chromian spinels in the basalts from the Lisbon volcanic complex (Portugal) and their petrogenetic implications

F. D'OREY*

T. PALACIOS **

* Departamento de Geologia, Faculdade de Ciências de Lisboa, R. da Escola Politécnica, 1294 Lisboa Codex.
** Departamento de Geologia, Faculdade de Ciências de Lisboa, Edifício C2, 5.º andar, Campo Grande, 1700 Lisboa Codex.

RESUMO

Palavras-chave : Cromite — Ferritchromit — *Basalto* — *Lisboa* — *Petrogénese.*

As espinelas cromíferas são muito comuns nos basaltos alcalinos do Complexo Vulcânico de Lisboa, cuja idade se atribui ao Cretácico Superior. Ocorrem como inclusões não zonadas no interior de olivinas magnesíferas em todos os tipos de basaltos, ou como grãos grosseiros espectacularmente zonados na matriz de basaltos porfíricos. Análises efectuadas com a microssonda electrónica, indicam a existência de trocas catiónicas complexas nos grãos zonados de cromite, devidas a reacções peritécticas simples que constituem respostas às mudanças de composição do líquido basáltico. Estas variações da distribuição catiónica nas espinelas zonadas reflectem, também, as relações parageneticas entre os óxidos e os silicatos. A cristalização das espinelas cromíferas iniciais processou-se a T$\sim$1200°C e $f_{O_2}\sim10^{-8.5}$ atm., anterior à (ou simultaneamente com a) formação de olivina magnesífera. Os mantos de titanomagnetite, que se depositaram sobre as espinelas cromíferas zonadas, cristalizaram a T$\sim$1200°C e a f_{O_2} inferior.

RÉSUMÉ

Mots-clés : Chromite — *Ferritochromite* — *Basalte* — *Lisboa* — *Petrogénèse.*

Les spinelles chromifères sont très communes dans les basaltes alkalins du «Complexe Volcanique de Lisbonne», d'âge Crétacé supérieur Les spinelles existent soit comme des inclusions à l'intérieur d'olivines. magnesifères dans tous les types de basaltes, soit en grains grossiers à zonation spectaculaire dans la matrice de basaltes porphyriques. Des analyses à la microsonde électronique indiquent des échanges cationiques complexes au sein des grains zonés de chromite, en conséquence de réactions péritectiques simples. Ces réactions représentent des réponses à des changements de la composition du liquide basaltique. Les changements concernant la distribution cationique chez les spinelles zonées traduisent également les rapports paragénétiques entre les oxydes et les silicates. La cristalisation des premières spinelles chromifères à eu lieu avec T$\sim$1200°C et $f_{O_2}\sim10^{-8.5}$ atm. (ou simultanément avec) avant la formation de l'olivine magnésifère. Les couches de titanomagnétite déposées sur les spinelles chromifères zonées ont crystallizé à T$\sim$1200°C avec f_{O_2} plus bas.

ABSTRACT

Key-words : Chromite — *Ferritchromit* — *Basalt* — *Lisbon* — *Petrogenesis.*

Chromian spinels are common in the late Cretaceous alkali basalts of the Lisbon volcanic Complex in Portugal. They occur as unzoned inclusions in magnesian olivines of all basalt types and as large spectacularly zoned grains in the groundmass of porphyritic basalts. Microprobe analysis indicate complex cationic exchange in the groundmass zoned spinels due to simple peritectic reactions and in response to changing composition of the basalt liquid. The variation of cationic distribution in zoned chromian spinels, reflects very accurately the changing chemistry of the cooling silicate melt and the paragenetical relations of mineral oxides and silicates. Crystallization of initial chromian spinels occurred at T$\sim$1,200°C and $f_{O_2}\sim10^{-8.5}$ atm. earlier or contemporaneously with magnesian olivine. The titanomagnetite mantles of zoned chromian spinels crystallized at T$\sim$1,200°C and much lower f_{O_2}.

INTRODUCTION

This study on the nature and origin of chromites, or more generally chromian spinels, is the first systematic research on opaque mineralogy being conducted in specimens of the Lisbon Volcanic Complex (ALVES *et al.* 1980). This Complex is mainly a thick sequence of erupted lava and pyroclastic piles in an area of moderate tectonic activity, which were emplaced in late Cretaceous.

The geology of the Lisbon Volcanic Complex was first described by P. CHOFFAT (1916, 1924) followed by A. JESUS & G. ZBYSZEWSKI (1952) and lately by A. SERRALHEIRO (1978) who mapped the volcanic formations in the area north of Lisbon.

A petrological and geochemical study was recently undertaken by C. A. ALVES *et al.* (1980) but with the exception of normative ilmenite and possibly titano-magnetite (?) no other opaque minerals were mentioned.

