Per. Mineral. (2001), ***70*****, 2, 205-230** http://go.to/permin

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environment, Archaeometry* and *Cultural Heritage*

Mantle xenoliths from Ñemby, Eastern Paraguay: O-Sr-Nd isotopes, trace elements and crystal chemistry of hosted clinopyroxenes

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Submitted, January 2001 - Accepted, April 2001

ABSTRACT. — Clinopyroxenes from protogranular spinel-peridotite mantle xenoliths in Eocenic melanephelinite of Ñemby hill, central eastern Paraguay (Asunción-Sapucai-Villarrica graben), are studied for: 1) crystal-chemical relationships between hosted clinopyroxenes and O isotopes; 2) trace element behaviour; 3) Sr-Nd relationships between whole rock and hosted pyroxenes. The mantle xenoliths are distinguished into two main suites, LK (relatively low in K and incompatible elements, IE) and HK (high in K and IE), both ranging from lherzolite to dunite and showing trends of «melt extraction». Clinopyroxenes crystal chemistry shows equilibration pressure over a range of 12-18 kb, in both suites. The hosted clinopyroxenes display extremely variable enrichment/depletion behaviours, mainly in LREE. The enriched components were mostly trapped in clinopyroxene which had previously crystallized from depleted to quasi-chondritic mantle sources. Oxygen isotopes (clinopyroxene-olivine pairs) suggest that equilibration temperatures were higher in the HK suite than in LK suite. On the whole, the isotopic Sr-Nd data indicate that, prior to enrichment, the lithospheric mantle was dominated by a depleted component, isotopically resembling a MORB source or even more depleted. Model ages ($Nd\text{-}T_{DM}$) of clinopyroxenes and host rocks confine the main enrichment, metasomatic, events to the Brasiliano cycle (i.e. 900-460 Ma). In contrast, Rb-Sr isotope systematics may be related with fluids induced by melting episodes occurred at Early Cretaceous times, during the different phases of lithospheric thinning in the area.

RIASSUNTO. — Clinopirosseni provenienti da xenoliti di mantello inclusi in lave melanefelinitiche Eoceniche affioranti nel Paraguay centro-orientale (graben Asunción-Sapucai-Villarrica) vengono studiati allo scopo di 1) definire le relazioni cristallochimiche con gli isotopi dell'ossigeno, 2) determinare il comportamento degli elementi in traccia, 3) verificare le relazioni tra gli isotopi radiogenici del clinopirosseno e quelli della roccia ospite. Gli xenoliti di mantello vengono distinti secondo due serie principali, «bassa» in K (ed elementi incompatibili, I.E.), LK, e «alta» in K (e I.E.), HK, entrambe con variazioni da lherzoliti a duniti, secondo evidenti indicazioni di variabile

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fusione parziale. La cristallochimica dei clinopirosseni evidenzia pressioni comprese tra i 12 e 18 kb per le due serie. Tale caratteristica non influenza in modo significativo i pirosseni ospitati che esprimono comportamenti estremamente variabili in termini di arricchimento/impoverimento, soprattutto per quanto riguarda la concentrazione di Terre Rare Leggere, indipendentemente dal grado di fusione parziale. I componenti arricchiti risultano in prevalenza concentrati nel clinopirosseno precedentemente equilibrato in una sorgente mantellica da impoverita a quasi chondritica. Gli isotopi dell'ossigeno (determinati per coppie clinopirosseno-olivina) suggeriscono temperature di equilibratura isotopica più elevate nella serie HK, rispetto alla serie LK. Nel complesso, i dati relativi agli isotopi radiogenici appaiono indicare un mantello litosferico dominato da una componente impoverita precedente agli eventi di arricchimento. Tale componente impoverita appare avere caratteristiche simili ai MORB e probabilmente è riferibile ad eventi antichi (Proterozoici) che hanno prodotto differenti residui in seguito a fusione parziale differenziata nel mantello. Le «età modello», riferite al Nd (rispetto a un mantello impoverito) calcolate sia per i clinopirosseni, sia per la roccia ospite, indicano un prevalente contributo metasomatico atrribuibile al Ciclo Brasiliano (900-460 Ma). La sistematica Rb-Sr sembra invece indicare il contributo di fluidi indotti da episodi di fusione parziale del mantello verificatisi durante differenti fasi di assottigliamento litosferico nella regione durante il Cretacico Inferiore.

KEY WORDS: *Eastern Paraguay, mantle xenoliths, clinopyroxenes, crystal chemistry, O-Sr-Nd isotopes, metasomatism.*

INTRODUCTION

Sodic melanephelinite/ankaratrite plugs, lava flows and dykes outcrop near Asunción town, Eastern Paraguay, at the westernmost fringe of the Paraná Basin (Comin-Chiaramonti *et al.*, 1991). This magmatism, dated at 61-32 Ma, is controlled by NW-SE trending rift structures (Asunción-Sapucai-Villarrica graben: ASV) and is associated with Early Cretaceous potassic magmatism (~128 Ma) and tholeiitic magmatism of the Serra Geral (Alto Paraná) Formation (~130 Ma). Sodic, potassic and tholeiitic magmatism is widespread mainly in the western, central and eastern sectors of ASV, respectively (fig. 1; see Comin-Chiaramonti and Gomes, 1996).

Spinel-bearing mantle xenoliths are common in all the ASV Tertiary occurrences. Previous studies (Comin-Chiaramonti *et al.*, 1986; Demarchi *et al.*, 1988; Petrini *et al.*, 1995) have shown that xenoliths from various localities have similar petrographic and chemical features. The main chemical characteristic is the very high content of incompatible elements (IE; e.g., ppm: K = 166-4898 ; Rb = 0.5-12 ; Sr = 2-75; Ba = 2-65) contrasting with the generally refractory character of the xenoliths. The latter are interpreted as residual mantle material which underwent partial melting and metasomatism; the lack of modal hydrous phases is attributed to their complete breakdown after pressure release during the rapid ascent of the host magma (Comin-Chiaramonti *et al.*, 1986; 1991).

Near Ñemby (25°24'S, 57°32' W), a small melanephelinitite plug, with elliptical topography (800 × 500 m, about 100 m above the plain), contains very abundant mantle xenoliths (~10-15% by volume of the plug) together with crustal xenoliths. The average size of the mantle xenoliths (10-12 cm as average, max 45 cm, i.e. the largest observed in ASV) and the compositional range (lherzolite to dunite) make these xenoliths particularly suitable for a study regarding metasomatic processe(s) affecting the region of the sampled mantle.

SUMMARY OF GENERAL FEATURES

Host lavas

The Ñemby lavas are nephelinites and subordinate ankaratrites, according to De La Roche (1986), and melanephelinites (CIPW Ab < 5 wt% and Ne > 20 wt%), according to Le Bas (1987), with mg# [MgO/(MgO+FeO), assuming Fe_2O_3/FeO ratio = 0.20] ranging from 0.64 to 0.67 (Comin-Chiaramonti *et al.*, 1991). The K/Ar age is 46 Ma (Bitschene,

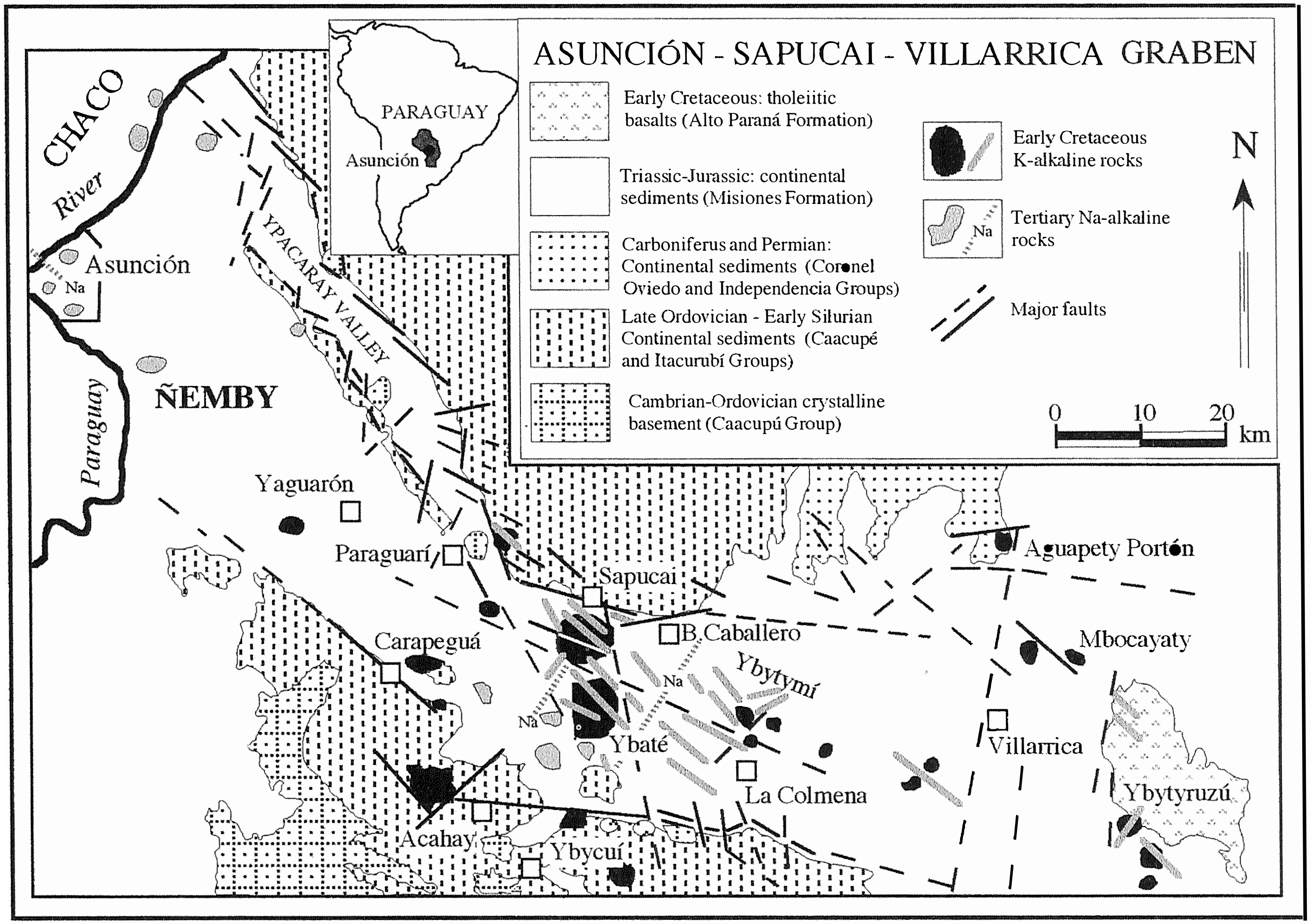

Fig. 1 – Sketch-map showing magmatic rocks in Central-Eastern Paraguay, after Comin-Chiaramonti and Gomes (1996).

