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GIOVANNI B. PICCARDO *, GIULIO OTTONELLO **

PARTIAL MELTING EFFECTS ON COEXISTING MINERALS COMPOSITIONS IN UPPER MANTLE XENOLITHS FROM ASSAB (ETHIOPIA) ***

RIASSUNTO. — In questo lavoro vengono studiati 9 xenoliti ultrafemici inclusi in vulcaniti alcaline recenti della regione di Assab (Etiopia): vengono analizzati e discussi in particolare la concentrazione in elementi maggiori ed elementi delle Terre Rare (REE) ed il loro partizionamento per le fasi mineralogiche coesistenti: olivina, ortopirosseno, clinopirosseno e spinello.

Dall'analisi delle concentrazioni e del partizionamento degli elementi maggiori fra coppie di minerali coesistenti, e tenendo conto delle caratteristiche strutturali e paragenetiche, si può concludere che l'associazione mineralogica complessiva dei diversi campioni analizzati ha subìto cristallizzazione all'equilibrio sotto condizioni relativamente uniformi. La stima di tali condizioni, secondo le metodiche dedotte dai più recenti dati sperimentali, indica temperature di circa 1100° C e pressioni comprese fra 9-10 e 21-22 kb, consistenti con il campo di stabilità delle peridotiti a spinello.

Questo evento di equilibratura metamorfica tende a mascherare gli effetti di qualsiasi processo la roccia abbia subìto in precedenza.

Nonostante ciò, variazioni più o meno regolari possono essere riconosciute per alcuni parametri composizionali delle diverse fasi mineralogiche (principalmente orto- e clinopirosseni) e, inoltre, risultano evidenti buone correlazioni in vari parametri composizionali fra le varie coppie di minerali. In particolare, clino- e ortopirosseni mostrano paralleli decrementi progressivi nei loro componenti Ca-Tschermakitici e ferriferi, accompagnati da incrementi nei componenti magnesiferi, l'olivina varia composizionalmente fra 7,89 e 11,61 in Fa, mentre gli spinelli mostrano solo una leggera variazione relativa nei loro componenti $MgAl_2O_4$ e $FeCr_2O_4$.

Il partizionamento fra fasi coesistenti mostra l'esistenza di ben definite correlazioni positive di vari parametri (ad esempio: Fe/Mg e Cr/Al) fra coppie di fasi coesistenti: in particolare per i pirosseni, il decremento parallelo del rapporto Fe/Mg, in entrambe le fasi, è accompagnato da incrementi paralleli del rapporto Cr/Al (e decremento nel contenuto in Al totale).

Può essere quindi concluso che le fasi silicatiche mostrano trends di variazione parallela verso composizioni arricchite in Mg, accompagnati, per clino- e ortopirosseni, da decremento nei loro componenti Ca-Tschermakitici.

Deve essere ricordato come i campioni analizzati, che mostrano una composizione harzburgitica (essendo il cpx presente soltanto in pochi %), abbiano mediamente contenuti in TiO_2, Al_2O_3, CaO, Na_2O e K_2O più bassi, e più elevati in MgO, rispetto alle composizioni stimate per il mantello superiore primitivo, e debbano essere quindi considerati come residui refrattari di un processo di fusione parziale, piuttosto che materiale non impoverito. I trends composizionali sopra descritti devono essere, a nostro parere, considerati come gli effetti di tale processo di fusione parziale sulle fasi costituenti, residuali dopo il processo di impoverimento.

In generale va ricordato come, sebbene tanti e tali siano stati i contributi sperimentali alla comprensione dei meccanismi genetici dei fusi basaltici per fusione del materiale del mantello,

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* Istituto di Petrografia dell'Università di Genova. ** Istituto Internazionale di Vulcanologia, Catania. Present address: Istituto di Mineralogia e Petrologia dell'Università di Pisa. *** Lavoro eseguito con il contributo finanziario del C.N.R.

non sufficienti dati paiono a tutt'oggi esistere sul comportamento delle fasi mineralogiche del mantello superiore (e cioè di soluzioni solide complesse) durante processi di fusione parziale progressiva sotto differenti condizioni P-T.

È generalmente riconosciuto come la fusione parziale progressiva produca continue variazioni nella composizione mineralogica dei residui refrattari, progressivamente eliminando diverse specie cristalline, ma le fasi residuali sono spesso considerate invariate in composizione, durante il progredire della fusione, oppure le loro variazioni non sono sufficientemente considerate (ad esempio: nella modellizzazione dei processi genetici dei fusi).

I risultati dei dati sperimentali esistenti (vedi ad esempio: MYSEN e BOETTCHER, 1977) mostrano un buon accordo con le nostre osservazioni, mentre analoghi trends composizionali sono evidenti per le fasi mineralogiche di vari massicci di peridotiti alpine, che mostrano di aver subìto processi più o meno spinti di fusione parziale sotto condizioni ascrivibili al mantello superiore (vedi ad esempio: PICCARDO, 1976; DICK, 1977).

Considerando i contenuti ed il frazionamento delle Terre Rare (REE) (dati in: OTTONELLO et al., 1978 a e b; OTTONELLO, in prep.), va innanzitutto osservato come i vari campioni analizzati per roccia totale mostrino patterns, normalizzati rispetto alle concentrazioni condritiche, arricchiti in LREE e relativamente impoveriti in HREE.

Sebbene tale carattere, comune agli xenoliti ultrafemici di questo tipo, sia interpretato da vari Autori come contrastante con il carattere residuale di questo tipo di rocce e ascritto a contaminazione da parte del fuso inglobante o da parte di componenti geochimici non meglio definiti, i dati di roccia totale per i nostri campioni mostrano un buon accordo con i risultati dei calcoli di bilancio di massa sulla base delle composizioni in REE delle singole fasi mineralogiche dei vari campioni (OTTONELLO, in prep.).

A riguardo della composizione in REE delle fasi mineralogiche (vedi: OTTONELLO et al., 1978 a e b; OTTONELLO, in prep.) e considerando in particolare il partizionamento fra clino- e ortopirosseni, va rimarcato come i rapporti fra le attività delle REE nelle due fasi mostrino caratteristiche simili per tutte le coppie investigate, con massimi localizzati al Ce. Le variazioni nel rapporto delle attività dello stesso elemento nelle diverse coppie di pirosseni è riferibile a sostituzioni parallele che interessano l'Al nei siti Z e le REE nelle posizioni M_2 della fase cpx.

Evidenti correlazioni con gli elementi maggiori suggeriscono l'esistenza di effetti di dipendenza dalla composizione in elementi maggiori per la distribuzione delle REE fra cpx e le fasi coesistenti.

Sebbene il quadro globale del partizionamento delle REE nelle fasi considerate sia molto complesso, comunque l'evoluzione dei valori del partizionamento sembra correlabile con le variazioni nei parametri considerati indicativi del carattere più o meno residuale dopo fusione parziale per questi materiali.

Variazione dei valori di partizionamento fra fasi solide coesistenti probabilmente si verifica durante un processo di fusione parziale progressiva. Inoltre, si può dimostrare che l'attività di tali elementi in fusi naturali è una funzione complessa dell'attività dell'O^{2-} in tali liquidi (FRASER, 1975).

Tali constatazioni, assieme alla mancanza di dati riguardanti l'attività delle REE nei fusi naturali, suggerisce cautela nell'utilizzazione di assunzioni semplicistiche (ad esempio: costanti coefficienti di partizionamento solido-solido e solido-liquido) durante la modellizzazione geochimica dei processi genetici dei fusi naturali.

ABSTRACT. — Reequilibrated tectonitic spinel peridotite xenoliths from Assab preserve evidences of a depletion event suffered by these residual materials prior to the equilibrium crystallization in a narrow range of temperatures (about 1100° C) in the spinel peridotite stability field.

Well defined correlations exist for the major compositional parameters among different mineral pairs. All the silicate phases show trends of parallel variations toward more Mg-rich compositions, accompanied by decrease in the Ca-Tschermak component in pyroxenes. The recognized compositional trends, which are ascribed to effects of progressive partial melting, are in good agreement with experimental results of quencing runs on similar materials.

REE partitioning picture in these materials appears quite complex but clear composition dependency effects of the REE distribution among clinopyroxene and the coexisting solid phases can be envisaged. These evidences, along with the lack of data concerning REE activities in natural melts, suggest great care in attempting geochemical modelling based on these elements.

Introduction

This paper is a report of present day knowledges on elemental distribution between coexisting solid phases in reequilibrated tectonitic spinel peridotite xenoliths from the Assab Range (Ethiopia).

Possible effects of a partial melting event, which operated on the solid assemblages prior to the equilibrium crystallization, are discussed in terms of crystal chemistry.

REE partitioning picture in these materials is also briefly resumed and attention is focused on possible composition dependency effects on the trace partitioning between coexisting residual solid phases and the liquid.

Bulk rock major element chemistry

As previously described (CIMMINO et al., 1976; OTTONELLO et al., 1978 a), the considered ultramafic xenoliths, on a textural basis, show the effects of a complete equilibration event, which operated on the whole four phases assemblage, without having recorded later reaction or exsolution phenomena.

Paragenetically, they mainly consist of olivine and orthopyroxene, whereas clinopyroxene and spinel are always confined to few percents. Their harzburgitic mineral assemblages are in agreement with the major element bulk rock chemistries (tab. 1): in fact, when the analyzed Assab spinel peridotites are compared with the estimated compositions for primitive upper mantle by different Authors (i.e. WYLLIE, 1971; MAALOE and AOKI, 1977), none of our samples approaches the proposed compositions.

