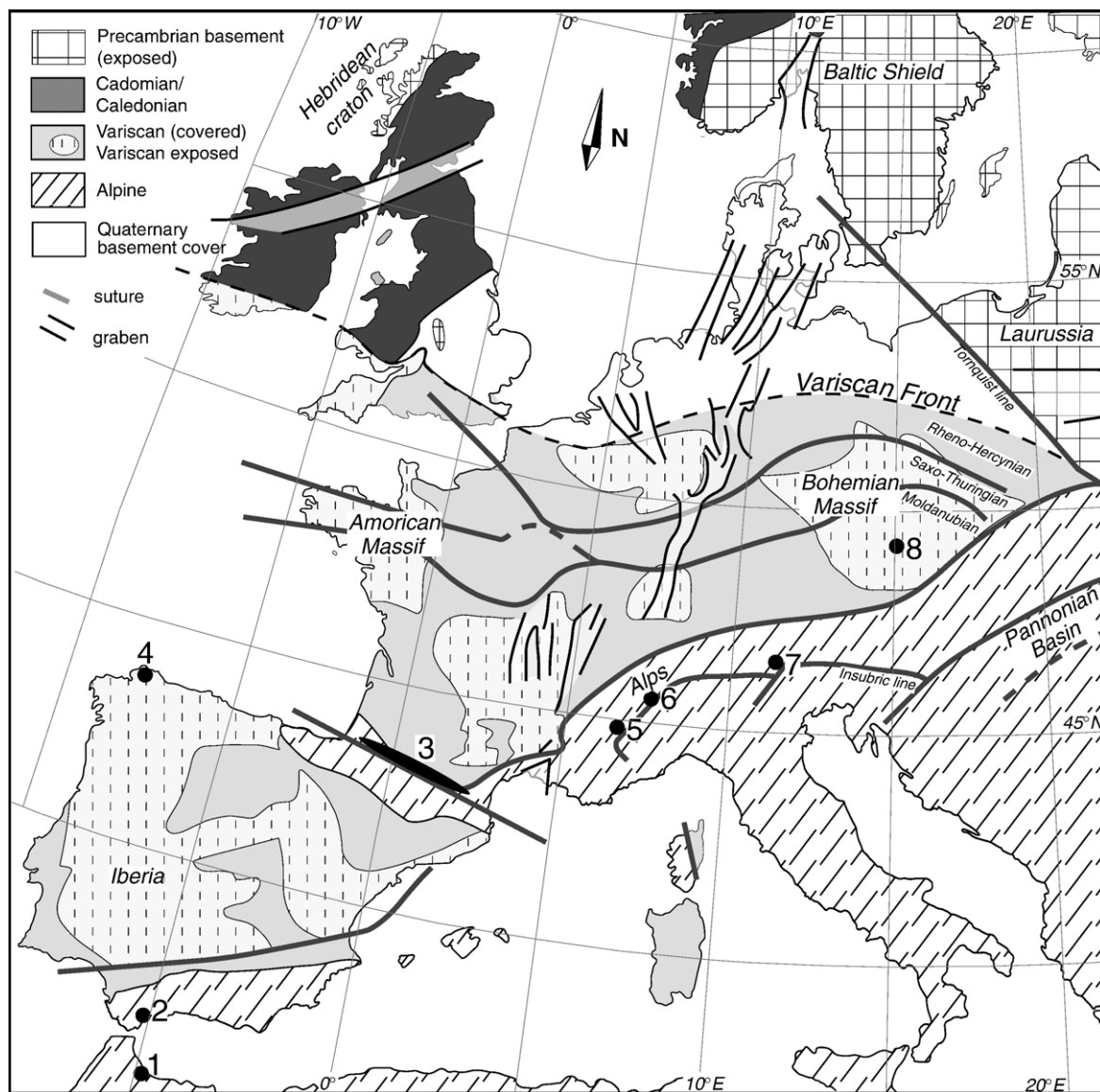


Fig. 2. Sketch map of geology of western Europe and northwest Africa, showing main localities of ultramafic massifs. Massifs: 1, Ronda (Spain); 2, Pyrenees (France); 3, External Ligurides (Italy); 4, western Alpine massifs (Italy); 5, Cabo Ortegal (Spain); 6 Beni Bousera (Morocco); 7, Eastern Alps (Italy); 8, Bohemian Massif (Austria).

Anhydrous spinel and garnet pyroxenites are also known from alkali basalt xenolith locations in Europe and worldwide. Pyroxenite xenolith suites in Italy, Scotland and Hungary have been studied by Ferrara et al. (1974), Montanini et al. (1992), Nimis and Vannucci (1995), Upton et al. (1998, 2003), Dobosi et al. (1998) and Kovacs et al. (2004). Pyroxenite veins in composite xenoliths have been studied by Irving (1980), Kempton (1987), Witt-Eickschen et al. (1993, 1998, 2003) and Witt-Eickschen and Kramm (1998). Other pyroxenite xenoliths are mentioned within reports

on peridotite xenolith suites from France, Romania, Hungary and Serbia, e.g., Downes and Dupuy (1987), Embey-Isztin et al (1990), Vaselli et al. (1995), Szabó et al. (1995), Wilson et al (1997), Féménias et al. (2003) and Cvetkovic et al. (2004). Outside Europe, Beeson and Jackson (1970), Shervais et al. (1973), Wilkinson (1974, 1976), Wilshire and Shervais (1975), Irving (1974), Wilkinson and Taylor (1980), Frey (1980), Mittlefehldt (1986), Esperanca and Garfunkel (1986), Sen (1988), Griffin et al. (1984, 1988), Sen and Leeman (1991), Stein et al (1993), Wilshire et al (1988), Adam

et al (1992), Ho et al. (2000), Chen et al (2001), Xu (2002) and Dessai et al (2004) studied pyroxenite xenolith suites in the USA, Hawaii, Israel, Australia, China and India. However, there are two main drawbacks to using xenolith data; firstly, the field relations of the different lithologies are unknown, and secondly the extent of interaction with and modification by the host magmatism is not clear. Significantly, many pyroxenite xenoliths show LREE-enriched compositions that are often thought to be the result of processes associated with the host basalts. This problem is even more acute for pyroxenite xenoliths from kimberlites (e.g. Boyd et al., 1984; Roden et al., 1999; Kopylova et al., 1999; Doyle et al. 2004). For these reasons, data from xenoliths have been omitted from this discussion.

3. Petrography of mantle pyroxenites

In the literature, mantle pyroxenites are also referred to as “mafic layers”, “metabasites”, “Type-II xenoliths” or “ultramafic granulites”. Pyroxenites are defined as ultramafic rocks containing >60% modal pyroxene (Streckeisen, 1976). Spinel, garnet and olivine are the most common varietal minerals. Relative proportions of the major minerals in pyroxenites are extremely variable so that lithologies range from orthopyroxenites, through websterites, to clinopyroxenites. Minerals such as amphibole and biotite may also be present in minor amounts. Less commonly, corundum, sapphirine, ilmenite, apatite, zircon, quartz, rutile and graphite can occur (Pearson et al., 1989; Kornprobst et al., 1990; Becker, 1996; Müntener and Hermann, 1996; Morishita et al., 2001; Montanini et al., 2006). Plagioclase, where present, is often of metamorphic origin, but the resulting rocks have sometimes been referred to as “olivine gabbros”.

The nature of the aluminous phase in mantle pyroxenites varies. Spinel is most common Al-host mineral in most massifs, with garnet being generally less abundant (Conqu  r  , 1977; Kornprobst et al., 1990). Plagioclase occurs in pyroxenites from Lanzo (Bodinier, 1988). These occurrences are mostly found within spinel peridotite-facies mantle, but garnet pyroxenite lenses also occur in garnet peridotite massifs in the Alps (Peters, 1963; Peters 1968; Morten and Obata, 1983; Green et al., 1997) and Austria (Becker, 1996). O’Hara (1967) designated two sub-facies of spinel peridotite mantle according to the nature of the aluminous phase in the pyroxenitic layers: the deeper “ariegite subfacies” for spinel peridotite in which the pyroxenites are garnet-bearing and the shallower “seiland sub-facies” for spinel peridotite in which the associated pyroxenites are

spinel-bearing. Phase relations of garnet pyroxenites have been determined by Kornprobst (1969), Irving (1974), Obata and Dickey (1976) and Herzberg (1978), and indicate that they were derived from pressures of 15–24 kbar. In some rare cases, graphite may form pseudomorphs after diamond as seen in Beni Bousera (Pearson et al., 1989) and Ronda (Davies et al. 1993), indicating exhumation of the host ultramafic massif from the diamond stability field (>45 kbar).

Ultramafic massifs provide valuable evidence for field relations between pyroxenites and their host peridotites (Spray, 1989; M  ntener and Hermann, 1996; Mukasa and Shervais, 1999). Two groups of pyroxenites are often evident in the field, defined by their pyroxene type: green Cr-diopside pyroxenites and black Al-augite pyroxenites. Such groupings are readily observed in the massifs of Beni Bousera (Kornprobst et al., 1990), Ronda (Obata, 1980; Garrido and Bodinier, 1999) and Balmuccia (Voshage et al., 1988; Shervais and Mukasa, 1991; Mukasa and Shervais, 1999). Pyroxenite layers often show a symmetrical zonation, e.g. cores of spinel-poor websterite with selvages of spinel pyroxenite (Mukasa and Shervais, 1999) or cores of garnet pyroxenite with websterite or orthopyroxenite edges (Pearson et al., 1993). Pyroxenite layers in Ronda show asymmetric zoning from garnet pyroxenites on one side to garnet-free websterite on the other (Garrido and Bodinier, 1999).

