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PETROLOGY OF ULTRAMAFIC XENOLITHS IN FISSURE ALKALI BASALTS OF THE ASSAB REGION (AFAR, ETHIOPIA) ***

Riassunto. — Oggetto della nota è la petrologia di alcuni xenoliti ultrafemici, inclusi nei basalti alcalini fissurali della Regione di Assab (Etiopia), rappresentati da harzburgiti tettonitiche a spinello e da pirosseniti oliviniche, interpretabili come materiale del mantello superiore sottostante l'areale.

Sulla base dei rapporti tessiturali e dei caratteri strutturali entrambe le famiglie di xenoliti mostrano di aver subìto una completa equilibratura della paragenesi durante lo stesso evento.

Sulla base della composizione chimica delle fasi mineralogiche all'equilibrio, olivina forsteritica, clinopirosseno diopsidico, ortopirosseno enstatitico e spinello cromifero, le temperature di equilibratura sono state valutate in accordo con le metodiche più realistiche finota proposte.

La stima delle temperature di equilibratura per rocce femiche ed ultrafemiche è fondamentalmente basata sulla determinazione sperimentale del solvus enstatite-diopside, nel sistema $Mg_2Si_2O_6$ - $MgCaSi_2O_6$ (fra gli altri citiamo Davis e Boyd, 1966; Warner e Luth, 1974; Nehru e Wyllie, 1974), e su modelli semiempirici che tendono a considerare gli effetti degli altri componenti, presenti nei complessi sistemi naturali (Wood e Banno, 1973; Saxena e Nehru, 1975).

A questi ultimi metodi, che sembrano ovviare, almeno in parte, ai limiti drastici di applicabilità dei dati sperimentali su semplici sistemi sintetici ai complessi sistemi multicomponenti naturali, sono da attribuire i dati più realistici: la loro utilizzazione per gli xenoliti harzburgitici e pirosseniti considerati fornisce valori di circa 1050°-1100° C per le temperature di equilibratura.

La ripartizione Mg - Fe^{++} fra coesistenti olivina e spinello, utilizzata da vari Autori (Irvine, 1967; Jackson, 1969; Medaris, 1975; Evans e Frost, 1975; Stroh, 1976), non sembra a tutt'oggi calibrata sperimentalmente in modo sufficiente per poter offrire buone garanzie di applicabilità, come funzione geotermometrica, ai complessi sistemi naturali.

La solubilità di Al_2O_3 negli ortopirosseni coesistenti con una fase alluminifera (granato o spinello) è considerata come una utile funzione geobarometrica ed è stata investigata sperimentalmente in semplici sistemi sintetici.

Nel tentativo di rendere utilizzabili i dati sperimentali per la stima delle pressioni di associazioni naturali Wood e Banno (1973), MacGregor (1974) e Stroh (1976) hanno proposto alcuni modelli di estrapolazione.

Utilizzando il grid proposto da MacGregor (1974), basato su dati sperimentali nel semplice sistema MgO - Al_2O_3 - SiO_2, e tenendo conto dei fattori correttivi indicati dall'Autore stesso, è stato ottenuto un valore medio di pressione di circa 20 Kb, per l'intervallo stimato di temperature.

Applicando la formula di Stroh (1976), basata sul modello di Wood e Banno (1973) e sui dati sperimentali di MacGregor (1974), sono stati ottenuti valori grossolanamente variabili da 8 a 16 Kb. L'eccessivo divario tra i valori ottenuti, che copre gran parte dell'intervallo di

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pressioni per il campo delle peridotiti a spinello alle temperature considerate, e la possibilità di valori non corretti (come sostenuto da Wood, 1975) nei dati di MacGregor (1974), supporto sperimentale di entrambi i metodi di estrapolazione, rendono praticamente non utilizzabili correttamente entrambi i metodi.

In conclusione per quanto riguarda le harzburgiti, interpretabili dal punto di vista composizionale come materiale del mantello impoverito per fusioni parziali, i valori di temperatura calcolati sono leggermente inferiori a quelli dedotti per fusioni parziali in condizioni anidre del materiale del mantello.

L'ipotesi di rapporti primari del tipo residuo refrattario-fuso prodotto tra questi noduli e le lave incassanti appare meno immediata rispetto all'ipotesi che questi materiali equilibrarono in tempi precedenti al loro inglobamento accidentale da parte dei basalti fissurali, anche se i limiti di attendibilità dei valori calcolati non consentono interpretazioni univoche.

ABSTRACT. — The temperature and pressure of equilibration of some ultramafic xenoliths enclosed in fissure alkali basalts of the Assab Region (Ethiopia) have been evaluated on the basis of mineral chemistry of pyroxenes, olivines and spinels, applying some of the methods so far proposed.

The more relyable values for temperatures, calculated by methods which more closely approach the real behaviour of complex natural systems, average 1050°-1100° C.

Methods for pressure evaluation seem to need further experimental improvements before being used with any degrees of confidence: pressure values for our xenoliths, evaluated by means of few proposed models, add no contributions to the petrographical evidences.

