Petrology of spinel Iherzolite xenoliths in alkali basalts from Liri, South of the Kapsiki Plateau (Northernmost Cameroon Hot Line)

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RESUME

Des xénolites de lherzolite à spinelle, composés d'olivine (Fo_{88-91}), d'orthopyroxène (En_{89-91}), de clinopyroxène (6,5 % d'Al₂O₃) et du spinelle riche Al sont présents dans les basaltes alcalins de Liri, Sud du plateau Kapsiki, extrême nord de la "Ligne chaude du Cameroun". Les données pétrographiques sont présentées et les analyses à la microsonde électronique des phases minérales coexistant dans six xénolites de lherzolite à spinelle sont reportées, avec les analyses des phases minérales des basaltes-hôtes. Des réactions d'échange et de transfert régies par des lois thermodynamiques sont examinées ; elles ont permis de conclure que les lherzolites à spinelle de Liri montrent une homogénéité chimique interne et qu'elles représentent un manteau supérieur normal. Leurs compositions minéralogiques suggèrent des conditions d'équilibre de 1050-1200°C et 1,4-2,3 GPa.

Mots clés : xénolites, ultramafique, lherzolite, Liri, Ligne Chaude du Cameroun, pétrologie.

ABSTRACT

Spinel Iherzolite xenoliths, composed of olivine (Fo₈₈₋₉₁), orthopyroxene (En₈₉₋₉₁), clinopyroxene (5.0 % Al₂O₃), and Al-rich spinel occur in alkali basalts from Liri, South of the Kapsiki plateau, northernmost Cameroon Hot Line. Petrographic data are given and microprobe analyses of coexisting phases in these spinel Iherzolite xenoliths are reported, along with the analyses of host-basalts. Exchange and transfer reactions rules based on thermodynamic equilibrium conditions are examined. The Liri spinel Iherzolites show internal chemical homogeneity and represented a normal upper mantle. Their mineral chemistries suggest equilibrium conditions of 1050-1200°C and 1.4-2.3 GPa.

Key words: xenoliths, ultramafic, Iherzolite, Liri, Cameroon Hot Line, petrology.

INTRODUCTION

The Liri region, South of the Kapsiki Plateau, belongs to the Cameroon Hot Line (Déruelle et al., 2007; Fig. 1), an active N30°E tectono-magmatic alignment, extending from Pagalu Island to Lake Chad. Its oceanic sector is comprised of six major volcanoes, and the continental sector of seven major volcanoes, numerous monogenic cones and more than sixty plutonic anorogenic ring complexes. The Kapsiki Plateau is the northernmost volcanic zone of the Cameroon Hot Line. The volcanism (27-35 Ma) is of alkaline type and has typical bimodal lava series diversity with basalts and hawaiite as mafic lavas and phonolites and trachytes, and rhyolites as felsic lavas (Ngounouno et al., 2000).

Ultramafic xenoliths described here were sampled in basaltic lava flows of the monogenic cone North-West

of Liri, and were first mentioned by Tamen (1998). Numerous occurrences of ultramafic xenoliths have been found in basaltic lavas all along the Cameroon Hot Line (Fig. 1) : six sites at Sao Tomé (Caldeira and Munha, 2002), two at Santa Isabel (Bioko) (Déruelle et al., 1991), and one in each of the other sites: Mt Cameroon (Ngounouno and Déruelle, 2007), Barombi-Mbo (Kumba) (Teitchou et al., 2007), Lake Enep (Oku) (Lee et al., 1996; Princivalle et al., 2000), and Nyos (Wum) (Nana et al., 1998). The rocks are mostly spinel Iherzolites; some pyroxenites occur at Sao Tomé and Mt Cameroon. Spinel (Girod et al., 1984) and garnet (Temdjim, 2005) Iherzolites are also present in the Adamawa. The purpose of the present study is to describe the petrography and composition of ultramafic xenoliths from Liri in order to determine their origin and their equilibrium conditions.

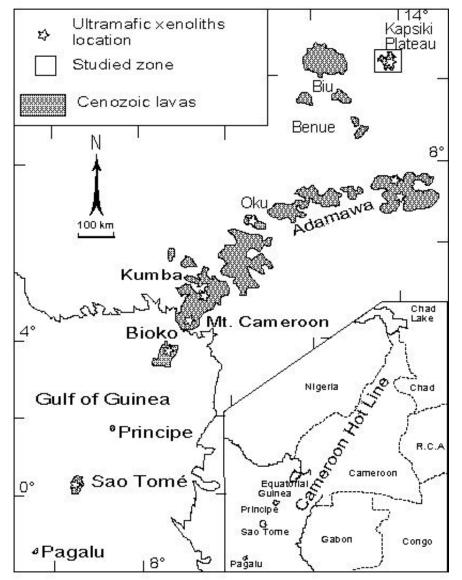


Fig. 1: Location of ultramafic xenoliths along the Cameroon Hot Line.

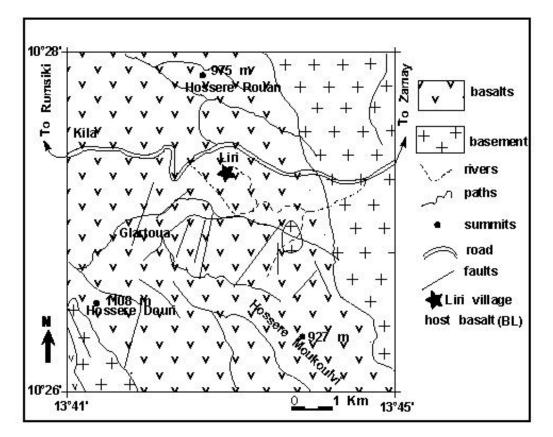


Fig. 2: Geological map of the Liri region and location of the spinel lherzolite xenoliths.