1987). These rocks are characterized by olivine phenocrysts (1-7 vol%, Fo 89-85) and microphenocrysts of olivine (1-6 vol%; Fo 82-77 mole%), clinopyroxene (1-6 vol%; mg# ~0.8) and Ti-magnetite (0.3-0.7 vol%; 37.9 ulv. mole%), set in a hypocrystalline groundmass (clinopyroxene 39-46 vol%, mg# ~0.75; olivine 3-6 vol%, Fo 74-76; magnetite 4-7 vol%, ulv. 42.8; nepheline 16-21 vol%; glass 11-25 vol%). Measured $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios range from 0.70362 to 0.70369 and from 0.512624 to 0.512803, respectively (Comin-Chiaramonti *et al.*, 1991). Geochemical data and the melting models show that the Ñemby lavas derived from liquids representing 4-6% degrees of partial melting of a garnet-peridotite (Comin-Chiaramonti *et al.*, 1997) and that these liquids cannot be derived from sources similar to those represented by the enclosed spinel-peridotite xenoliths (Comin-Chiaramonti *et al.*, 1991).

Mantle Xenoliths

The main Ñemby mantle xenoliths (101 analyzed samples) are spinel-lherzolites, harzburgites and subordinate dunites and correspond to the Cr-diopside series of Wilshire and Shervais (1975). The dominant texture is protogranular, rarely tabular or porphyroclastic. Detailed petrographic features are given in Demarchi *et al.* (1988). The Ñemby mantle xenoliths contain variable amounts of glassy patches («blebs»), and glassy drops in clinopyroxenes. The blebs (mg# 0.88-0.91) mainly consist of a glassy matrix containing microlites of olivine (mg# 0.91-0.92), clinopyroxene (mg# 0.91-0.93), Cr-spinel and (rarely) phlogopite (mg# 0.86-0.92). They are considered to have been formed by decompression melting of amphibole and phlogopite (Comin-Chiaramonti *et al.*, 1986). Assuming a diameter of 45 cm, corresponding to the size of the largest xenoliths, a density of 3.3 g/cm^3 and an origin at a depth ~70-75 km for host liquids (~boundary between garnet and spinel peridotite), the xenoliths were transported to the surface in a very short time (perhaps less than 9 days: cf. Spera, 1984). The glassy drops give an overprinted spongy texture, characteristic of the clinopyroxenes of the H-K suite.

The rapid rate of ascent is testified not only by the persistence of glassy drops and patches in the mantle xenoliths, but also by the lack of apparent interactions between the mantle xenoliths and host lavas (Demarchi *et al.*, 1988), and by lack of phase transitions in the associated crustal xenoliths (e.g. plagioclase-microcline, quartz-sillimanite pairs *etc.* for which calculated T-P equilibria are 570-700°C and 4-8.5 kbar, respectively; cf. Orué *et al.*, 1990).

The major elements show that the Ñemby xenoliths are characterized by a large range of the K_2O content (0.02 to 0.51 wt%). Some of them have K_2O abundances comparable with, or even higher than those reported for metasomatized mantle peridotites (e.g. Frey and Prinz, 1978; Roden *et al.*, 1984), in some cases resembling amphibole-mica-apatite-bearing mantle-xenolith suites (see O'Reilly and Griffin, 1988). K_2O contents and the occurrence of blebs and glassy drops allow the Ñemby xenoliths to be grouped into two main suites, low-K (LK, $K_2O < 0.1$ wt%), and high-K, with abundant glassy drops and/or variable amounts of blebs (HK, $K_2O \geq 0.2$ wt%). A complete set of chemical analyses may be found in Demarchi et al (1988). The analyses of some selected mantle xenoliths, blebs, glassy drops and average host lava are listed in Appendix (Tables I to III).

Major elements also display coherent variations throughout the two suites, and outlines a dunite-lherzolite sequence trending towards primitive mantle compositions (fig. 2). The population is mainly represented by harzburgitic compositions, being mostly within 0.55-0.63 range of $(SiO_2+Al_2O_3)/(MgO+FeO_t)$ molar ratio. The residual character of the mantle xenoliths, believed to be consistent with melting and basalt removal, is also shown by the correlation between clinopyroxene contents and the Cpx «fertility index» F (F = [Al+Fe+Na+Ti]/[Mg+Cr] *Cpx* atoms, inset A of fig. 2). This is further confirmed by the decrease in the *Cpx/Opx* modal ratio with

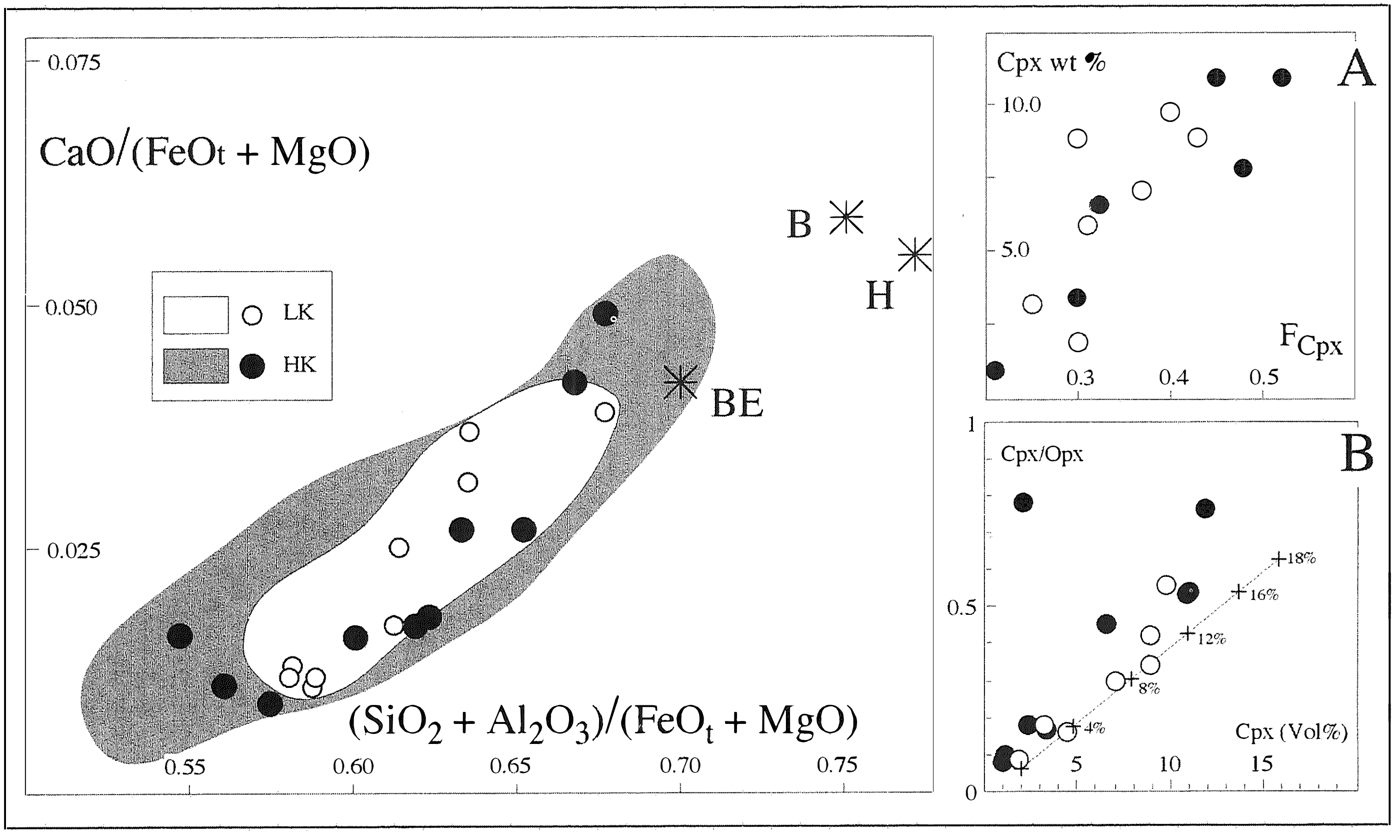

Fig. 2 – $(SiO_2 + Al_2O_3)/(FeO_{total} + MgO)$ *vs* $CaO/(FeO_{total} + MgO)$ diagram (molar ratios) for bulk-rock compositions of Ñemby xenoliths, LK and HK suites, respectively. Stars B, H and BE: pyrolite compositions (Bristow, 1984), primitive mantle (Hofmann, 1988) and Bulk Earth (McKenzie and O'Nions, 1991), respectively. Outlined fields are from Demarchi *et al.* (1988). Inset A: F (F_{cpx} = (Al+Fe+Na+Ti)/(Mg+Cr) atoms; cf. Tab. 4) *vs* clinopyroxene (*Cpx* vol%) contents of mantle xenoliths; inset B: variation of modal *Cpx vs* modal *Cpx/Opx* ratio. Line indicates model variation trends induced by 0-18% non-modal fractionation melting in a primitive mantle composition (cf. Rivalenti *et al.*, 2000) at 4% melting intervals.

decreasing modal *Cpx*, which fits the model variation trend induced by partial melting of lherzolite (inset B of fig. 2). K_2O contents are positively correlated with Na_2O, and to a lesser extent with incompatible elements such as Rb, Ba, Sr (cf. Demarchi *et al.*, 1988).

The most striking feature is the relative abundance of «blebs» and «spongy» clinopyroxene (i.e. rich in glassy drops) in the mantle xenoliths from the HK suite , correlated with: 1) relatively high abundances of Rb, Ba and La, compared to the primitive mantle estimates (fig. 3; see Jagoutz *et al.*, 1979; Sun and McDonough, 1989), and 2) depletion in Nb, Sm, Ti and Y.

The LK suite parallels to some extent the HK suite, with lower IE abundances, but with a Nb positive spike. LK suite shows the lowest enrichment in Rb, Ba, K relative to the primitive mantle (~2-3 times), depletion in Sr, and important depletion (up 10 times) in Nd, Sm and Ti.