Pyroxenite layers in ultramafic massifs range in thickness from thin centimetre-sized layers with diffuse margins to layers up to a metre thick showing a garnet pyroxenite core and spinel pyroxenite margins, indicating a long history of re-equilibration with their host peridotite (Sautter and Fabries, 1990). Thick layers are rare, whereas thin layers are much more abundant. In the Pyrenees massifs of Frechinde and Bestiac, layers of pyroxenite can locally predominate over the host peridotites (Conqu  r  , 1977), as is the case locally in Beni Bousera and Ronda, while in parts of the Cabo Ortegal complex (NW Spain) they constitute 80–90% of the mantle outcrop (Gil Ibarguchi et al., 1990). Pyroxenite layers have often been interpreted as originally having been formed as dykes that were rotated into the foliation plane of the surrounding peridotite (Fabri  s et al., 1991). Some can show folding and boudinage (e.g., Av   Lallemand, 1967; Nicolas and Boudier, 1975; Van der Wal and Vissers, 1996) and brittle faulting (Girardeau and Gil Ibarguchi, 1991). In some cases, discordance with the host peridotite can be observed and cross-cutting relations between pyroxenite layers indicate multiple periods of intrusion (Shervais and Mukasa, 1991). Careful field investigations have

revealed multiple episodes of pyroxenite formation, e.g. in Ronda (Garrido and Bodinier, 1999) and Balmuccia (Mukasa and Shervais 1999).

Pyroxenite emplacement can have an effect on the host peridotite. Pearson and Nowell (2004) have suggested that this may be due to melt-rock reaction between near-solidus partial melts of the pyroxenite and the surrounding peridotite. Reactions between the siliceous melt and the peridotite may increase the modal proportion of orthopyroxene in the wall-rock, forming orthopyroxenite margins to the clinopyroxenite layers (Yaxley and Green, 1998). Rivalenti et al. (1995) carefully studied the relation between websterite and enclosing peridotite in the Balmuccia massif and showed two different patterns of transition between the two rock-types. This was interpreted in terms of (a) infiltration of the melt that formed the pyroxenite and subsequent re-equilibration of the melt with the peridotite matrix, and (b) melt extraction from the peridotite wall-rock followed by diffusive redistribution after formation of the pyroxenite layer. Incorporation of pyroxenite layers into the host peridotite by deformation may also result in enrichment of the peridotite, as suggested for Beni Bousera by Tabit et al. (1997). Thus the former presence of a pyroxenite layer may be indicated only by a train of spinel or garnet grains.

A detailed field and petrographic study of pyroxenite layers in the Ronda massif (Garrido and Bodinier 1999) clearly demonstrated that different types of pyroxenite co-exist in a single massif. In Ronda, the oldest appear to be garnet pyroxenites that are LREE-depleted, sometimes show a positive Eu anomaly, have low mg-numbers and contain graphite pseudomorphs. These rocks resemble corundum-bearing garnet pyroxenites from Beni Bousera and may be related to subducted oceanic crust. A second group of spinel-garnet websterites are thought to have been formed by replacement of the pre-existing garnet pyroxenites by melt-rock reactions, while a third group formed by replacement of peridotites by melt-rock reactions with small volume melts, thus representing a metasomatic origin. These show along-strike transitions from peridotite-dominated areas with minor pyroxenite bands to pyroxenite-dominated regions with minor peridotite seams. Finally, green clinopyroxenites and pale brown orthopyroxenites were formed by replacement of pre-existing layers by reaction with a small degree volatile-rich melt. From this study it appears that pyroxenites can be formed by different processes that can be superimposed on each other. This can account for the wide range of compositions of pyroxenites in a given massif and indicates the complexity of their petrogenesis.

Bodinier and Godard (2003) divided pyroxenites into three groups, defined by their field relations to the

enclosing peridotite: dykes/veins, replacive pyroxenites, and deformed pyroxenites, all of which can be found within a single massif. However, some massifs appear to be dominated by one group or another, e.g. dykes and veins are prevalent in Balmuccia (Mukasa and Shervais 1999), Beni Bousera contains many ancient deformed layers (Kornprobst et al 1990), while many of the pyroxenites in Ronda are considered to be replacive in origin (Garrido and Bodinier 1999). These massifs may represent “end-member examples” of these processes, although detailed studies will probably reveal that many massifs contain pyroxenites of different origins and ages.

4. Whole-rock geochemical variation in mantle pyroxenites

If pyroxenites are derived from the solid-state recycling of oceanic crust, as proposed by Allegre and Turcotte (1986), then their average compositions should be similar to those of the bulk oceanic crust, some of them should have MORB compositions, and some should be plagioclase cumulates. On the other hand, if pyroxenites represent material crystallised from a magmatic liquid via liquid-crystal segregation processes, their whole-rock compositions should reflect (a) the nature of the magma from which they were formed and (b) the abundances of their constituent cumulate minerals plus any trapped liquid. The variety of pyroxenites may then be related to the wide range of magma-types that pass through the lithosphere in different tectonic settings, e.g. from small degree partial melts of enriched mantle, to large degree melts such as continental tholeiites, and even subduction-related magmas such as boninites and high-Al basalts. If, however, metamorphic segregation processes are involved in their formation, then pyroxenite whole-rock compositions should lie on tie-lines between constituent phases alone. Localised partial melting of the host peridotite should produce melts that lie on the extension of the lherzolite–harzburgite trend. Any subsequent processes such as partial melting, metasomatism or interaction of later melts with wall-rock will also affect the primary compositions. The geochemical variations in mantle pyroxenites will now be examined, in the light of these various hypotheses.

4.1. Major elements

Fig. 3 shows selected major elements in whole-rock mantle pyroxenites from ultramafic massifs plotted against MgO content, together with a field of European mantle spinel peridotites for comparison (Downes, 2001). Compositional fields for orthopyroxenes,

clinopyroxenes and garnet from pyroxenites are also shown. The chemical diversity of pyroxenites is immediately apparent, and a wide variety of compositions can be present in a single massif. Bodinier and Godard (2003) distinguished two groups of pyroxenites according to their Al-content (high Al with >10 wt.% Al_2O_3 ; low Al with <10 wt.% Al_2O_3). In this paper, no such distinction will be made because of the apparent continuum of compositions (Fig. 3). Pyroxenites always have lower MgO contents (9–33wt.% MgO) than mantle peridotites, yet are richer in MgO than most basalts including MORB. They have highly variable Al_2O_3 and CaO contents. In terms of their Al_2O_3 –CaO–MgO compositions, most pyroxenites plot in a triangle formed by orthopyroxene (high MgO, low Al_2O_3 , very low CaO), clinopyroxene (relatively lower MgO, high CaO, variable Al_2O_3) and a third component that has low CaO, high Al_2O_3 and low MgO. This latter component cannot be garnet (Fig. 3) but could be trapped melt of MORB composition. Many pyroxenites are similar in MgO, Al_2O_3 and CaO contents to MORB or MORB picrites. These tend to be from Beni Bousera and Ronda. In contrast, pyroxenites from Cabo Ortegal have unusually low contents of Al_2O_3 (and their constituent clinopyroxenes are similarly depleted in Al). Many pyroxenites, particularly those from Beni Bousera, Ronda and the Pyrenees massifs, have CaO/ Al_2O_3 ratios between 0.8 and 1.0, similar to those of the majority of mantle peridotites and basaltic magmas (Fig. 3). In contrast, those from Cabo Ortegal and the Alps show a wide range of CaO/ Al_2O_3 ratios up to 4.5. Some of these high CaO/ Al_2O_3 ratios may be due to seawater alteration of oceanic crust prior to subduction.

TiO_2 and Na_2O contents of mantle pyroxenites are very variable (Fig. 3), but are always lower than those of MORB. The MgO– TiO_2 plot again shows that three components are required to account for the chemical variation of pyroxenites: (a) a low-Ti, high-Mg component (probably orthopyroxene); (b) a low-Ti, low-Mg component (probably low-Ti clinopyroxene as found in Cabo Ortegal pyroxenites); (c) a high Ti, low Mg component that may be clinopyroxene but is also similar to basaltic magmas. There is a strong negative correlation between Na_2O and MgO, although Cabo Ortegal pyroxenites and some Alpine samples have unusually low Na_2O contents for their MgO content. A high-Na, low-Mg component is present in Beni Bousera and Ronda pyroxenites but is almost absent from Cabo Ortegal and Alpine pyroxenites. Clinopyroxene in some pyroxenites can contain significant quantities of Na_2O and TiO_2 , thus cumulus clinopyroxene may account for the high Na_2O and TiO_2 contents of some mantle pyroxenites. However, the Na- and Ti-rich compo-

nent within pyroxenites may also be due to the presence of trapped melt. Garrido and Bodinier (1999) pointed out that most pyroxenites are depleted in K_2O and P_2O_5 compared with basaltic magmas, and therefore they cannot be simple frozen melts.

When compared to MORB (Fig. 3), most mantle pyroxenites have lower TiO_2 and Al_2O_3 contents and many have higher CaO. This casts doubt on the view that such pyroxenites represent recycled ocean crust. However, samples from Beni Bousera and Ronda show a much stronger tendency to plot around the composition of picrites from the mid-ocean ridge which presumably are close to the composition of bulk ocean crust. Although there are wide ranges in pyroxenite composition within an individual massif (e.g. Ronda), significant differences are seen between pyroxenites from different groups of massifs. For example, Ronda and Beni Bousera pyroxenites have high Al_2O_3 and Na_2O contents whereas those from the Pyrenees and Alps have lower Al_2O_3 and Na_2O . Furthermore, many pyroxenites from Ronda and Beni Bousera have MgO compositions similar to that of MORB picrites, whereas those from massifs in the Alps and Pyrenees tend to be richer in MgO. Pyroxenites from Cabo Ortegal are very poor in Al_2O_3 , Na_2O and TiO_2 and plot away from those of other massifs on the MgO– Al_2O_3 variation diagram.