Regarding harzburgites, temperature values we have obtained are slightly lower than those inferred for melting conditions of anhydrous mantle material; the hypothesis that their equilibration is due to events earlier than the genesis of the enclosing lavas would appear more immediate.

Yet it is to be pointed out that the limits concerning the adequacy and the degree of relyability of the proposed methods for temperature and pressure evaluation might leave space to the hypothesis of genetic relationships between harzburgitic xenoliths, considered as refractory residua, and the enclosing fissure alkali basalts.

Introduction

The Afar and Red Sea geodynamic evolution was preceded and accompanied by continental and oceanic volcanism, the former related to continental rifting, the latter to crustal drifting away (as summarized by Barberi et al., 1972, and Gass, 1973).

A further, more recent, volcanism, whose composition ranges from ankaramitic to hawaiitic basalts (De Fino et al., 1973), developed in the Assab Region in connection with an E-W fault system, transverse to the main MNW-SSE structure.

Xenoliths considered in this paper are associated with these fissure alkali basalts.

As discussed by many Authors (Forbes and Kuno, 1967; White, 1966; Aoki, 1968; Jackson and Wright, 1970; Wyllie, 1970), xenoliths can represent extraneous material or can be genetically related to the enclosing lavas: if so, either they are products of magmatic crystallization (crystal adcumulates) or they are parts of the mantle material, primary or depleted, from which lavas generated by partial melting.

The different rock types enclosed as xenoliths in fissure alkali basalts of the Assab Region can be grouped, on structural, textural and compositional basis, in two main classes:

— Upper Mantle xenoliths;
— Crustal xenoliths.

To the first group belong tectonitic ultramafics, mainly represented by spinel harzburgites, minor green olivine-pyroxenites and spinel bearing olivine-pyroxenites, rarely websterites (according to the terminology of Moores, 1973): the various rock types can be primarily associated in one single xenolith, the pyroxenites occurring as bands within the harzburgites.

The second group consists of gabbroic rocks, with minor pyroxenites and peridotites, sometimes interlayered within one single xenolith, which are characterized by relic magmatic layered structures and complete metamorphic reequilibration textures.

As pointed out in a previous work (Ottonello et Al., 1975), only tectonitic ultramafic xenoliths can be genetically related to the enclosing lavas, of which may represent both parental material and refractory residua.

Aim of the present paper is to investigate the conditions of equilibration of some harzburgitic and ol-pyroxenitic xenoliths of the first group on the basis of mineral chemistry, and to discuss genetical relationships between harzburgites and the enclosing fissure alkali basalts.

Petrography

Two pyroxenitic xenoliths (labeled 2493 and 2490) and two harzburgitic ones (2488 and 2206) have been taken into consideration.

The modal analysis gave the following proportion for their four phases (olivine, ortho- and clinopyroxenes and spinel) assemblages:

	ol	opx	cpx	sp
2493	30	15	50	5
2490	40	15	44	1
2488	70	25	3,5	1,5
2206	75	20	3,5	1,5

For what concerns textures, harzburgite samples are characterized by xeno-morphic aggregates of poligonal grains with gently curved boundaries and almost no elongation; the grain size for olivine and orthopyroxene is medium to coarse, whereas clinopyroxene and spinel are much smaller and often cluster near greater enstatite crystals (« protogranular texture » according to Mercier and Nicolas, 1975).

This simple textural pattern involves all the mineral components and it suggests rearrangement of the whole assemblage during a single phase of equilibration: the extreme scarceness of reciprocal exsolutions in pyroxenes supports this fact.

Deformation effects occur but as kink bandings in both olivine and pyroxenes. Pyroxenites show a general smaller grain size, with olivine and pyroxenes in

equigranular and equidimensional individuals forming a mosaic-like textures, while spinel occurs as small grains confined along the boundaries of major phases.

Such textural relationships therefore testify that all the mineral phases in each xenolith have undergone crystallization in mutual equilibrium conditions.

Mineral chemistry

Analitical tecniques

Analyses were carried out with the M.A.C. electron microprobe of the Department of Geology, University of Western Ontario (Canada).

For all the elements the excitation voltage was 15 Kv, the specimen current approximately 0,01 ma and the electron spot size about 1,0 micron.