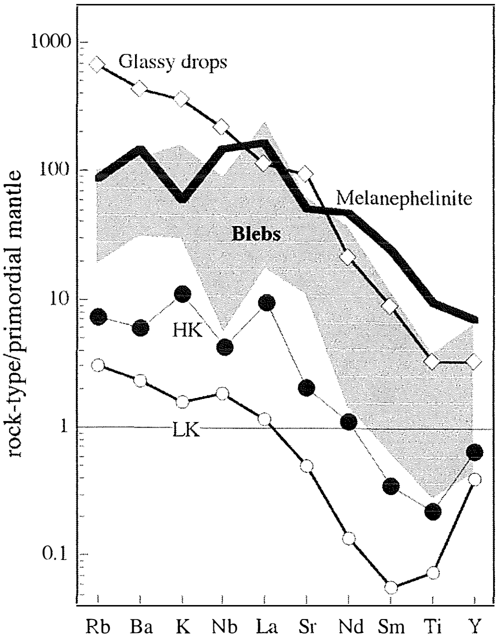

Fig. 3 – Incompatible elements of Ñemby mantle xenoliths (LK and HK suites), lavas, glassy drops (av. compositions) and blebs (field of the representative compositions), normalized to primitive mantle composition (Sun and McDonough, 1989).

Mineral Phases

Clinopyroxene (*Cpx*, mg# 0.90-0.96; 1 to 15 vol%) exhibits variable morphology, ranging from well preserved (lherzolite) to spongy relic (dunite) crystals. The most frequent *Cpx* habitus, at both core and rim of the xenoliths of the HK suite, is represented by crystals with partially to completely «spongy» texture, due to glassy drops. *Cpx* usually shows lamellar spinel (rarely orthopyroxene) exsolutions cut by the glassy drops, and because of these, *Cpx* was analized by microprobe in both spots and crosses (the latter obtained by shifting the sample under a defocussed beam in order to provide an extimate of composition before unmixing). The crosses compositions of spongy *Cpx* from highest K_2O-bearing xenoliths are anomalously rich in K_2O (up to 1.22 wt%). This reflect the occurrence of the glassy drops (up ~7.5% of the whole *Cpx* composition, as from mass balance) whose compositions are variable, but are systematically rich in K_2O, Al_2O_3, Rb, Sr, Ba (see Demarchi *et al.*, 1988).

Orthopyroxene (*Opx*, mg# 0.90-0.93; 3-26 vol%) is unzoned and rarely shows spinel exsolutions.

Olivine (*Ol*, 60-97 vol%) is chemically homogeneous within each sample and varies in composition mainly from Fo 90 (lherzolites) to Fo 93 (dunites) mole%.

Spinel (*Sp*, 0.6-4 vol%) from xenoliths with $K_2O \geq 0.20$ wt% (see later) is generally characterized by Cr increase from the core to the rim, particularly inside the blebs; spinels from xenoliths with $K_2O < 0.1$ wt% are unzoned (Demarchi *et al.* 1988); the Cr/(Cr+Al) atomic ratio shows a main variation range between 0.10 and 0.70.

Sulfides (pyrrhotite and pentlandite), *apatite* and *carbonate* occur in very small amounts as dispersed grains in almost all the xenoliths.

The «residual» character of the xenolith suites is reflected by the compositional

TABLE 1

Crystal-chemical data of selected clinopyroxene samples from Ñemby mantle xenoliths. L, lherzolite; H, harzburgite; D, dunite; (*), (**), (***), clinopyroxene containing scarce, abundant and very abundant glassy drops, respectively. Site and cell volumes, V(T), V(M1), V(M2), V_{Cell}, respectively, in Å^3. F, «fertility index», = (Al+Fe+Na+Ti)/(Mg+Cr), atoms; O- C isotopic data for clinopyroxene-olivine pairs expressed in δ‰ notation, temperatures calculated according to Kyser, 1990; T°C(BK), temperatures calculated using the Mercier's (1980) clinopyroxene geothermometer. Analytical methods from Kyser et al. (1981) and Princivalle et al. (2000).

	LK SUITE				HK SUITE			
Sample	3192	3221	3227	3269	3311	3307	3211	3284
Rock type	Lh	Lh	Hz	Hz	Lh	Lh	Hz	Hz
Cpx %	9.8	7.1*	3.2	1.9	11.0**	6.6°	3.4**	1.0***
F (°)	0.36	0.37	0.25	0.30	0.52	0.32	0.30	0.21
T-Site								
Si	1.905	1.924	1.952	1.956	1.903	1.914	1.962	1.957
Al	0.095	0.076	0.048	0.044	0.097	0.086	0.038	0.043
Sum	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
M1-Site								
Mg	0.776	0.833	0.871	0.857	0.743	0.827	0.844	0.901
Fe^{2+}	0.016	0.022	0.019	0.019	0.061	0.024	0.016	0.019
Al	0.128	0.091	0.059	0.077	0.167	0.086	0.083	0.006
Fe^{3+}	0.047	0.026	0.027	0.027	0.001	0.033	0.032	0.057
Cr	0.026	0.022	0.022	0.018	0.023	0.024	0.023	0.012
Ti	0.007	0.006	0.002	0.001	0.005	0.006	0.002	0.005
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
M2-Site								
Ca	0.822	0.837	0.871	0.857	0.776	0.892	0.828	0.903
Na	0.120	0.075	0.063	0.081	0.104	0.069	0.102	0.042
Mg	0.040	0.053	0.045	0.044	0.091	0.018	0.046	0.040
Fe^{2+}	0.018	0.033	0.020	0.018	0.025	0.019	0.023	0.013
Mn	0.000	0.002	0.001	0.000	0.004	0.002	0.001	0.002
Sum	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
VCell (Å^3)	432.96	435.33	436.67	435.68	433.56	436.29	435.59	437.10
V (T)	2.224	2.232	2.227	2.224	2.231	2.232	2.220	2.217
V(M1)	11.458	11.624	11.714	11.654	11.502	11.692	11.673	11.820
V(M2)	25.421	25.473	25.562	25.569	25.373	25.506	25.561	25.560
$\delta^{18}O_{cpx}$	5.8	5.9	5.8	6.0	5.5	5.9	5.6	6.0
$\delta^{18}O_{ol}$	5.0	5.2	5.3	5.6	5.3	6.0	5.8	6.1
T°C (K)	969	997	1048	1071	1113	1169	1183	1169
T°C (M)	976	1011	975	996	1053	1040	1025	1005

variation of mineral phases (Demarchi *et al.*, 1988; Petrini *et al.*, 1995), i.e. Mg/Fe$_{tot}$ (atomic ratio) of the orthopyroxene (9.7 to 11.8) is correlated with the Fo content of the olivine (90 to 93) and the Mg/Fe$_{tot}$ of clinopyroxene (9.2 to 15.3), as well as with the Cr/(Cr+Al) ratio of the spinel (0.10 to 0.70). Intercrystalline equilibration temperatures for orthopyroxene-clinopyroxene pairs (Wells geothermometer, 1977) and olivine-spinel pairs (Fabriès geothermometer, 1979) vary between 862 and 1075°C and between 748 and 968°C, respectively. Intracrystalline temperatures and pressures (calculated according to Mercier, 1980) vary between 907-1131°C and 950-1016°C, and between 11-23 kb and 17-20 kb for clinopyroxene and othopyroxene, respectively (see Petrini *et al.*, 1995; Princivalle *et al.*, 2000) in both the two suites.

CLINOPYROXENES

Mantle clinopyroxenes play an important role relative to the interpretation of mantle processes, such as melting and metasomatism (e.g. Salters and Shimizu, 1988; Takazawa *et al.*, 1992; Vannucci *et al.*, 1994). In general the decrease in modal clinopyroxene and decreasing of depletion indexes of peridotite and clinopyroxene (see fig. 2), towards harzburgite-dunite are consistent with extraction of melt fraction. These processes imply variations in the crystal-chemical configuration of the clinopyroxenes and on their concentrations of trace elements.

This section examines the characteristics of some clinopyroxenes from selected Ñemby mantle xenoliths, LK and HK suites, respectively, for 1) crystal-chemistry and structural results; 2) oxygen isotopes; 3) trace elements; 4) Sr-Nd isotopes.

Crystal Chemistry

Crystal chemical data are in Table 1 (see Princivalle *et al.*, 2000), together with oxygen isotopic data *Cpx-Ol* pairs and inferred temperatures calculated following Kyser *et al.* (1981) and Mercier (1980). The V(M1) *vs* V(Cell) diagram (fig. 4A) shows that the Ñemby *Cpx* equilibrated between the plagioclase-spinel and the garnet-bearing mantle peridotites (Princivalle *et al.*, 2000). Cell volumes are negatively correlated with modal *Cpx* (fig. 4B) in both two suites, according to the previously described chemical and mineralogical characteristics.

Crystal chemistry also shows that both LK- and HK-*Cpx* are characterized at similar V(T) by different V(M1), V(M2) and V(Cell) (Table 1), indicating variable equilibration pressure in the spinel-peridotite facies. Therefore, the Ñemby xenoliths represent mantle peridotites which underwent variable melting degrees and were sampled in a large pressure range between 12 and 18 kb (Princivalle *et al.*, 2000). It shoud be noted that the influence of «metasomatic processes», although very pronounced in the HK suite, is not appreciable on the cpx polyhedral variations.