4.2. Trace elements

Trace elements can broadly be divided into those that are compatible during fractionation of mafic magmas (Cr, Ni) and those that are incompatible (e.g. Sr, Zr). Whole-rock Ni contents of pyroxenites show a wide range (50–1500 ppm) but are always lower than those in mantle peridotites (Fig. 4). Most samples show a negative correlation with MgO and plot along the extension of the peridotite depletion trend (i.e. an olivine control line). However, pyroxenites from Cabo Ortegal and some other massifs fall off this trend and have lower Ni contents at a given MgO value. Cr contents in pyroxenites vary widely from <100 ppm to >7500 ppm (Fig. 4). The upper end of the range probably reflects accumulation of a Cr-rich phase, likely Cr-diopside or Cr-spinel. Other pyroxenites tend to fall on a trend of decreasing Cr content with decreasing MgO content, suggestive of mixing with a low-Mg, low-Cr component, perhaps trapped melt. Many Beni Bousera and Ronda pyroxenites are similar to MORB or oceanic crustal picrites in their Ni and Cr contents.

Mantle pyroxenites tend to have much higher Sc contents than peridotites and show much more scattered

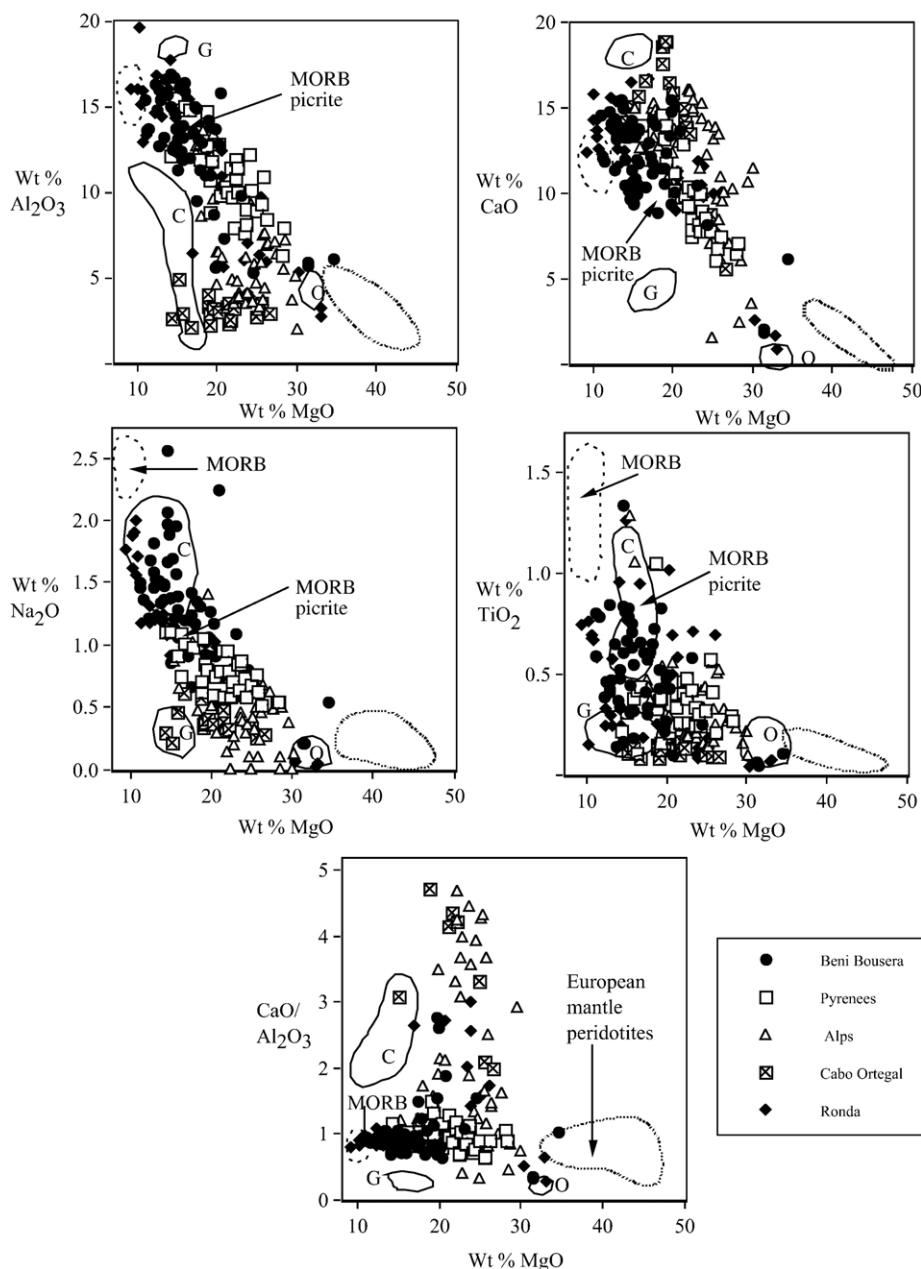


Fig. 3. Major element abundances and ratios, vs MgO contents in whole-rock mantle pyroxenites in ultramafic massifs. Data from: Alps (Bodinier, 1988), Pyrenees (Bodinier et al., 1987), Ronda (Schubert, 1977; Suen and Frey, 1987; Garrido and Bodinier, 1999), Beni Bousera (Pearson et al., 1993) and Cabo Ortegal (Gravestock, 1992). Fields of mineral compositions in pyroxenites from same authors (C=clinopyroxene; O=orthopyroxene; G=garnet). Stippled field=compositional variation of mantle peridotites from Europe (Downes, 2001); Field with dashed outline=variation in primitive MORB (Melson et al., 1976; Schilling et al., 1983; Korenaga and Kelemen, 2000). Data for MORB picrite from Elthon (1989).

distributions (Fig. 4). The Sc content of most pyroxenites greatly exceeds that of MORB. Samples from Cabo Ortegal tend to have higher Sc contents than pyroxenites from other areas. The data array formed by pyroxenites in the MgO–Sc diagram again requires a

minimum of three components. Sr is present in pyroxenites in concentrations ranging from near zero to values that are much higher than those in peridotites. Again, at least three components are required to explain the array of data. On the other hand, Sr is very abundant

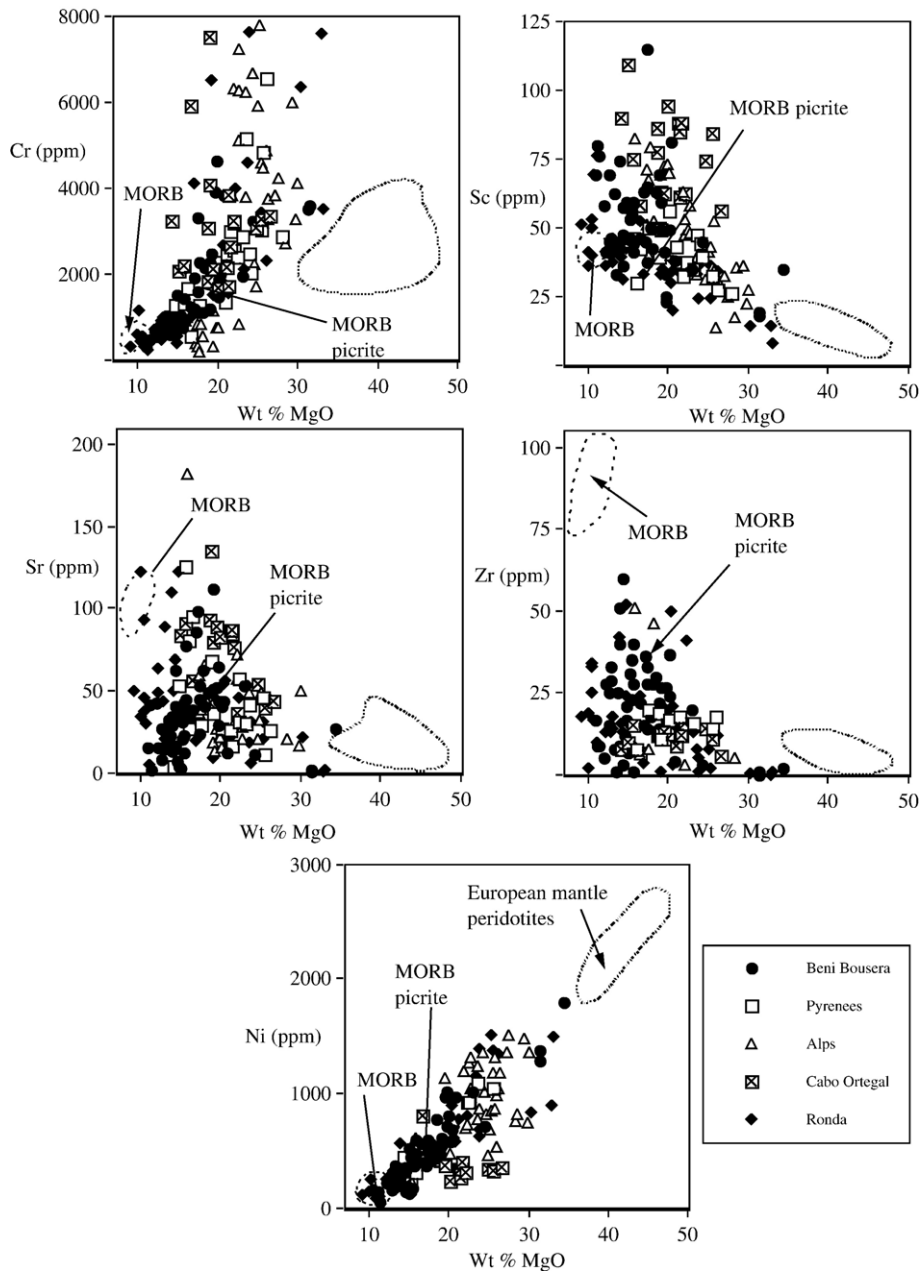


Fig. 4. Trace element concentrations vs MgO contents in whole-rock mantle pyroxenites in ultramafic massifs. Data sources: as for Fig. 3.

in sea-water, so alteration of the ocean crust could account for high Sr contents in pyroxenites if they represent subducted ocean crust. Zr contents of pyroxenites are much lower than those of MORB, possibly due to low K_d values for Zr in pyroxene in equilibrium with mafic magmas. The amount of trapped melt within mantle pyroxenites has not been quantified, although the low concentrations of strongly incompatible element suggest that it is not very significant.