The systematic differences in several components, and particularly the lower values for TiO_2, FeO, Na_2O, K_2O, Al_2O_3 and CaO, and the higher values for MgO, are on the whole in good agreement with a residual character after a partial melting event. Considering some compositional parameters, often utilized as indexes of depletion, rough covariances can be visualized among the different samples. In particular, the Al_2O_3 and CaO contents and the $FeO_{tot.}/MgO$ ratios show crude parallel decreases, accompanied by parallel opposite variation of the MgO contents.

Major element mineral chemistry

Constituent mineral phases of the harzburgite xenoliths have been separated by hand-picking, since optical investigations as well as microprobe surveys (see: CIMMINO et al., 1976) have shown no exsolution textures and a compositional homogeneity among and within crystal grains in the same sample. Pure clear mineral grains were separated and repeatedly cleaned by ultrasonic washing and rinsing with distilled water before crushing: purity is believed within 98 and 100 %.

Major element determinations were carried out by colorimetric and atomic absorption procedures (analyst: A. MAZZUCOTELLI, Istituto di Petrografia, Università di Genova; procedures as described in: BASSO and MAZZUCOTELLI, 1975; MAZZUCOTELLI, 1978, in press).

The analyzed minerals are 9 olivines, 9 orthopyroxenes, 9 clinopyroxenes and 6 spinels: data are presented in tables 2, 3, 4, 5. REE data are not reported, as they are available in other contributions (OTTONELLO et al., 1978 a and b; OTTONELLO, in prep.).

TABLE 1

Major elements bulk rock chemistry of Assab spinel peridotites and mantle estimated compositions after WHITE and HARRIS (*in* WYLLIE, 1971) and MAALOE and AOKI (1977) (*M.A*). *Data for samples 3G9, 3G17, 3G18, 3G19 from* OTTONELLO et al. (1978 a). *Total iron expressed as FeO*

	3G9	3G12	3G15	3G16	3G17	3G18	3G19	3G28	3G51	WHITE estim.	HARRIS estim.	(M.A.) estim.
SiO_2	44.23	44.75	45.00	44.50	44.39	44.46	44.52	44.50	43.60	44.50	44.20	44.71
TiO_2	0.03	0.03	0.02	0.02	0.07	0.02	0.04	0.03	0.03	0.15	0.10	0.16
Al_2O_3	0.98	0.80	1.00	0.99	1.04	0.78	0.78	0.78	1.01	2.55	2.70	2.46
Cr_2O_3	0.31	0.24	0.26	0.22	0.28	0.25	0.25	0.28	0.30	-	0.30	0.42
FeO tot.	7.95	7.66	8.57	8.03	8.90	7.94	7.87	7.99	7.94	8.65	8.29	8.15
MnO	0.12	0.12	0.10	0.10	0.14	0.12	0.12	0.11	0.13	0.14	0.15	0.18
NiO	0.32	0.32	0.30	0.31	0.31	0.32	0.32	0.30	0.33	-	0.20	0.26
MgO	44.88	44.50	43.02	44.68	42.57	44.95	45.06	44.81	45.84	41.70	41.30	41.00
CaO	0.85	1.09	1.25	0.78	1.76	0.73	0.68	0.80	0.60	2.25	2.40	2.42
Na_2O	0.06	0.09	0.11	0.09	0.11	0.08	0.04	0.07	0.05	0.25	0.25	0.29
K_2O	0.01	0.01	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.015	0.015	0.09
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	-	0.06
Total	99.75	99.62	99.66	99.74	99.60	99.68	99.70	99.69	99.85	99.98	99.90	100.20

All iron is considered as Fe^{2+} in the olivines and pyroxenes, although the minor amounts of Na in ortho- and clinopyroxenes may indicate small amounts of Fe^{3+} in the acmite end member. As for as spinels, the proportions of Fe_2O_3 and FeO are obtained assuming no cation omissions and the spinel stoichiometry.

Clinopyroxenes

Based on six oxigens, cation total average 4.016 ($\sigma = 0.013$), in good agreement with the theoretical value 4.000. Since silicon cations average 1.888 ($\sigma = 0.025$), more than one half of the total Al cations (mean value 0.180, $\sigma = 0.035$) appear to be tetrahedrally coordinated. It must be mentioned, however, that a small error in the Si determination leads to a large error in the Al^{IV}/Al^{VI} ratio, and it is better assumed that octahedrally coordinated aluminum reachs half of the total Al (see discussion in: WOOD, 1974).

On the whole, the analyzed clinopyroxenes fall in the diopside field and appear similar in their major element compositions, particularly for Ca (mean value 0.833, $\sigma = 0.018$), Mg (mean value 0.920, $\sigma = 0.025$) and Fe (mean value 0.099, $\sigma = 0.011$) atom proportions. Accordingly, the related elemental ratios range between narrow

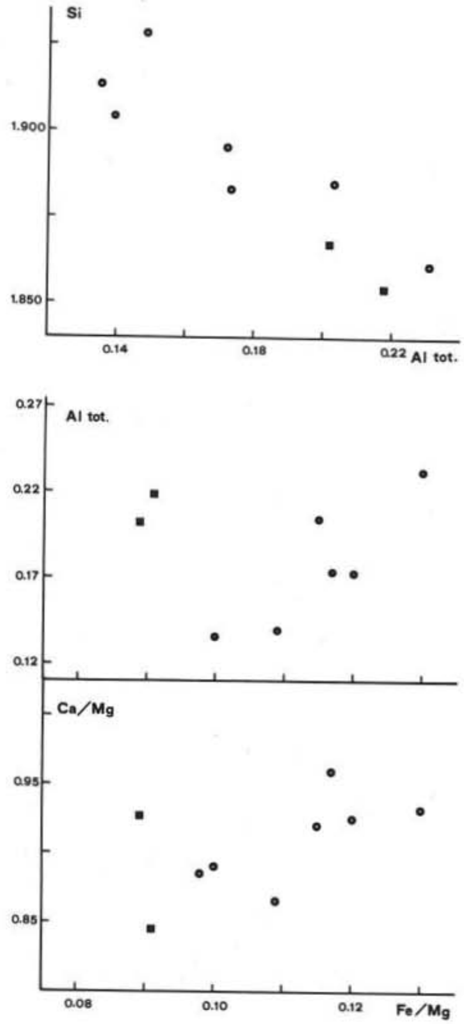

Fig. 1. — Compositional variations for clinopyroxenes. Full squares refer to samples 3G12 and 3G51, which show, mainly on the total Al versus Fe/Mg diagram, an anomalous behaviour with respect to the other samples. In particular, these samples clearly fall outside the trend of parallel increase of total Al and Fe/Mg, while they follow the Si-total Al co-variance trend: these features can be interpreted as differences in the relative variations of the Tschermakitic and Fe-bearing components. A similar anomalous behaviour is also shown by 3G12 opx (see Fig. 2).

limits, the Mg/Mg+Fe and Ca/Ca++Mg+Fe ratios averaging 0.903 ($\sigma = 0.012$) and 0.450 ($\sigma = 0.009$), respectively.

Relatively wider ranges are shown by Al (range 0.135 - 0.231), Na (mean value 0.050, $\sigma = 0.014$), Cr (mean value 0.039, $\sigma = 0.006$) and Ti (mean value 0.008, $\sigma = 0.002$).

The correlations existing among the various compositional parameters are not stricking, except for the good negative correlation between silica and total Al (see fig. 1): however, the Fe/Mg ratios show crude positive correlations with the Al and Na contents and the Ca/Mg ratios, and negative correlation with the Cr/Al ratio. Moreover, the Al content increases with increasing Ca/Mg ratio and with decreasing Cr and Al contents.

Taking into account such evidences, it can be recognized that the different clinopyroxene compositions indicate a rough trend of progressive parallel increase of Fe, Ca and Al, accompanied by more or less parallel increases in their Mg and Si contents. Such a compositional trend can be interpreted as a progressive parallel decrease of Fe, Ca and Al, accompanied by more or less parallel increases in their Mg and Si contents. Such a compositional trend can be interpreted as a progressive decrease of Ca-Tschermak ($CaAl_2SiO_6$) and Fe-bearing (i.e. $Fe_2Si_2O_6$) components of the clinopyroxenes solid solutions, accompanied by a parallel increase in Mg-bearing end members (i.e. $Mg_2Si_2O_6$). Less convincing deductions can be made on the behaviour of Na, since it shows positive correlation with the Fe/Mg ratio, suggesting co-variance with Fe as acmitic component, but slightly negative correlation with Al.