TABLE 1

Pyroxenes

Sample	2493		2490		2488		2206a		2206b	
Phase	cpx	opx	cpx	opx	cpx	opx	cpx	opx	opx	opx
SiO_2	50.55	54.44	49.85	53.62	51.30	55.77	52.33	55.32	52.97	54.83
TiO_2	0.30	0.08	0.22	0.06	0.10	0.04	0.36	0.12	0.28	0.10
Al_2O_3	5.52	3.98	5.75	5.34	4.75	3.66	4.12	3.01	3.85	2.82
FeO tot	3.62	7.16	3.58	8.02	2.59	4.56	2.50	5.25	2.53	5.14
MgO	16.31	32.26	17.19	31.20	17.15	34.00	17.41	34.92	17.21	35.21
CaO	22.01	0.82	21.66	0.78	22.14	0.94	21.17	1.05	21.12	1.00
Cr_2O_3	0.76	0.36	1.09	0.73	1.26	0.67	1.50	0.74	1.41	0.61
Na_2O	0.72	nd	0.75	nd	1.09	nd	0.85	nd	0.86	nd
Σ	99.79	99.10	100.09	99.75	100.38	99.64	100.24	100.41	100.23	99.70
Structural formulae (0 = 6)										
Si	1.851	1.906	1.823	1.874	1.864	1.919	1.894	1.901	1.914	1.898
Al^{IV}	0.149	0.094	0.177	0.126	0.136	0.081	0.106	0.099	0.086	0.102
Al^{VI}	0.089	0.070	0.071	0.094	0.067	0.067	0.070	0.023	0.078	0.013
Ti	0.008	0.002	0.006	0.002	0.003	0.001	0.010	0.003	0.008	0.003
Fe	0.111	0.210	0.109	0.235	0.079	0.131	0.076	0.151	0.076	0.149
Mg	0.890	1.683	0.937	1.625	0.929	1.744	0.939	1.789	0.927	1.817
Ca	0.864	0.031	0.849	0.029	0.862	0.035	0.821	0.039	0.818	0.037
Cr	0.022	0.010	0.030	0.020	0.036	0.018	0.043	0.020	0.040	0.017
Na	0.051		0.053		0.077		0.060		0.060	
X + Y	2.035	2.006	2.058	2.005	2.053	1.996	2.019	2.025	2.007	2.036
Z	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Ca/Ca+Mg	0.492	0.018	0.476	0.018	0.481	0.020	0.466	0.021	0.469	0.020

Elements were analyzed by using clinopyroxene (LUD-98), orthopyroxene (GER-99), olivine (MEX-133) and spinel (S-4) standards: Na and Ti were analyzed using an albite and an ilmenite standard respectively.

The original LUD-98 standard analysis was corrected by MACRAE (July 1971) and a slight correction was also yelded to MEX-133 standard analysis.

The data were reduced utilizing two computer programs, Cone and Abfan (Boyd, Finger and Chayes, 1968). The first program averages counts, evaluates statistical parameters and makes instrumental corrections. The output of Cone is the initial approximation to the composition. Abfan corrects the composition from Cone for assorption, fluorescence, backscatter and stopping power.

Piroxenes

Five pyroxene pairs are listed in Tab. 1. As for sample 2206, which presents a thin (few mm) clinopyroxene-rich band, the mineral phases were analyzed in both harzburgite (2206a) and cpx-rich band (2206b). Plotting the data on the Ca - Mg - Fe diagram (Fig. 1) the compositions of clinopyroxenes are quite similar and fall
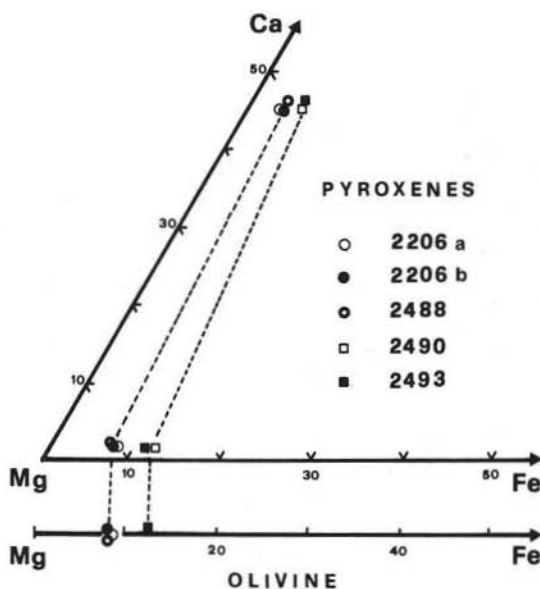
Fig. 1. — Pyroxene pairs compositions on Ca - Mg - Fe diagram and Mg - Fe ratios of coexisting olivines. Correlations (dashed lines) show parallel shift for harzburgite and pyroxenite minerals.

in the diopside field near to the diopside-endiopside boundary: the only difference between harzburgite and ol-pyroxenite clinopyroxenes is given by a slight shift toward more ferriferous compositions for the latter ones.

Further differences are shown in Al contents, which are some higher for ol-pyroxenites, and in Cr contents, which are slightly higher in harzburgites.

Greater separation characterizes orthopyroxenes where higher Mg contents correspond to the harzburgites: Al contents follow the same behavior as in clino-pyroxenes.

Olivines

Olivines (Tab. 2) are rich in forsterite (Fo_{92} for harzburgites), with a slightly lower value for the pyroxenite one ($Fo_{87.5}$) (Fig. 1), and relatively high in Ni content.