4.3. REE and trace element patterns

Whole-rock REE patterns (normalised to chondrite values of Nakamura, 1974) should provide a powerful indicator of the origin of mantle pyroxenites. A variety of analytical techniques have been used to determine the REE abundances in these rocks, including isotope dilution, INAA and solution ICPMS. Some of these techniques are limited to certain elements. Layered

pyroxenites from Ronda, Beni Bousera, the Pyrenees and the Alps tend to show LREE-depletion (Fig. 5). This is more likely due to an original LREE-depletion in the magma that formed the pyroxenite than because of subsequent equilibration with surrounding LREE-depleted mantle peridotites. A single layer from Beni Bousera (Kumar et al., 1996) shows variation from LREE-depletion in garnet pyroxenites to LREE-enrich-

ment in websterites. Strong Eu anomalies in whole-rock compositions, as would be expected if fractionation or accumulation of plagioclase had occurred in oceanic crustal magma chambers, are rare, but minor positive and negative Eu anomalies are quite common, especially in Beni Bousera. Compared with N-MORB (Sun and McDonough, 1989), layered pyroxenites from many massifs have lower concentrations of REE and stronger

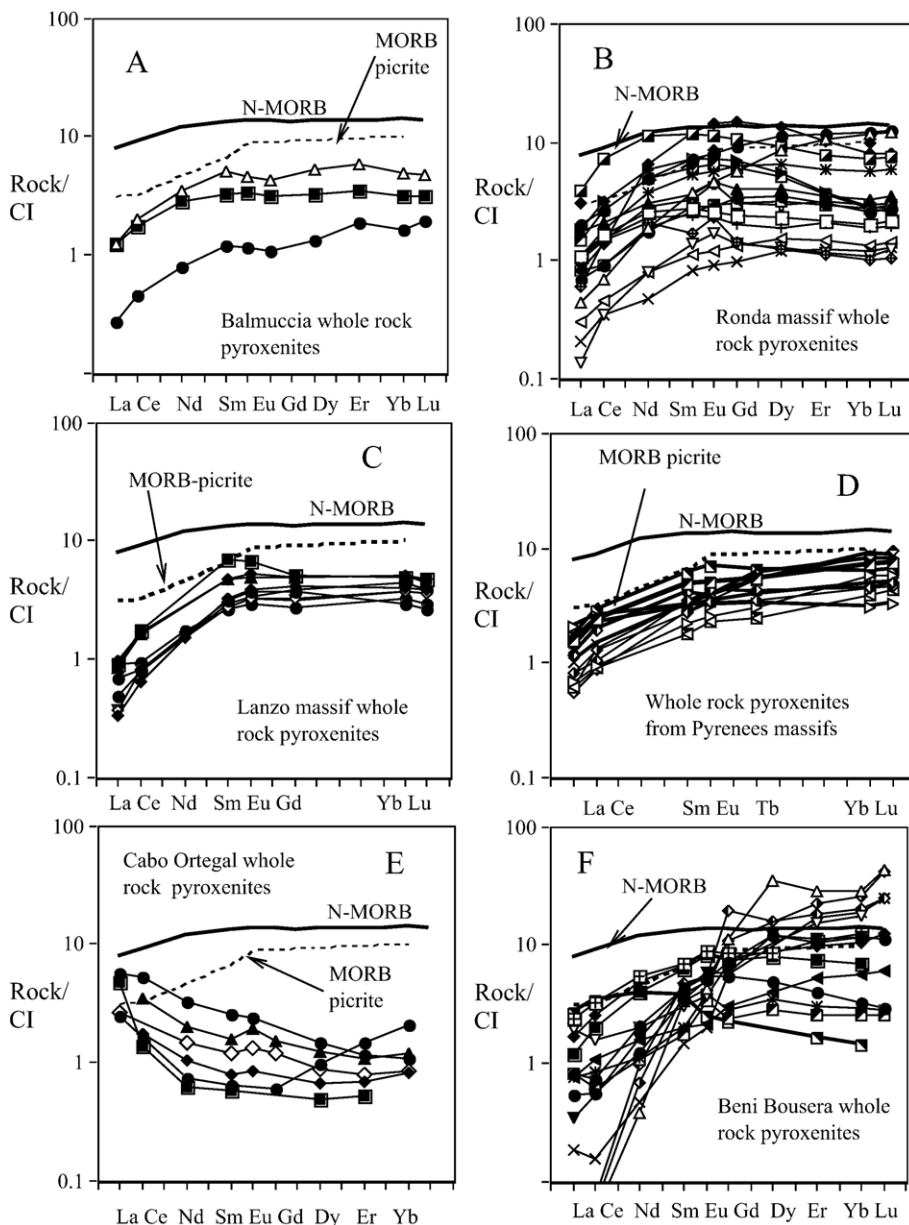


Fig. 5. Chondrite-normalised (Nakamura, 1974) whole-rock REE patterns for mantle pyroxenites from ultramafic massifs: (A) Balmuccia, (B) Ronda (Garrido and Bodinier (1999), (C) Cabo Ortegal (Gravestock, 1992), (D) Pyrenees (Bodinier et al., 1987), (e) Lanzo (Bodinier, 1988), (F) Beni Bousera (Pearson et al., 1993). Patterns for N-MORB (Sun and McDonough, 1989) and MORB-picrite (Elthon, 1989) shown for comparison.

LREE-depletion. Many of them resemble the MORB-picrite analysed by Elthon (1989) but with considerably lower abundances. In contrast, websterite layers in the Cabo Ortegal massif have extremely low HREE concentrations (around $0.8\text{--}2.0\times$ chondritic Yb) and show significant LREE-enrichment. These pyroxenites are so unusual in their REE compositions that they must have experienced processes quite different from those that formed pyroxenites of other massifs.

Whole-rock trace element data for the Large Ion Lithophile (LIL) such as Rb, Sr, Ba and Cs, and High Field Strength Elements (HFSE) such as Nb, Zr and Hf, are fairly sparse in the literature for pyroxenites. Solution ICP-MS analyses of unaltered, uncontaminated samples are required to produce meaningful results at the chondritic levels found in pyroxenites. There is evidence that more than 60% of the budget of elements such as Rb, Ba, Nb, Ta and Sr is hosted in grain boundary components and inclusions within ultramafic mantle rocks (Garrido et al., 2000), so whole rock data may not be particularly useful for petrogenetic interpretations. Fig. 6 shows the mantle-normalised whole-rock compositions of pyroxenites from Ronda and Cabo Ortegal analysed by solution ICPMS. Garrido and Bodinier (1999) found different whole-rock trace element patterns for the different groups of pyroxenites in Ronda. Most samples show low abundances of the HFSE, particularly Nb and Ta but there is also a conspicuous Zr–Hf trough in many. LILE are very variable in their abundances, with some samples showing high Ba and Sr contents. In contrast, Cabo Ortegal pyroxenites (Santos et al., 2002) are strongly enriched in LIL, Nb, Ta and Zr; they also have distinct negative Hf anomalies.

5. Geochemistry of clinopyroxenes from pyroxenites

Trace element analyses of separated or in situ clinopyroxenes have been widely used to determine the origin of mantle pyroxenites. Garrido et al. (2000) studied the partitioning of REE and other trace elements between constituent minerals in anhydrous spinel pyroxenites from Ronda. They showed that clinopyroxene is the main host of REE, so its pattern should reflect that of the whole-rock. In contrast, in garnet pyroxenites the REE are distributed between garnet and pyroxene, and hence the clinopyroxene will not mirror the whole-rock pattern but will tend to be more HREE-depleted (Fig. 7). Sub-solidus re-equilibration may also affect the REE distribution (Bodinier et al., 1987).

Clinopyroxenes from spinel pyroxenites from the Balmuccia massif have the simplest REE patterns (Fig. 7)

that are slightly LREE-depleted and sinusoidal, with some samples showing the highest normalised REE content at Nd–Sm. Those from Ronda tend to be similar although a few very rare examples display stronger LREE-enrichment. Massifs such as Beni Bousera and the Pyrenees generally have more variable and more strongly LREE-depleted patterns in their clinopyroxenes. In addition, clinopyroxene from garnet pyroxenites often show a HREE-depleted signature caused by equilibration with garnet. As with their whole-rock compositions, clinopyroxenes from pyroxenites of Cabo Ortegal show LREE-enrichment (Fig. 7). These are the only samples that are

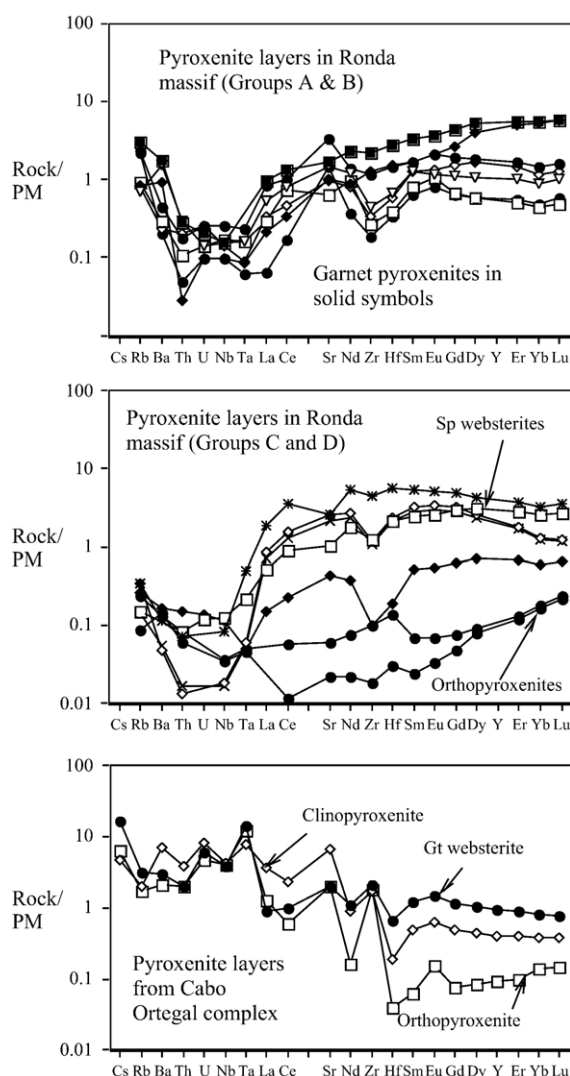


Fig. 6. Mantle-normalised (Sun and McDonough, 1989) whole-rock compositions of selected pyroxenites from ultramafic massifs. Solution ICP-MS data for Ronda samples from Garrido and Bodinier (1999), Cabo Ortegal samples from Santos et al. (2002).