Oxygen Isotopes

The oxygen isotope compositions of separates of clinopyroxene and coexisting olivine ($\delta^{18}O$‰) range from 5.5 to 6.0‰, and from 5.0 to 6.1‰, respectively (Table 1). These ratios fall in the range of values for worldwide mantle phases (olivine 4.4 to 7.5‰, clinopyroxene 4.8 to 6.7‰; cf. Chazot *et al.*, 1994 and therein references) and South America mantle xenoliths (olivine 4.9 to 6.4‰, clinopyroxene 5.0 to 6.0‰; cf. Kyser, 1990). The calculated *Cpx-Ol* isotopic temperatures (calculated according Kyser *et al.*, 1981) are around 970-1070°C (LK suite) and 1101-1180°C (HK suite), respectively, whereas the Mercier's intracrystalline temperatures are 970-1011°C (LK) and 1005-1053°C (HK), respectively. Notably, the $\delta^{18}O_{cpx}$ *vs* $\delta^{18}O_{\bullet l}$ diagram (fig. 4C) shows different trends for the two suites, reflecting differences that vary with apparent isotopic equilibration temperatures (fig. 4D). In

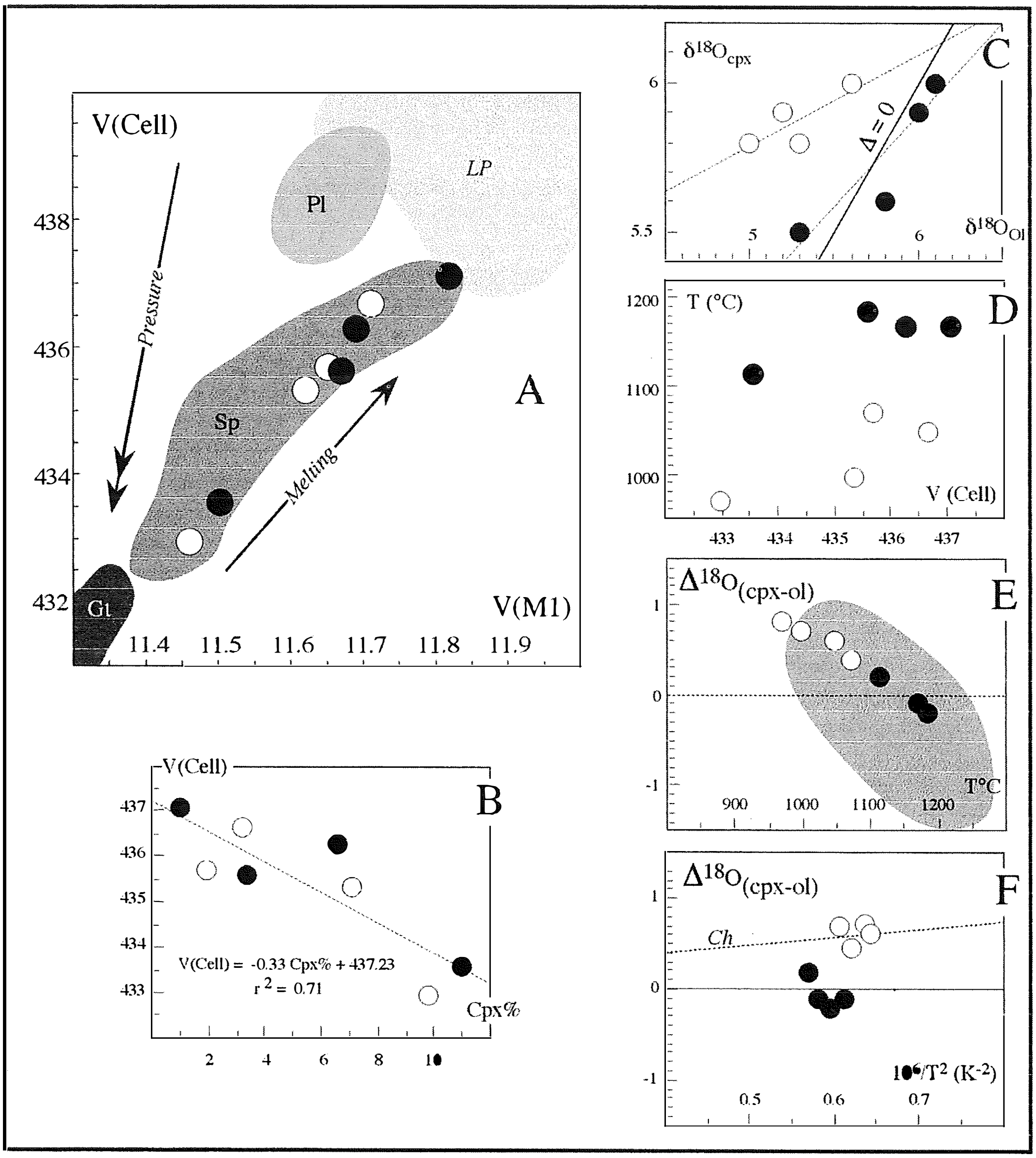

Fig. 4. A) – Variations in M1 *vs* cell volumes [V(M1) and V(Cell), Å^3] of representative Ñemby clinopyroxenes from LK and HK suites. Symbols as in fig. 2. Arrows: «dominant» effects on the clinopyroxene structures, i.e. pressure and progressive melting; fields define variations in cell and M1 volumes of clinopyroxenes in garnet (Gt), spinel (Sp) and plagioclase (Pl) mantle peridotites, and in low-pressure (LP) environment (cf. Princivalle *et al.*, 2000). B) Modal *Cpx vs* V(Cell). C) $\delta^{18}O_{cpx}$ *vs* $\delta^{18}O_{ol}$; regression lines for LK and HK suites and equilibration line ($\Delta = 0$), respectively, are shown. D) Isotopic equilibration temperatures (T°C, Kyser, 1981) *vs* V(Cell). E) $\Delta^{18}O_{cpx\text{-}ol}$ *vs* isotopic equilibration temperatures, T°C; field represents the clinopyroxene-olivine pairs from South America mantle xenoliths (Kyser, 1990). F - Clinopyroxene-olivine fractionation as a function of clinopyroxene intracrystalline temperatures (Mercier, 1980); fractionation line (*Ch*) from Chiba *et al.* (1989).

TABLE 2

Representative ion microprobe analyses of selected clinopyroxenes (Cpx), orthopyroxene exsolutions (Opx), and glassy drops (GD) in Cpx from Ñemby xenoliths (Lh, lherzolite; Hz, harzburgite). Also shown volume % of the clinopyroxene and the «fertility index» F_{Cpx} *= (Al+Fe+Na+Ti)/(Mg+Cr). X/X*: PM-normalized, (Hofmann, 1988),* $(X/X)_N$*: CH, Chondrite-normalized (Boynton, 1984). Analytical methods from Petrini et al. (1995).*

	LK suite			HK suite										
	3252 Cpx	3254 Cpx	3254 Opx	3221 Cpx	3227 Cpx	3269 Cpx core	3269 Cpx rim	3311 Cpx	3222 Cpx core	3222 Cpx rim	3307 Cpx	3211 Cpx	3284 Cpx	3284 GD
	Lh	Lh	Lh	Lh	Hz	Hz	Hz	Lz	Lz	Lz	Lz	Hz	Hz	
Rb	0.08	0.01		1.20	1.70	1.30	0.74	1.30	0.07	0.10	0.30	1.80	1.40	120
Ba	0.59	0.85	0.39	0.60	0.60	0.90	0.51	0.50	0.50	0.60	0.25	3.50	2.10	1781
Nb	0.11	0.10	0.09	0.10	0.10	0.10	0.18	0.20	0.11	0.15	0.30	0.70	0.30	155
K	142	90	11.4	118	8.50	12.50		30.00	63	90	10	397	81	82453
La	22.84	10.87	0.32	23.70	0.41	33.32	28.01	36.14	0.58	2.83	23	119.40	38	77.39
Ce	20.98	8.72	0.07	23.64	2.18	47.48	34.77	45.55	0.38	2.24	22	121.50	98	106.25
Sr	106	132	1.70	425	38	187	234	336	18.4	26.1	130	977	525	1414
Nd	3.85	0.88	0.18	3.36	2.21	9.30	5.13	10.37	1.67	1.99	4.86	15.13	62	27.74
Zr	0.53	0.13	0.16	0.80	11.50	9.20	5.07	14.00	12.30	11.10	14	2.60	97	189
Sm	0.80	0.14	0.09	0.85	0.92	0.79	0.31	1.26	1.20	1.21	1.16	1.23	13.20	4.16
Eu	0.27	0.05	0.06	0.29	0.28	0.21	0.12	0.54	0.56	0.54	0.39	0.23	4.37	1.00
Ti	750	260	314	1065	420	160	178	955	2157	1727	1253	405	483	4888
Gd	1.08	0.37	0.36	1.29	0.95	0.12	0.21	1.87	2.02	1.45	1.60	0.56	9.71	2.92
Dy	1.75	0.75	0.85	1.67	0.57	0.26	0.22	1.63	2.58	2.27	1.54	0.55	7.80	2.61
Y	12.00	6.20	7.50	2.30	3.70	11.00	3.20	10.40	16.80	15.30	9.00	3.60	39	14.70
Er	1.24	0.73	0.71	1.15	0.29	0.38	0.25	1.10	1.63	1.58	1.12	0.69	3.95	1.68
Yb	1.26	0.73	0.93	0.96	0.41	0.36	0.30	1.20	0.60	1.38	0.96	0.82	3.24	1.23
Sc	74	86	84	90	41	84	81	85	77	79	74	93	93	
V	214	230	213	173	173	194	143	220	252	225	221	166	180	32
Cr	4006	9424	5299	3479	8566	4706	4327	4998	4940	4919	4229	4674	9217	2
Cpx %	8.9	8.9		7.1	3.2	1.9		11.0	10.9		6.6	3.4	1.0	
F	0.43	0.30		0.37	0.25	0.30		0.52	0.45		0.32	0.30	0.21	

TABLE 2: *continued*

	LK suite				HK suite									
	3252	3254	3254	3221	3227	3269	3269	3311	3222	3222	3307	3211	3284	3284
	Cpx	Cpx	Opx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	GD
						core	rim		core	rim				
	Lh	Lh	Lh	Lh	Hz	Hz	Hz	Lz	Lz	Lz	Lz	Hz	Hz	
PM														
Zr/Zr*	0.02	0.02	0.08	0.03	0.56	0.19	0.20	0.24	0.56	0.47	0.41	0.03	0.23	1.14
Ti/Ti*	0.35	0.45	0.52	0.44	0.20	0.18	0.26	0.24	0.51	0.49	0.40	0.28	0.02	0.72
Y/Y*	1.06	1.07	1.25	0.22	1.18	4.23	1.72	1.02	1.07	1.06	0.89	0.72	0.91	0.92
$(La/Sm)_N$	17.97	17.71	2.24	17.55	0.28	26.55	56.88	18.06	0.30	1.47	12.48	61.12	1.81	11.71
$(Sm/Dy)_N$	0.75	0.31	0.18	1.09	2.66	5.01	2.44	1.28	0.98	1.38	1.24	3.69	2.79	2.63
$(Gd/Yb)_N$	0.69	0.41	0.31	1.09	1.87	0.27	0.57	1.26	2.72	0.85	1.35	0.55	2.42	1.92
CH														
Eu/Eu*	0.89	0.63	0.88	0.85	0.91	1.28	1.36	1.07	1.09	1.25	0.87	0.74	1.13	0.84
$(La/Yb)_N$	12.2	10.0	0.2	16.6	0.7	62.4	62.9	20.3	0.7	1.4	16.2	98.2	7.9	42.4

particular the O-isotope temperatures vary coherentely with the $\delta^{18}O(cpx\text{-}ol)$ which tends to 0 in the HK (fig. 4E). Mercier's temperatures vs $\Delta^{18}O(cpx\text{-}ol)$ show that LK samples plot along the experimentally determined fractionation line (Chiba *et al.*, 1989), whereas, compared with LK samples, the HK types have less significant O-isotopic fractionation between minerals (fig. 4F).

