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Research paper

Behavior of the clinopyroxenes trace elements in spinel-lherzolite xenoliths from Liri (Kapsiki plateau, Cameroon line)

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Abstract

Spinel-lherzolite xenoliths trapped within the alkali basalts flow in the Liri region (Kapsiki Plateau) have a protogranular texture and consist of olivine, orthopyroxene, clinopyroxene and spinel crystals. These xenoliths are residues of partial melting of the primitive mantle, with the low titanium content in clinopyroxene crystals (TiO_2 < 0.5 wt.%). The clinopyroxene of the spinel-lherzolite xenoliths from Liri, are divided into two distinct groups according to their trace element characteristics. The variations in the rare earths elements make it possible to classify the different clynopyroxenes in two groups: the first group consisting of the samples of Liri (Liri 1, Liri 02, Liri 3, Liri 05 and Liri 5) rich in light rare earths elements (LREEs), with ratios (Ce/Yb)N normalized which vary between 3.00 and 7.78. It is probably a cryptic metasomatism due to the absence of hydrated minerals (such as amphibole) which caused these enrichments. The second group comprises samples of Liri (Liri 01, Liri 2, Liri 04, Liri 4) depleted in light rare earths elements, with the ratio in (Ce/Yb) N < 1.2. This depletion in rare earths elements results from the extraction of the melting liquid.

Keywords: *Spinel-Lherzolite Xenoliths; Clinopyroxene; Cryptic Metasomatism; Liri; Cameroon Line.*

1. Introduction

Peridotite nodules broken to the surface by alkaline basalts provide us direct information on the processes and composition of the upper mantle. These nodules constitute the major source of information concerning the state of stress, pressure and temperature in the upper mantle. Mantle xenoliths occur in the basaltic plug from Liri (south of the Kapsiki Plateau, Cameroon Line). Alkali basaltic lavas exhumed these ultramafic xenoliths consisting of olivine, clynopyroxene, orthopyroxene and spinel. In the formerly petrological study on the Liri sector, major and trace elements of the host-basalt and the mineral chemistry of the spinel-lherzolite xenoliths are presented. According to these data, [1] proposed that the spinel-lherzolite xenoliths from Liri are the residues of partial melting of an initial mantle with a small degree of partial melting. However, clinopyroxene is a major host for many incompatible trace elements in peridotite xenoliths and as such its trace-element composition is a useful indicator of chemical modification in the mantle. In this respect, clinopyroxenes in mantle xenoliths from Liri would furnish opportunities to better understand Liri's peridotite formation processes. Since crystal chemical studies have demonstrated that site configurations may be related to specific suites of possible mantle residue from partial melting and metasomatism ([2]; [3]).

This study is focused on the behavior of the clinopyroxenes trace elements, analyzed in spinel lherzolte xenoliths from Liri, in order to establish their petrological origin and thermobarometric stability conditions in the mantle, according to the mineral chemistry and crystal structure.

2. Geological setting

The Kapsiki plateau (altitude ≈ 1000 m) is a volcanic zone located northern of the "Cameroon Line" [4]. The Precambrian base of this area is intersected by numerous needles and dykes of trachyte, phonolite and rhyolite, and partially covered by basaltic flows. The age of the basalts is included between 33.2 ± 1.3 Ma [5] and 27.0 ± 0.5 Ma [6]. The trachytes were dated at 29.6 ± 0.6 Ma [6] and 35.3 ± 2.4 Ma [5]. The age of rhyolites is between 32 ± 0.5 Ma and 29.0 Ma [5]. The presence of xenoliths in the Liri sector (south of the Kapsiki Plateau) was initially reported by [7]. According to the work of [8], it is proved that the structural and Geophysical (gravimetric and seismological) features of the granite-gneissic base complex are still poorly defined.