TABLE 2

Major element chemistry of clinopyroxenes from spinel peridotite xenoliths of the Assab Range (Ethiopia)

	3G9	3G12	3G15	3G16	3G17	3G18	3G19	3G28	3G51
SiO_2	52.97	50.97	50.86	52.14	51.20	52.31	51.90	51.80	51.00
Al_2O_3	3.46	5.09	5.36	4.23	3.99	3.14	3.22	4.75	4.68
TiO_2	0.16	0.31	0.21	0.22	0.31	0.41	0.40	0.32	0.28
Cr_2O_3	1.50	1.30	1.20	1.46	1.06	1.74	1.20	1.22	1.60
FeO tot.	2.97	2.88	3.81	3.54	3.44	3.04	3.36	3.38	2.67
MgO	16.98	17.81	16.48	16.50	16.54	17.05	17.35	16.54	16.90
CaO	20.96	20.97	21.34	21.26	22.09	21.16	20.88	21.21	21.80
Na_2O	0.60	0.60	0.48	1.00	0.77	0.60	0.72	0.56	0.52
Total	99.57	99.93	99.74	100.35	99.40	99.45	99.32	100.02	99.45
Si	1.928	1.854	1.861	1.895	1.883	1.913	1.904	1.885	1.967
Al^{IV}	0.072	0.146	0.139	0.105	0.117	0.087	0.096	0.115	0.133
Al^{VI}	0.076	0.072	0.092	0.076	0.056	0.048	0.043	0.088	0.069
Ti	0.004	0.008	0.006	0.006	0.009	0.011	0.011	0.009	0.008
Cr	0.043	0.037	0.035	0.042	0.031	0.050	0.035	0.035	0.046
Fe^{2+}	0.090	0.088	0.117	0.108	0.106	0.093	0.103	0.103	0.082
Mg	0.921	0.966	0.899	0.894	0.907	0.929	0.949	0.897	0.922
Ca	0.816	0.817	0.836	0.828	0.871	0.829	0.821	0.827	0.855
Na	0.042	0.042	0.034	0.070	0.055	0.043	0.072	0.056	0.037
Total	3.993	4.031	4.018	4.023	4.003	4.004	4.034	4.015	4.019

TABLE 3

Major element chemistry of orthopyroxenes from spinel peridotite xenoliths of the Assab Range (Ethiopia)

	3G9	3G12	3G15	3G16	3G17	3G18	3G19	3G28	3G51
SiO_2	54.77	53.80	54.68	54.96	55.30	54.36	54.82	54.22	54.22
Al_2O_3	2.79	4.04	4.63	3.39	2.50	2.78	2.83	3.82	3.74
TiO_2	0.02	0.06	0.02	0.06	0.02	0.02	0.06	0.08	0.02
Cr_2O_3	0.73	0.74	0.80	0.79	0.62	0.26	0.68	0.01	0.70
FeO tot.	6.19	5.72	7.18	6.72	6.45	6.29	5.93	6.97	6.70
MgO	33.38	34.65	30.96	32.54	33.55	34.49	33.96	32.21	32.67
CaO	1.58	1.54	1.12	1.22	1.13	1.24	1.18	1.15	1.44
Na_2O	0.12	0.03	0.08	0.12	0.22	0.08	0.11	0.08	0.02
Total	99.58	100.58	99.47	99.80	99.79	99.52	99.57	99.34	99.51
Si	1.909	1.857	1.908	1.912	1.922	1.896	1.907	1.898	1.894
Al^{IV}	0.091	0.143	0.092	0.088	0.078	0.104	0.093	0.102	0.106
Al^{VI}	0.024	0.021	0.098	0.051	0.025	0.010	0.023	0.055	0.048
Ti	0.001	0.002	0.001	0.002	0.001	0.001	0.002	0.002	0.001
Cr	0.020	0.020	0.022	0.022	0.017	0.007	0.019	0.022	0.019
Fe^{2+}	0.180	0.165	0.210	0.195	0.187	0.183	0.172	0.204	0.196
Mg	1.735	1.783	1.610	1.687	1.738	1.793	1.761	1.680	1.701
Ca	0.059	0.057	0.042	0.045	0.042	0.046	0.044	0.043	0.054
Na	0.008	0.002	0.005	0.008	0.015	0.005	0.007	0.005	0.001
Total	4.029	4.050	3.988	4.010	4.025	4.046	4.028	4.013	4.020

Orthopyroxenes

Cations totals average 4.023 ($\sigma = 0.019$) per formula unit, close to the ideal 4.000 value. Silicon and aluminum cations average 1.900 ($\sigma = 0.017$) and 0.139 ($\sigma = 0.029$), respectively. Similar to clinopyroxenes, much more than half of the Al cations apparently occupies tetrahedral sites, but the real Al partitioning among four-fold and six-fold positions can be masked by small analytical errors involving systematically low values for silicon.

Orthopyroxenes are enstatites and show no important variations in their compositions, as for as Ca (mean value 0.048, $\sigma = 0.007$), Mg (mean value 1.721, $\sigma = 0.058$) and Fe (mean value 0.188, $\sigma = 0.015$) cations per six oxigens, and consequently in their Mg/Mg+Fe and Ca/Ca+Mg+Fe ratios, averaging 0.901 ($\sigma = 0.010$) and 0.024 ($\sigma = 0.003$), respectively.

Aluminum shows a small range of variation (0.103 - 0.190); average numbers of other cations, occurring in small concentrations, are: Ti = 0.001 ($\sigma = 0.001$), Na = 0.006 ($\sigma = 0.004$) and Cr = 0.019 ($\sigma = 0.005$).

As for clinopyroxenes, rough correlations are recognizable among some compositional parameters, concordant, on the whole, with those ones identified in the cpx compositions: in particular, the Al contents increases with increasing Fe/Mg and Ca/Mg ratios and decreasing Si contents (see fig. 2). Accordingly, progressive decreases in Ca-Tschermakitic and Fe-bearing components, accompanied by parallel increase in enstatitic components, can be visualized.

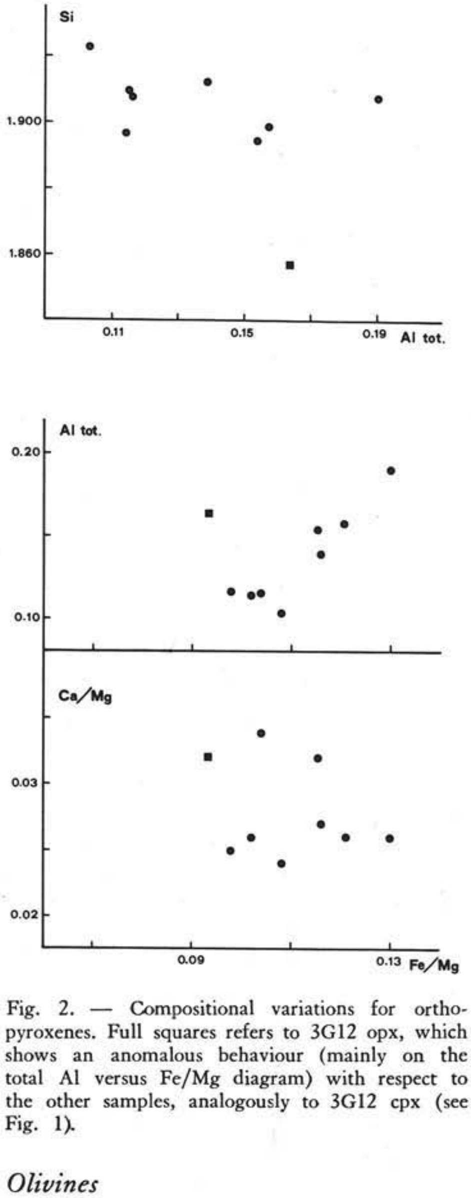

Fig. 2. — Compositional variations for orthopyroxenes. Full squares refers to 3G12 opx, which shows an anomalous behaviour (mainly on the total Al versus Fe/Mg diagram) with respect to the other samples, analogously to 3G12 cpx (see Fig. 1).

Olivines

Based on four oxigens, cation totals average 3.029 ($\sigma = 0.029$), close to the stoichiometric value 3.000. There are only little deficiencies of silicon (mean value 0.971, $\sigma = 0.020$) and excesses of six-fold coordinated cations, being 2.058 ($\sigma = 0.040$) the mean value of Σ (Fe + Mg + Ni).

The Fa contents of the analyzed olivines show a relatively narrow range of variation (7.89 - 11.61), the mean values being 9.13 ($\sigma = 1.23$). The Ni contents range from 0.005 to 0.010 (mean value 0.007, $\sigma = 0.002$), in good agreement with contents shown by olivines from mantle materials.

Spinels

When recalculated on the basis of four oxigens, assuming spinel stoichiometry and no cation omissions, the spinel compositions show a remarkable homogeneity in the Mg (range 0.702 - 0.755, mean value 0.729, $\sigma = 0.019$) and Fe^{2+} (range 0.245 - 0.295, mean value 0.270, $\sigma = 0.018$) contents. Cr and Al contents exhibit a significant nearly reciprocal variation, their range being 0.337 - 0.526 and 1.565 - 1.390, respectively. Accordingly, the Cr/Cr + Al ratios vary over the range 0.177 - 0.276 (mean value 0.206, $\sigma = 0.038$), with only a relatively small variation in the $Mg/Mg+Fe^{2+}$ ratio (range 0.704 - 0.755, mean value 0.729, $\sigma = 0.018$) (fig. 3).