As a general principle, because FeO, TiO_2 and Cr_2O_3 increase with decreasing SiO_2, basic rocks tend to contain larger concentrations of oxides than either intermediate suites or acid end members. Therefore, the presence of opaque mineral oxides in the Lisbon basalts can not be ignored for they form an ubiquitous constituent in all basic igneous rocks and are an important group for their yielding data on geothermometry and oxygen geobarometry.

The volcanic rocks where chromian spinels occur both in the groundmass and as inclusions in olivine, are coarsely crystalline and were prone to accumulative processes dictated by gravity. These rocks consist of olivine, pyroxene and minor plagioclase phenocrysts, with some sparse phenocrysts of chromian spinels and small grains of titanomagnetite intergrown with sandwich and trellis textured ilmenite in a darkish groundmass. Several other iron and titanium oxides together with rare copper, nickel and iron sulphides occur in these rocks. The composition of lavas where zoned chromian spinels are abundant, place them in the titanium and alkali rich end of the basalt range with an ankaramitic composition (Table I).

In the present study, chromian spinels occurring in the basalts have been analysed in detail with regard to their overall chemical variability and relationship to silicate phases. Phase relations in the pertinent parts of the systems $MgO-Cr_2O_3-SiO_2$ and $CaO-MgO-Al_2O_3-SiO_2$ suggest that a spinel phase should crystallize at or near the liquidus in melts of basaltic composition (HENDERSON, 1975). Basalts commonly contain a few percent of spinel but the modification or disappearence of this phase as crystallization proceeds, indicates a reaction relationship between spinel and liquid (RIDDLEY, 1977). Peritectic reaction involving spinel may be predicted from phase relations in the above synthetic systems (IRVINE, 1967; HENDERSON, 1975). The chemical variability in the chromian spinels of the groundmass is related to the extent to which they have been exposed to the cooling basalt magma, hence it is possible to document the changes that took place during reaction of spinels with silicate liquid.

MINERALOGY

Idiomorphic or rounded crystals of chromian spinels are of ubiquitous occurence in the basalts of the Libon

Volcanic Complex. The occurence of chromian spinels in this volcanic complex has not previously been known. Nearly equant habits in the groundmass are typical of chromian spinels, the degree of idiomorphism decreasing with increasing iron and titanium content in the spinels. If the early chromian spinels have grown free in the magma, the paragenetically later xenomorphic titano-magnetite crystals were constrained to fill available spaces within a framework of silicates.

In most chromian spinels, the oxides MgO, Cr_2O_3, Al_2O_3, Fe_2O_3, and FeO sum more than 98 % (HAGGERTY, 1976). In the Lisbon Volcanic Complex, TiO_2 and MnO are typically present in small amounts but CaO, ZnO, SiO_2, CoO and VO_3 were not detected and NiO just occurs in trace amounts.

The simplest chemical formula of a spinel mineral is $R^{++}R_2^{+++}O_4$, the theoretical end members are many but the following six predominate (HAGGERTY, 1976) and hereafter referred to by the indicated names or symbols:

$Fe^{++}Cr_2O_4$ ——— chromite (ch)
$Fe^{++}Al_2O_4$ ——— hercynite (hc)
$Fe^{++}Fe_2^{+++}O_4$ ——— magnetite (mt)
$MgCr_2O_4$ ——— picrochromite (pc)
$MgAl_2O_4$ ——— spinel (sp)
$MgFe_2^{+++}O_4$ ——— magnesioferrite (mf)

The later iron/titanium spinels are predominantly solid solutions of the following end members:

$Fe_2^{++}Ti^{++++}O_4$ ——— ulvospinel (uv)
$Fe^{++}Fe_2^{++++}O_4$ ——— magnetite (mt)

The chromian spinels included in olivine (figure 1) are generally homogeneous, but larger grains in the groundmass are strikingly zoned. In the latter, zoning is generally gradational (figure 2) and very rarely sharp (figure 3).

The zonation of chromian spinel is seen in reflected light by an increase in reflectance from the cores to the
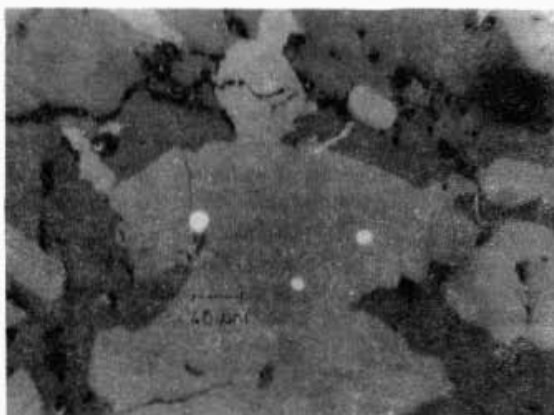