TABLE 2

Olivines

Sample	2493	2488	2206a	2206b
SiO_2	40.71	41.16	40.81	40.32
Feo tot	11.69	8.00	8.13	8.13
MgO	47.32	50.83	51.03	51.50
NiO	0.30	0.32	0.29	0.32
Σ	100.02	100.31	100.26	100.27
Structural formulae (0 = 6)				
Si	1.005	0.998	0.990	0.981
Fe	0.241	0.162	0.165	0.165
Mg	1.742	1.836	1.845	1.867
Ni	0.006	0.006	0.005	0.006

Spinels

Spinels (Tab. 3) show quite constant $Mg/Mg+Fe^{++}$ ratios, ranging from 0,727 for the pyroxenite to 0,734-0,738 for harzburgites, whereas they exibit a wider range in $Cr/Cr+Al$ ratios from 0,181 for the pyroxenite to 0,281-0,430 for harzburgites.

The Fe^{+++} content is low for all the samples, values for $Fe^{+++}/Cr+Al+Fe^{+++}$ being 0,053 for pyroxenite and ranging from 0,020 to 0,044 for harzburgites.

TABLE 3

Spinels

Sample	2493	2488	2206a	2206b
MgO	18.19	18.21	17.24	17.26
FeO*	12.16	11.45	10.85	11.12
Fe_2O_3*	4.98	1.88	3.68	3.98
Al_2O_3	49.69	44.62	33.06	36.26
Cr_2O_3	15.47	24.55	35.15	33.73
Σ	100.49	100.71	99.98	100.35
Structural formulae (0 = 32)				
Mg	6.016	6.097	6.055	6.021
Fe^{++}	2.256	2.151	2.138	2.177
Fe^{+++}	0.831	0.318	0.652	0.701
Al	12.273	11.156	8.671	8.925
Cr	2.714	4.360	6.548	6.242

* Fe cations distribution is calculated from total Fe, assuming the spinel stoichiometry.

In spite of the compositional variation among the harzburgite samples, these rocks are characterized by lower Al and Fe^{+++} and consequently higher Cr contents in comparison with the pyroxenite xenolith.

Geothermometry

The physical parameters of equilibration for olivine - orthopyroxene - clino-pyroxene - spinel assemblages have been investigated by many Authors: tempe-rature evaluations are mainly based on elements partitioning among coexisting phases and on molecular components activities.

Pyroxenes thermometry

Regarding temperature, on the basis of the mineral chemistry of coexisting Ca-poor and Ca-rich pyroxene pairs, different methods have been proposed: a first one consisting in the calculation of elements partitioning among coexisting phases (KRETZ, 1963), the others based on the evaluation of solid solution proportions and pyroxenes components activities (DAVIS and BOYD, 1966; WOOD and BANNO, 1973; NEHRU and WYLLIE, 1974; WARNER and LUTH, 1974; SAXENA and NEHRU, 1975).

Limits to the applicability of the KRETZ's method, based on the calculation of K_D(Mg-Fe) between coexisting pyroxene pairs, arise from the effect of cations other than Fe and Mg, namely Al and Ca, which superimposes to the non-ideal two-sites occupacy effect of Fe and Mg; in addition the K_D coefficient can also be affected by the total rock composition (as summarized by MAXEY and VOGEL, 1973).

Moreover the K_D values we have obtained for our samples (ranging from 0,806 to 1,124), consistently with KRETZ's results for ultramafic inclusions in basalts, are remarkably higher than the range of values calculated by KRETZ for both magmatic pyroxene pairs (K_D ranging from 0,65 to 0,86) and the metamorphic ones (K_D ranging from 0,51 to 0,65); since they fall outside the proposed K_D/T plot they are ineffective in order to evaluate temperatures.

The two components Diopside - Enstatite system has been investigated estensively on theoretical and experimental basis.

Special attention has been given to subsolidus equilibria boundaries owing to the experienced correlation between the molecular proportion of enstatite exsolved in orthopyroxene - coexisting diopside and temperature of equilibration.

This proportion has been assumed as geothermometric function, since it is considered, on the whole, virtually insensitive to pressure variations between 1 and 30 Kb, in the range 900°-1400° C, in spite of the slightly different beaviours of the pyroxene solvii explored at different pressures (DAVIS and BOYD, 1966; NEHRU and WYLLIE, 1974; WARNER and LUTH, 1974).

The temperature evaluation accomplished by applying the different criteria proposed by the cited Authors, according to their experimentally determined solvii, gave for our samples values averaging about 960° C, 910° C and 1070° C, respectively.

Limits to the applicability of these metods arise from the various problems involved in applying experimental data from simple syntetic systems to complex natural mineral parageneses, namely the effect of additional elements, as Fe, Al, Cr and Na, which are present in natural pyroxene solid solutions, and non-ideal sites occupancy for clino- and orthopyroxenes.

Experimental works confirm that the orthopyroxene component solubility in the clinopyroxene phase increases with Fe addition to the system, whereas the Al effect is less understood (as summarized by Wood and Banno, 1973): as a whole Authors agree that the experimental results on the $CaMgSi_2O_6$ - $Mg_2Si_2O_6$ join are useful for equilibration temperature determination of pyroxenes containing up to 3-4 Al_2O_3 wt % and few percents of $FeSiO_3$.