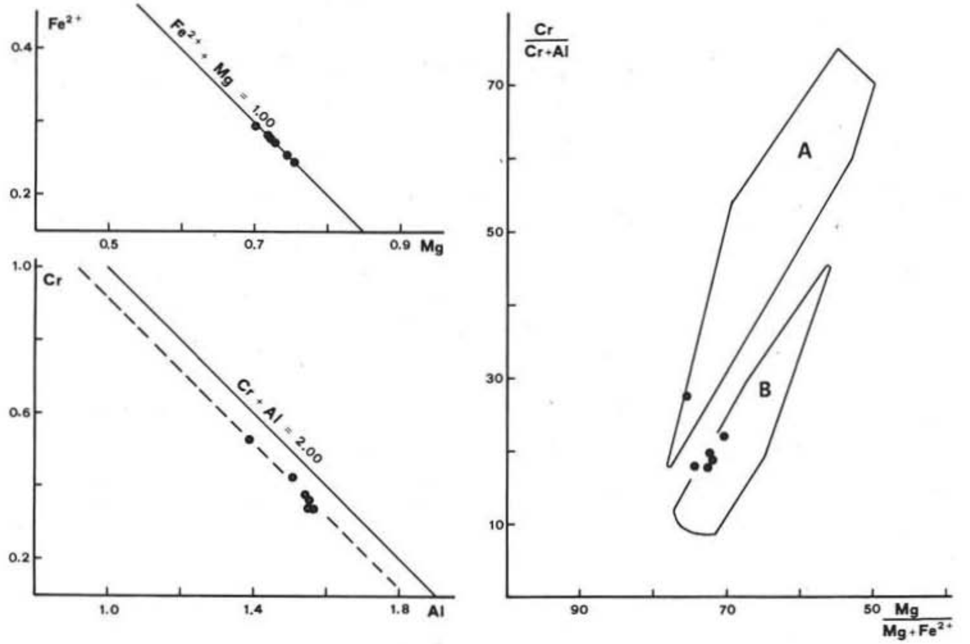

Fig. 3. — Atomic proportions of Fe^{2+} versus Mg (Fig. 3-I) and Cr versus Al (Fig. 3-II) for the analyzed spinels. The lines in I and II define solid solutions for which $Mg + Fe^{2+} = 1.00$ and $Al + Cr = 2.00$, respectively: the dashed line in II indicates the mean value 1.912 of (Al + Cr) for our analyzed samples. In Fig. 3-III the analyzed samples are plotted on the $Cr/Cr+Fe^{2+}$ diagram. Fields A and B refer, respectively, to spinel compositional variations for alpine peridotites of the Klamath Mountains (Dick, 1977) and of the Western Alps and Northern Apennines (Piccardo, 1976; Ernst, 1978; Ernst and Piccardo, 1978, in press).

The Fe^{3+} values show a significant range of variation, 0.062 - 0.112, without having sure correlations to the other chemical parameters, but a dubitative negative correlation with the Cr/Al ratio.

Owing to the relatively homogeneous $Mg/Mg+Fe^{2+}$ values, no clear co-variance can be recognized with the Cr/Cr + Al ratio: only disregarding sample 3G18, a rough negative correlation seems to exist (see fig. 3-III) between the two chemical parameters, indicating that the small compositional variation could be mainly due to opposite parallel variations of the $MgAl_2O_4$ and $FeCr_2O_4$ components.

TABLE 4

Major element chemistry of olivines from spinel peridotite xenoliths of the Assab Range (Ethiopia)

	3G9	3G12	3G15	3G16	3G17	3G18	3G19	3G28	3G51
SiO_2	39.85	38.40	40.51	40.00	40.00	38.90	38.80	39.90	38.83
MgO	51.00	52.17	47.96	52.17	47.55	52.21	51.82	50.64	52.10
FeO tot.	8.43	8.94	10.24	8.91	11.11	8.25	8.61	9.25	7.97
NiO	0.38	0.40	0.30	0.28	0.46	0.32	0.48	0.31	0.42
Total	99.66	99.91	99.01	101.36	99.12	99.68	99.71	100.10	99.32
Si	0.977	0.946	1.005	0.967	0.997	0.956	0.956	0.978	0.957
Mg	1.865	1.916	1.773	1.880	1.766	1.912	1.902	1.849	1.914
Fe^{2+}	0.173	0.184	0.212	0.180	0.232	0.170	0.177	0.190	0.164
Ni	0.007	0.008	0.006	0.005	0.009	0.006	0.010	0.006	0.008
Total	3.022	3.054	2.996	3.032	3.004	3.044	3.045	3.023	3.043

TABLE 5

Major element chemistry of spinels from spinel peridotite xenoliths of the Assab Range (Ethiopia)

	3G12	3G15	3G16	3G18	3G28	3G51
Al_2O_3	47.43	48.84	48.93	42.54	48.00	49.80
Cr_2O_3	20.00	16.81	15.90	24.01	17.51	16.00
Fe_2O_3	3.06	4.30	5.55	4.01	4.28	4.86
FeO	13.05	12.41	11.32	10.58	12.15	12.22
MgO	17.51	17.90	18.62	18.27	17.89	18.31
Total	101.05	100.26	100.32	99.41	99.83	101.19
Al	1.510	1.554	1.550	1.390	1.537	1.565
Cr_{3+}	0.427	0.359	0.338	0.526	0.376	0.337
Fe_{2+}	0.062	0.087	0.112	0.084	0.087	0.098
Fe^{2+}	0.295	0.280	0.254	0.245	0.276	0.273
Mg	0.702	0.720	0.746	0.755	0.724	0.728
Total	2.996	3.000	3.000	3.000	3.000	3.001

Major element partitioning

After the pioneering paper on element partitioning between coexisting phases by RAMBERG and DE VORE (1951), numerous workers dealt with experimental and theoretical aspects of element fractionation as a way for investigating crystallization conditions of natural assemblages (see: SAXENA, 1973, for main references).

Prior to discussing the main characteristics of major element partitioning in our analyzed samples, let us briefly recall few fundamental statements, particularly considering the simple partition reaction involving exchange of two components (A and B) between two coexisting phases (I and II) (as recently summarized by ERNST, 1976). Such a reaction may be written as

$$1A_I + mB_{II} = 1B_I + mA_{II} \qquad (1)$$

(where 1 and m are the exchanged moles of ions), or as

$$A_I + nB_{II} = B_I + nA_{II} \qquad (2)$$

(dividing by l and letting m/l = n), and it is related to the Gibbs free energy change (ΔG) by means of the Van't Hoff equation, in the form

$$\Delta G = \Delta G^\circ + RT\ln\,(a_B/a_A)_I\,(a_A/a_B)^n_{II} \qquad (3)$$

(where a indicates element activity), or in the form

$$\Delta G = \Delta G^\circ + RT\ln\,(X_B/X_A)_I\,(X_A/X_B)^n_{II} \qquad (4)$$

(where X_A and X_B are mole fractions), if the activity coefficients are of unit value as for ideal solutions.

At equilibrium conditions ($\Delta G = 0$)

$$-\frac{\Delta G^\circ}{RT} = \ln\,(X_B/X_A)_I\,(X_A/X_B)^n_{II} = \ln K_D \qquad (5)$$

Regarding the temperature and pressure influence on the distribution coefficient, it appears evident from the enthalpy change (ΔH°) and the volume change (ΔV°) of the reaction (differentiating with respect to T and P) that the K_D variation with T should be smaller at higher temperatures, where K_D will more closely approach unity: on the contrary, K_D does not appear to be significantly affected by pressure variation.

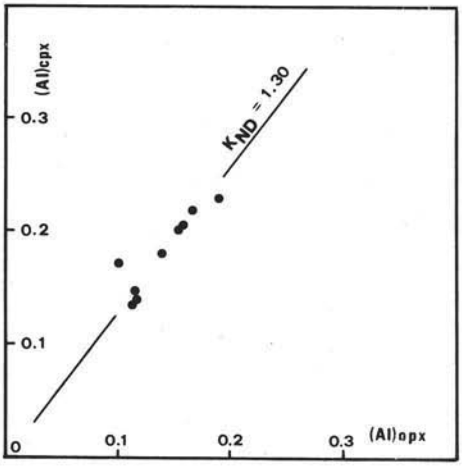

Fig. 4. — Total Al co-variance in the different pyroxene pairs. The Al_{cpx}/Al_{opx} mean value is expressed as mean Nernst distribution coefficient (K_{ND}), even if Al appears to be too concentrated for Nernst infinite dilution.

Finally, it must be mentioned that the K_D values for crystallochemically complex silicates possessing different structural sites for the exchangeable cations, strongly depend on sublattice distributions and, moreover, that the treatment of element partitioning among coexisting complex natural solid solutions suffers for the simple assumption of ideal, ion-for-ion, exchange behaviour.

Regarding the analyzed Assab Range mantle xenoliths, their bulk rock and constituent mineral chemistries generally range over relatively narrow limits: accordingly, hereafter we'll simply discuss distributions of those elements (i.e. Fe, Mg, Cr, Al) which show clear relationships and systematic variations, disregarding less convincing correlations among other chemical variables.

Firstly, before analyzing Fe/Mg and Cr/Al partitioning among the suitable mineral pairs, let us emphasize the well defined positive correlation between the total Al contents of the coexisting pyroxene pairs (fig. 4), accompanied by less evident parallel variations for both spinel-clinopyroxene and spinel-orthopyroxene pairs.

Fe and Mg partitioning

Fe^{2+} and Mg partitioning among coexisting olivine and orthopyroxene, firstly theoretically discussed by RAMBERG and DE VORE (1951) and MUELLER (1964), have been demonstrated by experimental investigations (i.e. LARIMER, 1968; MEDARIS, 1969) to be not significantly sensitive to temperature effects in the range 800-1300° C and, accordingly, not useful for geothermometry.