Fig. 1 — Rounded inclusions of homogeneous chromian spinels (white) enclosed in olivine phenocrystals (light grey)

Fig. 2 — Irregulary shaped core of aluminous chromian spinel (C) enveloped by *ferritchromit* (F) showing symplectic intergrowth plagioclase (dark grey) mantled by lighter titanomagnetite (M)
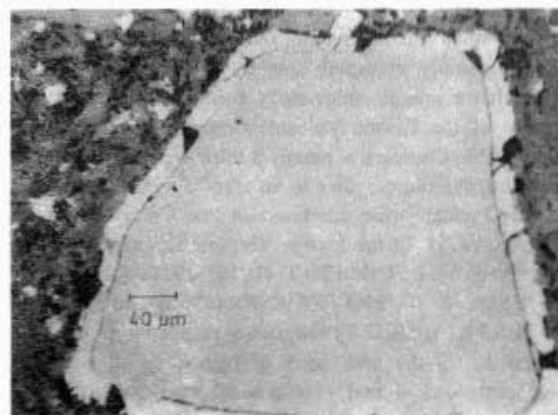

Fig. 3 — Euhedral but partly corroded dark core of chromian spinel sharply mantled by lighter titanomagnetite

borders. Chemical changes due to these alterations are great and because iron increases in the border phases, the external material has been termed *ferritchromit* by SPANGENBERG (1943). Quantitative electron microprobe analysis indicates that alteration of the cores display the following trend: increase in Fe and decrease in Mg and Al, with Cr remaining almost constant. This alteration zone *(ferritchromite)* is surrounded by a titanomagnetite rim with higher reflectance resulting of sharp increase in Ti and Fe, and decrease in Al, Cr, and Mg.

CHEMISTRY

Chromian spinels were alalysed with a Jeol Superprobe JCXA 733 and the results are given in Table II. The analysis for Fe were recalculated to give FeO and Fe_2O_3 assuming stoichiometry of the spinels. Major element electron microprobe profile across one gradationally zoned chromian spinel is shown in figure 4.
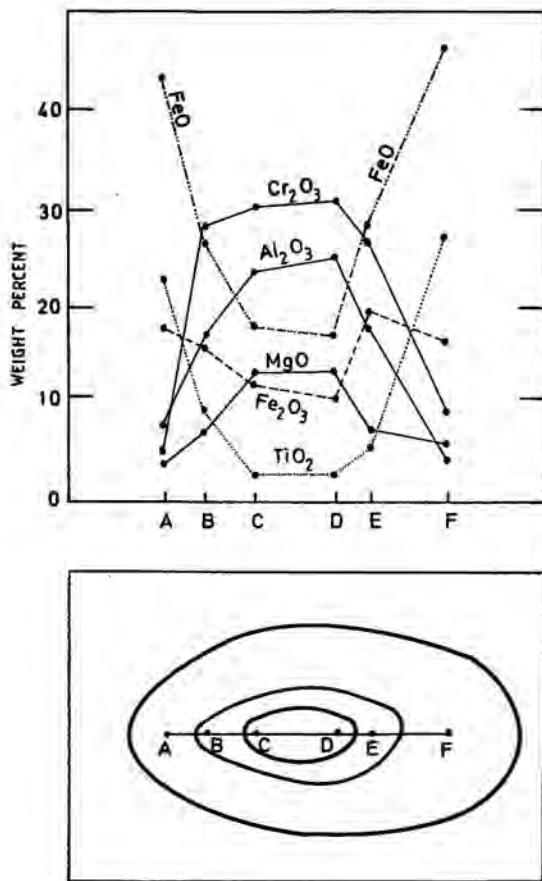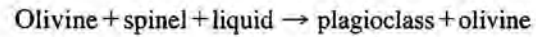
196

Fig. 4 — Electron microprobe profile across a zoned chromian spinel occurring in the groundmass of a porphyritic basalt. The cores are TiO₂ and FeO poor and MgO, Cr₂O₃ and Al₂O₃ rich. Analytical data for the A-B profile is listed in table 1 (grain 1)

Zoned chromian spinels in the groundmass were only identified in the coarsely crystalline porphyritic basalts which were prone to acumulative processes. The non porphyritic basalts only contain unzoned chromian spinels as inclusions in magnesian olivines, this being also common in porphyritic basalts. Apparently, in non porphyritic basalts the chromian spinels in the groundmass have disappeared by simple peritectic reactions of the type

Olivine + spinel + liquid → plagioclass + olivine

as would be predicted in simple synthetic systems as suggested by THAYER (1946) and IRVINE (1967).