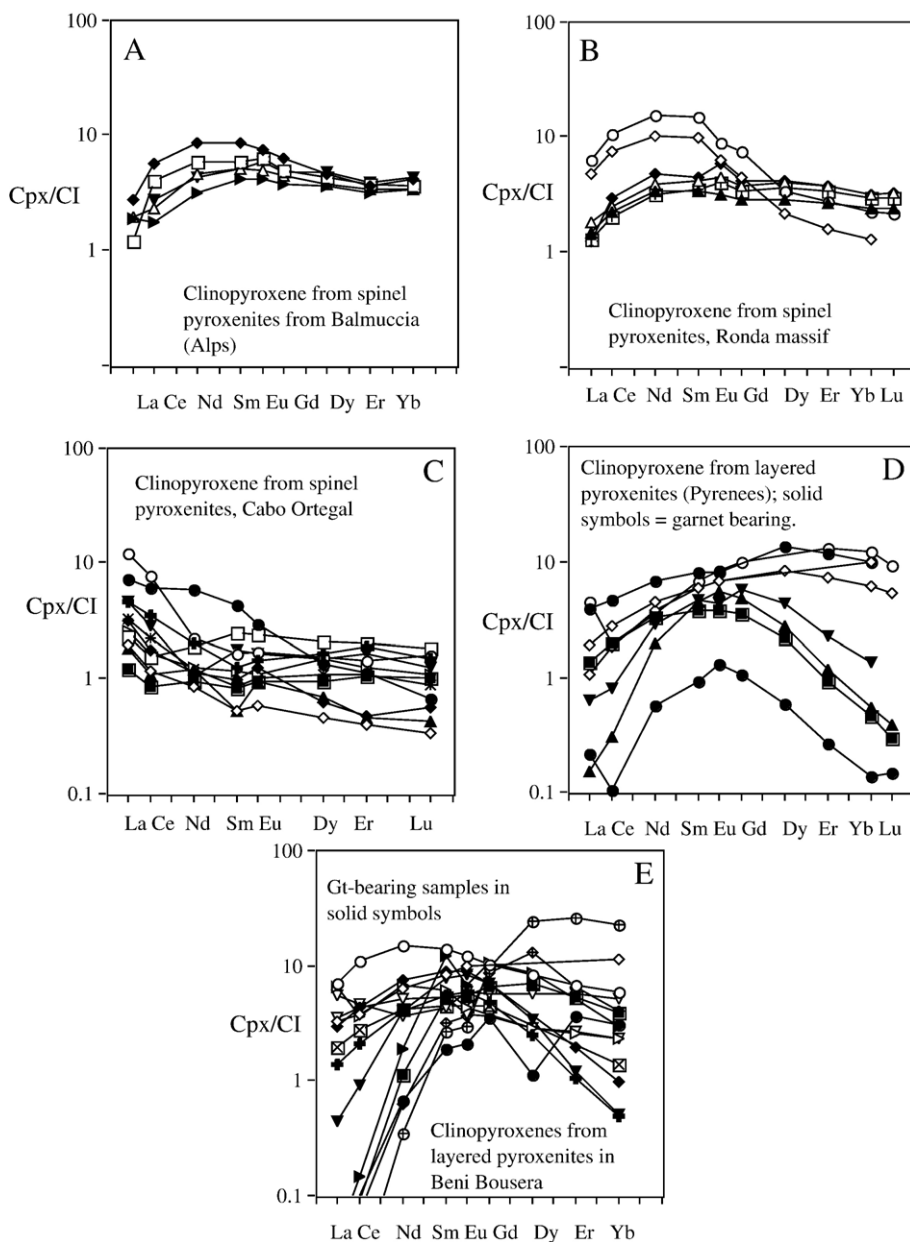


Fig. 7. REE patterns for clinopyroxene from mantle pyroxenites in ultramafic massifs, normalised to chondrite (Nakamura, 1974). Data sources: Beni Bousera (Pearson et al., 1993), Pyrenees (Downes et al., 1991), Balmuccia (Rivalenti et al., 1995), Cabo Ortegal (Gravestock, 1992), Ronda (Garrido and Bodinier, 1999).

consistently LREE-enriched. They are also distinguished by their very low HREE concentrations, which are much lower than in clinopyroxene from most other spinel pyroxenites. This supports the idea that Cabo Ortegal has undergone a significantly different process from other ultramafic massifs.

In mantle-normalised trace element diagrams (Fig. 8), clinopyroxenes from Balmuccia spinel pyrox-

enite layers show relatively flat patterns with a large Zr trough and minor depletion in Sr. Clinopyroxenes from pyroxenite layers from Ronda have very similar patterns, although the number of samples analysed does not accurately reflect the complexity of Ronda pyroxenites. New data for clinopyroxenes from Beni Bousera pyroxenites (Appendix A) are much more complex, showing both depletion and a rare example of

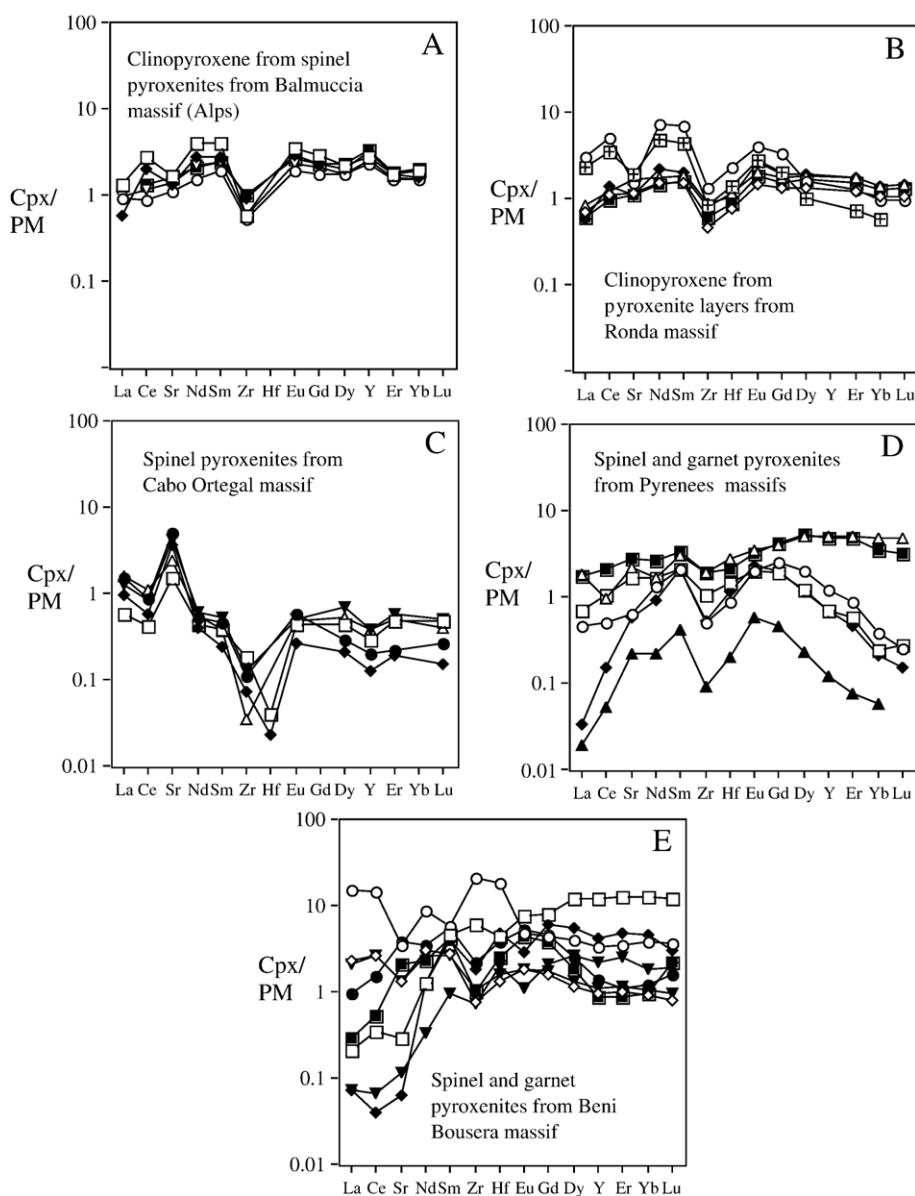


Fig. 8. Trace element data for clinopyroxene from mantle pyroxenites in ultramafic massifs, normalised to primitive mantle (Sun and McDonough, 1989). Data from: Balmuccia (Rivalenti et al., 1995; Mukasa and Shervais, 1999), Ronda (Garrido and Bodinier, 1999), Cabo Ortegal (Gravestock, 1992), Pyrenees (Appendix A), Beni Bousera (Appendix A).

enrichment in Zr and Hf in a Cr-diopside websterite. Clinopyroxenes that co-exist with garnet in garnet clinopyroxenites tend to have lower concentrations of HREE and Y, compared with spinel pyroxenites (Fig. 8) but otherwise their trace element patterns are similar to those of spinel pyroxenites, showing large negative Zr–Hf anomalies. This is particularly strongly displayed in clinopyroxene from garnet pyroxenites in the Pyrenees (Appendix A). However, clinopyroxene from the Cabo

Ortegal spinel pyroxenites show even stronger depletion in Zr and Hf, much stronger peaks in Sr, and generally lower overall trace element enrichment, with the exception of La and Ce.