2. GEOLOGICAL SETTING AND SAMPLES LOCATION

The volcanism of the Liri region (Dumort and Péronne, 1966) is alkaline (Tamen, 1998) and characterized by a few small basaltic lava flows (Figure 2) intruded along the N65°E, N30°E and N165°E fractures (Moreau et al., 1986) of the Precambrian basement (Regnoult and Déruelle, 1983). The ages of these basalts are not precisely known. Nevertheless, similar basalts samples 15 km northwards in the Kapsiki Plateau gave K-Ar ages between 27.4 \pm 0.5 Ma and 33.21 \pm 1.33 Ma (Dunlop, 1983). The host rock (BL) represents basaltic lava flows and contains numerous spinel Iherzolite xenoliths with sub-rounded shapes (7 to 30 centimetres in diameter).

3. ANALYTICAL METHODS

Mineral analyses reported here (Table 1) were made with the "Microscan 5" electro-probe microanalyser, Titanomagnetite (53 < Usp % < 62).....10-10 ($\pm 0.5 \times 10^{-10}$) and at the CAMPARIS analytical centre, Université Pierre et Marie Curie, Paris, on either a Cameca CAMEBAX or SX-50 microprobe, using the wavelength dispersive method. Pure elements, oxides, simple silicate compositions or sulphides were used as standards. Corrections were made for dead-time, atomic number, absorption and fluorescence using computer programes based on the methods of "PAP" (Pouchou and Pichoir, 1991). The analytical conditions (by element) are : olivine: 15 kV, 40 nA, 20 s, except Si: 10 s; orthopyroxene and clinopyroxene : 15 kV, 40 nA, 20 s, except Ti: 30 s (Fe³⁺ recalculated after Droop, 1987), Fe-Ti oxides: 20 kV, 40 nA, 40 s except Al and Cr: 30 s (Fe³⁺ recalculated after Stormer, 1983); plagioclase: 15 kV, 10 nA, 10 s; spinel: 10 kV, 80 nA, 40 s except Al and Cr : 30 s, and Zn and Ni: 15 s. For pyroxenes, the nomenclature used is that of Morimoto et al. (1988). For spinel, Fe³⁺ is calculated by stoichiometry.

Major elements (Table 2) of the host basalt (BL) were made by inductively coupled plasma emission (ICP). Trace elements, including rare earth elements, were analyzed by inductively coupled plasma emission mass spectrometry (ICP-MS) at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy, France. A full description of the techniques used, including analytical conditions and precision estimates, is given in Carignan et al. (2001).