In porphyritic basalts, zoned chromian spinels in the groundmass were preserved due to the limited proportions of intercumulus liquid or like RIDLEY (1977) suggested for the Rhum and Muck basalts, it was due to the limited temperature range over uhich spinel was in contact with intercumulus liquid or the major element buffering effect of surrounding cumulus silicate phase. In porphyritic basalts, total reaction of chromian spinels could have occured once pyroxene crystallized (RIDLEY, 1977) although this was precluded by precipitation of titanomagnetite which effectively shielded spinels from further reaction with the liquid.

The data in table II, shows that there is a wide range in compositions for the chromian spinels, the highest level for Cr_2O_3 and Al_2O_3 are 32.13 and 27.77 per cent respectively. TiO_2 content of chrome bearing titanomagnetite mantles may reach 25.48 percent. The zoned grains in the

TABLE 1

Representative analysis of aluminous chromian spinels, «ferrichromits) and titanomagnetite mantles occurring in the Lisbon Volcanic Complex

	1C′	1C″	1F′	1F″	1M′	1M″	2C	2M	3	4	5	6	7
TiO_2	2.13	2.43	4.09	5.12	23.57	25.48	2.71	24.06	2.17	5.76	4.36	4.41	6.12
Al_2O_3	24.18	25.03	17.32	16.86	5.45	4.68	27.77	3.64	22.36	18.51	21.36	21.48	13.23
Cr_2O_3	30.18	30.43	27.66	27.41	4.63	3.42	24.56	4.04	32.13	17.79	22.63	22.26	27.68
Fe_2O_3 *	12.34	10.35	15.84	19.61	18.23	15.71	10.79	19.35	22.15	36.38	33.07	32.70	22.77
FeO *	16.71	16.97	26.36	27.64	44.25	46.27	24.39	44.00	6.55	11.34	4.51	6.46	23.78
MgO	13.30	13.41	7.22	6.02	3.62	3.77	9.02	3.27	14.13	8.74	12.88	12.17	5.42
MnO	0.27	0.17	0.51	0.53	0.67	0.79	0.43	0.84	0.23	0.33	0.25	0.26	0.49
ToTal	99.11	98.79	99.00	99.32	100.42	100.12	99.67	99.20	99.72	98.85	99.06	99.74	99.49
cations per 32 oxygens													
Ti	0.40	0.45	0.82	1.03	5.04	5.46	0.51	5.26	0.41	1,15	0.83	0.84	1.26
Al	7.03	7.26	5.41	5.33	1.82	1.57	8.14	1.25	6.53	5.79	6.40	6.42	4.27
Cr	5.89	5.92	5.80	5.81	1.04	0.77	4.83	0.93	6.30	3.74	4.55	4.46	6.00
Fe³	1.55	1.27	2.08	2.78	3.07	2.73	1.29	3.30	2.36	4.17	3.39	3.43	3.21
Fe²	4.19	4.15	6.93	6.51	11.34	11.67	5.80	11.64	3.13	5.62	3.9o	4.19	6.93
Mg	4.89	4.92	2.85	2.41	1.53	1.61	3.34	1.42	5.22	3.46	4.88	4.60	2.21
Mn	0.05	0.03	0.11	0.12	0.16	0.19	0.09	0.20	0.05	0.07	0.05	0.06	0.12

* FeO and Fe₂O₃ were computed from total iron assuming complete stoichiometry of the spinels.

Note — C refers to core, F to ferritchromit bands and M to titanomagnetite mantles. Grain 1 is in the groundmass and shows gradational zoning. Grain 2 in the groundmass is sharply zoned. Grain 3 in the groundmass does not show zoning. Grains 4, 5, 6 and 7 are not zoned and occur in magnesian olivine phenocrystals.

groundmass, present rims that are more ferriferous than cores and inversely for magnesium, the cores being high in Cr_2O_3 and Al_2O_3 and low in TiO_2 and FeO. Comparatively, homogeneous xenomorphic grains in olivine are lower in Cr_2O_3 and Al_2O_3 and higher in FeO and Fe_2O_3 than cores of zoned grains in the groundmass. Homogeneous chromian spinels hosted in olivines of all basalt types tende to have lower $Mg/Mg+Fe^2$ ratios and lower Al than those in the groundmass.

Observation of the compositional ranges of the zoned chromian spinels in the groundmass reveals the following evolution stages:

1) *Initial stage*: simple substitutions Al-Fe^3 and 2Cr--Fe^2Ti;

2) *Intermediate stage*: decrease in Al and Mg, slight increase in Fe^3 and Ti, and increase in Fe^2;