Trace Elements

Trace element analyses are given in Table 2. The main characteristics are summarized in the incompatible element and REE diagrams of fig. 5 (normalization to primitive mantle and to chondrites, respectively). In general, the clinopyroxenes from both LK and HK suites present various profiles, with flattened behaviours or enrichments in La, Ce, Sr and Nd, independently of *Cpx* content (i.e. melting degree of the xenoliths) and of the calculated temperatures. The orthopyroxene exsolutions (e.g. LK-3254 specimen) have the same profile as the host clinopyroxene, except for strong depletion in K, LREE and Sr (panel A of fig. 5). In particular, the HK-3284 sample (*Cpx* = 1%, with glassy drops up to 7.5%; panel D of fig. 5) is strongly enriched in REE, like as the hosted glassy drops. On the whole, MREE to HREE from Ñemby clinopyroxenes are in the same range as clinopyroxenes from northeastern brazilian protogranular mantle xenoliths, except for sample 3284 which is characterized by the highest REE concentrations (see panel D, fig. 5).

LREE are usually strongly enriched (La_N/Yb_N, LK suite: lherzolite = 16.6-10.0, harzburgite ~62-63; HK suite: lherzolite = 20.3 - 16.2, harzburgite = 98.2 - 7.9), excluding samples 3227 (LK harzburgite with La_N/Yb_N = 0.67) and 3222 (HK lherzolite with La_N/Yb_N = 0.65 - 1.38; cf. Table 2).

In general, trace elements behaviour is not consistent only with fractional melting processes: only one sample (HK lherzolite 3222; panel C of fig. 5) may be modelled by a low degree (6%) of non-modal fractional melting of primitive mantle (see also Rivalenti *et al.*, 2000).

In detail, in the primitive-mantle-normalized trace element diagrams (fig. 5), all samples have profiles depleted in Ba, Nb, Zr and Ti ; Zr and Ti systematically display negative spikes (see Rampone *et al.*, 1991), indicating HFSE depletion (see Zr/Zr* and Ti/Ti* of Table 2). Sr shows both positive and negative anomalies in LK and HK suites (Sr /Sr* = 2.34 to 0.51), with the minimum in HK harzburgite 3284 (Sr/Sr* = 0.51). Y/Y* ratio generally approaches one (av. 1.07 ± 0.26) but shows a positive anomaly in the *Cpx* from LK harzburgite 3269 (4.23 to 1.72, core and rim, respectively) and negative anomaly in *Cpx* from LK lherzolite 3221 (0.22). Compared with the host *Cpx*, the glassy drops (e.g. HK 3284 *Cpx*) are strongly enriched in Rb, Ba, K, La, Ce, Sr, Zr and Ti and depleted in Nd, HREE, Sc, V and Cr (fig. 5 and Table 2), and are characterized by Eu negative anomaly (glassy drop, Eu/Eu* = 0.84; host *Cpx*, Eu/Eu* = 1.13). Notably, the geochemical features of the glassy drops fit those of a material rich in a phlogopite-like component (see McKenzie and O'Nions, 1991: Ti = 4796 ppm and K= 78786 ppm). Lastly, it is worth noting that some harzburgites display U-shaped patterns (e.g. LK 3269 and HK 3211), with La_N/Sm_N ~60

Fig. 5 – Trace element patterns of clinopyroxenes (ion microprobe data) from Ñemby xenoliths, normalized to the primitive mantle (Hofmann, 1988), and REE normalized to chondrites (Boynton, 1984), subdivided following LK and HK typology and petrography (panels A and B: LK; panels C and D: HK). *Cpx*, clinopyroxene, Opx, orthopyroxene, GD, glassy drop; PMCE: clinopyroxene trace element composition in primitive mantle (Hofmann, 1988; Rivalenti *et al.*, 1996); NEB: clinopyroxene field from protogranular mantle xenoliths of NE Brazil (Rivalenti *et al.*, 2000). In panel C, clinopyroxene pattern in residue from non-modal fractional melting (6%) of primitive mantle (Hofmann, 1988) is reported; fractional melting parameters and partitions coefficients, after Johnson *et al.* (1990) and Rivalenti *et al.* (1996), respectively.

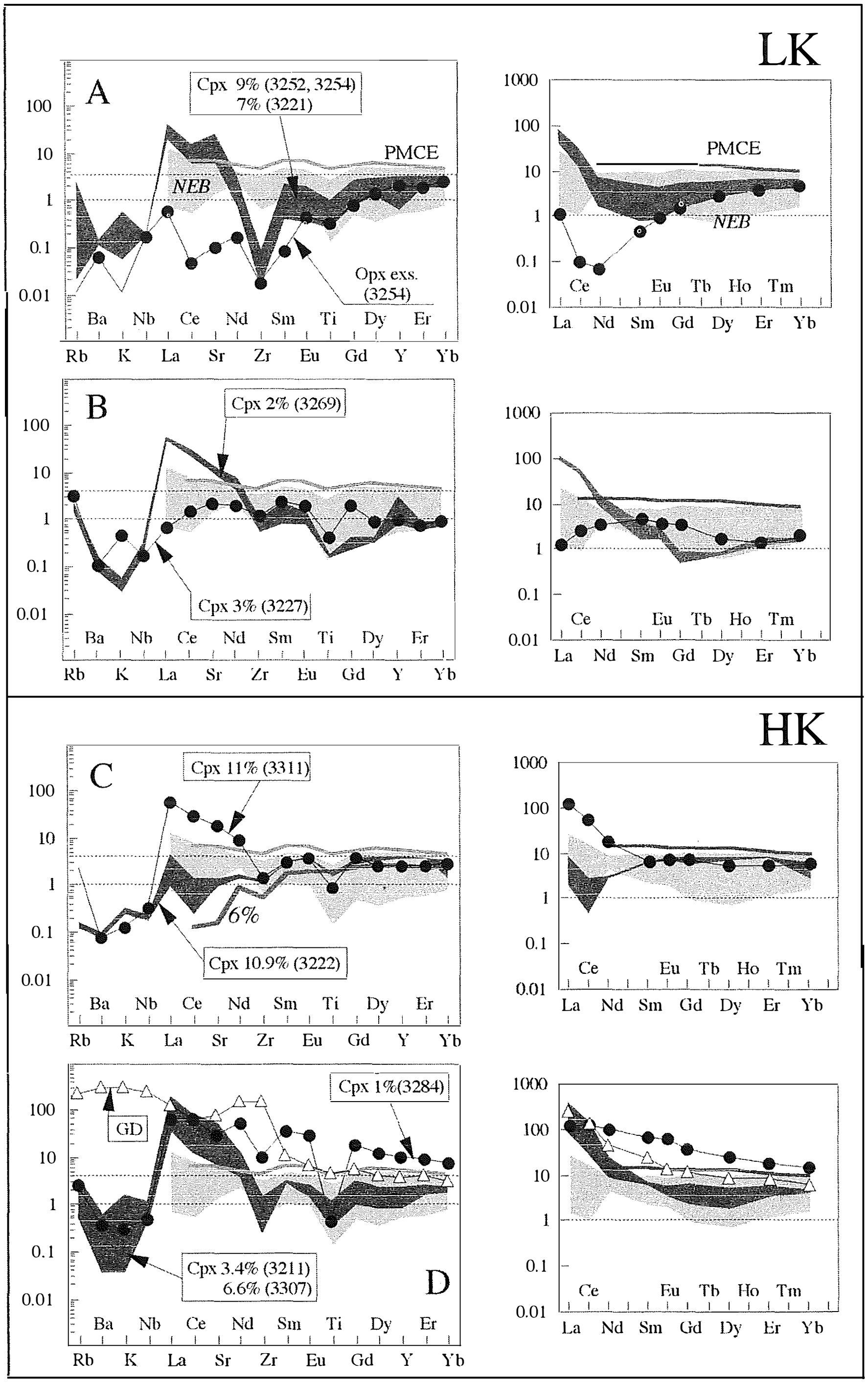
LK
A
Cpx 9% (3252, 3254)
7% (3221)
PMCE
NEB
Opx exs.
(3254)
100
10
1
0.1
0.01
Ba Nb Ce Nd Sm Ti Dy Er
Rb K La Sr Zr Eu Gd Y Yb
1000
Ce Eu Tb Ho Tm
La Nd Sm Gd Dy Er Yb
B
Cpx 2% (3269)
Cpx 3% (3227)
HK
C
Cpx 11% (3311)
6%
Cpx 10.9% (3222)
GD
Cpx 1%(3284)
Cpx 3.4% (3211)
6.6% (3307)
D

Fig. 5

and Gd_N/Yb_N ~0.55 (cf. Table 2). This characteristic was in general attributed to a «carbonatitic component» by Hauri (1997).

Correlations between $\delta^{18}O$ and IE contents were not observed: the lack of significant differences in oxygen isotopic composition between LREE-depleted and REE-enriched samples from both LK and HK suites suggests that metasomatism did not appreciably affect oxygen isotope systematics.

In summary, the trace elements patterns of clinopyroxenes from Ñemby xenoliths are probably the result of different, overlapping processes affecting the upper mantle beneath central-eastern Paraguay:

1) depletion by variable degrees of partial melting, as shown by the «residual» character of mantle xenoliths and by the «fertility index» of clinopyroxenes;

2) subsolidus re-equilibration, as indicated by spinel and orthopyroxene exsolution in clinopyroxenes;

3) metasomatic processes l.s. as shown by variable enrichment of incompatible elements, in both clinopyroxenes and host xenoliths;

4) decompression and partial melting after sampling by host lavas, as shown by the presences of glassy phases, i.e. glassy drops in clinopyroxenes «cutting» the spinel exsolutions, and blebs in the host xenoliths.

