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

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RESUMO


As espinelas cromíferas são muito comuns nos basaltos alcalinos do Complexo Vulcânico de Lisboa, cuja idade se atribui ao Cretáceo 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 catiônicas complexas nos grãos zonados de cromite, devidas a reações peritécticas simples que constituem respostas às mudanças de composição do líquido basáltico. Estas variações da distribuição catiônica nas espinelas zonadas reflectem, também, as relações paragenéticas entre os óxidos e os silicatos. A cristalização das espinelas cromíferas iniciais processou-se a \(T \sim 1200^\circ C\) e \(f_o_2 \sim 10^{-8.5}\) 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 \(T \sim 1200^\circ C\) e a \(f_o_2\) inferior.

RÉSUMÉ

Mots-clés : Chromite — Ferritchromite — Basalte — Lisboa — Petrogénèse.

Les spinelles chromièfres 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 magnesíferes 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 catiôniques complexes au sein des grains zonés de chromite, en conséquence de réactions peritéctiques simples. Ces réactions représentent des réponses à des changements de la composition du liquide basaltique. Les changements concernant la distribution catiônique chez les spinelles zonées traduisent également les rapports paragenétiques entre les oxydes et les silicats. La cristallisation des premières spinelles chromièfres à eu lieu avec \(T \sim 1200^\circ C\) et \(f_o_2 \sim 10^{-8.5}\) atm. (ou simultanément avec) avant la formation de l'olivine magnésièfere. Les couches de titanomagnétite déposées sur les spinelles chromièfres zonées ont cristallisé à \(T \sim 1200^\circ C\) avec \(f_o_2\) plus bas.

ABSTRACT

Key-words : Chromite — Ferritchromite — 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 spectac­cularly 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 \(T \sim 1,200^\circ C\) and \(f_o_2 \sim 10^{-8.5}\) atm. earlier or contemporaneously with magnesian olivine. The titanomagnetite mantles of zoned chromian spinels crystallized at \(T \sim 1,200^\circ C\) 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, TiO₂ and Cr₂O₃ increase with decreasing SiO₂, 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).

| TABLE I |
| Average composition of three ankaramitic basalt samples containing large zoned chromian spinels |
| SiO₂ | 44.7 |
| TiO₂ | 2.9 |
| Al₂O₃ | 12.7 |
| Cr₂O₃ | 3.3 |
| FeO | 7.7 |
| MnO | 0.2 |
| MgO | 12.2 |
| CaO | 11.2 |
| Na₂O | 2.0 |
| K₂O | 1.4 |
| P₂O₅ | 0.3 |
| H₂O⁺ | 1.4 |
| H₂O⁻ | 0.4 |

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-Cr₂O₃-SiO₂ and CaO-MgO-Al₂O₃-SiO₂ 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 disappearance 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 occurrence in the basalts of the Libon...
Volcanic Complex. The occurrence 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 titanomagnetite crystals were constrained to fill available spaces within a framework of silicates.

In most chromian spinels, the oxides MgO, Cr$_2$O$_3$, Al$_2$O$_3$, Fe$_2$O$_3$, 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$_2$ were not detected and NiO just occurs in trace amounts.

The simplest chemical formula of a spinel mineral is R$^{3+}$R$^{4+}$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$^{3+}$Cr$_2$O$_4$ — chromite (ch)
- Fe$^{2+}$Al$_2$O$_4$ — hercynite (hc)
- Fe$^{2+}$Fe$_2$$^{3+}$O$_4$ — magnetite (mt)
- MgCr$_2$O$_4$ — picrochro mismatch (pc)
- MgAl$_2$O$_4$ — 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$^{4+}$O$_4$ — ulvospinel (uv)
- Fe$^{2+}$Fe$_2$$^{3+}$O$_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 borders. Chemical changes due to these alterations are great and because iron increases in the border phases, the external material has been termed ferrichromite 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 (ferrichromite) 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 analysed with a Jeol Superprobe JXA 733 and the results are given in Table II. The analysis for Fe were recalculated to give FeO and Fe$_2$O$_3$ assuming stoichiometry of the spinels. Major element electron microprobe profile across one gradationally zoned chromian spinel is shown in figure 4.
Zoned chromian spinels in the groundmass were only identified in the coarsely crystalline porphyritic basalts which were prone to accumulative 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

\[ \text{Olivine} + \text{spinel} + \text{liquid} \rightarrow \text{plagioclase} + \text{olivine} \]