The Liri sector is located along the Cameroon Line with a basement constituted of granite and gneiss (Fig. 1). This basement is crossed by faults and locally covered by basaltic lava flows. The lava flows are broken up into the small centimetric blocks. The spinel-lherzolite xenoliths (size: 7-30 cm) with sub-rounded shapes were discovered in these dark basaltic lavas.

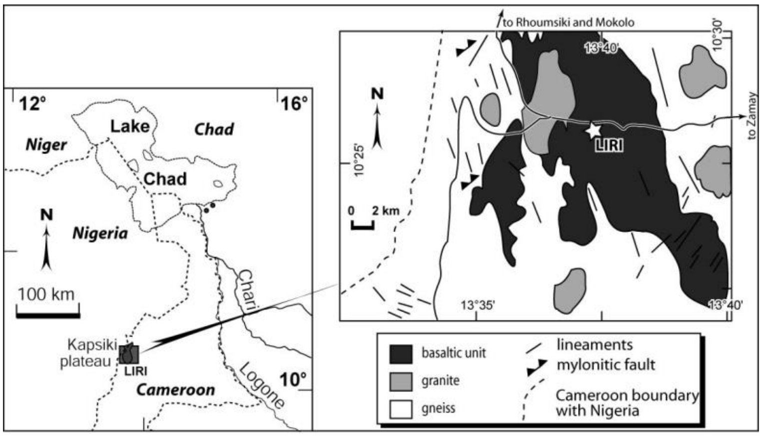

Fig. 1: Location of the Ultramafic Xenoliths from Liri Within the Kapsiki Plateau and the Geological Sketch of the Studied Sector.

3. Analytical methods

The polished thin sections of the different rock-types were observed under an Olympus BH2-HLSH microscope. The minerals of the different thin sections were observed at magnifications x5, x10, x25 and x50. Chemical analyzes ("Université de Bretagne Occidentale-Brest, France") of major elements were performed using an electron microprobe with beams of: 10 and 40 μm, 15 kV and 15 nA. Errors considered for these analyzes are between 5% and 10% of measured values < 1% and between 1% and 5% of the measured values > 1%. Measurements of trace elements of the different phases have been produced using a technique laser ablation of a mass spectrometer coupled plasma source (LA-ICP-MS). The analyzes are done on polished sections. Before each analysis, the samples are metallized with carbon. Then a very fine incident beam of electrons comes into contact with the sample. In order to test the homogeneity of the peridotite minerals, several grains on the samples were analyzed. To verify the zonation in composition, we analyzed several points in the same grain. Overall, no chemical variation from one grain to another in the sample was observed for olivine and spinel. The olivine and spinel analyzes were performed punctually in the core of the crystals.

4. Results

Spinel-lherzolite xenoliths from Liri (south of the Kapsiki Plateau) have a protogranular texture and consist of olivine (50−60 vol.%), orthopyroxene (20−25 vol.%), clinopyroxene (10−16 vol%) and spinel (2−4 vol.%) crystals [9]. Clinopyroxene phases occur in these lherzolite xenoliths as interstitial crystals between olivine and orthopyroxene. These clinopyroxene crystals (Fig. 2, Table 1) have the compositions of Cr-diopside ($Wo_{45.67-47.99}En_{53.92-51.77}Fs_{0.41-0.24}$) and augite ($Wo_{43.85-44.86}En_{54.13-53.44}Fs_{2.03-1.70}$) with M2-Site characterized by high Ca (≈ 0.830 atoms per formula unit, a.p.f.u.) and Mg_2 (≈ 0.850 a.f.u.) components (Tab. 1).