In order to show the sizes of the Zr trough and Sr peak in these diagrams, Zr and Sr have been ratioed to their adjacent REE on the primitive-mantle normalised diagram (Fig. 9). Clinopyroxenes from most mantle pyroxenites fall in a common field with high Zr/Sm and

moderate Sr/Nd ratios. This group includes layered pyroxenites from Balmuccia, Beni Bousera, Ronda and the Pyrenees massifs. In contrast, clinopyroxenes in spinel pyroxenite layers in Cabo Ortegal tend to have significantly higher Sr/Nd values and a tendency to lower Zr/Sm ratios. One possibility that could explain this unusual chemistry has been suggested by Santos *et al.* (2002), who consider that Cabo Ortegal may represent supra-subduction zone mantle, with the increase in Sr relative to Nd being due to the subduction flux. The Zr–Hf trough may in part be the result of equilibration of clinopyroxene with orthopyroxene, which has a higher K_d for these two elements (Garrido *et al.*, 2000). However, the Zr–Hf trough is also seen in the whole rock compositions (Fig. 6) and thus cannot be entirely explained by this effect.

6. Isotopic compositions of mantle pyroxenites

6.1. Stable isotope compositions

Oxygen isotope analysis of clinopyroxenes separated from pyroxenites (Fig. 10) generally show typical mantle values. The new laser fluorination data for clinopyroxenes from pyroxenites in the Alpine and Ronda massifs (Appendix B) yielded $\delta^{18}\text{O}$ values between 5.3 and 5.6‰. In the Pyrenees, however, a zoned pyroxenite layer with a garnet clinopyroxenite

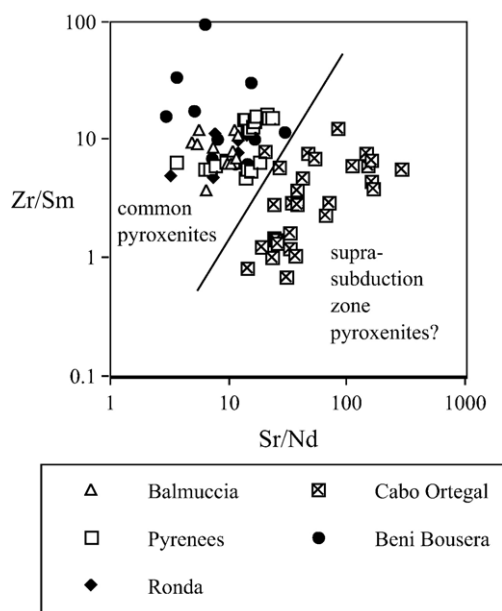


Fig. 9. Sr/Nd vs Zr/Sm ratios in clinopyroxenes from pyroxenite layers in ultramafic massifs. Data sources as in Fig. 8.

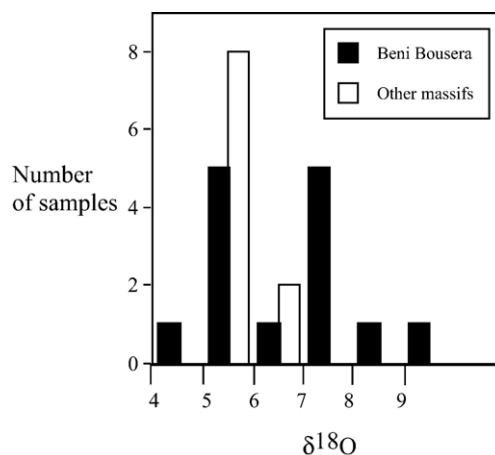


Fig. 10. Oxygen isotope variations in clinopyroxenes from mantle pyroxenites in ultramafic massifs. Data from: Beni Bousera (Pearson *et al.*, 1991a,b), other massifs including the Pyrenees (Appendix B).

core and a spinel websterite margins gave a value of 6.2–6.3‰ (Appendix B), whilst other pyroxenite samples yielded values between 5.5 and 5.8‰. Only pyroxenites from the Beni Bousera massif (Pearson *et al.*, 1991a) show a wide range of $\delta^{18}\text{O}$ values from typical mantle values (5–6‰) up to >9‰, which are values more akin to those found in altered ocean crust (e.g. in ophiolites).

Graphite pseudomorphs after diamond in the Beni Bousera pyroxenites have an isotopically light $\delta^{13}\text{C}$ composition (–16 to –28‰), which is distinctly more negative than typical mantle carbon (–4 to –8‰) (Pearson *et al.*, 1991b). This has been interpreted to indicate that the precursor diamonds formed from isotopically light carbon which was derived from the surface of the earth and taken to mantle depths by subduction of hydrothermally altered ocean crust. Significantly, graphite pseudomorphs have only been found in Ronda and Beni Bousera, the two massifs in which some pyroxenites have whole-rock compositions most similar to ocean crust.

6.2. Radiogenic isotope compositions

Since clinopyroxenes are the host of most of the Sr and Nd within mantle pyroxenites, isotopic compositions of these elements are usually determined on separated and leached clinopyroxenes, rather than on whole-rock powders. In particular, Garrido *et al.* (2000) showed that 65% of the trace element budget of Sr in a ultramafic rock can be housed in grain boundary phases, so the significance of whole-rock Sr isotopes in mantle

pyroxenites is very questionable. The data of Polvé and Allègre (1980) for the Pyrenees have therefore been excluded. Wide variations in the initial ratios $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are present in clinopyroxenes from mantle pyroxenites (Fig. 11). Many pyroxenites have identical isotope compositions to mantle peridotites, forming a cluster in the depleted mantle field with $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7025–0.7035 and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.5128–0.5133. A few pyroxenites from Beni Bousera and the Pyrenees show either much higher Nd isotope ratios or much higher Sr ratios. Those with elevated $^{87}\text{Sr}/^{86}\text{Sr}$ could be the result of hydrothermal processes in the oceanic crust. Cabo Ortegal pyroxenites tend to have slightly higher $^{87}\text{Sr}/^{86}\text{Sr}$ values than many other pyroxenites but with a relatively high $^{143}\text{Nd}/^{144}\text{Nd}$ value (Fig. 11), pointing to addition of a Sr-rich fluid, possibly derived from an enriched subducted component. Garnet pyroxenites from Hercynian ultramafic massifs in Austria are anomalously enriched in radiogenic Sr and unradiogenic Nd, which Becker (1996) related to a component derived from subducted upper crustal rocks.

Pb isotope analyses on unleached clinopyroxenes or whole-rock powders are prone to serious error due to alteration and environmental contamination, and therefore the data of Hamelin et al. (1984) on the Pyrenees massifs have been excluded. There are only small differences between pyroxenites and peridotites for Pb isotope data (Fig. 12). Leached clinopyroxenes from pyroxenite layers in ultramafic massifs lie above the NHRL in $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ space, but closer to it in $^{208}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ space. The displacement above the MORB field may indicate an enriched subduction-related component in some pyroxenites.

Mantle pyroxenites have much more radiogenic $^{187}\text{Os}/^{186}\text{Os}$ isotope ratios than mantle peridotites (Reisberg et al., 1991; Roy-Barman et al., 1996; Pearson and Nowell, 2004). This is interpreted as being due to Re/Os fractionation during partial melting. However, high γOs values are also characteristic of continental crust, eclogite xenoliths and unaltered ocean island basalts. Therefore Os isotopes do not help to distinguish between the different hypotheses of formation, except to cast doubt on the hypothesis of metamorphic segregation without partial melting. Becker et al. (2004) suggested that the radiogenic Os was derived from melting of subducted sediments.

Mantle pyroxenites from Beni Bousera have been analysed for Hf isotopes by Blichert-Toft et al. (1999) and Pearson and Nowell (2004). The former authors considered that the pyroxenites represented residues left by melting of oceanic crust. The latter authors used calculated whole-rock Hf and Nd compositions to suggest that some of the pyroxenites appear to have originated from a source composed of old subducted MORB, whereas others were formed from a source that contained 2–5% terrigenous sediment. This result is in keeping with previous suggestions of multiple origins for different types of pyroxenites in Beni Bousera by Kornprobst et al. (1990) and Pearson et al. (1993).

6.3. Geochronological constraints on mantle pyroxenites

From field evidence, it is clear that pyroxenites were formed prior to emplacement of the ultramafic massif into the continental crust (Dick and Sinton, 1979;

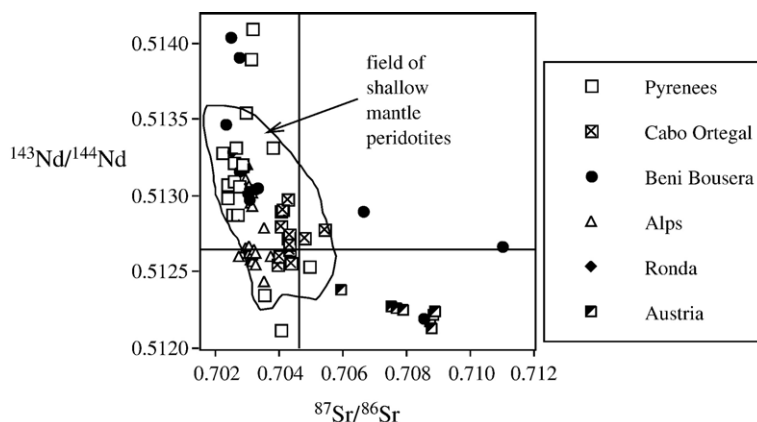


Fig. 11. Sr–Nd isotope variations in separated and leached clinopyroxenes from mantle pyroxenites in ultramafic massifs. Data sources: Cabo Ortegal (Gravestock, 1992; Santos et al., 2002), Pyrenees (Downes et al., 1991; Mukasa et al., 1991), Beni Bousera (Pearson et al., 1993), Western Alps (Voshage et al., 1988; Mukasa et al., 1991; Mukasa and Shervais, 1999), Ronda (Zindler et al., 1983). Field of European mantle peridotites from Downes (2001).