3) *Late stage*: rapid depletion in Cr and rapid increase in Ti and Fe^2 as well as slight increase in Mn.
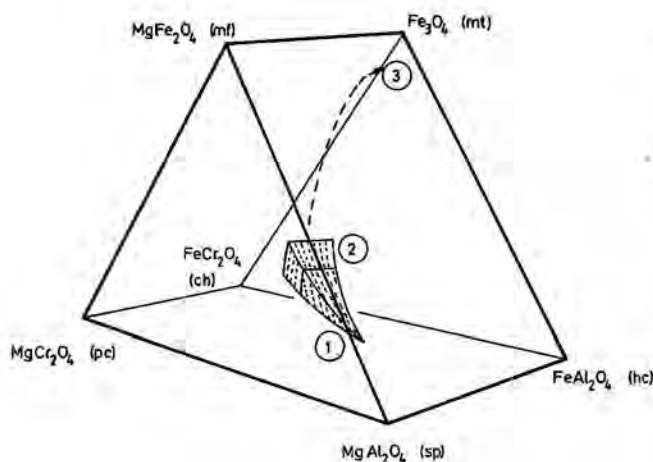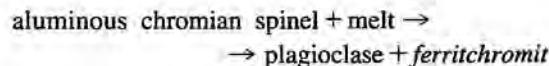
These stages are shown in figure 5.

Fig. 5 — Evolutionary trend of chromian spinel crystallization as projected in the multicomponent spinel prism: (1) initial Al/Mg chromite; (2) intermediate stage of *ferritchromite* (ferriferous chromite); (3) projection field of late titanomagnetite mantles

The evolution of the chromian spinel compositions in the groundmass through these stages, may be interpreted in terms of the crystallization of the associated silicates. ALVES *et al.* (1980) state that the Lisbon Volcanic Complex is characterized by the appearence of the phases pyroxene, olivine, amphibole and plagioclase, in this order. We find it difficult to agree with this order not only for textural reasons, for augite commonly replaces and corrodes pre-existent olivine, but mainly based on chemical evidence shown by zoned chromian spinel trends.

Chromian spinel grains are also found enclosed in olivine crystals and this is taken to indicate that the chromian spinel crystallized before or possibly at the same time as olivine. Thus, the initial stage was characterized by crystallization of chromian spinel prior to and concurrently with olivine phenocrystals leading to a minor increase in the level of Al in the residual liquid with

depletion in Cr due to its partition into the chromite phase. Crystallization of olivine implied a rapid depletion of Mg in chromian spinel. The trend of chromite cores to *ferritchromit* bands involved an increase in the Cr/Al ratio. This increase coincided with a textural change in which tiny grains of plagioclese are intergrown with chromite (figure 2) in a symplectic texture reflecting a peritectic reaction:

aluminous chromian spinel + melt →

→ plagioclase + *ferritchromit*

This intermediate stage was therefore initiated by the crystallization of calcic plagioclase which reversed the trend of Al enrichment in the residual liquid. The resulting removal of Al from the liquid caused Al depletion in *ferritchromit* with only limited depletion in Cr. Spinelids continued to be the only phase in which Cr was partitioned. The changes are accompanied by a gradual increase in Fe^3, Fe^2 and Ti content of the spinels, the ratio Fe^3/Fe^2 remaining constant and only decreasing once titanomagnetite precipitates. As pointed out by RIDLEY (1977) due to the the large octahedral site preference energy of Cr and none for either Al or Fe^3, the increase in Fe^3 reflects the substitution of $Fe^3 →$ Al rather than $Fe^3 →$ Cr as is evident in the gradual decreasing spinel (sp) and hercynite (Hc) component in the Johnstone spinel prism (figure 5).

Crystallization of pyroxene depleted the residual liquids driving spinel compositions towards titanomagnetite, contemporaneously with the crystallization of the outer rims of titaniferous augite. In this late stage, after the initiation of pyroxene crystallization, Cr was rapidly consumed. The titanomagnetite rims were precipitated directly from the cooling melt upon the surface of previously reacted chromian spinel/*ferritchromit*, essentially protecting the spinels from further cation exchange and reaction with the silicate melt. These are the main trends revealed by the common zoning of chromian spinels. However, some grains do not show the intermediate *ferritchromit* bands (figure 3) and frequently the external rims of the *ferritchromit* bands are not parallel to the chromite cores (figure 2). This shows that some resorption occurred during the crystallization of the spinels. The frequent irregular zonation also shows that in the chromian spinels of the groundmass Fe and Ti diffused inwards and replaced Al, Mg and Cr which diffused outwards. The high content of Cr in titanomagnetite mantles (up to 4.63 %) as compared to xenomorphic contemporaneous titanomagnetite grains (Cr up to 0.4 %) also shows the existence of an outwards diffusion of Cr.

Summing up, the initial spinels to crystallize from the basaltic liquids were aluminous chromian spinels (figure 5). Exposure to the cooling silicate liquid gave rise to an enrichment of the magnesioferrite-chromite-magnetite components as compared to the initial spinel-hercynite-picrochromite solid solutions. The gradual increase in the Fe^2/Mg ratio, the enrichment in the Ti content, but constancy in the Fe^3/Fe^2 ratio, reflect the changing chemistry of the cooling silicate melt.