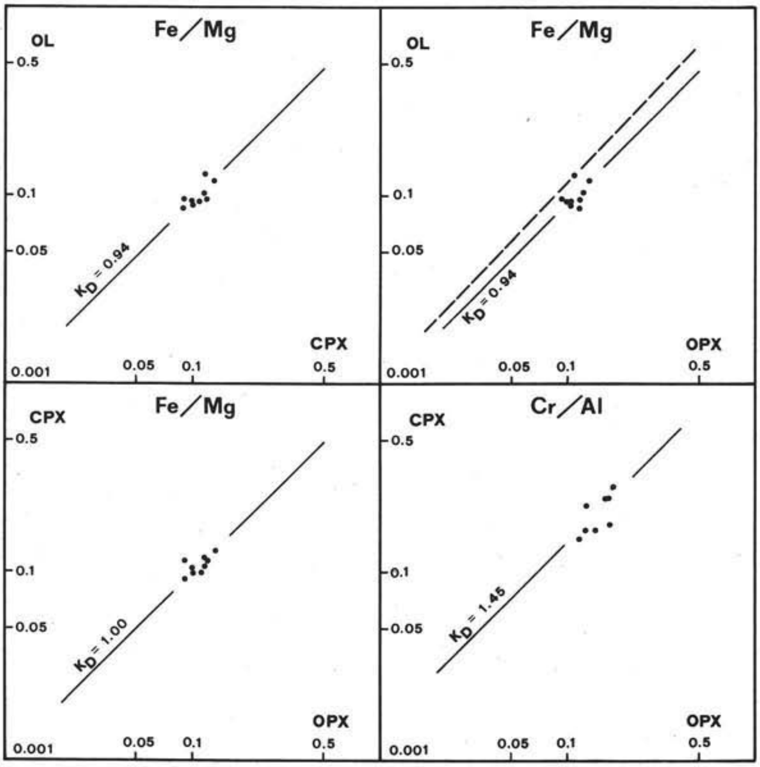

Fig. 5. — Fe/Mg and Cr/Al partitioning among suitable mineral pairs from the analyzed xenoliths. Lines representing the K_D mean values are also reported (see text for discussion). The dashed line on the ol-opx diagram represents the 1100-1300° C experimental partitioning curve by LARIMER (1968).

The range 0.748 - 1.213 (mean value 0.941, $\sigma = 0.145$) in the K_D values obtained from our analyzed ol-opx pairs is greater than the restricted range (1.06 - 1.21), experimentally determined by LARIMER (1968), and the representative points of our samples (as shown in fig. 5) fall below the experimental distribution curve.

The departure from the experimental partitioning of the K_D values for ol-opx pairs from ultramafic xenoliths (as discussed by MEDARIS, 1969) can be imputed to introduction of alumina in natural orthopyroxene solid solutions rather than to disequilibrium. This seems to be the case, even if a clear correlation does not exist between K_D and Al content of the orthopyroxenes.

Fe^{2+} and Mg fractionation between coexisting pyroxene pairs has been firstly discussed by KRETZ (1961, 1963) and BARTHOLOMÉ (1961, 1963), who recognized that different K_D values are shown by magmatic (K_D range 0.65 - 0.86) and metamorphic (K_D range 0.51 - 0.65) pyroxene pairs, whereas K_D values for pyroxene pairs from ultramafic xenoliths in basalts are generally remarkably higher. In the hypothesis of ideal solid solutions, Fe-Mg partitioning has been utilized by these Authors in order to evaluate temperature of equilibration.

The calculated cpx-opx K_D values for our analyzed pyroxene pairs (utilizing the total Fe as divalent) range over rather narrow limits (0.940 - 1.112, disregarding the anomalous value 0.774 of sample 3G51), approaching unity and averaging 0.984 ($\sigma = 0.097$) (see fig. 5). These homogeneous K_D values testify for relatively uniform conditions of equilibration for all the analyzed pyroxene pairs.

It must be mentioned that, besides the quite similar distributions, the different pyroxene pairs show a certain range of variation in their Fe/Mg ratios, obviously for both clino- and orthopyroxenes, and positively related, going from relatively Fe-richer pairs (i.e. 3G15 and 3G28) to relatively Fe-poorer pairs (i.e. 3G9 and 3G19).

The distribution of Fe and Mg between olivine-clinopyroxene pairs show rather similar K_D values, ranging from 0.800 to 1.120 (mean value 0.939, $\sigma = 0.099$), confirming relatively uniform conditions of equilibration (fig. 5). Moreover, similarly to the co-variance of the Fe/Mg ratio for cpx and opx, a concordant small range of variation is also shown by the Fe/Mg ratios of the olivine-clinopyroxene pairs, from relatively more Fe-rich pairs (i.e. 3G15 and 3G28) to relatively more Fe-poor pairs (i.e. 3G9 and 3G19).

Fe-Mg partitioning among coexisting ol-cpx pairs has been recently calibrated as a geothermometer (POWELL and POWELL, 1974): the proposed formula is not used hereafter, since the elemental partitioning among coexisting pyroxene pairs seems, at present, a more reliable approach to geothermometric measurements on natural assemblages (see next section).

Not very different K_D values are shown by the Fe-Mg fractionation among olivine-spinel pairs, ranging from 0.229 to 0.308 (mean value 0.265, $\sigma = 0.031$).

The element partitioning between coexisting ol-sp pairs, firstly investigated by IRVINE (1965, 1967), has been subsequently utilized by JACKSON (1969) and MEDARIS (1975) in the attempt of evaluating temperatures of equilibration for natural assemblages, and it has been recently calibrated (EVANS and FROST, 1975; STROH, 1976) by using temperature estimates from natural mineral assemblages. Such a thermometric method is so far generally considered not sufficiently calibrated for geothermometry (see: STROH, 1976) and less reliable with respect to the pyroxene thermometry: accordingly, it has not here been used for this purpose.

Fe/Mg K_D values for clinopyroxene-spinel and orthopyroxene-spinel pairs are quite similar, the mean values being 0.310 ($\sigma = 0.050$) and 0.306 ($\sigma = 0.045$), respectively, testifying for a strong relative iron enrichment in the spinel phase and relatively narrow limits of equilibration conditions.

Cr and Al partitioning

Cr and Al fractionation between coexisting spinel-clinopyroxene and spinel-orthopyroxene pairs (as Cr/Al ratios) from our xenoliths, on the whole, do not allow any important conclusion, but a relatively uniform distribution. In fact (disregarding 3G18 K_D, which shows quite different values with respect to the other analyzed pairs), sp-cpx K_D range from 0.893 to 1.665 (mean value 1.289, $\sigma = 0.350$) and sp-opx K_D range from 1.380 to 2.320 (mean value 1.838, $\sigma = 0.347$).

Considering Cr-Al fractionation between clino- and orthopyroxenes, concordant partitioning is shown by the different pairs, with a slight disproportionation in favour of the Ca-rich phase, the K_D averaging 1.453 ($\sigma = 0.249$). A well defined correlation exists among the Cr/Al ratios of the coexisting pyroxene pairs, varying from relatively Al-richer pairs (i.e. 3G15 and 3G28) to relatively Al-poorer pairs (i.e. 3G9 and 3G19).

Pyroxene thermometry

The elemental partitioning among coexisting pyroxene pairs have been experimentally and theoretically investigated by several Authors (Davis and Boyd, 1966; Wood and Banno, 1973; Warner and Luth, 1974; Saxena and Nehru, 1975; Mysen and Boettcher, 1975 a and b; Mysen, 1976; Lindsley and Dixon, 1976; Wells, 1977; and many others) in order to evaluate the temperature conditions of equilibration for natural assemblages.

Firstly, experimental data on the Di-En solvus have been empirically applied to natural Fe-Al-poor pyroxene pairs by Davis and Boyd (1966), which recognized that the $Ca/Ca+Mg+Fe^{2+}$ ratio in clinopyroxene solid solution, coexisting with $Mg_2Si_2O_6$-rich orthopyroxene, is a function of temperature, since this solvus limb appears practically insensitive to pressure.

Later on, Wood and Banno (1973), starting from the solvus data by Davis and Boyd (1966), introduced a correction procedure which adapts binary Di-En relations to multicomponent system behaviour, using an ideal two-sites solution model and correcting the activities of $Mg_2Si_2O_6$ in both opx and cpx phases for concentrations of cations other than Ca and Mg, according to the formula:

$$T = \frac{-10202}{\ln\left(\frac{a^{cpx}_{Mg_2Si_2O_6}}{a^{opx}_{Mg_2Si_2O_6}}\right) - 7.65X^{opx}_{Fe} + 3.88(X^{opx}_{Fe})^2 - 4.6} \qquad (6)$$

where

$$a^{cpx}_{Mg_2Si_2O_6} = (X^{M1}_{Mg} \cdot X^{M2}_{Mg})_{cpx} \qquad (7,1)$$

$$a^{opx}_{Mg_2Si_2O_6} = (X^{M1}_{Mg} \cdot X^{M2}_{Mg})_{opx} \qquad (7,2)$$

and X's are molar fractions, assuming

$$\left(\frac{Mg}{Mg + Fe^{2+}}\right)_{M1} = \left(\frac{Mg}{Mg + Fe^{2+}}\right)_{M2} = \left(\frac{Mg}{Mg + Fe^{2+}}\right)_{mineral} \qquad (8)$$

Subsequently, new experimental data by dissolution and reversed runs have been performed (i.e. Nehru and Wyllie, 1974; Mori and Green, 1975, 1976; Mysen and Boettcher, 1975 a and b; Mysen, 1976; Lindsley and Dixon, 1976) on this solvus.