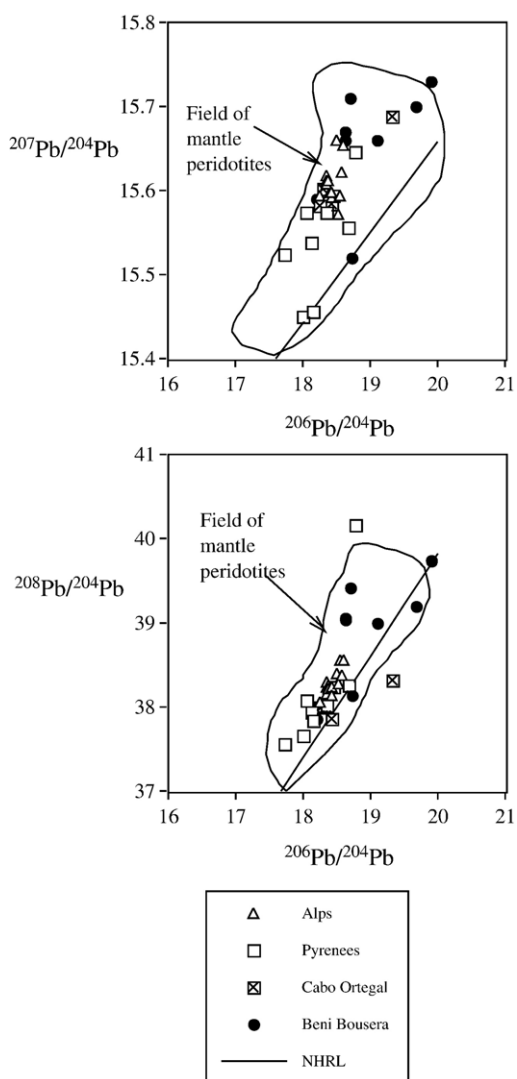


Fig. 12. Pb isotope data for separated and leached clinopyroxenes from mantle pyroxenites in ultramafic massifs. Data from Santos et al. (2002), Pearson et al. (1993), Mukasa et al. (1991), Mukasa and Shervais (1999). Field of European mantle peridotites from Downes (2001).

Mukasa and Shervais, 1999). Isotope geochronology can shed some light on the dating of pyroxenite-forming events and of the timing of exhumation of massifs. Lu–Hf ages of garnet–clinopyroxene mineral pairs from Beni Bousera pyroxenites yield ages of ca 24–26 Ma (Blichert-Toft et al., 1999; Pearson and Nowell, 2004), similar to the Sm–Nd age of 21.5 ± 1.8 Ma for Ronda (Zindler et al., 1983). This is considered to be the age of emplacement of Beni Bousera and Ronda into the continental crust. In contrast, Sanchez-Rodriguez and Gebauer (2000) have shown that magmatic zircons from

pyroxenite layers in Ronda yield crystallisation ages of 130–180 Ma (i.e. Jurassic) with older inherited cores. Henry et al. (1998) determined Sm–Nd ages of 138–177 Ma on minerals from within garnet pyroxenite layers from the Pyrenees massifs, but considered that a 450–500 Ma Sm–Nd errorchron on whole-rock samples represents the age of fractionation from the mantle. Pyroxenites in the Cabo Ortegal massif yielded internal Sm–Nd isochrons interpreted as crystallisation ages of 390 Ma (Santos et al., 2002) and zircon ages of 406 Ma (Santos Zalduegui et al., 1996). In some instances, ages of mantle pyroxenites appear to be related to known events in the adjacent crust, e.g. Voshage et al., (1988) considered that the whole-rock Sm/Nd isochron of 270 Ma for layered pyroxenites in Balmuccia was related to a period of late-Hercynian magmatic activity in the southern Alps. Bodinier et al. (1987) proposed that Triassic tholeiitic magmas associated with opening of the Atlantic Ocean were responsible for forming pyroxenites in the Pyrenees ultramafic massifs.

Re–Os systematics of pyroxenite layers in Ronda have been investigated by Reisberg et al (1991) who obtained model ages between 1 and 2 Ga. Model ages of 1.1–1.2 Ga were obtained on pyroxenites from Beni Bousera and Lanzo by Roy-Barman et al. (1996). Recent work by Pearson and Nowell (2004) on Beni Bousera yielded Re–Os model ages in a narrow range of 1.2–1.4 Ga. Although these results do not yield precise ages, the Proterozoic ages contrast strongly with the much younger zircon ages discussed above and indicate that some mantle pyroxenite layers have had a long and complex history.

7. Discussion

The whole-rock major element compositions of pyroxenites (Fig. 3) are more Mg-rich than most basaltic magmas and do not always lie in the area of oceanic crustal compositions. Frey (1980) demonstrated that pyroxenite xenoliths from Hawaii have compositions that cannot represent magmatic liquids and this conclusion is supported strongly by the compilation of pyroxenite data presented here. The scatter observed in the major element variation diagrams argues against an origin as incipient partial melts of the host peridotite or metamorphic segregations, because the compositions do not lie along either the extension of the peridotite melting trend or along the opx–cpx join. Binary variation diagrams also suggest that at least three components are required to explain the spread of data for mantle pyroxenites. The majority of whole-rock REE patterns for mantle pyroxenites from massifs are LREE-depleted

(Fig. 5), although with lower absolute concentrations than MORB or bulk oceanic crustal estimates. They therefore appear to be cumulates from large-degree partial melts; in some cases they are formed from melts that have experienced melt-rock reactions (Garrido and Bodinier, 1999).

Whole-rock mantle-normalised trace element diagrams (Fig. 6) show that pyroxenites often have distinct negative anomalies in the HSFE (Nb, Ta, Zr, Hf), strong variation in HREE and variable enrichment in the LIL. These patterns are unlike those of any mafic melts. Some of this variation reflects the K_d values between pyroxene and magma; some may be inherited from pre-existing rocks (replacive pyroxenites). Radiogenic isotope systematics also point to an origin in the depleted mantle, albeit with some possible enrichment from subduction zone processes. The lack of strong positive or negative Eu anomalies in whole-rock REE compositions (Fig. 5) also suggests the absence of plagioclase in the processes that formed pyroxenites.

7.1. Ocean crust recycling

The view of Allegre and Turcotte (1986) that mantle pyroxenites generally represent recycled ocean crust does not seem to be applicable to the majority of pyroxenites discussed here. Whole-rock compositions of pyroxenites do not resemble the composition of the bulk ocean crust, but form a triangular field in most diagrams in which two apices are orthopyroxene and clinopyroxene and the third is probably trapped melt. The evidence for the previous existence of plagioclase that characterizes the oceanic crust (e.g. Eu anomalies) is weak. It is difficult to account for multiple generations of pyroxenites, or the modal variation within thick pyroxenite layers, using this model. Only some pyroxenite layers in Ronda and Beni Bousera show features such as the presence of graphite with anomalous light carbon isotopes and silicates with a wide range of oxygen isotope compositions that are characteristic of altered oceanic crust. Other pyroxenites, including most of those analysed for this study (Appendix B), have mantle-type oxygen isotope ratios.

One of the main arguments in favour of recycled ocean crust is the apparent antiquity of garnet pyroxenite layers in ultramafic massifs, suggested from Os-isotope evidence. Using the model age approach, ages of 1.1–1.4 Ga have been obtained for pyroxenite layers from Beni Bousera, Lanzo, and Ronda. Such ages would be consistent with the expected time-scale for oceanic crustal recycling. However, Permian and Jurassic ages of magmatic zircons from Ronda pyroxenites (Sanchez-

Rodriguez and Gebauer, 2000) are very much younger than the Os model ages and strongly support a direct magmatic origin for pyroxenites. The inherited component in zircons from Ronda pyroxenites (Sanchez-Rodriguez and Gebauer, 2000) may support the suggestion by Garrido and Bodinier (1999) of reaction between infiltrating melts and older pyroxenites; the Os model ages imply that the older pyroxenites might be >1 Ga.

7.2. Metamorphic segregation/in situ melting

The “metamorphic segregation” theory put forward by Dick and Sinton (1979) is a concept of metamorphic layering formed as a response to stress in the lithosphere. It satisfactorily accounts for the multiple generations of pyroxenites, mantle-like oxygen isotope compositions and whole-rock LREE-depletion, but it is unclear why such segregations should contain the three end-members seen in the bulk rock compositions of pyroxenites (Fig. 3), when most segregations would presumably be composed of pyroxene minerals alone (i.e. should lie on tie-lines between ortho- and clinopyroxene). It also cannot easily account for mineralogical layering within single pyroxenite bands. This solid-state process also does not readily account for the presence of garnet pyroxenite layers within spinel peridotite massifs (ariegite sub-facies). The metamorphic segregation process also cannot explain the enriched Sr, Nd and Pb isotopic signatures shown by many pyroxenites (Figs. 11 and 12), nor for the unusual stable isotope compositions of some (Fig. 9). However, many pyroxenites have whole-rock compositions dominated by one or two pyroxenes. The concept of localised “mantle anatexis”, i.e. incipient melting and melt segregation without the formation of large magma batches, producing a banded structure analogous to gneissose texture in continental rocks, may be applicable in some cases. This mode of origin may form an end-member of a continuum of processes within the lithosphere that culminates in modal crystal accumulation of pyroxenes ± garnet (and trapping of interstitial liquid) from batches of asthenosphere-derived mafic melts.