| rock | lherzolite | | | | | | | | host-basalt | | | | | | |
|-------------------------|------------|-------|-------|-------|--------|-------|--------|--------|-------------|-----------|-------|-------|-------|-------|---------|
| mineral | ol | | opx | | срх | | sp | | ol (ph) | ol (xeno) | opx | срх | ilm | mt | plag |
| SiO ₂ (wt %) | 39.73 | 40.53 | 54.81 | 55.92 | 48.50 | 49.05 | | | 38.66 | 40.72 | 55.99 | 47.85 | 0.02 | 0.01 | 50.89 |
| TiO ₂ | | | 0.01 | 0.06 | 0.18 | 0.25 | 0.07 | 0.07 | | | 0.10 | 2.35 | 51.57 | 19.09 | |
| Al_2O_3 | | | 2.38 | 3.04 | 4.44 | 4.93 | 50.53 | 52.49 | | | 3.16 | 6.59 | 0.07 | 2.85 | 30.89 |
| Cr_2O_3 | 0.03 | 0.03 | 0.58 | 0.23 | 0.78 | 0.92 | 15.01 | 14.54 | | 0.05 | 0.26 | | 0.19 | 1.28 | |
| FeO* | 10.10 | 9.31 | 5.47 | 6.13 | 2.91 | 2.67 | 12.59 | 12.75 | 14.69 | 8.94 | 5.98 | 9.38 | 40.56 | 68.37 | 0.57 |
| MnO | 0.20 | 0.14 | 0.15 | 0.21 | 0.11 | 0.01 | 0.09 | 0.11 | 0.26 | 0.13 | 0.18 | 0.29 | 0.83 | 0.57 | |
| MgO | 48.94 | 49.26 | 34.68 | 33.02 | 20.87 | 19.50 | 19.58 | 19.51 | 45.12 | 49.06 | 33.06 | 11.22 | 5.44 | 3.17 | |
| CaO | 0.12 | 0.11 | 0.80 | 0.39 | 20.99 | 21.21 | 0.01 | 0.00 | 0.12 | 0.13 | 54.00 | 21.41 | 0.23 | 0.03 | 13.87 |
| Na ₂ O | | | 0.12 | 0.11 | 1.07 | 1.02 | 0.01 | 0.00 | | | | 0.96 | | | 3.31 |
| K ₂ O | | | | | | | | | | | | | | | 0.12 |
| NiO | 0.40 | 0.31 | 0.12 | 0.11 | 0.03 | 0.08 | 0.35 | 0.29 | 0.35 | 0.41 | 0.13 | | 0.11 | 0.00 | |
| Total | 99.55 | 99.71 | 99.12 | 99.22 | 99.87 | 99.64 | 97.89 | 99.76 | 99.20 | 99.43 | 99.53 | 99.38 | 99.02 | | 99.66 |
| FeO recalc. | | | 1.83 | 6.13 | 1.47 | 1.58 | 9.376 | 10.12 | | | | 5.95 | 35.47 | | 0.57 |
| Fe_2O_3 recalc. | | | 4.04 | 0.00 | 1.59 | 1.21 | 3.58 | 2.92 | | | | 2.89 | | 27.90 | 0.00 |
| Total recalc. | | | 99.52 | 99.22 | 100.03 | 99.76 | 98.25 | 100.05 | | | | 99.51 | 99.59 | 98.17 | 99.53 |
| Si | 0.984 | 0.996 | 1.895 | 1.946 | 1.903 | 1.892 | | | 0.982 | 1.001 | 1.941 | 1.816 | 0.001 | 0.000 |) 2.325 |
| Ti | | | 0.000 | 0.002 | 0.003 | 0.215 | 0.011 | 0.011 | | | 0.003 | 0.057 | 1.890 | 0.531 | |
| Al | | | 0.097 | 0.124 | 0.193 | 0.215 | 12.809 | 13.082 | | | 0.130 | 0.241 | 0.004 | 0.124 | 1.664 |
| Cr | 0.001 | 0.001 | 0.016 | 0.006 | 0.023 | 0.027 | 2.553 | 2.431 | | 0.001 | 0.007 | | | 0.037 | |
| Fe ³⁺ | | | | 0.000 | 0.044 | 0.034 | 0.620 | 0.464 | | | 0.000 | 0.084 | 0.207 | 0.776 | 5 0.000 |
| Fe ²⁺ | 0.209 | 0.191 | 0.053 | 0.178 | 0.046 | 0.049 | 1.645 | 1.791 | 0.303 | 0.184 | 0.173 | 0.208 | 1.445 | 1.337 | 0.022 |
| Mn | 0.004 | 0.003 | 0.004 | 0.006 | 0.003 | 0.002 | 0.016 | 0.020 | 0.005 | 0.003 | 0.005 | 0.009 | 0.034 | 0.018 | 8 |
| Mg | 1.807 | 1.804 | 1.787 | 1.712 | 0.874 | 0.856 | 6.279 | 6.151 | 1.725 | 1.798 | 1.708 | 0.624 | 0.395 | 0.175 | 5 |
| Ca | 0.003 | 0.003 | 0.030 | 0.015 | 0.831 | 0.842 | 0.002 | 0.000 | 0.002 | 0.003 | 0.020 | 0.856 | 0.012 | 0.001 | 0.679 |
| Na | | | 0.008 | 0.007 | 0.077 | 0.073 | 0.004 | 0.000 | | | | 0.077 | | | 0.294 |
| K | | | | | | | | | | | | | | | 0.007 |
| Ni | 0.008 | 0.006 | 0.003 | 0.003 | 0.001 | 0.002 | 0.061 | 0.050 | 0.007 | 0.008 | 0.004 | | 0.004 | 0.000 |) |
| Mg# | | | 97.1 | 90.6 | 95.0 | 94.6 | 79.2 | 77.4 | | | 90.8 | 75.0 | | | |
| Cr# | | | | | | | 17.9 | 15.7 | | | | | | | |
| Usp (%) | | | | | | | | | | | | | | 59.0 | |
| Fo | 89.4 | 90.3 | | | | | | | 84.9 | 90.6 | | | | | |
| Fa | 10.6 | 9.7 | | | | | | | 15.1 | 9.4 | | | | | |
| Wo | | | 1.6 | 0.9 | 47.5 | 48.2 | | | | | 1.0 | 45.7 | | | |
| En | | | 95.6 | 91.2 | 49.9 | 49.0 | | | | | 89.9 | 40.8 | | | |
| Fs | | | 2.8 | 7.8 | 2.6 | 2.8 | | | | | 9.1 | 13.5 | | | |
| An | | | | | | | | | | | | | | | 69.2 |
| Ab | | | | | | | | | | | | | | | 30.0 |
| Or | | | | | | | | | | | | | | | 0.7 |

Table 1: Chemical compositions of representative host-basalt from Liri (BL). The Mount Cameroon (C10J) and Kapsiki Plateau (52X) host-basalts are used in comparison.

4. RESULTS

4.1. Petrography

4.1.1. The host basalt

The host rock (BL) is an alkaline basalt (D.I. ≈ 25 ; normative nepheline ≈ 7 %), with porphyritic texture containing abundant (30 % vol.) euhedral phenocrysts of olivine (0.7-3 mm), clinopyroxene (1-2 mm), spinel

and Ti-magnetite in a groundmass of lath-shaped crystals of clinopyroxene (< 0.05 mm), plagioclase microlites (0.01-0.05 mm) and a heterogeneous glass. The basalt also contains olivine, and angular and fractured orthpyroxene xenocrysts with well-developed undulose extinction.