A rough evaluation of the temperature value underestimation, due to the Fe content disregarding, can be visualized utilizing a correct $Ca/Ca+Mg+Fe$ ratio instead of the $Ca/Ca+Mg$ ratio in applying the Davis and Boyd method.

Wood and Banno (1973), in the aim of taking into account the effect of additional components besides Ca and Mg and the different occupancies of the two cations sites in the pyroxene structure, assume that large ions occupy the M_2 site and the smaller ones of the octahedrally coordinated ions the M_1 site, whereas Fe^{++} and Mg randomly distribute over the two sites in both pyroxene phases.

To calculate equilibrium temperature of two - pyroxenes assemblages they propose the following formula:

$$T = \frac{-10202}{\ln\left(\frac{a_{Mg_2Si_2O_6}^{cpx}}{a_{Mg_2Si_2O_6}^{opx}}\right) - 7,65\ x_{Fe}^{opx} + 3,88\ (x_{Fe}^{opx})^2 - 4,6}$$

where

$$a_{Mg_2Si_2O_6}^{cpx} = (X_{Mg}^{M_1} \cdot X_{Mg}^{M_2})_{cpx}$$

$$a_{Mg_2Si_2O_6}^{opx} = (X_{Mg}^{M_1} \cdot X_{Mg}^{M_2})_{opx}$$

and X's are molar fractions, assuming

$$\left(\frac{Mg}{Mg + Fe^{++}}\right)_{M_1} = \left(\frac{Mg}{Mg + Fe^{++}}\right)_{M_2} = \left(\frac{Mg}{Mg + Fe^{++}}\right)_{mineral}$$

Such formula gives for our samples the following T values:

Samples	T (°C)
2493	1022
2490	1045
2488	1015
2206a	1116
2206b	1119

Recently Saxena and Nehru (1975), pointing out the limits involved in the use of solvus data for petrogenetical considerations, discussed thermodynamic and crystal-structural problems concerning the Enstatite-Diopside solvus, considered as parts of two solvi, respectively with ortho- and clino-structure for the $CaMgSi_2O_6$ and $Mg_2Si_2O_6$ endmembers.

They present a non-ideal solution model for pyroxenes, according to which Fe and Mg mix ideally on M_1 sites for both clino- and orthopyroxenes, while M_2 sites occupancy might be attributed to as ternary solutions of Ca, Mg and Fe; Ca - Mg mixing is a non-ideal one and different in ortho- and clinopyroxene, whereas Ca and Fe may be assumed as ideally substituting at temperatures above 1000° C.

With this assumption, they proposed the following formula for the equilibrium constant of two-pyroxenes assemblages:

$$K_a = \frac{X^{M_1}_{Mg-cpx} \cdot X^{M_2}_{Mg-cpx} \cdot \exp\left[\frac{6531}{RT} \cdot X^{M_2}_{Ca-cpx} \cdot (X^{M_2}_{Ca-cpx} + X^{M_2}_{Fe-cpx})\right]}{X^{M_1}_{Mg-opx} \cdot X^{M_2}_{Mg-opx} \cdot \exp\left[\frac{7184}{RT} \cdot X^{M_2}_{Ca-opx} \cdot (X^{M_2}_{Ca-opx} + X^{M_2}_{Fe-opx})\right]}$$

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

The solution of such expressions gave for our samples the following temperature values:

Samples	T (°C)
2493	1074
2490	1194
2488	1077
2206a	1085
2206b	1051

The different criteria followed in the aim of solving temperature determination problem by the Authors quoted above show an improvement of the methods mainly due to more accurate approach to the real behaviour of complex systems.

Namely the tentative evaluation of effects of cations other than Ca and Mg, taken into account by Wood and Banno (1973), and the hypothesis of non-ideal distribution, put forward by Saxena and Nehru (1975), represent most effective improvements with respect to the traditional solvus methods, and therefore data obtained applying their formulas seem to be more realistic and reliable.

The slight discrepancies among the two sets of data obtained applying their formulas are to be referred to the different assumptions on which the two methods are based: anyway, the differences between the mean values given by the two methods ($\simeq 1050°$ C and $\simeq 1100°$ C, respectively) being confined within less than 5 %, the degree of consistency seems quite satisfactory.
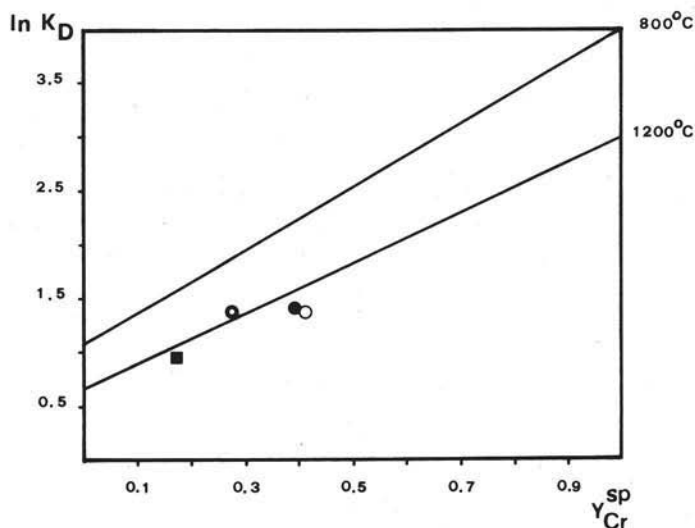
Fig. 2. — Plotting of our samples on the ln K_D versus Y_{Cr}^{sp} diagram of MEDARIS (1975). Samples symbols as in Fig. 1.