Nehru and Wyllie experimentals, together with a simple mixing model for the pyroxenes solid solutions, were utilized by Saxena and Nehru (1975) for deriving the following semi-empirical formula, applyable to natural Al-Fe-bearing pyroxene pairs:

$$Ka = \frac{X^{M1}_{Mg-cpx} \cdot X^{M2}_{Mg-cpx} \cdot \exp\left[\frac{6531}{RT} \cdot X^{M2}_{Ca-cpx} \cdot (X^{M2}_{Ca-cpx} + X^{M2}_{Fe-cpx})\right]}{X^{M1}_{Mg-opx} \cdot X^{M2}_{Mg-opx} \cdot \exp\left[\frac{7184}{RT} \cdot X^{M2}_{Ca-opx} \cdot (X^{M2}_{Ca-opx} + X^{M2}_{Fe-opx})\right]} \qquad (9)$$

where X's are molar fractions and T (in °K) is the pyroxenes crystallization temperature, provided that the $-RT \ln K_a = 500$ is satisfied.

The Mysen and Boettcher (1975 a and b) and Mysen (1976) experimental data on natural lherzolitic materials duplicated the Davis and Boyd (1966) results, confirming the pressure-indipendent nature of the diopside limb, after correction for the presence of Ca-Tschermak components.

On the other hand, Lindsley and Dixon (1976), after investigations by reversed runs on the synthetic binary Mg_2-Si_2O_6-$CaMgSi_2O_6$ system under different pressure conditions, pointed out that increasing pressure is accompanied by rising temperature on the diopside limb, and that sensible differences exist at high temperatures with respect to the Davis and Boyd data. In order to utilize the solvus data of Lindsley and Dixon (1976) a provisional assignement of the confining pressure is required.

Following a recent contribution (Ernst and Piccardo, 1979, in press), hereafter we utilize as geothermometric function the partitioning of Mg and Ca between coexisting pyroxene pairs employing the experimental determination of the Di-En miscibility gap at 15 kb total pressure by Lindsley and Dixon (1976, fig. 1, pg. 1292).

According to the scheme proposed by Wood and Banno (1973) for assignement of site occupancies (e.g. Ca on M_2 sites for both cpx and opx), M_2 structural sites are involved and the exchange reaction may be written:

$$(M2)Mg^{opx} + (M2)Ca^{cpx} = (M2)Ca^{opx} + (M2)Mg^{cpx} \qquad (10)$$

and the equilibrium constant $K_D^{(M_2)}$

$$\ln K_D^{(M2)} = \ln\left(\frac{a^{cpx}_{Mg}}{a^{opx}_{Mg}}\right)\left(\frac{a^{opx}_{Ca}}{a^{cpx}_{Ca}}\right) = \Delta G°/RT \qquad (11)$$

Since phase equilibrium data and mineral analyses are available in terms of mole fractions, utilizing mole fractions quotients (rather than activity quotients) extrapolated by the Lindsley and Dixon experimentals, the plot of their natural logarithms versus the reciprocal of the absolute temperature defines a slightly curved line (see: Ernst and Piccardo, 1979, in press, fig. 7 *a*), instead of the theoretical straight line, reflecting the non-ideality of this system.

In order to evaluate equilibration temperatures for our analyzed samples, Ca and Mg activities for both cpx and opx have been calculated according to the scheme proposed by Wood and Banno (1973), corrected for the presence of other cations, but leaving the activity quotients only in terms of M_2 site populations (see: Ernst and Piccardo, 1979, in press, for more details).

Table 6

Nominal temperatures of equilibration for cpx-opx pairs of the Assab spinel peridotite xenoliths calculated with the method proposed by Ernst and Piccardo (1979, in press), *together with values obtained by the* Wood and Banno (1973) (*WB*) *and* Saxena and Nehru (1975) (*SN*) *methods*

Sample	Temperatures in °C		
		(W.B.)	(S.N.)
3G9	1170	1135	1102
3G12	1164	1144	1107
3G15	1118	1099	1178
3G16	1099	1113	1108
3G17	1048	1015	1037
3G18	1131	1111	1060
3G19	1104	1088	1107
3G28	1112	1082	1120
3G51	1128	1082	1105
Average	1119	1097	1103
Std.deviation	$1\sigma=36$	$1\sigma=38$	$1\sigma=39$

The nominal temperature values obtained in such a way, together with the temperature estimates by the Wood and Banno (1973) and the Saxena and Nehru (1975) methods (see tab. 6) show narrow ranges of variation, differences among the values obtained with the same method being confined within 10 %.

It must be concluded that the mantle tectonite xenoliths so far analyzed from the Assab Region have undergone complete equilibrium subsolidus crystallization under remarkably similar temperature conditions. Regarding the temperature absolute values of such equilibration, the mean values of the nominal temperatures obtained using the quoted methods show an excellent agreement at about 1100° C.

Geobarometry

Methods for evaluating pressure conditions of equilibration have been developed in recent years (i.e. O'Hara, 1967; MacGregor, 1974; Wood, 1974; Akella, 1976; Herzberg and Chapman, 1976; Stroh, 1976) by utilizing experimental results on the Al contents of ortho- and clinopyroxenes in equilibrium with pyrope-rich garnet, spinel or plagioclase, using synthetic and natural peridotite compositions.

Particularly for the spinel peridotite field, based on experimental data on the ternary MgO-Al_2O_3-SiO_2 system, MacGregor (1974) emphasized that the Al content of opx in equilibrium with $MgAl_2O_4$ spinel markedly increases with increasing temperature and decreasing pressure, resulting in Al_2O_{3opx} isopleths with positive P-T slope, similar to the isopleth trending in the garnet stability field.

The methods for evaluating pressure (i.e. MacGregor, 1974; Stroh, 1976) based on MacGregor's experimentals seem actually not useful for geobarometry, since more recent experimental data (see data and discussions in: Wood, 1975; Obata, 1976; Herzberg and Chapman, 1976; Presnall, 1976), in contrast with MacGregor's results, all have demonstrated that the pressure effects on Al_2O_3 solubility in pyroxenes coexisting with spinel is much more temperature than pressure dependent, the Al_2O_3 isopleths being more or less parallel to the pressure axis and the solubility increasing with increasing temperature.

Knowing the nominal temperature of equilibration, pressure limits may be roughly evaluated from the experimentally determined petrogenetic grids for aluminous lherzolite bulk compositions (i.e. Willie, 1970; Green and Ringwood, 1970): at equilibrium temperatures of 1100° C (as for our analyzed samples), two pyroxenes spinel-bearing assemblages are stable between 9-10 and 21-22 kb.

It must be concluded that the analyzed xenoliths testify for a mantle section which underwent a complete subsolidus equilibration at about 1100° C and 15 ± 6 kb.

Rare earth element composition and partitioning

As it has been previously described (see: Ottonello et al., 1978 a and b), the Assab spinel peridotites so far analyzed for rare earth elements (REE) display a LREE enrichment relative to chondrites, while depletion in HREE are observed.

It is at present well known that the LREE over HREE enrichments shown by residual spinel peridotite xenoliths is a common feature of this assemblage (see: Nagasawa et al., 1969; Frey et al., 1971; Reid and Frey, 1971; Philpotts et al., 1972; Frey and Green, 1974). Some Authors consider this feature contrasting with the residual character of these rocks, mainly on the basis of argumentations concerning the more or less « incompatible » character of the different rare earth elements. However, as it will be briefly discussed hereafter, these argumentations seem to be not compelling.

Moreover, the measured REE concentrations in the Assab xenoliths (see data in: Ottonello et al., 1978 a and b; Ottonello, in prep.) exhibit good concordance with the results of mass balance calculation involving REE compositions of single phases in the different samples (Ottonello, in prep.). This observation indicates that the measured REE fractionation in the materials under consideration is a typical feature of this assemblage and cannot be ascribed to contamination from the host magma.

Regarding the constituent mineral compositions, clinopyroxenes show chondrite-normalized REE patterns widely variable both in shape and absolute REE contents,