4.1.2. The xenoliths

Lherzolites display a protogranular texture (terminology

| | | Kapsiki | Mt |
|-------------------------|-------|---------|----------|
| | Liri | Plateau | Cameroon |
| Sample | BL | 2X | C10J |
| SiO ₂ (wt %) | 43.99 | 42.87 | 45.00 |
| TiO ₂ | 2.86 | 2.74 | 2.27 |
| Al_2O_3 | 12.55 | 11.35 | 8.43 |
| FeO* | 11.47 | 12.19 | 11.07 |
| MnO | 0.17 | 0.17 | 0.18 |
| MgO | 13.11 | 15.13 | 14.46 |
| CaO | 10.07 | 10.16 | 14.57 |
| Na ₂ O | 3.07 | 2.72 | 1.26 |
| K ₂ O | 0.81 | 1.06 | 0.59 |
| P_2O_5 | 0.58 | 0.83 | 0.32 |
| L.O.I. | 1.18 | 0.20 | 1.87 |
| Total | 99.84 | 99.62 | 100.02 |
| Ne | 7.31 | 15.80 | 2.88 |
| D.I. | 24.57 | 21.92 | 11.71 |
| Mg# | 79.4 | 80.1 | 80.3 |
| Rb (ppm) | 22.7 | 22.0 | 14.3 |
| Sr | 732 | 1105 | 473 |
| Cs | 0.39 | 0.00 | 0.27 |
| Ba | 345 | 360 | 205 |
| V | 223 | 105 | 235 |
| Cr | 669 | 1101 | 1304 |
| Со | 53 | 62 | 57 |
| Ni | 361 | 0 | 279 |
| Cu | 50 | 105 | 55 |
| Zn | 127 | 92 | 88 |
| Y | 22.22 | 22.00 | 18.30 |
| Zr | 250.8 | 163 | 183 |
| Nb | 53.0 | 52.0 | 39.0 |
| Hf | 5.49 | | 4.45 |
| Та | 3.89 | | 2.88 |
| Th | 4.31 | | 3.26 |
| | | | |
| U | 1.19 | | 0.88 |
| La | 38.2 | 35.5 | 32.7 |
| Ce | 77.7 | 85.0 | 70.0 |
| Pr | 9.49 | | 8.70 |
| Nd | 38.8 | 38.3 | 35.1 |
| Sm | 7.91 | 8.30 | 6.80 |
| Eu | 2.60 | 2.67 | 2.10 |
| Gd | 6.68 | 7.70 | 5.51 |
| Tb | 0.93 | | 0.76 |
| Dy | 4.76 | 4.40 | 3.97 |
| Yb | 1.56 | 1.23 | 1.37 |
| Lu | 0.22 | 0.22 | 0.19 |

Table 2: Chemical composition of representativeminerals of the Iherzolite and the host-basalt from Liri.

Kansiki

Mt

after Mercier and Nicolas, 1975) and have a modal composition comprising olivine: 50-60 %, orthopyroxene: 20-25 %, clinopyroxene: 10-16 %, spinel: 2-4 %. Olivine is colourless and often contains deformation lamellae. It is generally coarse-grained (3-6 mm in diameter) with curved joints and is surrounded by subhedral clinopyroxene crystals with well-developed kink bands. Small polygonal olivine grains (down to 0.1 mm or less in diameter) are present and represent recrystallized olivine grains. Orthopyroxene is usually colourless, but occasionally with a brown tint. Unmixing of clinopyroxene in orthopyroxene is uncommon. Cleavage traces are commonly visible. Clinopyroxene (2-5 mm) is colourless to brown grey, and occurs as interstitial crystals between olivine and orthopyroxene crystals, displaying well-developed undulose extinction. Spinel occurs as interstitial or vermicular crystals (20-30 m), sometimes in grains (3-4 mm long) concentrated in distinct planes in the xenoliths.

4.2. Mineral chemistry

Lherzolite olivine has Fo contents between 89 and 91. It is homogeneous and shows very similar composition in different xenoliths samples. There is no chemical distinction between porphyroclastic olivine and the polygonal recrystallized varieties; a feature also observed by Temdjim (2005) in garnet Iherzolites from the Adamawa. MgO and NiO (0.30-0.44 %) contents are similar to those of xenocrysts from the host basalt (Fo₈₈₋₉₂; 0.13-0.26 %). Mg-rich olivine phenocrysts are homogeneous and show very similar compositions in different samples of the host basalt. They are unzoned but sometimes have cores richer in Mg (Fo₈₅₋₇₅) than rims (Fo₇₂).

Lherzolite orthopyroxene is Al-rich enstatite (En₈₉₋₉₂). As in the case of coexisting olivine, the orthopyroxene has very constant composition from grain to grain as well as from xenolith to xenolith. Rounded and fracturated Al-rich enstatite (En93; Mg# 94) xenocrysts are present.

Clinopyroxene from Iherzolite xenoliths is AI and Crrich diopside ($Wo_{45-48}En_{46-49}Fs_{9-3}$). Like the coexisting enstatite, the diopside to show minor variations in Al content. The average AI content in Liri Iherzolite diopside is 0.71 %, which is twice the amount present in the coexisting enstatite. The clinopyroxene contains 0.4 to 2.0 % Fe₂O₂ averaging 1.2 %. When considering calculated pyroxene end-member proportions special attention is drawn to the contents of jadeite, Ca-Titschermak's molecule and Ca-tschermak's molecule because of the pressure and temperature dependencies of these components. The small compositional range of the Iherzolite diopside is reflected in the fact that the end-member proportions show only 11.9 mole percent, and jadeite + Ca-tschermak's molecule constitute 17.0 to 20.1 mol. %, while the amount of

Ca-Ti-tschermak's molecule are low (1.7 mol. % on average). The host basalt contains phenocrysts of diopside ($Wo_{45-47}En_{43-38}Fs_{12-15}$) with Mg# values and TiO₂ of 77-78 and 1.3-2.8 %, respectively.

Spinel from the lherzolite xenoliths is spinel sensu strictu in the terminology of Deer et al. (1975): (Mg > Fe²⁺; Al > Cr) with Cr (Cr# = 14-17 with Cr# = Cr x 100/(Cr+Al)) and Mg (Mg# 79-82) contents similar to those of spinel from Nyos (Nana et al., 1998; Temdjim, 2005), Dibi (Girod et al., 1984) and Barombi and Enep (Lee et al., 1996). A certain variation in Al and Cr contents of individual spinels gives rise to a range of Cr#.