Olivine-spinel thermometry

IRVINE (1965, 1967) and JACKSON (1969) developed a method to evaluate equilibration temperatures based on Mg and Fe^{++} partitioning between coexisting spinel and olivine.

MEDARIS (1975), utilizing the thermochemical data compiled by JACKSON (1969), presented a ln K_D versus Y_{Cr}^{sp} diagram, where

$$Y_{Cr}^{sp} = \frac{Cr}{Cr + Al + Fe^{++}}$$

in spinel, and

$$K_D = \left(\frac{X_{Mg}}{X_{Fe}}\right)^{ol} \cdot \left(\frac{X_{Fe}}{X_{Mg}}\right)^{sp}$$

with X's representing molar fractions (Fig. 2).

Our data:

Samples	K_D	Y_{Cr}^{sp}
2493	1,00	0,17
2488	1,39	0,28
2206a	1,37	0,41
2206b	1,41	0,39

show a good agreement among the harzburgites, whereas the pyroxenite 2493 is characterized by lower values for both K_D and Y_{Cr}^{sp}.

By plotting the data on the MEDARIS diagram, which reports calculated isotherms from 800° C to 1200° C, we obtain temperature values higher than 1200° C for samples 2493, 2206a and 2206b, and a slightly lower value for the sample 2488 (Fig. 2).
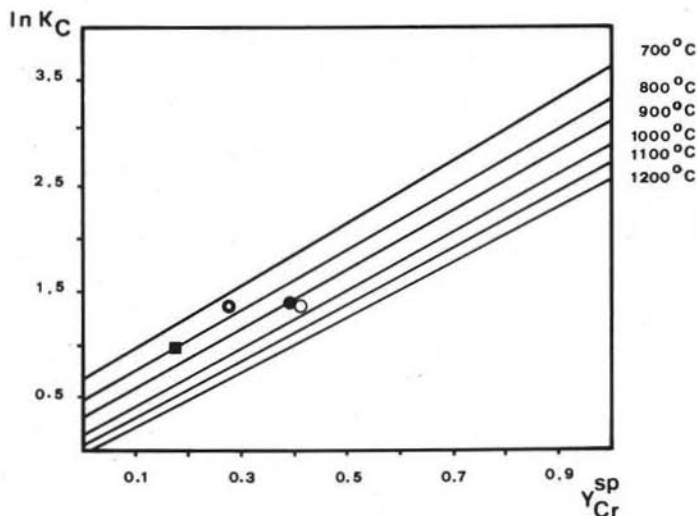

Fig. 3. — Plotting of our samples on the ln K_c versus Y_{Cr}^{sp} diagram of STROH (1976). Samples symbols as in Fig. 1.

As JACKSON (1969) and MEDARIS (1975) pointed out, severe limits in such temperature evaluation arise from the uncertainties in the thermochemical data, which could affect the calculated temperature values by errors as much as ± 300° C.

Temperature values obtained by the method of JACKSON appear to be too high (EVANS and WRIGHT, 1972; EVANS and FROST, 1975), namely 100°-300° higher than temperatures of equilibration obtaied by other methods, such as those based on pyroxenes chemistry.

In the aim of obtaining more realistic values, EVANS and FROST (1975) propose a tentative empirical calibration of the spinel-olivine geothermometer: on the basis of microprobe-analyzed high-grade metamorphic and magmatic pairs, they draw the 700° C and 1200° C geotherms on the ln K_D versus Y_{Cr}^{sp} diagram.

Recently STROH (1976), revising and interpreting the thermochemical data in JACKSON (1969), matches them with the ln K_c values at 700° C, deduced from the data of EVANS and FROST (1975), to give the variation in ln K_e with temperature (Fig. 3).

By using the calibrated ln K_D versus Y_{Cr}^{sp} diagrams by EVANS and FROST (1975) and by STROH (1976), we obtain remarkably lower values of the spinel-olivine equilibration temperature for our samples: they range from ≃ 750° C to ≃ 950° C

for the harzburgites (2488 and 2206), and $\simeq 800°$ C for the pyroxenite (2493).