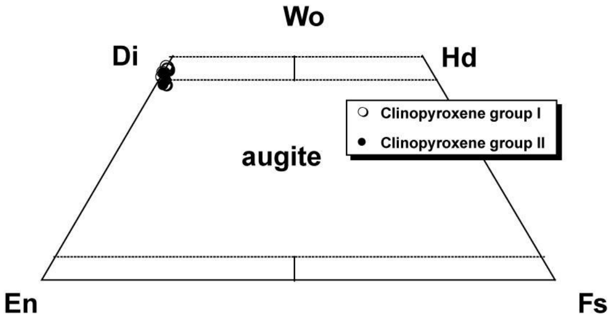

Fig. 2: Compositions of the Clinopyroxenes Analyzed in the Spinel-Xenoliths of Liri.

Two groups (I and II) of clinopyroxene are identified according to the trace elements contents. In some crystals (group I) the trace elements are enriched than in the others (see Table 2). Excepted for Er and Yb contents, where the compositions are similar in the both groups; the seggragation are shown in the normalized REE patterns (Fig. 3). Even the Sr and Zr contents (see Table 2) are enriched in the group I clynopyroxenes from the spinel-xenoliths of Liri.

Table 1: Chemical Analyses of Major Element, Cation Partition Among of T, M1, M2 Sites and V(Cell), V(M1) Volume for Liri Clinopyroxenes

Samples	LIRI-01	LIRI-02	LIRI-04	LIRI-05	LIRI1	LIRI2	LIRI3	LIRI4	LIRI5	LIRI5
SiO_2(wt %)	52.28	51.59	52.48	52.63	52.75	52.05	52.13	51.26	52.68	51.42
TiO_2	0.26	0.32	0.23	0.30	0.22	0.16	0.22	0.27	0.29	0.45
Al_2O_3	5.14	5.87	5.04	4.99	5.14	5.05	4.90	5.84	5.22	5.87
Cr_2O_3	0.93	1.01	0.91	0.90	1.00	1.02	0.94	1.14	0.97	0.94
FeO*	2.64	2.76	2.97	2.26	2.35	2.50	2.35	3.24	2.10	3.30
MnO	0.10	0.10	0.05	0.05	0.04	0.02	0.12	0.14	0.12	0.14
MgO	15.84	15.66	16.15	15.68	15.50	15.86	15.74	15.80	15.46	15.84
CaO	21.50	21.42	21.18	22.14	21.80	21.78	21.63	20.85	22.24	20.81

Na_2O	1.37	1.36	1.31	1.40	1.58	1.35	1.41	1.23	1.50	1.25
Sum	100.06	100.10	100.34	100.35	100.38	99.79	99.45	99.76	100.58	100.03
T-Site										
Si(a.p.f.u)	1.886	1.861	1.889	1.893	1.896	1.882		1.858	1.890	1.859
Al^{iv}	0.114	0.139	0.111	0.107	0.104	0.118	0.109	0.142	0.110	0.141
Sum	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
M1-Site										
Al^{vi}	0.105	0.111	0.102	0.105	0.114	0.097	0.101	0.107	0.111	0.109
Fe^{3+}	0.064	0.076	0.062	0.057	0.060	0.076	0.069	0.073	0.060	0.068
Ti	0.007	0.009	0.006	0.008	0.006	0.004	0.006	0.007	0.008	0.012
Cr	0.027	0.029	0.026	0.026	0.028	0.029	0.027	0.033	0.028	0.027
Mg_1	0.742	0.708	0.740	0.767	0.753	0.731	0.744	0.705	0.760	0.713
Fe_1	0.055	0.067	0.063	0.037	0.039	0.062	0.054	0.074	0.033	0.070
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
M2-Site										
Mg_2	0.069	0.074	0.088	0.047	0.048	0.062	0.056	0.097	0.036	0.098
Fe_2	0.001	0.001	0.003	0.001	0.001	0.000	0.000	0.003	0.000	0.004
Mn	0.003	0.003	0.002	0.001	0.001	0.001	0.004	0.004	0.004	0.004
Ca	0.831	0.828	0.817	0.853	0.839	0.844	0.841	0.810	0.855	0.806
Na	0.096	0.095	0.091	0.098	0.110	0.094	0.099	0.086	0.105	0.088
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Wo (%)	45.98	45.67	44.86	47.47	47.40	46.72	46.79	44.06	47.99	43.85
En	53.05	53.92	53.44	51.88	51.94	53.12	53.01	54.36	51.77	54.13
Fs	0.97	0.41	1.70	0.64	0.66	0.16	0.20	1.58	0.24	2.03
Vcell (Å)	436.107	436.029	436.143	436.27	435.829	436.522	436.19	436.074	436.051	436.042
V_{M1}(Å)	11.5544	11.5344	11.5713	11.5484	11.5209	11.5803	11.5651	11.5511	11.5267	11.5433