GEOTHERMOMETRY AND OXIGEN GEOBAROMETRY

Compositions intermediate between chromite and tita-nomagnetite rich spinels, have frequently been interpreted as formed by reaction of early formed chromite with the residual magmatic fluid during the end stages of crystallization (GUNN *et al.*, 1970). However, R. THOMPSON (1973) has suggested that spinels intermediate between titanian chromite and chromian titanomagnetite occurring in a Snake River basalt, formed directly from the melt. Experimental studies in the system MgO-iron oxide-Cr_2O_3--SiO_2 (ARCULUS *et al.*, 1974) illustrates in principle how both interpretations can be correct in individual circunstances. Evidence in the study of zoned chromian spinels in the groundmass of the Lisbon basalts suggests that the chemical zoning resulted from a reaction between spinel and liquid.

The chromian spinel inclusions within olivine phenocrysts are more likely to represent original liquidus compositions for they were prevented of subsequent reactions with silicate melt and apparently do not appear to have undergone important subsolidus cation exchange with olivine.

Studies of E. JACKSON (1969) emphasized the correlation between declining T and the $Mg/Mg+Fe^2$ ratio. T. IRVINE (1965) and G. ULMER (1969) laid more stress on increase of $Mg/Mg+Fe^2$ ratio with increasing f_{O_2}. R. HILL & P. ROEDER (1974) based on experimentel work have showed that the ratio is lowered by increase in f_{O_2} between 10^{-9} and 10^{-6} atm. at 1.200°C and only at higher f_{O_2} does the ratio increase. According to data provided by R. HILL & P. ROEDER (1974) at constant f_{O_2} the $Mg/Mg+Fe^2$ ratio declines steadily with falling T. The declining $Mg/Mg+Fe^2$ ratio in the Lisbon zoned spinels follows the pattern established by R. HILL & P. ROEDER (1974).

The lower thermal stability of titanomagnetite relative to chrome spinel is well illustrated by results of melting experiments (YODER & TILEY, 1962) in which titanomagnetite melted completely below 1.160°C in an olivine tholeite and below 1.200°C in a high alumina basalt. The chrome spinel in the olivine tholeite had only partly melted at 1.225°C while in the high alumina basalt it melted at 1.250°C. B. EVANS & J. MOORE (1968) reported that chrome spinels crystallized between 1.200 and 1.150°C in the Makaopuhi lava lake, whereas titanomagnetite crystallization only commenced below 1.070°C. The temperature interval corresponding to the paragenetic gap may thus be considered to be approximately 100°C.

The T. IRVINE (1965, 1967) olivine/spinel geothermometer as formulated by E. JACKSON (1969) can not be applied to terrestrial volcanic chromian spinels for according to B. EVANS & T. WRIGHT (1972) it gives temperatures in excess of 2.000°C. A re-evaluation of this geothermometer was undertaken by P. ROEDER *et al.* (1979) and the calculated temperature using his formulation are geologically most reasonable. Comparison of our data which includes analysis of olivine in equilibrium with chromian spinel, with data published by P. ROEDER

et al. (1979), confirm that the chromian spinels in the Lisbon Volcanic Complex begun to crystalize at approximately 1.200°C. Experimental data obtained by R. HILL & P. ROEDER (1974) on the composition of spinels in basalts crystallizing over a range of T and f_{O_2} provide a number of additional trends for the behaviour of major elements. Thus, for the Lisbon Volcanic Complex (figure 6) at constant T=1.200°C $Fe^3/Fe^3+Al+Cr$ and Fe^3/Fe^3+Fe^2 ratios, indicate an approximate $f_{O_2}=10^{-8.5}$ atm.