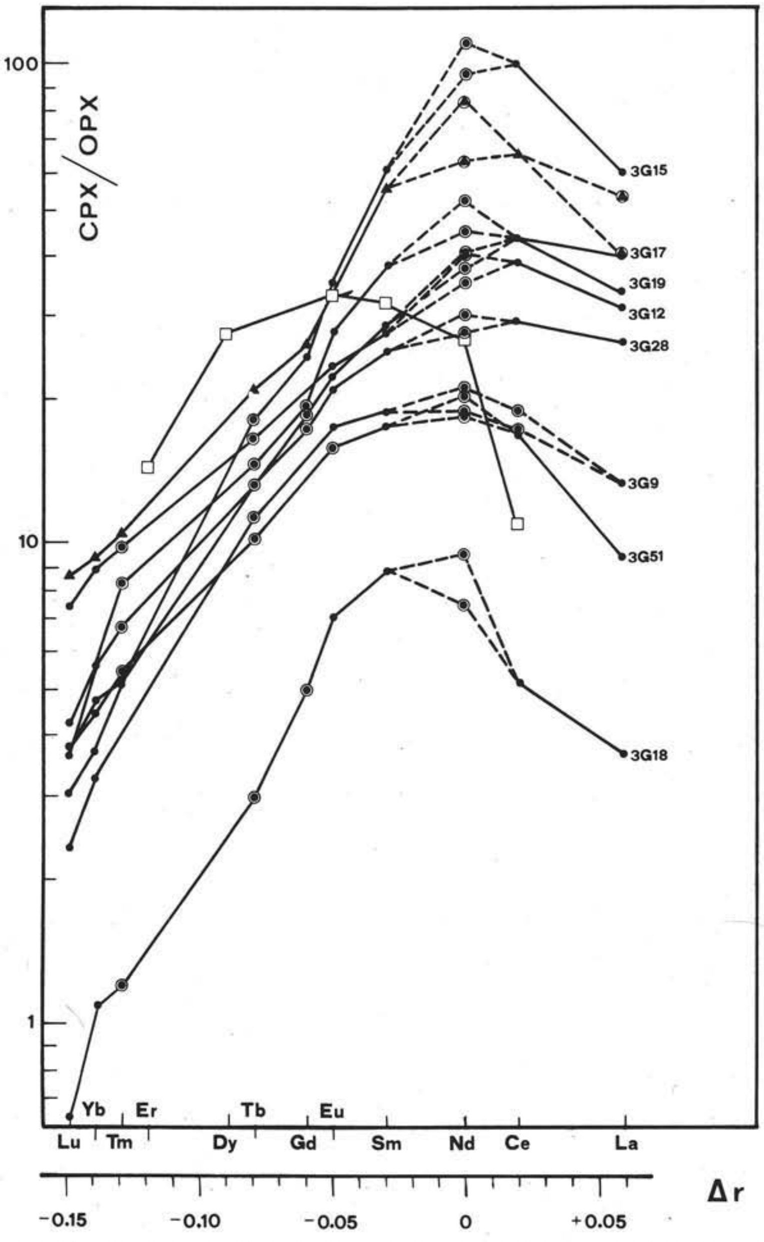

Fig. 6. — Cpx/opx REE partitioning versus differences in the ionic radii of single REE relative to Ca in VIII-fold coordination with oxigen (for value on the abscissa axis) (after Ottonello et al., 1978b, modified). Areas comprised between dashed lines reflect uncertainty in the Nd value for opx. Data from Onuma et al. (1968) (solid triangles) and from Philpotts et al. (1972) (open squares) are reported for comparison. (●) (▲) = extrapolated values.

which range over about one order of magnitude, orthopyroxenes exhibit a more restricted range in their REE concentrations and have weakly U-shape profiles (with a negative La/Lu fractionation) (Ottonello et al., 1978 b).

Olivines display quite irregular REE patterns: this feature may be imputed to the fact that REE do not occupy definite positions in the olivine crystal lattice but, more probably, occur as clusters or aggregates (Morris, 1975; Ottonello, in prep.).

Spinels exhibit a strong LREE/HREE fractionation, and most of the analyzed samples have higher LREE contents with respect to chondrites. Either positive and negative Eu anomalies can be visualized in the spinel patterns (Ottonello, in prep.).

The main features of REE partitioning between coexisting pyroxene pairs from the analyzed samples are visualized in fig. 6 (from Ottonello et al., 1978 b, modified), where cpx/opx REE concentration ratios are plotted versus the difference between the Ca ionic radius value in VIII-fold coordination (selected as optimum site dimension for M_2 site in clinopyroxenes) and REE ionic radius values in VIII-fold coordination with oxygen. The partition patterns drawn in fig. 6 consist of two branches departing from an inflection point located at Nd or Ce (which ionic radii in VIII-fold coordination are almost equal to that one of Ca).

Taking into account the structural effects of the two phases and applying the Iiyama's (1974) theory on local lattice deformation, Ottonello et alii (1978 b), have shown that the patterns of REE activity ratios between the two phases exhibit constant features for the investigated pyroxene pairs with maxima of activity ratios located at Ce.

The variability in the activity ratio for a same rare earth element in different pyroxene pairs has been imputed by Ottonello et alii (1978 b) to coupled substitutions involving Al in Z positions and REE in M_2 positions in the cpx phase. This inference is supported by the existence of a clear correlation between the ratio of the total REE content in the two phases and their silica ratio at given Ca values in clinopyroxene (see fig. 7, from Ottonello et al., 1978 b). This correlation can be in fact imputed to analogy of substitution of an hypothetical $Tr^{3+}R^{3+}Al_2O_6$ component and a Ca-Tschermak component in the cpx phase (see: Ottonello et al., 1978 b, for more detailed discussion).

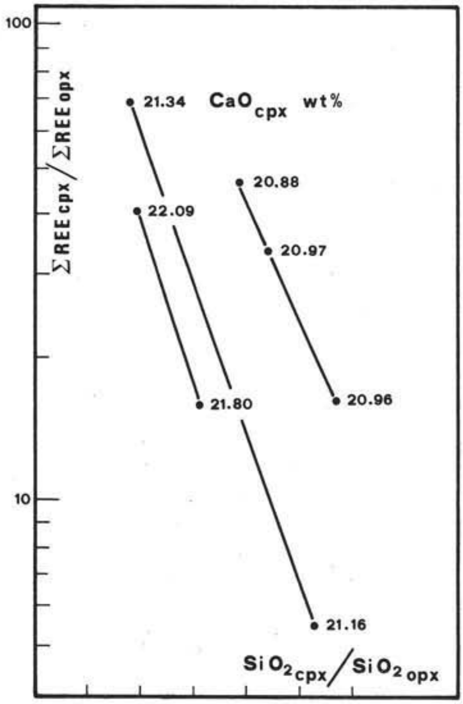

Fig. 7. — REE concentration ratios versus silica ratios for the analyzed pyroxene pairs: CaO isopleths in clinopyroxenes are also reported (after Ottonello et al., 1978 b).

The above argumentations imply the recognition of composition dependence effects on the REE distribution between cpx and the coexisting solid phases. In summary, the REE partitioning picture in the solid assemblages under consideration appears quite complex: however, the evolution of partition values can be correlated with parameters which are generally believed to be indicative of the residual character of the whole assemblage and, moreover, crude correlations can be visualized with the major element compositional trending, as described in the former section. As an example, the two pairs of samples (3G15 - 3G28 and 3G9 - 3G19, respectively), previously taken as indicative of slightly different stages of depletion (the former ones indicating less depleted lithotypes), on the basis of major element compositions, in a concordant way plot along different trends on the diagram of fig. 7.

This should allow the modellization of partial melting events operating on these materials provided a sufficient knowledge on P, T and compositional effects on REE activities in the liquid phase. Unfortunately, little is known on this subject and some thermodynamic considerations suggest great care in formulating oversimplified assumptions.

It has been shown recently (Fraser, 1975) that the ionic concepts on the nature of silicate liquids, expressed by Toop and Samis (1962 a and b), can be improved taking better into account the real complexities of their structure and explaining the behaviour of altervalent trace elements (Morris and Haskin, 1974; Paul and Douglas, 1965).

According to Fraser (1975), three types of matrices can be envisaged in the silicate liquid: the cation and the anion matrices, as already described by Toop and Samis (1962 a and b) and Masson (1968) deriving the Temkin's (1946) approximation for ionic solutions, and the structon matrix, which is defined by the atoms which form the centers of polyanions or « structons ». The importance of this third set of sites is evident when it is considered that REE could dissociate in the silicate liquid according to two different reaction schemes:

$$Ln_2O_3\,{}_{(liquid)} \rightleftarrows 2Ln^{3+}_{(liq.)} + 3O^{2-}_{(liq.)} \qquad (12)$$

or

$$Ln_2O_3\,{}_{(liq.)} + O^{2-}_{(liq.)} \rightleftarrows 2LnO_2^-\,{}_{(liq.)} \qquad (13)$$

where in reaction (12) Ln_2O_3 is seen as a basic oxide (Ln = lanthanides) and in reaction (13) as an acidic oxide. At equilibrium, two constants for reactions (12) and (13) can be described as:

$$Kb = \frac{a^2_{Ln^{3+}} \cdot a^3_{O^{2-}}}{a_{Ln_2O_3}} \qquad (14,1) \qquad\qquad Ka = \frac{a^2_{LnO_2^-}}{a_{Ln_2O_3} \cdot a_{O^{2-}}} \qquad (14,2)$$

where a represents activity and K_b and K_a are the constants for basic and acidic dissociation, respectively.

From expressions (14-I) and (14-II) it can be derived the activity ratio between species Ln^{3+} and LnO_2^-:

$$\frac{a_{LnO_2^-}}{a_{Ln^{3+}}} = a^2_{O^{2-}} \sqrt{\frac{Ka}{Kb}} \qquad (15)$$

Assuming ideal mixing (TEMKIN, 1946) of Ln^{3+} in the cation matrix and of LnO_2^- in the structon matrix, i.e.:

$$a_{Ln^{3+}} = \frac{nLn^{3+}}{\Sigma n \text{ cations}} \qquad (16,1) \qquad\qquad a_{LnO_2^-} = \frac{nLnO_{2-}}{\Sigma n \text{ structons}} \qquad (16,2)$$

and expressing the total content of Ln^3 as:

$$nLn^{III}_{total} = nLn^{3+} + nLnO_2^- \qquad (17)$$

FRASER (1975) derived a general expression for the activity of trace elements with amphotheric behaviour in the liquid:

$$a^{liquid}_{Ln} = \left[\frac{\alpha nLn^{3+}}{n \text{ cations}} \cdot \frac{(1-\alpha)nLnO_2^-}{n \text{ structons}}\right]^{\frac{1}{2}} \qquad (18)$$

(equation 25 of FRASER, 1975). Equation (18) says that the activity of Ln^3 in the liquid is dependent on the relative proportions α and $(1\text{-}\alpha)$ of Ln^{3+} and LnO_2^- in the cation and structon matrices, respectively, while equation (15) describes the relative activities of the Ln^{3+} and LnO_2^- species as a function of $a^2_{O^{2-}}$ and the square root of the K_a/K_b ratio.

Activity of O^{2+} in magmas of complex composition depends on the nature and relative concentrations of metal oxides and on the degree of polymerization of functional groups SiO_4^{4-}, wich in turn depend on silica content for a given liquid (cf. TOOP and SAMIS, 1962 a and b; HESS, 1971; FRASER, 1975).