Sr-Nd Isotopes

Rb-Sr and Sm-Nd isotope data were collected on whole rock and on clinopyroxene-orthopyroxene separates (Table 3). Both display a very wide isotopic variation, with $^{87}Sr/^{86}Sr$ isotope ratios in the ranges 0.70380 - 0.70480 and 0.70326 - 0.70461, respectively, and $^{143}Nd/^{144}Nd$ in the ranges 0.51246 - 0.51346 and 0.51260 - 0.51348, respectively. In the $^{87}Sr/^{86}Sr$ - $^{143}Nd/^{144}Nd$ diagram (fig. 6A), the compositions of whole rocks and clinopyroxenes encompass the whole range of isotopic ratios observed in NE Brazil (Pico Cabugi), Fernando de Noronha island and Patagonia (Stern *et al.*, 1989; Barbieri *et al.*, 1997; Rivalenti *et al.*, 2000).

A positive correlation ($r^2 > 0.8$) between $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ is shown by whole rocks from the two suites, from which a reference lines of 128 Ma may be calculated (inset of fig. 6B). This Early Cretaceous age approaches those inferred for potassic and tholeiitic rocks (128 and 133 Ma, respectively; Comin-Chiaramonti and Gomes, 1996; Ernesto *et al.*, 1996) from Asunción-Sapucai-Villarrica graben. Notably, the Early Cretaceous age may indicate the latest thermal event interesting the lithospheric mantle before sampling by ascending melanephelinite magma in Eocene times.

The clinopyroxenes are systematically characterized by $^{87}Sr/^{86}Sr$ ratios lower than those of the host rocks, and by a cluster of $^{87}Rb/^{86}Sr$ ratios between 0.0002 and 0.0086; only one sample from LK suite and two samples from the HK suite have $^{87}Rb/^{86}Sr$ ratios greater than 0.1 (cf. Table 3). On the whole, these values correlated poorly with the 128 Ma reference line (cf. inset of fig. 6B), reflecting substantial isotopic disequilibria between whole rock and hosted clinopyroxene (cf. Song and Frey, 1989). $^{87}Sr/^{86}Sr$ whole rock - clinopyroxene disequilibria may be ascribed to contributions of a component enriched in radiogenic Sr in the bulk xenoliths (cf. Downes and Dupuy, 1987); this component may actually be confined to blebs, glassy drops, and/or at grain boundaries. This suggests that leaching of whole rock samples was not strong enough to dissolve such an enriched phase, as in the case of the glassy component of the clinopyroxene. Leaching solutions produce error-chron lines (Table 4) between 129 Ma (LK sample 3192) and 61 Ma (HK sample 3307), approaching the ages of the K-alkaline magmatism (128 Ma) and nephelinitic magmatism of the region (61-32 Ma), respectively (Comin-Chiaramonti *et al.*, 1991; Comin-Chiaramonti and Gomes, 1996). Isotopic mixing between an old whole-rock component (?) and the magmatic-decompressional event at Ñemby hill (46 Ma) probably affected the xenoliths.

The measured $^{143}Nd/^{144}Nd$ ratio ranges from slightly enriched (0.51246) to depleted

TABLE 3

Rb, Sr, Sm, Nd abundances (ppm) and $^{87}Rb/^{86}Sr$, $^{147}Sm/^{144}Nd$, $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ measured ratios in Ñemby mantle xenoliths (WR, whole rock; Cpx, clinopyroxene; Opx, orthopyroxene; leached, leaching solutions from Cpx). T_{DM} values (calculation of model dates relative to depleted reservoir, $^{143}Nd/^{144}Nd$ = 0.513114 and $^{147}Sm/^{144}Nd$ = 0.222) are presented for plausible solutions. Analytical methods are described in Castorina et al. (1997). The samples are ordered in decreasing content of cpx (see Appendix).

SAMPLE	Rb	Sr	^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr	Sm	Nd	^{147}Sm/^{144}Nd	^{143}Nd/^{144}Nd	T_{DM} (Ma)
LK-Suite									
3192 WR	1.07	6.80	0.45511	0.70433 (4)	0.040	0.25	0.09667	0.51258 (6)	713
Cpx	*0.136*	*45.85*	*0.00860*	*0.70332 (1)*	*1.595*	*4.71*	*0.20461*	*0.51344 (5)*	
Leached			*0.54830*	*0.704330*					
“			*0.33700*	*0.703815*					
3252 WR	0.70	6.12	0.33097	0.70420 (8)	0.040	0.15	0.16055	0.51311 (6)	145
Cpx	*0.011*	*103.30*	*0.00032*	*0.70382 (8)*	*0.65*	*3.70*	*0.10619*	*0.51291 (2)*	*354*
Opx				*0.70360 (10)*	*0.03*	*0.18*	*0.10075*	*0.51305 (6)*	*148*
3254 WR	0.48	2.11	0.65827	0.70480 (4)	0.017	0.04	0.25590	0.51346 (7)	1065
Cpx	*1.45*	*9.80*	*0.43019*	*0.70461 (3)*	*0.089*	*0.18*	*0.29889*	*0.51348 (8)*	*568*
3221 WR	1.99	19.80	0.29068	0.70410 (8)	0.042	0.31	0.08186	0.51263 (7)	581
Cpx	*0.001*	*12.74*	*0.0002*	*0.70384 (1)*	*0.575*	*4.21*	*0.08252*	*0.51272 (5)*	*483*
3199 WR	1.92	16.94	0.32797	0.70426 (5)	0.012	0.20	0.03612	0.51264 (7)	447
3213 WR	1.20	14.50	0.23947	0.70392 (5)	0.038	0.22	0.10399	0.51246 (6)	974
3253 WR	0.65	8.98	0.20945	0.70399 (4)	0.036	0.20	0.10837	0.51305 (8)	160
3227 WR	1.01	8.75	0.33386	0.70446 (8)	0.054	0.55	0.05932	0.51301 (5)	135
Cpx	*0.022*	*199.43*	*0.00032*	*0.70375 (1)*	*0.469*	*4.80*	*0.05909*	*0.51277 (3)*	*387*
3269 WR	1.74	9.94	0.50653	0.70452 (8)	0.010	0.29	0.02076	0.51267 (8)	387
Cpx	*0.02*	*415.62*	*0.00014*	*0.70444 (1)*	*0.594*	*6.64*	*0.05408*	*0.51253 (2)*	*605*
Leached			*0.02950*	*0.704329*					
“			*0.04681*	*0.704398*					
“			*0.77595*	*0.704712*					
“			*0.89880*	*0.705543*					

TABLE 3: *continued*

SAMPLE	Rb	Sr	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$	Sm	Nd	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	T_{DM} (Ma)
HK-Suite									
3288 WR	4.62	41.22	0.32432	0.70420 (3)	0.150	0.90	0.10028	0.51279 (4)	406
Cpx	*28.66*	*250.51*	*0.33088*	*0.70408 (3)*	*2.410*	*16.80*	*0.08671*	*0.51267 (3)*	*587*
3222 WR	1.38	14.33	0.27866	0.70412 (4)	0.470	1.12	0.25367	0.51325 (5)	347
Cpx	*0.12*	*44.8*	*0.00775*	*0.70361 (3)*	*0.873*	*2.40*	*0.21987*	*0.51317 (3)*	*260*
3311 WR	3.86	68.15	0.16381	0.70399 (3)	0.320	2.20	0.08792	0.51286 (5)	363
Cpx	*15.96*	*309.91*	*0.14815*	*0.70422 (6)*	*0.980*	*6.70*	*0.08838*	*0.51283 (1)*	*314*
3307 WR	0.05	28.20	0.00513	0.70366 (6)	0.190	2.05	0.05602	0.51254 (6)	599
Cpx	*0.04*	*173.74*	*0.00066*	*0.70389 (2)*	*0.841*	*4.13*	*0.12309*	*0.51277 (2)*	*653*
Leached			*0.71477*	*0.704519*					
"			*0.00668*	*0.703912*					
"			*0.09366*	*0.703991*					
3211 WR	2.85	44.15	0.18669	0.70380 (7)	0.180	2.16	0.05037	0.51258 (5)	541
Cpx	*0.11*	*977.26*	*0.00033*	*0.70326 (6)*	*1.993*	*26.04*	*0.04626*	*0.51260 (6)*	*510*
3313 WR	3.93	58.02	0.19590	0.70397 (2)	0.210	2.42	0.05245	0.51288 (5)	265
3301 WR	4.23	22.97	0.53287	0.70464 (4)	0.140	1.13	0.07459	0.51254 (6)	680
3220 WR	0.59	14.22	0.12006	0.70383 (4)	0.076	0.56	0.08170	0.51276 (4)	463
3284 WR	6.58	63.12	0.30140	0.70401 (7)	0.390	2.65	0.08896	0.51261 (6)	671
Cpx	*1.73*	*653.79*	*0.00765*	*0.70350 (1)*	*16.145*	*84.34*	*0.11790*	*0.51272 (1)*	*678*
Leached			*0.37758*	*0.703862*					
"			*0.29199*	*0.703774*					

(0.51348) signature (Table 3; fig. 6). On the whole, the Nd isotope ratios of the Ñemby xenoliths and hosted pyroxenes encompass almost the entire range of values reported for mid-ocean ridge basalts (MORB) and ocean-island basalts (OIB) (cf. White, 1985; Galer and O'Nions 1989; Stosch and Lugmair, 1986). Significant correlations between $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ were not observed ($r^2 \leq 0.85$), but the best fit is along a 0.5 Ga line (cf. Table 4). By contrast, strongly positive correlations are shown by clinopyroxenes from Pico Cabugi (NE Brazil; $r^2 = 0.99$, best fitting at 1114 Ma) and from Fernando de Noronha ($r^2 = 0.90$, best fitting at 413 Ma; see Table 4 and fig. 6B).

In particular, the $^{143}Nd/^{144}Nd$ ratios of clinopyroxenes and orthopyroxene from Ñemby indicate isotopically heterogeneous mantle sources, ranging from values approaching the Bulk Earth estimate (e.g. HK-3288-*Cpx*: measured $^{143}Nd/^{144}Nd = 0.51267$) to a variably LREE depleted source (e.g. LK-3254-*Cpx*: $^{143}Nd/^{144}Nd = 0.51348$). Sample 3252 (LK) shows significant whole rock-clinopyroxene-orthopyroxene isotopic disequilibria, i.e. $^{143}Nd/^{144}Nd = 0.51311$, 0.51291, 0.51305, respectively, and $^{147}Sm/^{144}Nd = 0.16$, 0.11 and 0.10, respectively (fig. 6). Thus, decoupling between $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios suggests a complex history of REE depletion and enrichment events in the mantle, as indicated by the trace element patterns.