Temperature values are not in good agreement with the most reliable values obtained from the pyroxenes thermometry, even if it is not necessary (as pointed out by EVANS and FROST, 1975) that the quenching-in temperature for Ca - Mg - Fe exchanges in pyroxenes is the same as for Mg - Fe exchanges between olivine and spinel.

These sensible differences between the values obtained by pyroxenes and olivine-spinel thermometry confirm that Mg - Fe partitioning between olivine and spinel, in natural systems with FeO, Fe_2O_3, along with MgO, SiO_2 and Al_2O_3, seems to be so far not sufficiently calibrated for geothermometry (STROH, 1976), in respect of the pyroxenes thermometry; then it should not be used for that purpose.

Pressure evaluation

The solubility of alumina in orthopyroxene coexisting with an Al_2O_3-rich phase is considered as a geobarometric function and it has been experimentally tested in simple systems (BOYD and ENGLAND, 1964; MACGREGOR, 1964; BOYD, 1970; MACGREGOR, 1974).

WOOD and BANNO (1973), WOOD (1974) and STROH (1976), in the aim of improving pressure estimates for natural multicomponent systems, developed models taking into account the effects of additional components.

We have attempted an estimation of equilibration pressure for our xenoliths using the petrogenetic grid proposed by MACGREGOR (1974), based on experimental data in the three components MgO - Al_2O_3 - SiO_2 system, and the formula developed by STROH (1976), which is based on the model of WOOD and BANNO (1973) and on the experimental results of MACGREGOR (1974) and implies a simple solution model for olivine, aluminous orthopyroxene and spinel.

On structural and paragenetical basis we recognized that both harzburgitic and pyroxenitic xenoliths underwent a crystallization event responsible for their four phases equilibrium assemblages in spinel peridotite facies.

Assuming an averaged temperature range of about 1050°-1100° C, the representative points of our samples fall within the garnet peridotites field of the MACGREGOR's grid, in contrast with the petrographic characters (Fig. 4).

They give an average pressure value of $\simeq 25$ Kb, with partial averages of $\simeq 22$ Kb for pyroxenites and $\simeq 27$ Kb for harzburgites, using T = 1050° C, and slightly higher values assuming T = 1100° C.

MACGREGOR (1974) points out that the grid is valuable for Ca-free ultramafic rocks, while corrections are required when applied to two pyroxenes assemblages, as Al_2O_3 content in enstatite decreases of about 2 wt % from Ca-undersaturated to Ca-saturated assemblages in the same pressure and temperature conditions (BOYD, 1970).

Taking into account such suggestions and making coarse corrections to the

analytical data, sample points plot within the spinel field or along the spinel-garnet boundary, in better agreement with the petrographic characters, giving an average value of pressure of $\simeq$ 19 Kb, with partial averages of $\simeq$ 15,5 Kb for pyroxenites
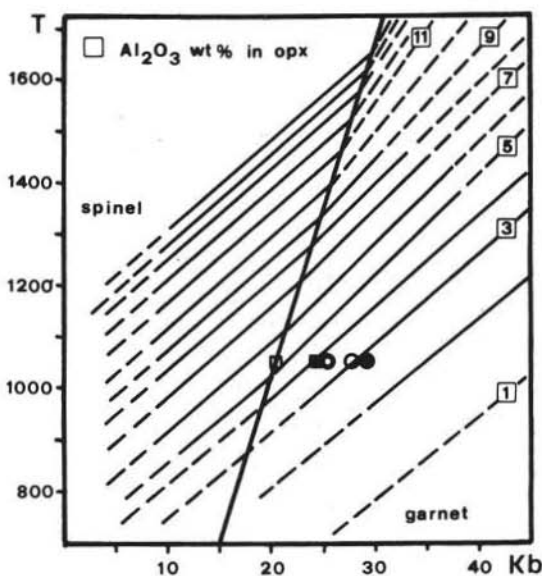

Fig. 4. — Plotting of our samples on the grid of MacGregor (1974), without any correction. Samples symbols as in Fig. 1.

and of $\simeq$ 21 Kb for harzburgites, using $T = 1050°$ C, and slightly higher values assuming $T = 1100°$ C.

The discrepancy can be referred both to the different bulk composition effect (as pointed out by FRISCH, 1974) and to the nature and proportions of the coexisting minerals: in fact the two rock types we are considering show a systematic variation in the pyroxenes Al_2O_3 content (lower for the harzburgites), obviously owed to the different processes responsible for their formation.

In effects, while harzburgites should represent refractory residua of a depletion process by partial melting on primary mantle material, pyroxenites are to be ascribed to deep seated crystallization of melts.
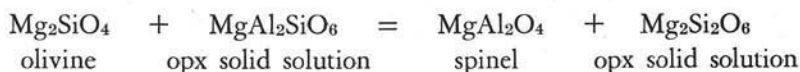
Regarding the method of evaluating pressure of equilibration, severe limits to the applicability of the grid lie in the extension of experimental data on simple systems to complex natural multicomponent systems, where the Al_2O_3 content is lower than in simple MgO - SiO_2 - Al_2O_3 or $MgSiO_3$ - $CaSiO_3$ - Al_2O_3 systems (STROH, 1976).