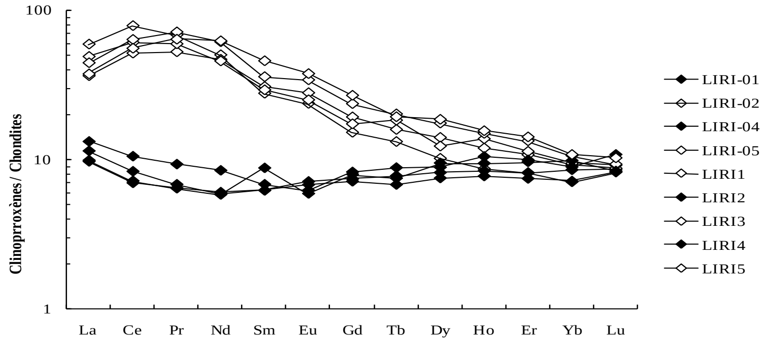

Fig. 3: Normalized REE Patterns of the Studied Clinopyroxenes From the Xenoliths from Liri (White Square for Group I And Black Square for Group II). Values Are Normalized to Chondrites [10].

Indeed, the clinopyroxene crystals of group-I are enriched in LREE and the patterns display a convex shape. However, the patterns of the group-II are more or less flat and low. The heavy rare earth contents (Er, Yb) are homogeneous for both groups (I and II). The Ti/Zr, Sm/Dy, Ce_N/Yb_N, La/Sm, Sm/Yb and La/Yb ratios (see Table 2) are similar in each group and entirely different from group I to group II. The Ce_N/Yb_N ratio is high in the clynopyroxene of group I and low for the group II.

Table 2: A) Trace Elements of the Analyzed Clinopyroxene from Liri Spinel-Lherzolite

Samples	La	Ce	Sr	Nd	Zr	Sm	Eu	Gd	Ti	Dy	Er	Yb
LIRI-01	11.427	8.322	49.450	5.818	10.320	6.193	6.768	7.126	1723.940	7.499	7.445	7.151
LIRI-02	59.310	78.863	207.230	50.243	48.510	27.736	23.696	15.158	745.460	10.136	8.087	7.046
LIRI-04	9.655	6.946	45.960	6.012	11.430	6.193	7.089	7.375	1874.840	8.138	8.131	8.486
LIRI-05	36.557	51.790	130.960	47.038	39.470	30.931	28.125	19.379	2527.290	14.133	10.824	9.280
LIRI1	49.041	60.925	163.110	45.800	40.490	29.368	25.179	17.396	2057.800	12.361	11.391	9.477
LIRI2	13.251	10.527	55.550	8.444	15.780	6.798	6.196	8.240	2339.610	8.859	9.943	8.923
LIRI3	44.440	63.727	154.250	61.472	58.450	35.826	34.107	23.601	2790.920	17.470	13.279	10.585
LIRI4	9.885	7.162	43.450	5.791	9.570	8.770	5.875	7.935	2119.660	9.477	9.629	9.846
LIRI5	37.665	56.018	143.590	62.843	59.730	46.159	37.857	27.060	2924.750	18.665	14.223	10.831

Table 2: B) Ratio of Some Analyzed Chemical Element from Liri Clinopyroxene.