Titanomagnetite (53 < Usp % < 62) and ilmenite (TiO₂ \approx 52 %) from the host basalt have similar compositions to those of basalts from Kapsiki Plateau (Ngounouno et al., 2000). Equilibrium Fe-Ti oxide temperatures are between 980 and 1000°C (± 20°C) and corresponding oxygen fugacities of 10-10 (± 0.5 x 10-10) atmospheres according to Spencer and Lindsley (1981).

Plagioclase microlites from the host basalt are Ca-rich (An_{68-53}) .

The above composition of various phases in the Iherzolites confirms that the Liri Iherzolites are typical members of the Cameroon Hot Line Iherzolite xenolith suite (e.g. Lee et al., 1996; Nana et al., 1998; Princivalle et al., 2000 ; Caldeira and Munha, 2002, Déruelle et al., 1991, Teitchou et al., 2007) and of the Adamawa Plateau (Temdjim, 2005).

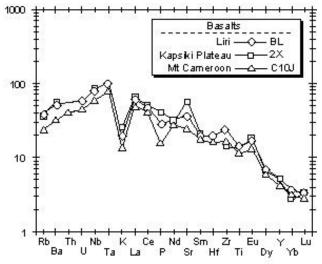


Fig. 3: Multielement spidergram of the host-basalts from Liri (BL). Basalt from Kapsiki Plateau (2X) and Mount Cameroon (C10J) are used for comparison. (normalizing values from McDonough and Sun (1995).

4.3. Geochemistry

The host basalt (BL) displays primitive characteristics (Mg# 79) with high Cr (669 ppm) and Ni (361 ppm) contents (Table 2). In primitive mantle normalized spidergrams, the host basalt and the less evolved basalts of Kapsiki Plateau and Mt Cameroon have similar patterns (Fig. 3). These are characterized by negative Rb and K and positive Zr anomalies, and have high (La/Yb)N \approx 17 and (La/Sm)_N \approx 3. The host basalt spectra are similar to those of the Cameroon Hot Line basalts (e.g. Déruelle et al., 2007).

5. DISCUSSION

The triple-point junctions (V app. 120°) seen between the silicate phases suggest that a certain degree of intergrain adjustment possibly annealing, has taken place (Vernon, 1970). The protogranular texture, undulose extinction of olivine and clinopyroxene and local recrystallization suggest that the studied xenoliths were deformed after they crystallized. In addition, Iherzolites are crosscut by a thin basaltic vein. These observations suggest that it is highly unlikely that the xenoliths are cognate to their host-basalts. Also, there is no trace of plagioclase, garnet, or accessory hydrated minerals (amphibole, phlogopite, and apatite) in the mode of the xenolith.

5.1. Exchange reactions and equilibrium state

Elements are not randomly distributed between the four mineral phases (ol, opx, cpx, and sp) of the Iherzolite xenoliths from Liri. In fact, their distribution is governed by a set of exchange and transfer reactions rules based on thermodynamic equilibrium conditions (Mercier and Bertrand, 1984). Here, we should review some of these reactions which must later allow to characterize the chemical composition of the upper mantle beneath the Liri region and to test the equilibrium state between these mineral phases.

In the case of the Liri peridotites, olivine and orthopyroxene constitute more than 70-90 vol.% of the rock, and their compositions very closely approach compositions of the FeO-MgO-SiO₂ (FMS) system. We could then characterize the chemical variation of Fe/Mg systems using the olivine/orthopyroxene pair. According to Matsui and Nishizawa (1974), the Fe-Mg exchange between olivine and orthopyroxene can be described allowing behaviour of a monosite, ideal solution for these two phases at high temperatures (> 1000°C). We must then use the following reaction to express this exchange:

The partition coefficient is expressed as follows: $K_{D} = ((X_{Fe})_{ol} * (X_{Mg})_{opx} / ((X_{Mg})_{ol} * (X_{Fe})_{opx}))$

In application to natural system and considering that Fe/Mg exchange is limited to octahedral sites (not occupied by Ca, Na, Cr and Al), the concentrations corresponding to the FMS-system can be estimated as: $(X_{Mg})_{ol} = (Mg/Mg + Fe^{2+})_{ol}$ $(X_{Fe})_{ol} = 1 - (X_{Mg})_{ol}$ $(X_{Mg})_{opx} = (Mg/Mg + Fe^{2+})_{opx}$ $(X_{Fe})_{opx} = 1 - (X_{Mg})_{opx}$

Assuming the Mg/(Mg + Fe) ratio of olivine and orthopyroxene of peridotites, the Mg/(Mg + Fe)ol versus (Mg/(Mg + Fe)_{opx} diagram (Fig. 4) is constructed and the partition coefficient is determined and compared to a theoretical model. Figure 4 shows an excellent correlation between olivine and orthopyroxene indicating partition coefficients higher than 1, except for peridotites from Ngaoundéré and Dibi (Dautria and Girod, 1986; Lee et al., 1996) for which the average partition coefficient is 0.94. The small compositional range of the Fo content of olivine is in the same general range of the mantle rocks (90-92; Sato et al., 1991).