For a path of crystallization described by R. HILL & P. ROEDER (1974) for basalts slightly more siliceous than the ones of Lisbon, at 1.230°C the first crystallization phase is a chrome rich spinel. As T is lowered, the chromite becomes slightly rich in Fe and Ti with a concomitant decrease in Cr, Al and Mg. At a T=1.196°C olivine begins to crystallize together with chromite. At a T=1.168°c plagioclase crystallizes and below this T is clinopyroxene which starts crystallizing. The amount of chromite progressively decreases until it disappears and is no longer stable in equilibrium with the liquid. This occurs because the trace amount of Cr in the system readily enters the clinopyroxene structure, as it happens in the Lisbon basalts where clynopiroxene may contain up to 0.7 % Cr.
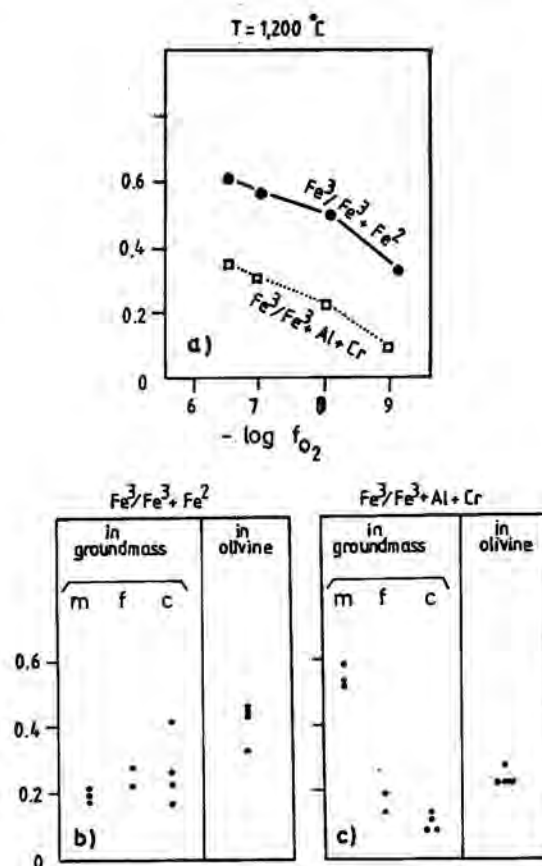

Fig. 6 — (a) Variation diagrams of spinel compositions Compiled by H. EALES & D. SNOWDEN (1979) from data of R. HILL & P. ROEDER (1974) at constant T=1.200°C and variable f_{O_2}; (b) & (c) Fe^3/Fe^3+Fe^2 and $Fe^3/Fe^3+Al+Cr$ ratios of chromian spinels in the Lisbon basalts occurring both in the groundmass and in Olivine phenocrysts (C=cores; F=ferrichromit bands; M=titanomagnetite mantles)
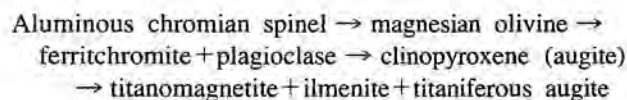
The intervening *spinel absent field* is approximately $10^{-8.5}$ atm. and 1.125-1.150°C. However at f_{O_2} greater than $10^{-8.5}$ atm. spinel crystallization is continuous (HAGGERTY, 1976). This demonstrates that in the Lisbon basalts, interruptions in the trend continuities from the base of the spinel Johnstone prism to the apices (figure 5) is a function of f_{O_2}. Thus, the main reason for the discontinuity in composition between chromian spinel and titanomagnetite in the Lisbon basalts is the reaction at low f_{O_2} between chromite, pyroxene and liquid. At about 1.120°C and much lower f_{O_2} the content of Fe^3, Fe^2 andTi of the residual liquid have increase sufficiently to cause a new spinel to precipitate: *the mantles of titano-magnetite*.

CONCLUSIONS

Chromian spinels were identified in basalts of the Lisbon Volcanic Complex as either small rounded homogeneous inclusions in magnesian olivine or as large zoned grains in the groundmass. Textural evidence and microprobe analysis of zoned chromian spinels revealed that an initial aluminous chromian spinel evolved to ferrous titanian spinel in response to changing compositions of the basalt liquid together with peritectic type reactions in which the initial aluminous chromian spinel became a chromian spinel with precipitation of plagioclase. This chromian spinel *(ferritchromit)* was later mantled by direct precipitation of titanomagnetite which protected the initial spinels from further cation exchange with the silicate melt.

Interpreting the evolution of spinel compositions in terms of the crystallization of associated silicates, the basalts of the Lisbon Volcanic Complex are characterized by the appearence of the following phases:

Aluminous chromian spinel → magnesian olivine → ferritchromite + plagioclase → clinopyroxene (augite) → titanomagnetite + ilmenite + titaniferous augite

The chromian spinels enclosed in olivine, do not appear to have undergone cation exchange with its host and the Fe/Mg ratio of the olivine seems to have remained unaffected by the enclosed spinel. Consequently these spinels were prevented from subsquent reaction with the silicate melt and may represent original composition. If this is so, the composition of these spinels indicate that they have crystallized at $f_{O_2} \sim 10^{8.5}$ atm. at T of about 1.200°C.

General increases in $Fe^3/Fe^3 + Al + Cr$ and $Fe^3/Fe^3 + Fe^2$ ratios and decrease in $Mg/Mg + Fe^2$ ratio of zoned chromian spinels represent crystallization of *ferritchromit* and titanomagnetite under conditions of decreasing f_{O_2} and T. The sharp contacts between rims and cores of some zoned spinels as well as sharp variations in composition, suggest a hiatus between crystallization of high Cr cores and low Cr high Ti mantles at low f_{O_2}. The mantles of titanomagnetite must have precipitated at T of about 1.120°C at much lower f_{O_2}.