For a given Σn cations/Σn structons ratio in a silicate liquid, equation (18) predicts that the activity of a trace element with amphotheric behaviour will depend on its relative proportions as ion and structon. Equation (15) indicates that $n\alpha$ and $n(1-\alpha)$ proportions are influenced by $a_{O^{2-}}$. Magma composition will thus affect the activities of the trace elements with amphotheric behaviour and, generally, an increase of $a_{O^{2-}}$ will result in divergency of the activity values of the two species, which will tend to decrease and increase, respectively.

Effects of $a_{O^{2-}}$ on these values will be different for different trace elements and the divergency will be more pronounced for elements whose oxides have a better defined basic or acidic behaviour, than for elements with intermediate character.

Variations of K_a and K_b can be expected ranging from La to Lu: these variations should likely results in an increase of the K_a/K_b ratio through the REE series. Unfortunately, to our knowledge, no quantitative data are at present available concerning these values, thus calculations of REE's activities in melts of different composition cannot be performed.

Nevertheless, it is evident from the above argumentations that great care is needed in defining the character of these elements during magmatic processes involving liquid and solid phases of changing composition. For instance, owing to present day lack of experimental and theoretical data, we do not believe that it is at present possible to state unambiguously that LREE are more easily stabilized than HREE in the liquid phase. This assumption, however, has been made by several Authors and has lead to built-in deductions about the nature of residual materials which, at least in some cases, contrast with the natural evidences.

Discussion

When major element compositions and elemental partitioning among coexisting mineral pairs are considered, it can be concluded that the whole assemblages of the different analyzed samples have been equilibrated under relatively uniform conditions: such equilibration partly tends to mask the effects of whatever process the rocks had undergone prior to that event.

However, as it has been shown in the previous sections, more or less regular variations in some chemical parameters are recognizable within the compositions of the different mineral phases, mainly for clino- and orthopyroxenes, and, moreover, co-variances of several chemical parameters between different mineral pairs are still recognizeable.

Summing up the data discussed in previous sections, it can be emphasized that clino- and orthopyroxenes show progressive decreases of their Ca-Tschermakitic and Fe-bearing components, and olivine compositions vary from Fa 7.89 to Fa 11.61, whereas spinels only show small parallel variations in their $MgAl_2O_4$ and $FeCr_2O_4$ components.

The elemental partitioning among different mineral pairs indicates that well defined positive correlations exist for the main compositional parameters (i.e. Fe/Mg and Cr/Al ratios) among different mineral pairs. Considering in particular the variations of the Fe/Mg and Cr/Al ratios (as well as the Al absolute values) for the different pyroxene pairs, the parallel decrease of the Fe/Mg ratio in both phases appears to be accompanied by increase in the Cr/Al ratio (and lowering in the total Al content).

Disregarding less convincing correlations, it can be concluded that all the silicate phases show trends of parallel variations towards more Mg-rich compositions, accompanied by decrease in the Ca-Tschermak component for both clino- and orthopyroxenes.

We must here recall that the analyzed xenoliths, which show on the whole an harzburgitic composition (cpx being generally confined to few percents in volume), are lower in TiO_2, Al_2O_3, CaO, Na_2O and K_2O, and higher in MgO, than primitive upper mantle estimated compositions (see: WYLLIE, 1971; MAALOE and AOKI, 1977), suggesting a residual character after a partial melting process.

We believe that the outlined compositional trends can be easily recognized as effects of that partial melting event on the constituent minerals, resulting in the depleted character of the whole rock.

To this purpose, let us briefly discuss some points concerning present day knowledges on partial melting of mantle material, particularly for the effects on the residual mineral concentrations and compositions.

On the whole, it must be outlined that, even if so many experiments have been developed in recent years concerning the mechanisms of magma genesis by partial melting of peridotitic upper mantle (see REAY and HARRIS, 1964; KUSHIRO, 1969, 1971; KUSHIRO et al., 1968, 1972; SCARFE et al., 1972; GREEN, 1973; YODER, 1976), not sufficient data seem so far to exist on the behaviour of the upper mantle minerals (i.e. complex solid solutions) during progressive partial melting processes under different P and T conditions.

It is generally believed that progressive partial melting produces continuous changes in the compositions of the refractory residua, successively eliminating different crystalline phases, but the residual phases are often considered as unchangeable in composition during partial melting, or their variations are not sufficiently taken into account (i.e. in models for magma genesis).

Some experimental works (i.e. KUSHIRO et al., 1972; MYSEN and KUSHIRO, 1977), on the other hand, have described the compositional variations of coexisting phases with degree of melting on natural mantle compositions. MYSEN and KUSHIRO (1977) experimentals on a starting material similar to the estimated composition of primitive upper mantle (their 1611 sample) during incremental melting under 20 kb total pressure, can be taken as the experiments the most closely approaching the physico-chemical conditions of depletion for our analyzed samples.

The chemical trends of their analyzed silicate minerals show progressive loss in Fe, Al, Na and Ca, in the suitable phases, accompanied by Mg and Cr gain, during increasing melting. Particularly for the initial stages of depletions, when a clinopyroxene phase is still present among the crystalline residua, the Al- and Fe-bearing components in orthopyroxenes and Al- and Na-bearing components in clinopyroxenes seem to be the most rapidly released.

A main discrepance exists with our analyzed samples, since their clinopyroxene phase show a pigeonitic rather than a diopsidic character. However, similar runs on different stating material (i.e. sample 66 SAL-1 of MYSEN and KUSHIRO, 1977), richer in Al and Ca and poorer in Mg, have shown qualitatively similar overall chemical trends for the silicate minerals, the presence of diopsidic clinopyroxene within the residual crystalline phases and, moreover, the existence of a chemical trend for the spinel phase towards more Cr-rich compositions.

Similar compositional trends are shown by the suitable residual minerals of different alpine peridotite bodies, which are believed to have undergone partial melting processes under upper mantle conditions (i.e. PICCARDO, 1976; DICK, 1977): in particular, the orthopyroxene gets progressively depleted in Al, Fe and Ca, and relatively enriched in Mg, and the spinel depleted in the $MgAl_2O_4$ component, going from more lherzolitic (less depleted) to more harzburgitic and dunitic (more depleted) types.

Considering the available mineral chemistry data on alpine spinel peridotites (see discussion and references in: DICK, 1977), similar mineralogical trends are clearly recognizeable, apparently recording different degrees of melting and depletion for the different peridotite bodies.

In conclusion, the recognized compositional trends for our analyzed samples can be ascribed to effects of progressive partial melting, within a restricted range of variation. Our data are, on the whole, in good agreement with existing experimental results as well as mineral chemistry data on mantle compositions. Moreover, since recrystallized clinopyroxene is still present in our samples, it has been shown that this phase is progressively depleted in its Ca-Tschermakitic and Fe-bearing components.

Our results, together with the discussed experimental data, strongly suggest that residual minerals continuously change their compositions during progressive partial melting: thus, such effects must be no more disregarded when models of magma genesis are discussed.

In attempting the geochemical modelling of magmatic processes, it is actually a general rule to describe trace partitioning between liquid and solid phases by means of partition values, thought as simple concentration ratios of the single trace elements between the phases of interest. This approach largely derives from the consideration that trace elements obey to the laws of dilute solutions, but also from the necessity of comparing calculated and observed concentrations in natural melts.

However, the partition of a trace element between two phases (either liquid or solid phases) is governed by the ratio of the activities of the element in the phases of interest. Concentrations are linked to activities by activity and solvent coefficients, which depend on structural and compositional parameters (cf. IIYAMA, 1974; MORRIS and HASKIN, 1974; FRASER, 1975). These coefficients may or may not be constant, for a given system, depending on the ideality of the distribution process: nevertheless, activities and activity and solvent coefficients are pressure, temperature and composition dependent.

All these complexities make extremely difficult to evaluate distribution laws (as the partition values are) which could approach the real process. The introduction of a « carrier » in the expression of the distribution coefficient, as suggested by MCINTIRE (1963), is useful only in the rather improbable case that trace an carrier ions behave identically (see also: FRASER, 1975). Moreover, it is almost trivial to recall that activity coefficients of ions of different valence could exhibit divergent relations in liquids of different compositions (Lewis and Randall, 1923; McIntire, 1963).

In spite of the complexities above outlined, REE partitioning between solid and liquid phases has been often interpreted by Authors only in terms of simple control by structure and composition of the solid phases, ignoring REE activities in the liquid phase. Moreover, almost dogmatic assumptions about the more or less incompatible or residual character of these elements during partial melting or crystallization processes has led to dangerous circular paralogisms about the nature and relations of materials involved in natural processes. The commonly accepted views that oceanic tholeiites result by partial melting on an already depleted mantle material and that residual mantle cannot exhibit LREE over HREE enrichments seem to pertain to this kind of reasoning.

Concerning our analyzed Assab spinel peridotite xenoliths, the REE partitioning picture appears quite complex. REE partitioning among coexisting solid phases appears to be mainly governed by composition dependency effects, which lead to continuous modifications of the REE partition values between coexisting solid phases.

The evolution of the partition values likely occurred during a partial melting event at different degrees of partial melting are testified by major element bulk and constituent mineral chemistries.

These evidences, along with the impossibility of describing rigorously REE activities in melts of different compositions, suggest great care in geochemical modelling mainly based on mass balance argumentations concerning these elements.

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