The higher $^{87}Sr/^{86}Sr$ ratios for whole rocks and acid leachate relative to clinopyroxenes indicate that the Sr isotopic ratio was affected by secondary processes. Therefore, model age calculations based on Rb/Sr systematics are not as reliable as those based on Sm/Nd systematics. Sm/Nd model ages (T_{DM}), calculated with respect to a depleted reservoir (Table 2), range from 135 to 1065 Ma (averaged $T_{DM} = 0.5 \pm 0.3$ Ga; LK, 0.51 ± 0.29, HK, $0.49 \pm 0{,}2$ Ga, respectively).

This complexity of the Sm/Nd systematics suggests a multi-stage history, such as repeated melt extraction and fluid diffusion, undergone by the lithospheric mantle beneath Paraguay at various times (*e.g.* Transamazonic, Uruaçano and Brasiliano cycles). Thus various metasomatic events may have overlapped, giving a mixed isotopic character to the Ñemby mantle xenoliths (cf. reference lines, fig. 6A).

CONCLUSIVE REMARKS

Ñemby spinel peridotites are variable in major element compositions, ranging from relatively «fertile» to very depleted in basaltic component. Some of the xenoliths have exceedingly high K_2O and incompatible element (IE) contents compared with the composition of lherzolites which underwent partial melting during basalt-extraction (see Frey and Green, 1974). The IE contents of clinopyroxenes encompass world-wide occurrences (see e.g., Salters and Shimizu, 1988). This suggests that processes, other than depletion, occurred. Demarchi *et al.* (1988) have shown that K is mostly partioned into blebs in the xenoliths and glassy drops in clinopyroxenes. The blebs have been interpreted as derived from the breakdown of volatile-bearing wet phases, such as amphibole and/or phlogopite, which melted during ascent to the surface; the glassy drops in clinopyroxenes are generally interpreted as products of incongruent partial melting induced by decompression (Comin-Chiaramonti *et al.*, 1986; see O'Reilly and Griffin, 1988; Chen *et al.*, 1989; Luhr and Aranda-Gomes, 1997). Both probably represent the remnants of hydrous phases such as micas and/or amphiboles, and/or products induced by the influx of small-volume, volatile-rich melts (Petrini *et al.*, 1994).

In summary, most of the major element chemistry of the Ñemby xenoliths (except K_2O and to a lesser extent Na_2O) are consistent with 1) residual compositions after variable degrees of partial melting and 2) metasomatic effects shown by alkali and IE enrichments in both whole rock and clinopyroxene.

It has been shown that clinopyroxenes display variable REE enrichments, more

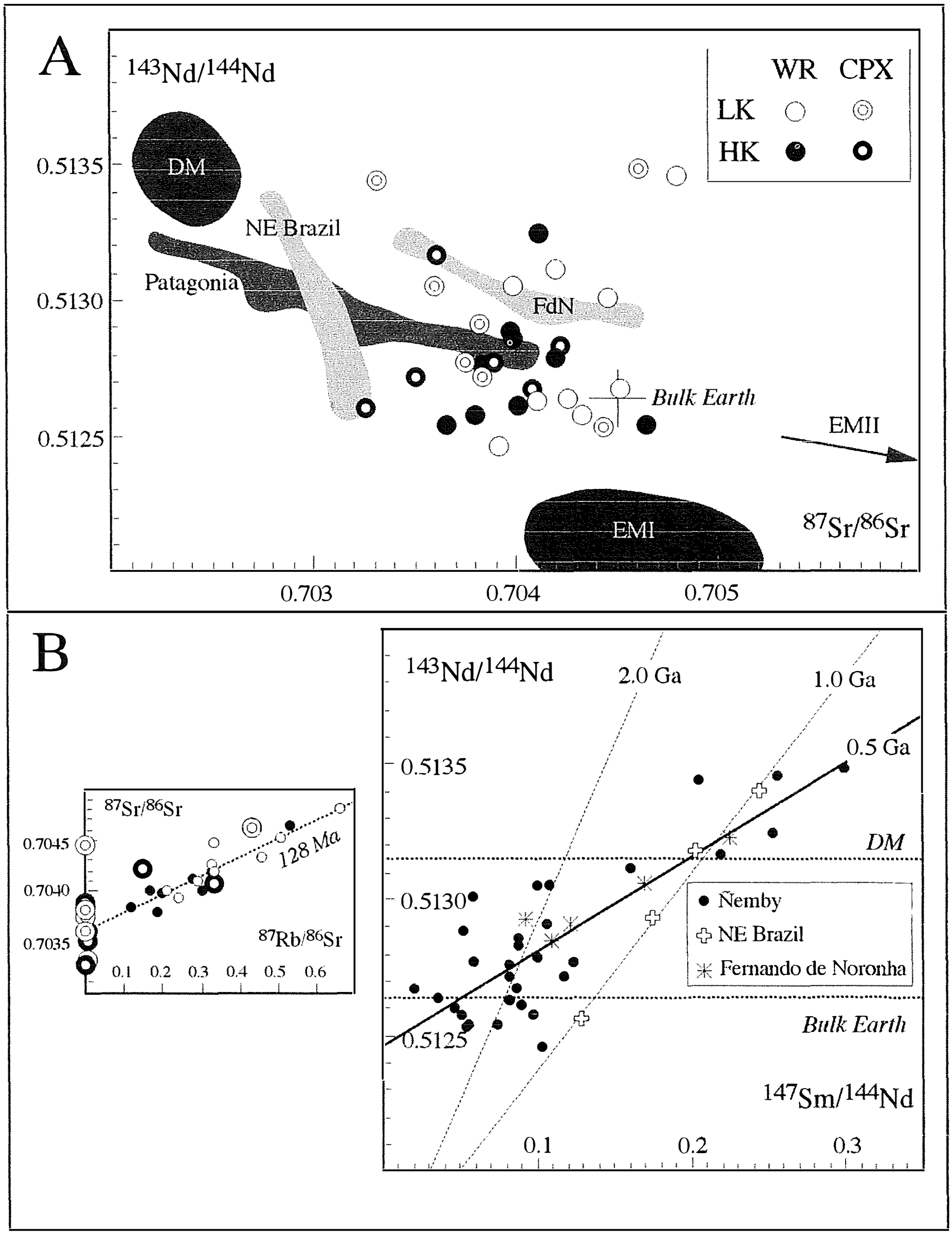

Fig. 6. – A) $^{87}Sr/^{86}Sr$ *vs* $^{143}Nd/^{144}Nd$ plot for Ñemby clinopyroxenes and host mantle xenoliths; for comparison the compositions of the cpx from NE Brazil and Fernando de Noronha (Rivalenti *et al.*, 2000), Patagonia (Stern *et al.*, 1989; Barbieri *et al.*, 1997) are also plotted. B) $^{147}Sm/^{144}Nd$ *vs* $^{143}Nd/^{144}Nd$ plot for Ñemby clinopyroxenes and xenoliths, and 0.5 — 2.0 Ga reference lines, together with NE Brazil and Fernando de Noronha clinopyroxene plots; inset: $^{87}Rb/^{86}Sr$ *vs* $^{87}Sr/^{86}Sr$ plot and 128 Ma reference line.

TABLE 4

Correlations between $^{87}Rb/^{86}Sr$ *and* $^{87}Sr/^{86}Sr$*, and* $^{147}Sm/^{144}Nd$ *and* $^{143}Nd/^{144}Nd$ *and inferred ages, following the usual equation* $y = m(e^{\lambda t} - 1) + R_0$*, where* R_0 *is the initial isotopic radiogenic ratio,* λ *is the decay constant (*^{87}Rb*: 1.42* $\times 10^{-11}$*year*$^{-1}$*;* ^{147}Sm*: 6.54* $\times 10^{-12}$*year*$^{-1}$*) and t is time.*

^{87}Rb/^{86}Sr *vs* ^{87}Sr/^{86}Sr	"m"	R_0	r^2	AGE (Ma)
LK				
WR	0.001796	0.70362	0.85	126
Cpx	0.001876	0.70379	0.44	132
3192: *Cpx* + Leaching solutions	0.001840	0.70327	0.98	129
3269: *Cpx* + Leaching solutions	0.000962	0.70435	0.74	68
HK				
WR	0.001820	0.70360	0.91	128
Cpx	0.001884	0.70360	0.48	133
3284: *Cpx* + Leaching solutions	0.000975	0.703492	0.99	69
3307: *Cpx* + Leaching solutions	0.000866	0.703901	1.00	61
^{147}Sm/^{144}Nd *vs* ^{143}Nd/^{144}Nd				
LK				
WR	0.003398	0.512497	0.55	519
Cpx	0.003703	0.512506	0.85	565
HK				
WR	0.003015	0.512473	0.68	460
Cpx	0.003174	0.512432	0.86	484
NE BRAZIL				
CPX	*0.007312*	*0.511636*	*0.99*	*1114*
FERNANDO DE NORONHA				
CPX	*0.002704*	*0.512608*	*0.90*	*413*

evident in those crystals characterized by spongy texture and abundance of glassy drops (e.g. 3284 sample). Some of the investigated clinopyroxenes show U-shaped (and spoon) patterns which also characterize clinopyroxenes from shallower (i.e. more depleted) mantle levels beneath Oahu (Hawaii; Sen *et al.*, 1993). A possible explanation for the progressive enrichment of samples characterized by similar HREE and different LREE abundances, is different ion-exchange processes (cf. «simple mixing metasomatism model» of Song and Frey, 1989; Sen *et al.*, 1993), due to the passage of a LREE-rich chemical front on depleted compositions, in both LK and HK suites.

It is believed that «residual» pyroxenes incorporated REE during later metasomatic events (cf. Chen *et al.* 1989). The above observation is consistent with the Nd isotope ratios measured on clinopyroxenes, indicating a LREE-depleted source for some samples and supporting the hypothesis that clinopyroxenes from some lherzolites (eg 3222, 3252 and 3254) did not crystallize from an original LREE enriched component; other samples (e.g. 3288) approache enriched or undifferentiated compositions (cf. Table 3).

Alkaline basaltic magmas from deeper, garnet-bearing mantle may be suitable enriching agents (cf. Comin-Chiaramonti *et al.*, 1997). Moreover, the Ñemby xenoliths were probably involved in carbonatite metasomatism (Comin-Chiaramonti *et al.*, 1991), as indicated by the IE patterns of some clinopyroxenes. The latter are characterized by high LREE and Sr abundances coupled with depletion in Nb, Ti, Zr. Notably, similar behaviour has already been described for clinopyroxenes from peridotite xenoliths hosted in ocean island basalts from Samoa and Tubai, which, according to Hauri *et al.* (1993), show clear evidence of carbonatitic metasomatism.