AKNOWLEDGEMENTS

BIBLIOGRAPHY

ALVES, C. A. M.; RODRIGUES, B.; SERRALHEIRO, A. & FARIA, A. F. (1980) — *O Complexo Basáltico de Lisboa*. Com. Serv. Geol. de Portugal, 66, pp. 111-134.

ARCULUS, R. J.; GILLBERG, M. E. & OSBORN, E. F. (1974) — *The system MgO — Iron Oxide — Cr_2O_3 — SiO_2: Phase relations among olivine pyroxene, silica and spinel in ais at 1 atm*. Carnegie Institution, Ann. Rept. Director, Geophys. Lab., Year Book 73, pp. 317-322.

CHOFFAT, P. (1916) — *Sur le volcanisme dans le litoral portuguais au nord du Tage*. C. R. Acad. Sc. Paris, 162, pp. 981-983.

———— (1924) — *Esquises de la carte des regions éruptives du Nord du Tage*. Mem. Soc. Phy. H. H. de Genève, 39(8), pp. 461-467.

EALES, H. V. & SNOWDEN, D. V. (1979) — *Chromiferous spinels of the Elephant's Head Dike*. Mineral. Deposita, 14, pp. 227-242.

ENDERSON, P. (1975) — *Reaction trends show by chrome spinels of the Rhum layered intrusion* Geochim. Cosmochim. Acta, 39, pp. 1035-1044.

EVANS, B. W. & MOORE, J. G. (1968) — *Mineralogy as a function of depth in the prehistoric Makaopuhi lava lake*. Contr. Min. Petrol., 14, pp. 429-465.

EVANS, B. W. & WRIGHT, T. L. (1972) — *Compositions of liquid chromite from the 1959 (Kilauea Iki) and 1965 (Makahopuhi) eruption of Kilauea volcano, Hawaii*. Amer. Mineral., 57, pp. 217-230.

GUNN, B. M. R.; COY-YLL, R.; WATKINS, N. D.; ABRAMSON, C. E. & NOUGUIER, J. (1970) — *Geochemistry of an oceanite-ankaramite-basalt suite from East Island, Crozet Archipelago*. Contrib. Mineral. Petrol., 28, pp. 319-339.

HAGGERTY, S. (1976) — *Opaque Mineral Oxides in terrestrial igneous rocks*. Mineral. Soc. America, Spec. Publ. no. 3, Hg101-Hg300.

HILL, R. & ROEDER, P. (1974) — *The crystallization of spinel from basaltic liquid as a function of oxygen fugacity*. Journ. Geol., 82, pp. 709-729.

IRVINE, T. N. (1965) — *Chromian spinel as a petrogenetic indicator. Part. 1: Theory.* Canad. J. Earth Sci., 2, pp. 648-672.

———— (1967) — *Chromian spinel as a petrogenetic indicator. Part. 2: Petrological applications.* Canad. J. Earth Sci., 4, pp. 71-103.

JACKSON, E. D. (1969) — *Chemical variation in coexisting chromite and olivine in the chromitite zone of Stillwater Complex.* Econ. Geology Monograph, 4, pp. 41-71.

JESUS, A. M. & ZBYSZEWSKI, G. (1952) — *Contribution à l'étude du Complexe Basaltique de Lisbonne.* Com. Soc. Geol. de Portugal, 33, pp. 185-220.

RIDLEY, W. I (1977) — *The crystallization trends of spinels in Tertiary basalts from Rhum and Muck and their petrogenetic significance.* Contrib. Mineral. Petrol., 64, pp. 243-255.

ROEDER, P. L.; CAMPBELL, I. H. & JAMIESON, H. E. (1979) — *A Re-Evaluation of the olivine-spinel geothermometer.* Contrib. Mineral. Petrol., 68, pp. 325-334.

SERRALHEIRO, A. (1978) — *Contribuição para a actualização do conhecimento do Complexo Vulcânico de Lisboa.* Univ. of Lisbon unpublished report, 39 pages.

SPANGENBERG, K. (1943) — *Die Chromitelagerstätte von Tampadel am Zobten.* Zeitscher. prakt. Geologie, 51, pp. 13-23 & 25-35.

THAYER, T. P. (1946) — *Preliminary chemical correlation of chromite with the containing rocks.* Econ. Geology, 41, pp. 202-217.

THOMPSON, R. N. (1973) — *Titanian chromite and chromian titanomagnetite from a Snake River Plain basalt, a terrestrial analogue to lunar spinels.* Amer. Mineral., 58, pp. 826-830.

ULMER, G. C. (1969) — *Experimental investigations of chromite spinels.* Econ. Geology Monograph 4, pp. 114-130.

YODER, H. S. & TILLEY, C. E. (1962) — *Origin of basalt magmas.* J. Petrol., 3, pp. 342-352.