Due to the fact that AI and Cr contents are concentrated in spinel, but are also present in pyroxene in small amounts, the second exchange reaction is:

 $(Mg, Fe)_{3}AI(AISi_{3}O_{12}) + \frac{1}{2} (Mg, Fe)Cr_{2}O_{4}$

(sp)

(xqo)

$$\begin{array}{c} <=> & (Mg, Fe)_{3}Cr(AlSi_{3}O_{12}) + \frac{1}{2} (Mg, Fe)A_{12}O_{4} \\ (opx) & (sp) \end{array}$$

In fact, Ganguly and Ghose (1979) pointed out by experimentally measuring the interatomic lattice in pyroxene, that AI occupies both tetrahedral and octahedral sites while Cr is restricted to the octahedral sites. They concluded that the Cr-AI exchange is limited to octahedral sites. To maintain the electroneutrality of the phase, the presence of Na in the pyroxene needs an equivalent amount of trivalent cations (AI, Cr and Fe³⁺). The content of these three elements is relatively constant in the presence of a given Al-rich phase for peridotites derived from the upper mantle (Mercier, 1980; Bertrand et al., 1987). In our case, for the spinel facies, the amount of ferric iron in the pyroxenes (Table 1) is very low and any significant value could be calculated from electron microprobe results. In summary, to express AI-Cr exchange between orthopyroxene and spinel, we should calculate the amount of Al^{VI} (none associated with Na): (AI - Cr - Na)/2 and $AI^{IV} = (AI + I)^{IV}$ Cr - Na)/2). The (Cr/Cr + AI)sp versus (Cr/AI^{IV})_{onx} diagram (Fig. 5) is used in order to describe in appropriate manner this exchange. The pattern observed implies a non-ideal spinel composition with respect to the Y-site for a Cr-Al substitution. This agrees with

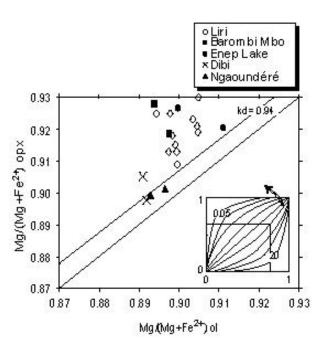


Fig. 4: Fe-Mg exchange diagram between olivine and orthopyroxene. The inset is calculated by a model of fictive ideal solution assuming octahedral sites for the two phases.

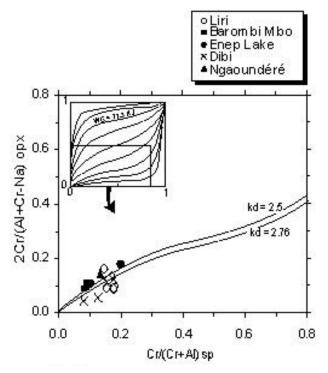


Fig. 5: Cr-Al exchange diagram between spinel and orthopyroxene. The model of regular solution has been calculated at 900 °C (inset) with an excess energy of 11.3 kj (Webb and wood, 1986) for Cr/Al interactions in Y-sites of the spinel.

experimental and theoretical data showing that a simple model of regular solution will be convenient to describe this AI-Cr partitioning between spinel and orthopyroxene.

Note that:

 $X_2 = X_1/(X_1 + K (1 - X_1) \exp(W_G (2X_1 - 1)/RT \text{ for } T$ fixed with; where

 $X_1 = (Cr/(Cr + AI))_{sp}$ and $X_2 = (2Cr/(AI + Cr - Na))_{opx'}$ WG (2X1 - 1)

RT being excess of energy with a value of 11.3 kJ for the parameter of Margules WG, according to Webb and Wood (1986). This expression allows calculating the theoretical AI - Cr partition between spinel and orthopyroxene which is represented by asymmetrical curves contrasting with those shown in Figure 4. The majority of representative compositions plot on the curve corresponding to an equilibrium constant of 2.5.

The AI-Cr exchange between the two pyroxenes is well described by a model of ideal solution using the $(Cr/^{IV}AI)_{cpx}/(Cr/^{IV}AI)_{opx}$ pair and an equilibrium constant written as follows: $K_D = (X_{AI})_{opx}(X_{Cr})_{opx}/(X_{Cr})_{opx}$ with $(X_{Cr})_{opx} = 2Cr/(AI + Cr ? Na)$ and $(X_{AI})_{opx} = 1 - (2Cr/(Cr + AI - Na))$. The equilibrium constant is significantly different from unity and is about 3.3 for peridotites from Liri (Fig. 6). Cr and AI contents of clinopyroxene are twice the amount of those of orthopyroxene. The observed correlation

confirms what was seen in the previous diagrams (Figs 3, 4): Iherzolite samples from Liri as well as those from the Barombi Mbo, Lake Enep, and Ngaoundéré and Dibi attest a good internal equilibrium, and quite represent a normal mantle.

Due to the effects of interactions of Fe and Mg cations in the X-sites and AI and Cr in the Y-sites, spinel could not be considered as a monosite ideal solution for the Fe-Mg substitution. These interactions can be described by the following reaction:

 $\text{FeAl}_2\text{O}_4 + \text{MgCr}_2\text{O}_4 < = = > \text{FeCr}_2\text{O}_4 + \text{MgAl}_2\text{O}_4$

This is well described using the $(Mg/Mg+Fe^{2+})_{sp}$ versus $(Cr/Cr+AI)_{sp}$ diagram (Fig. 7). As spinel is richer in Cr than other minerals, the Cr#_{sp} reflects the system and controls the Mg#_{sp}. For comparison, the composition of Iherzolites from Liri, Barombi Mbo, Lake Enep, and Ngaoundéré and Dibi, and ophiolitic peridotites (Cabanes and Mercier, 1988) are also reported on Figure 7. The investigated Iherzolites and those from other parts of the Cameroon Hot Line, and Ngaoundéré and Dibi (Dautria and Girod, 1986; Lee et al., 1996) are clearly distinct in chemistry and are located above the field of ophiolites (Cabanes and Mercier, 1988), in the domain of spinel peridotites derived from lithospheric mantle (Conticelli and

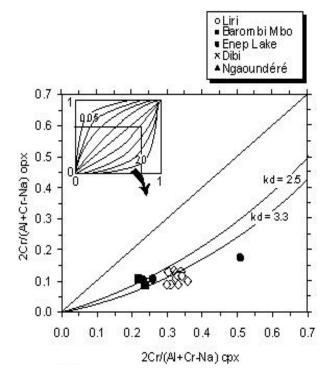


Fig. 6: Cr-AI exchange diagram between the two pyroxenes. Only Cr and AI in octahedral sites have been taken into account in the exchange.