The effects of «metasomatic processes» are not appreciable on the *cpx* polyhedral variations, even in the HK suite. Systematic isotope differences between LK and HK xenoliths were not observed, excepting those related to $\Delta^{18}O$(*cpx-ol*). This suggests buffering dominated by olivine in the upper mantle (cf. Mattey *et al.*, 1994), where the equilibration was supported by coherence between observed O-isotopic fractionation and clinopyroxene temperatures.

The observed radiogenic isotope trend (Bulk Earth *vs* Depleted Mantle) is not consistent with major element refractory parameters, suggesting that mixing with enriched components is also recorded on a whole-rock scale. The enriched components were mostly trapped in some clinopyroxene which had previously crystallized from depleted to quasi-chondritic mantle sources. On the whole, the isotopic data indicate that the lithospheric mantle prior to the enrichment was dominated by a depleted component, isotopically resembling MORB sources (cf. Menzies *et al.*, 1985; Stosch and Lungmair, 1986; Menzies and Hawkesworth, 1987; Song and Frey, 1989; Comin-Chiaramonti *et al.*, 1997) or even more depleted, probably related to the occurrence of residua which differentiated from ancient events of partial melting.

The Nd-T_{DM} (model ages referred to depleted mantle) of clinopyroxenes and host rocks record earlier fluid-infiltrations events. These are defined between 135 and 1065 Ma (Table 3), with more than 50% model ages spanning the Brasiliano cycle (i.e. 900-460 Ma).

Considering that magmatism in the Asunción-Sapucai-Villarrica region (Early Cretaceous: tholeiitic and K-alkaline-carbonatitic rocks; Late Cretaceous to Tertiary: Na-alkaline rocks) requires their parental magmas to have been derived from a heterogeneous subcontinental mantle (garnet peridotite; Comin-Chiaramonti *et al.*, 1997), significant fluids are expected to modify the isotope ratios of the overlaying spinel peridodites.

On this respect, the younger Nd-T_{DM} and the Rb-Sr systematics may reflect to some extent the main melting episodes occurring in the mantle regions during the various phases of lithospheric thinning (cf. Comin-Chiaramonti and Gomes, 1996) and repeated interactions between fluids and overlaying peridotites.

APPENDIX

Selected whole-rock chemical analyses of LK (K_2O < 0.1; Table I) and HK (K_2O > 0.1; Table II) mantle xenoliths from Ñemby hill, central-eastern Paraguay, and representative «blebs», glassy drops in clinopyroxene and averaged host melanephelinites (Table III). Modal analyses are also reported, as well mg# [Mg/(Mg+Fe)] and cr# [(Cr/(Cr+Al)] of coexisting clinopyroxene *(Cpx)*, olivine *(Ol)*, orthopyroxene *(Opx)* and spinel *(Sp)*, respectively. Lh, lherzolite; Hz, harzburgite; Dun, dunite. For a complete list and analytical methods, s. Demarchi *et al.*, 1988.

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APPENDIX

TABLE I

Mantle xenoliths from LK suite.

LK Suite	1-3192	2-3252	3-3254	4-3221	5-3199	6-3213	7-3253	8-3227	9-3269
wt%									
SiO_2	44.68	43.82	44.15	43.74	44.19	43.56	43.37	43.31	43.66
TiO_2	0.05	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.01
Al_2O_3	2.56	1.81	1.74	1.31	1.09	0.86	0.79	0.85	0.77
FeO_t	7.88	8.03	7.55	8.04	7.83	7.85	7.60	7.85	7.66
MnO	0.12	0.12	0.11	0.13	0.11	0.11	0.11	0.11	0.11
MgO	41.37	42.94	43.48	44.11	44.71	45.80	46.32	46.09	46.10
CaO	2.27	2.19	1.91	1.54	1.09	0.79	0.80	0.82	0.71
Na_2O	0.10	0.13	0.15	0.11	0.09	0.03	0.11	0.05	0.05
K_2O	0.09	0.04	0.06	0.09	0.02	0.04	0.04	0.03	0.06
P_2O_5	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	99.13	99.12	99.16	99.10	99.12	99.05	99.15	99.12	99.13
ppm									
Cr	2968	2226	2872	2255	2650	2840	2010	2616	2379
Ni	2131	2193	2169	2349	2342	2333	2380	2386	2377
Sc	12	11	11	9	7	7	7	6	6
Rb	3	1	1	2	2	2	2	1	2
Sr	7	9	4	20	18	20	12	9	16
Y	2	2	1	3	1	2	nd	nd	nd
Nb	nd	2	2	1		1	nd	1	1
Ba	17	15	17	20	14	17	18	18	11
La	2	4	2	4	3	3	2	2	3
Cpx vol%	9.8	8.9	8.9	7.1	4.5	4.0	3.5	3.2	1.9
Ol	70.3	62.2	68.5	65.2	65.5	69.5	69.7	77.2	76.4
Opx	17.5	26.0	21.1	23.9	27.8	24.8	25.3	18.1	21.1
Sp	2.4	2.9	1.5	3.8	2.2	1.7	1.5	1.5	0.6
mg#*Cpx*	0.91	0.92	0.93	0.94	0.93	0.95	0.95	0.96	0.96
mg#*Ol*	0.91	0.91	0.91	0.91	0.91	0.92	0.92	0.92	0.92
mg#*Opx*	0.91	0.91	0.91	0.91	0.92	0.92	0.92	0.92	0.92
cr#*Sp*	0.13	0.13	0.15	0.16	0.30	0.23	0.25	0.27	0.31
Rock	Lh	Lh	Lh	Lh	Lh	Hz	Hz	Hz	Hz

TABLE II

Mantle xenoliths from HK suite.

HK Suite	10-3288	11-3222	12-3311	13-3307	14-3211	15-3313	16-3301	17-3220	18-3284
wt%									
SiO_2	44.19	44.35	44.05	43.81	42.42	44.36	41.03	43.15	42.92
TiO_2	0.04	0.09	0.06	0.06	0.01	0.02	0.05	0.01	0.06
Al_2O_3	2.37	2.32	2.35	1.90	0.86	1.37	1.56	0.790	1.32
FeO_t	7.68	8.02	8.15	7.89	7.78	7.44	8.35	7.50	9.09
MnO	0.12	0.12	0.12	0.12	0.11	0.11	0.12	0.11	0.16
MgO	41.51	40.86	42.15	43.20	46.94	44.20	46.67	46.73	43.67
CaO	2.45	2.78	1.59	1.65	0.74	1.09	1.03	0.60	0.98
Na_2O	0.29	0.27	0.21	0.13	0.11	0.16	0.12	0.13	0.32
K_2O	0.49	0.29	0.42	0.28	0.15	0.32	0.14	0.13	0.41
P_2O_5	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.06
Sum	99.15	99.11	99.12	99.05	99.13	99.09	99.08	99.16	98.99
ppm									
Cr	2298	2422	3038	3170	2606	2656	5630	2201	2586
Ni	2122	2117	22127	2189	2443	2255	2436	2403	2290
Sc	12	13	9	10	6	8	5	6	5
Rb	5	2	5	nd	2	6	3	1	6
Sr	45	15	63	27	46	60	21	13	63
Y	4	4	3	3		2	2		5
Nb	2		2	1		1	1		13
Ba	65	23	55	34	35	29	50	18	42
La	9	3	5	5	7	8	6	4	10
Cpx vol%	11.9	10.9	8.8	6.6	3.4	2.4	2.1	1.1	1.0
Ol	71.1	67.0	67.7	76.9	75.5	83.6	89.6	86.6	84.1
Opx	15.6	20.6	20.5	14.5	19.9	13.4	2.7	11.2	12.5
Sp	1.4	1.5	0.8	2.0	1.2	0.6	5.6	1.1	2.4
mg#*Cpx*	0.90	0.91	0.90	0.93	0.96	0.92	0.93	0.93	0.97
mg#*Ol*	0.90	0.90	0.90	0.91	0.91	0.92	0.91	0.92	0.88
mg#*Opx*	0.90	0.91	0.90	0.92	0.92	0.92	0.92	0.93	0.90
cr#*Sp*	0.11	0.12	0.18	0.21	0.40	0.27	0.34	0.40	0.70
Rock	Lh	Lh	Lh	Lh	Hz	Hz	Dun	Hz	Hz

TABLE III

Blebs, glassy drops and averaged melanephelinite composition.

	Blebs	Glassy drops				Host
	3091	3283	3284	3301	3313	lavas
			***	**	**	(N=31)
wt%						
SiO_2	45.81	46.17		59.83	64.17	42.53 (0.67)
TiO_2	0.69	0.06	0.82	0.68	0.49	2.10 (0.06)
Al_2O_3	10.03	6.30		22.42	19.91	13.59 (0.40)
FeO_t	6.69	6.86		0.83	0.12	10.26 (0.59)
MnO	0.14	0.13		0.00	0.01	0.21 (0.02)
MgO	23.49	35.78		1.35	0.19	9.23 (0.51)
CaO	6.51	2.25		3.14	0.45	10.32 (0.30)
Na_2O	1.99	0.73		3.85	0.55	5.62 (0.56)
K_2O	3.08	0.90	10.00	7.78	14.58	1.82 (0.39)
P_2O_5	0.83	0.07				1.18 (0.06)
Sum	99.26	99.25		99.88	99.98	96.86
ppm						
Cr	38114	16622	2	803	134	519 (65)
Ni	1124	1740				255 (15)
Rb	41	12	120	380	760	56 (9)
Sr	873	234	1414	2800	1700	1074 (54)
Y	26	2	14.7			32 (3)
Nb	55	4	155			107 (7)
Ba	462	213	1781	2700	4650	1029 (87)
La	142	12	77.4			116 (7)
Nd	46	2	27.7			64 (5)
Sm			4.2			11 (3)

ACKNOWLEDGMENTS

The authors are grateful to L. Civetta, F. Castorina, R. Petrini and A. Barbieri for analyses of radiogenic isotopes, particularly those for leaching solutions, and to P. Censi for O isotope analyses. This paper benefitted by review comments from G. Piccardo, E. Rampone, G. Rivalenti and R. Vannucci. Acknowledgements are due to the CNR for the use of the ion microprobe installed at CSCC-Pavia. The research was supported by MURST (COFIN 1998 and 1999, Comin-Chiaramonti and Princivalle, respectively), CNR (1997 and 1998) and FAPESP grants.

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