7.3. Crystal accumulation

The crystal accumulation model still best explains the compositions of the majority of mantle pyroxenites. The view of pyroxenites being cumulates from passage of mafic magma within the lithospheric mantle is a frequent interpretation of the LREE-enriched spinel

pyroxenites that occur within spinel peridotite xenolith suites (Frey, 1980; Vaselli et al., 1995; Witt-Eickschen and Kramm, 1998; Dobosi et al., 1998). It has also been suggested as the origin of many pyroxenite dykes and layers in ultramafic massifs (Obata, 1980; Sinigoi et al., 1983; Suen and Frey, 1987; Bodinier et al., 1987; Shervais and Mukasa, 1991; Mukasa and Shervais, 1999). The majority of pyroxenites for which whole-rock major element data are available (Fig. 3) do not lie between the composition of the peridotite mantle and that of common basalts (e.g. MORB) and so they must represent mineral cumulates in the broadest sense. Plagioclase was not present during accumulation as the whole-rocks lack strong positive or negative Eu anomalies (Fig. 5). However, the LREE-depletion in most pyroxenites argues against an origin as cumulates from small-degree melt fractions, and points towards larger degrees of melting and tholeiitic parental magmas. This model can also explain the generally mantle-like oxygen isotope compositions and the modal variation within layers. The enriched radiogenic isotopic compositions can be related to introduction of an enriched component via subduction.

Open system magmatic replacement of pre-existing mantle ultramafic rocks has been suggested as the origin of several groups of pyroxenites in the Ronda massif (Garrido and Bodinier 1999) but this hypothesis has not yet been extended to other massifs. The hypothesis is hard to test except on field evidence, although it would predict variable whole rock compositions that would not resemble magma compositions, and that pyroxenites would generally have mantle-derived isotopic compositions. It is possible that many pyroxenites are the products of this process, but without good field relations they may not be easily distinguishable from crystal cumulates.

7.4. Subduction-zone processes

Some pyroxenites, such as those that form the abundant layers in the Cabo Ortegal massif, have such different whole-rock compositions (low Al, Na, Ti and Ni) and REE patterns (LREE-enriched but with extremely low HREE contents), that an entirely different mode of origin must be implied. Clinopyroxenes from pyroxenites in the Cabo Ortegal massif have LREE-enriched compositions with strong Sr-peaks. Santos et al. (2002) suggested that they formed via introduction of melts from a subducting slab, whereas the previous extensive depletion by partial melting within the overlying mantle wedge would account for the low contents of Al, Na and Ti. Crystallisation from LREE-

enriched melts of subduction affinity may explain high Sr/Nd and low Zr/Sm ratios in their clinopyroxene (Fig. 9), but the high Nb and Ta contents is not consistent with this hypothesis. Clearly more work needs to be undertaken on this massif to determine the origin of these anomalous pyroxenites.

7.5. Mantle recycling

It is clear from the above discussion that several different processes can form mantle pyroxenites. However, no matter how they were formed, pyroxenites are a well-documented example of enrichment of the lithospheric mantle. Recycling of such material into the asthenosphere, by delamination of the sub-continental lithosphere, would enrich the resulting mixture. Pyroxenite layers may have lower melting temperatures compared to the host peridotite and may melt preferentially to form enriched magmas. Sobolev et al. (2005) and Tuff et al. (2005) have proposed such an origin for basalts and ferropicrites, respectively, using major and minor element arguments. However, the wider role of mantle pyroxenites in magmagenesis could be difficult to track using Sr, Nd and Pb isotope compositions as these are often similar to the host peridotites. Trace element compositions such as Sm/Nd ratios are also hard to distinguish from those of peridotites. Os isotope compositions are significantly different between pyroxenites and peridotites, but the range of pyroxenite data overlaps that of basalts, eclogites and continental crust, making it hard to discriminate between the relative contributions of these lithologies.

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Appendix A

LA-ICPMS data for clinopyroxenes from layered pyroxenites from ultramafic massifs in the Pyrenees (Pyr) (samples from [Downes et al., 1991](#)) and Beni Bousera (BB) (samples from [Pearson et al., 1993](#)), analysed at University of Utrecht (P R D Mason, analyst) and at Birkbeck University of London (A D Beard, analyst). b.d.l.=below detection limit; n.a.=not analysed; *n*=number of points analysed and averaged.

	70–148	70–375	70–358	70–379G	70–379W	72–375	GRD33	GRD101a	GRD101b	GP130	GP37	PHN42	GP147	GP81
	Pyr	Pyr	Pyr	Pyr	Pyr	Pyr	BB	BB	BB	BB	BB	BB	BB	BB
	<i>n</i> =8	<i>n</i> =10	<i>n</i> =7	<i>n</i> =6	<i>n</i> =8	<i>n</i> =9	<i>n</i> =2	<i>n</i> =9	<i>n</i> =4	<i>n</i> =5	<i>n</i> =10	<i>n</i> =10	<i>n</i> =2	<i>n</i> =1
Ni	597	257	300	229	220	224	258	443	340	469	544	473	63	81
Rb	<0.26	0.23	<0.67	0.23	<0.67	<0.26	0.38	0.22	0.18	0.16	0.48	0.22	0.85	0.33
Sr	4.6	12	36	48	60	11.8	6	28.4	73	28	44.2	79	2.2	1.3
Y	0.55	3.0	3.5	23	19.2	5.7	54.1	4.4	15.3	5.1	3.9	6.2	9.6	18.6
Zr	1.03	5.9	13	21.5	22	6	68.4	8.4	238	11.9	11.3	24.8	7.8	20.7
Nb	<0.009	<0.012	<0.05	0.36	<0.05	0.038	0.039	0.40	1.6	0.061	0.07	0.09	<0.06	<0.04
Ba	<0.011	<0.015	2.12	0.06	<0.06	0.059	1.86	0.05	0.16	0.057	<0.87	<0.63	0.36	1.32
La	0.013	0.024	0.53	1.32	1.24	0.26	0.145	1.59	10.4	1.46	0.19	0.65	<0.05	<0.05
Ce	0.093	0.265	2.07	1.75	3.90	0.86	0.605	4.75	26.0	4.7	0.95	2.69	0.124	<0.08
Pr	0.030	0.111	0.39	0.3	0.69	0.23	0.19	0.79	3.3	0.75	0.34	0.67	0.068	0.068
Nd	0.303	1.23	2.32	2.18	4.20	1.94	1.69	4.02	11.6	3.56	3.06	4.76	0.44	1.7
Sm	0.185	0.91	0.97	1.39	1.57	1.02	2.00	1.22	2.54	1.19	1.81	2.48	0.44	1.78
Eu	0.096	0.42	0.38	0.62	0.60	0.35	1.28	0.31	0.81	0.31	0.72	8.75	0.185	0.48
Gd	0.27	1.20	1.19	2.55	2.9	1.57	4.7	0.95	2.55	1.05	2.26	2.77	1.11	3.57
Tb	0.035	0.17	0.18	0.52	0.51	0.26	1.19	0.13	0.49	0.16	0.23	0.37	0.27	0.59
Dy	0.17	0.88	0.96	3.93	3.8	1.44	8.88	0.85	2.96	0.99	1.34	1.84	1.83	3.98
Ho	0.024	0.126	0.14	0.86	0.74	0.22	2.05	0.17	0.59	0.20	0.19	0.29	0.42	0.77
Er	0.036	0.221	0.26	2.50	2.0	0.43	6.15	0.49	1.7	0.54	0.42	0.53	1.14	2.26
Tm	<0.001	0.020	0.025	0.37	0.24	0.045	n.a.	n.a.	n.a.	n.a.	<0.12	0.085	0.108	0.34
Yb	0.028	0.104	0.13	2.45	1.50	0.22	6.23	0.45	1.84	0.51	0.47	0.59	0.91	2.22
Lu	<0.005	0.010	0.016	0.37	0.19	0.025	0.88	0.06	0.27	0.07	0.165	0.12	0.14	0.228
Hf	0.063	0.35	0.51	0.86	0.78	0.28	1.35	0.40	5.65	0.50	0.78	1.2	0.55	1.46
Ta	<0.001	<0.001	0.009	0.156	<0.005	0.006	0.023	0.028	0.60	0.02	0.12	<0.12	<0.12	<0.08
Pb	0.15	0.052	0.59	0.247	0.49	0.096	0.22	0.24	0.18	0.25	<0.54	<0.40	2.31	1.15
Th	<0.001	<0.001	0.007	0.229	<0.003	0.013	0.02	0.30	0.91	0.17	<0.37	<0.29	<0.26	<0.19
U	<0.002	<0.002	<0.008	0.091	<0.008	0.004	0.011	0.105	0.21	0.104	<0.32	<0.26	<0.23	<0.21

Separated pyroxenes were mounted in an epoxy resin circular blocks and polished. Analysis method for mantle clinopyroxenes in Utrecht is described by [Downes et al. \(2003\)](#). The analytical instrumentation at Birkbeck/UCL consists of a New Wave Research UP213 Nd:YAG solid state laser operating at a wavelength of 213 nm, coupled to an Agilent 7500a quadrupole ICP-MS. Time-resolved analysis was employed during data acquisition. Ablation was carried out in a He atmosphere and mixed with Ar carrier gas before the plasma torch. NIST 612 was used as an external calibration standard. Calcium (^{43}Ca) was determined on all samples and used as the internal calibration.

Appendix B

Oxygen isotope data for clinopyroxenes separated from mantle pyroxenites (analysed by N Grassineau, Royal Holloway University of London), using the laser fluorination technique of [Mattey and Macpherson \(1993\)](#). Details of methodology are given by [Dobosi et al. \(1998\)](#). Reproducibility is ± 0.03 per mil. All samples gave yields $>90\%$.

Sample	per mil $\delta^{18}\text{O}$
‰	
Pyrenees massifs: (samples from Downes et al., 1991)	
70–148	5.53
70–357	5.52
70–358	5.64

(continued on next page)

Appendix B (continued)

Sample	per mil ^{δ18O}
‰	
70–379G	6.23
70–379W	6.28
72–357c	5.77
<i>Alpine massifs spinel pyroxenites</i>	
Balmuccia-1	5.50
Finero-1	5.60
<i>Ronda massif spinel pyroxenites</i>	
Ron-6	5.55
Ron-9	5.33

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