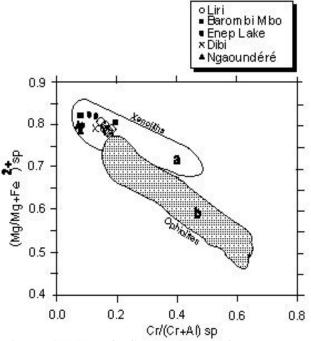


Fig. 7: Fig. 7: Mg-Cr diagram for spinel.

a: Domain of ultrabasic xenoliths (lherzolites and harzburgites) in basaltic lavas (after Conticelli and Piccerillo, 1990).

b: Domain of ultrabasic xenoliths in ophiolites (Cabanes and Mercier, 1988b).

Piccerillo, 1990). The distinct chemical differences between Iherzolite xenoliths and ophiolites were explained by kinetics of this exchange reaction (Cabanes and Mercier, 1988).

5.2. Geothermometry and geobarometry of spinel Iherzolite xenoliths

We evaluated three different geothermometers for the Liri Iherzolite xenoliths. Equilibrium temperatures of 1050-1100°C are estimated using the olivine/spinel geothermometer of Fabriès (1979), using crystal cores analyses. As the Fo content of olivine from Iherzolites is obviously high, (between 89 and 91 %) and spinel and orthopyroxene contain very small amounts of Fe³⁺, (which could only have insignificant effect on temperature calculations), it seems reasonable to use this geothermometer. Equilibrium temperature estimates fall between 1130 and 1190°C, using Bertrand and Mercier's (1985) two-pyroxene geothermometer. Applying the geothermometer of Bertrand et al. (1987), based on the solubility of Al₂O₂ in clinopyroxene and orthopyroxene, the temperature expression calibrated at 1.5 GPa in a natural spinel Iherzolite system, gives the equilibrium temperatures of individual Liri Iherzolite xenoliths as 1158-1166°C. In conclusion, the overall impression is that the equilibrium temperatures of spinel lherzolite xenoliths from Liri lie in the same general range as equilibrium temperatures of a number of other lherzolite xenoliths along the Cameroon Hot Line, and Ngaoundéré and Dibi (Dautria and Girod, 1986; Lee et al., 1996). More specifically, Liri Iherzolite equilibrium temperatures lie 200°C below the dry peridotite solidus at 1.5 GPa (Wyllie, 1970), but nearly 300°C above the water saturated peridotite solidus at the same pressure (Mysen

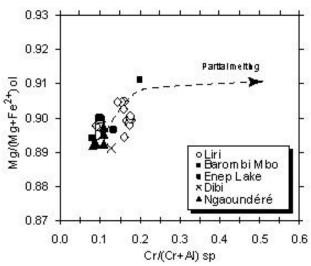


Fig. 8: Mg# versus Cr# diagram illustrating the compositional evolution of the peridotite system strongly depending on partial melting.

and Boettcher, 1975).

The lack of plagioclase or garnet in Iherzolites and the fact that the Iherzolite xenoliths have reached a high degree of internal chemical equilibrium, indicate that equilibration took place at pressures ranging between 1.4 and 2.3 GPa (55-80 kms). Liri xenoliths have probably been sampled by the host-basalt in the upper mantle. At depths of 60-80 kms, the calculated temperatures are about 200°C above those of the oceanic geotherm of Clarke and Ringwood (1964). It seems noteworthy that Iherzolite xenoliths along the Cameroon Hot Line likewise have equilibrium temperatures about 200°C above the oceanic geotherm (Lee et al., 1996).

5.3. Origin of spinel Iherzolite xenoliths

Lherzolite xenoliths, characterized by the presence of Cr-diopside, in alkaline basaltic rocks represent portions of the earth's upper mantle (cf. Green and Ringwood, 1967) or represent cumulates crystallized from their host rocks (O'Hara and Mercy, 1963; O'Hara, 1968, 1970). How do these two competing models compare in the light of mineral chemistry evidence from the Liri Iherzolite xenoliths?

The composition of olivine and spinel is strongly dependent on the degree of melting, a feature characterized firstly by a regular increase of $(Mg\#)_{ol}$, $(Mg\#)_{sp}$ and $(Cr\#)_{sp}$ values and secondly by the fact that these values remain nearly constant through the melting process (Mysen and Kushiro, 1977). As Cr is a refractory element, it is enriched in the residue. The overall representative analyses are grouped around a restricted range (Fo89-91) (Fig. 8). Based on these data, the xenoliths from Liri represent a residual sequence issued from partial melting of a mantle source.

Experiments have shown that the composition of solid solutions, such as olivine, is very sensitive to temperature changes, and olivine could therefore evolve towards refractory compositions during the partial melting. So, an extraction of the melt could leave a residue depleted in highly incompatible elements (e.g. Na, AI, K, and Ti) and enriched in Cr and Ni relative to the most primitive mantle (Hart and Zindler, 1985). Na and Ti contents decrease with $(Cr#)_{sp}$ (Fig. 9), a pattern similar to that previously observed in the precedent figures. But, while the chemical evolution of Ti contents is well explained by a melting process, the highly incompatible behaviour of Na is more complicated, with many analyses plotting above the region predicted for primitive mantle. These discrepancies could certainly imply metasomatic effect.