Samples	Ti/Zr	Sm/Dy	Ce_N/Yb_N	La/Sm	Sm/Yb	La/Yb
LIRI-01	167.05	0.826	1.110	1.845	0.866	1.598
LIRI-02	15.367	2.736	7.780	2.138	3.936	8.417
LIRI-04	164.03	0.761	0.854	1.559	0.730	1.138
LIRI-05	64.031	2.189	3.665	1.182	3.333	3.939
LIRI1	50.822	2.376	4.929	1.670	3.099	5.175
LIRI2	148.26	0.767	1.188	1.949	0.762	1.485
LIRI3	47.749	2.051	3.648	1.240	3.385	4.199
LIRI4	221.49	0.925	0.756	1.127	0.891	1.004
LIRI5	48.966	2.473	3.001	0.816	4.262	3.478

5. Discussion

The investigations of trace elements in single grain clinopyroxenes provide reliable information about chemical composition. The trace-elements composition of clinopyroxene analyzed in spinel-lherzolite xenoliths from Liri is therfore a useful indicator of chemical modification in the mantle. Thus, ion microprobe investigation allowed two groups incompatibility diagrams in Liri clinopyroxenes to be distinguished (Fig. 3). The first one is highly LREE-enriched (Ce_N/Yb_N: from 3.00 to 7.78). The second one has concave-upward REE patterns (Sm_N/Dy_N) and is less LREE-enriched (Ce_N/Yb_N: from 0.75 to 1.18). According to [11], for peridotites that do have LREE-depleted clinopyroxenes, a correlation of HREE with other incompatible trace elements (e.g., strontium, zirconium) requires fractional melting to be the principal means of depletion in the mantle.

The slight depletion of rare earths elements in the analyzed clinopyroxenes (Liri 01, Liri 2, Liri 04, Liri 4) compared with the other REE observed in the others clinopyroxenes from Liri is indicative of a partial melting episode, whereas light rare earth elements enrichments observed for other samples (Liri 1, Liri 02, Liri 3, Liri 05 and Liri 5) are significant for cryptic metasomatism [12]. It is probably a cryptic metasomatism due to the absence of hydrated minerals (such as amphibole).

It is suggested that this enrichment in light rare earth element (LREE), at times, is closely related to the host alkali basaltic volcanism. The host xenoliths of studied clinopyroxenes have had a substantial component of mantle metasomatism that dominates partial melting and basaltic extraction effects. Incompatibility diagrams clearly demonstrate that clinopyroxenes have been in part modified or produced by mantle metasomatism.

Our results are similar to those described by [13], that clinopyroxenes which survived larger degrees of melting were easily enriched by the successive interaction with metasomatic agents due to the more appropriate site volumes, we suggest also that crystal chemistry and trace-element variations of clinopyroxenes from group I and group II are the result of highly complex processes including: 1) partial melting at different depths, 2) crystallization from alkaline magmas, cryptic metasomatism by 3) alkaline magmas. And then we can imagine that during metasomatism of group I and group II, clinopyroxenes incorporated significants amounts of LREE and Sr (interaction with alkaline melts), Zr (interaction with alkaline melts), but not Ti. However, present data indicate that the mineral chemistry of clinopyroxenes may be also significantly modified by interaction with alkaline. A remarkable feature in the variation of REE shows the depletion of higher rare earths elements (HREE), interpreted as absence of garnet in the source liquid.

6. Conclusion

Spinel-lherzolite xenoliths from Liri (south of the Kapsiki Plateau) have a protogranular texture with the particular clinopyroxenes composition. Two clinopyroxenes groups have been identify according to their trace-elements compositions. In some crystals (group I) the trace elements are enriched than in the others (group II). The slight depletion of REE in the group II clinopyroxene from Liri is indicative of a partial melting episode. However, the LREE enrichments observed in the others samples (group II) are significant for cryptic metasomatism.

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