Accordingly WILSHIRE and JACKSON (1975) urge caution in application of MacGREGOR's grid, since they note large inconsistencies in calculated temperatures and pressures.

The equation of STROH (1976):

$$P = 1 + \frac{(9 \cdot 116 - 5{,}065\ T_0) - RT_0\ \ln \left(\dfrac{(X_{Mg})_{sp} \cdot (X_{Al})^2_{sp} \cdot (X^{M_1}_{Mg})_{opx}}{(X_{Mg})^2_{ol} \cdot (X^{M_1}_{Al})_{opx}} \right)}{\Delta V_{reaction}}$$

is based on equilibrium between olivine, aluminous orthopyroxene and spinel, according to the reaction:

$$Mg_2SiO_4 \quad + \quad MgAl_2SiO_6 \quad = \quad MgAl_2O_4 \quad + \quad Mg_2Si_2O_6$$

    olivine   opx solid solution   spinel   opx solid solution

Applying this model to our samples (for explanation of theoretical and calculative supports to the STROH's formula, see Appendix in STROH, 1976), we obtain pressure values broadly ranging from 8 to 16 Kb, for $T = 1100°$ C, the harzburgites being characterized by the lower values, the pyroxenite by the higher one.

As pressure values determined utilizing MACGREGOR's experimental system must be systematically high for complex system where the $(X_{Mg})_{ol}$, $(X_{Mg})_{sp}$ and $(X_{Al})_{sp}$ terms are important, the pressure values obtained following the STROH's method could be more reliable, at least taken as nominal values, with all the uncertainties involved in the method.

As pointed out by STROH (1976), an incorrect model or incorrect initial experimental calibration could be at fault singly or in combination, to give physically impossible results.

WOOD (1975), testing MACGREGOR's experimental data from the thermodynamical point of view, shows that MACGREGOR's data are correct in the garnet field, whereas the data in the spinel field are incorrect, and in disagreement with other experiments.

Since these data represent the experimental support for both the proposed methods, large uncertainties arise about their applicability, expecially for pressure evaluation of natural spinel peridotites.

In conclusion it is apparent that further improvements on experimental data are needed on the olivine, orthopyroxene and spinel system, before the relationships in the system can be used with any degree of confidence (WOOD, 1975) to deduce realistic values of equilibration pressures for natural assemblages.

Regarding our xenoliths, the range in pressure values, obtained by applying MACGREGOR's and STROH's methods, covers largely the spinel peridotites field for the considered temperature values, and adds no contribution to the petrographical evidences.

Final remarks

The comparison of the above discussed methods for temperature and pressure evaluation on the basis of mineral chemistry stresses how, in spite of recent

improvements, their application to complex natural systems still faces against important problems at least partially unsolved, namely the values of thermodynamical parameters involved in phase reactions, the crystallochemical properties of mineral phases at different temperature and pressure conditions and the effect of bulk chemistry on the element partitioning among coexisting phases.

Moreover, expecially for what concerns harzburgites and other depleted ultramafics affected by partial melting processes, further uncertainties are due to the still scarce knowledge of the cristallochemical behaviour of the refractory phases during the melting processes and its possible dependence on the degree of partial melting.

Discussion

Summing up previous data, the conclusion can be drawn that the examined xenoliths have undergone a complete equilibration at temperatures of 1050°-1100° C and at upper mantle depth.

Focussing the attention on harzburgites, significant problems arise on the interpretation of their petrological and textural characters from a genetical point of view, in the aim of a tentative correlation with the geodynamical evolution of the Afar - Red Sea system.

The different stages of this evolution (continental rifting, crustal drifting, transverse faulting) are marked by different volcanic events connected to partial melting processes, and consequent depletion, of the upper mantle.

The petrographic features of the harzburgite xenoliths support the hypothesis of a strict connection with such processes, since their « protogranular texture » should be referred, according to MERCIER and NICOLAS (1975), to an equilibrium recrystallization during the partial melting of mantle primary peridotites.

In a previous work (OTTONELLO et Al., 1975), in which the genetic relationships of harzburgites with enclosing fissure alkali basalts have been investigated on the basis of trace elements distribution, the conclusion has been drawn that these xenoliths represent neither primary mantle material nor the parental rock of the enclosing lavas but they can be considered the refractory residua of a small-degree (6-10 %) partial melting process which produced the enclosing basalts.

Temperature values we have obtained are slightly lower than those inferred for melting conditions of anhydrous mantle material, then the hypothesis that the equilibration of harzburgite xenoliths is due to events earlier than the genesis of the enclosing lavas would appear more immediate.

Yet it is to be pointed out that the limits above mentioned concerning the adequacy and the degree of reliability of the proposed methods for temperature and pressure evaluation might leave space to the hypothesis of genetic relationships between the harzburgite xenoliths, considered as refractory residua, and the enclosing fissure alkali basalts.

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