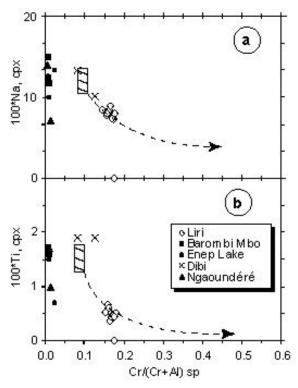


Fig. 9: Correlation between incompatible elements and the degree of partial melting in clinopyroxene and spinel.

a: (100*Na)cpx versus (Cr/Cr+Al)sp. **b:** (100*Ti)cpx versus (Cr/Cr + Al)sp.

The range of Ni contents of olivine of Iherzolites from Liri confirms that they are residue of melting. This is illustrated in Figure 10 and can be deduced from the non-modal batch melting equation of Shaw (1970): $CNi^{s}/CNi^{0} = D_{Ni}^{s/l}/(D_{Ni}^{s/l}(1 - F) + F)$ where F is the degree of melting; C_{Ni}^{s} and C_{Ni}^{0} are the concentration of Ni in the residue and the source; $D_{Ni}^{s/l}$ is the bulk distribution coefficient of Ni in the initial assemblage and for the minerals entering into the liquid, respectively.

The fact that Ni behaves as a highly compatible element, i.e. $D_{Ni}^{s/l} >> 1$ allows us to assume that $D_{Ni}^{s/l} >> F$ (e.g. Hart and Davis, 1978) and simplify the partial melting expression as follows: $C_{Ni}^{s}/C_{Ni}^{0} = 1/(1 - F)$. The degree of melting can be accurately estimated taking into account this approach and also the high proportion of olivine.

The Ni content is very high (2190-3331 ppm) in olivine, while it is only 130-936 ppm in clinopyroxene and 285-1181 ppm in orthopyroxene. For spinel, the Ni content is somewhat similar to that of olivine, but spinel is a minor mineral phase (< 5 vol. %) and so its role is still insignificant. The Ni content of olivine could

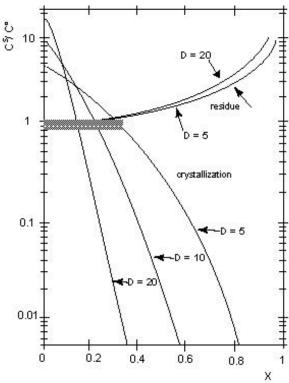


Fig. 10: Variation of the theoretical C^s/C^o ratio during the partial melting and fractional crystallization for different partition coefficients. X is the degree of melting or crystallization. The grey part indicates the variation of Ni contents for the studied xenoliths

represent the maximum content of the bulk-rock compositions. Assuming that the initial concentration of Ni in the primitive mantle is $C_{Ni}0 = 2108 \text{ ppm}$ (Jagoutz et al., 1979), the Ni contents of the Liri samples were plotted in Fig. 10. It can be observed that for an interval degree of melting or crystallization, the range of Ni content resulting from fractional crystallization is larger than that generated from the residue. For example, the Cs/Co ratio varies from 5 to 1.2 with $D^{s/l} = 5$ and requires 30 % of crystallization. This is particularly obvious for the highest D^{s/l} values. On the other hand, under similar conditions, the C^{s}/C^{o} ratio changes from 1 to 1.33 during partial melting. To summarize, it appears that high content of Ni (2190-3331 ppm) in olivine suggests that xenoliths from Liri could derive from a low degree of melting (< 30 %) of a relatively homogeneous mantle source.

There is thus no need to appeal to a cumulate crystallized rocks model of the kind proposed by O'Hara and Mercy (1963), O'Hara (1968, 1970). Rather, the model of Green and Ringwood (1967) for portions of the earth's upper mantle appears appropriate for the origin of the Liri Iherzolite xenoliths.

5.4. Origin of the host basalt

The host basalt (BL) represents the most primitive lava erupted in the Liri region. It has high MgO (13.0 wt %), Ni (361 ppm) and Cr (669 ppm) and high *mq*number (79), consistent with a derivation from partial melting of a peridotite mantle source. Xenocrysts of olivine (Fo₈₈₋₉₂) and orthopyroxene (Mg# 94) have been found in this basalt. They may be individual crystals resulting from the disaggregation of peridotite xenoliths. The modal abundances of these xenocrysts is very low (< 0.1 vol. % for orthopyroxene and < 0.2 vol. % for olivine) so that the chemistry of the host basalt is not significantly affected by their occurrence. The parental magma of the Liri basalts could have incorporated accidental fragments of a spinel-peridotite during their rise through the lithosphere. These rising magmas may have accumulated in reservoirs at the crust-mantle boundary beneath the Liri shield, as suggested by the presence of orthopyroxene and olivine xenocrysts in the basalt (BL) which implies a minimum depth of \approx 30-50 km, estimated (e.g. Walter and Presnall, 1994) from the stability field of spinel peridotite at liquidus temperature (1300-1400°C). This depth is consistent with the crust-mantle boundary locally estimated at 37-44 km from seismic refraction studies (Dorbath et al., 1986).

6. CONCLUSION

The ultramafic xenoliths exhumed by alkali basalts from Liri South of Kapsiki Plateau are classical spinel Iherzolites. Major and trace elements and mineral chemistry indicate that these Iherzolites are residues of partial melting of an initial mantle with a degree of melting lower than 30 %. The spinel Iherzolites show internal chemical homogeneity, and their mineral chemistries suggest equilibrium conditions of 1050-1200°C and 1.4-2.3 GPa. Major and trace element contents of the investigated host basalt suggest derivation from the earth's upper mantle by a small degree of partial melting.

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