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 which 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 occurred once pyroxene crystallized (RIDLEY, 1977) although this was precluded by precipitation of titano-magnetite which effectively shielded spinels from further reaction with the liquid.

The data in Table 1, shows that there is a wide range in compositions for the chromian spinels, the highest level for \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) are 32.13 and 27.77 per cent respectively. \( \text{Ti}_2\text{O}_3 \) content of chrome bearing titanomagnetite mantles may reach 25.48 percent. The zoned grains in the

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### Table 1

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<td>2M</td>
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<td>TiO₂</td>
<td>2.13</td>
<td>2.43</td>
<td>4.09</td>
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<td>25.48</td>
<td>2.71</td>
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<td>5.76</td>
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<td>Al₂O₃</td>
<td>24.18</td>
<td>25.03</td>
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<td>27.77</td>
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<tr>
<td>Cr₂O₃</td>
<td>30.18</td>
<td>30.43</td>
<td>27.66</td>
<td>27.41</td>
<td>4.63</td>
<td>3.42</td>
<td>24.56</td>
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<td>17.79</td>
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<td>FeO*</td>
<td>12.34</td>
<td>10.35</td>
<td>15.84</td>
<td>19.61</td>
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<td>15.71</td>
<td>10.79</td>
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<td>36.38</td>
<td>33.07</td>
<td>32.70</td>
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<tr>
<td>MgO</td>
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<td>26.36</td>
<td>27.64</td>
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<td>46.27</td>
<td>24.39</td>
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<td>11.34</td>
<td>4.51</td>
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<tr>
<td>MnO</td>
<td>0.27</td>
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<td>0.51</td>
<td>0.53</td>
<td>0.67</td>
<td>0.79</td>
<td>0.43</td>
<td>0.84</td>
<td>0.23</td>
<td>0.33</td>
<td>0.25</td>
<td>0.26</td>
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<tr>
<td>Total</td>
<td>99.11</td>
<td>98.79</td>
<td>99.00</td>
<td>99.32</td>
<td>100.42</td>
<td>100.12</td>
<td>99.67</td>
<td>99.20</td>
<td>99.72</td>
<td>98.85</td>
<td>99.06</td>
<td>99.74</td>
</tr>
</tbody>
</table>

* \( \text{FeO} \) and \( \text{Fe}_2\text{O}_3 \) were computed from total iron assuming complete stoichiometry of the spinels.

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Note — C refers to core, F to ferrichromite 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 phenocrysts.
groundmass, present rims that are more ferriferous than cores and inversely for magnesium, the cores being high in Cr$_2$O$_3$ and Al$_2$O$_3$ and low in TiO$_2$ and FeO. Comparatively, homogeneous xenomorphic grains in olivine are lower in Cr$_2$O$_3$ and Al$_2$O$_3$ and higher in FeO and Fe$_2$O$_3$ than cores of zoned grains in the groundmass. Homogeneous chromian spinel host in olivines of all basalt types tend 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$^3+$Ti;
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.

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 appearance 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-existant 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. This increase in the level of Al caused Al 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 ferritchromite bands involved an increase in the Cr/Al ratio. This increase coincided with a textural change in which tiny grains of plagioclase are intergrown with chromite (figure 2) in a symplectic texture reflecting a peritectic reaction:

aluminous chromian spinel + melt → plagioclase + ferritchromite

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 ferritchromite 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 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).

Cry stalization 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/ferritchromite, 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 ferritchromite bands (figure 3) and frequently the external rims of the ferritchromite 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 titanomagneteite 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-magneteite components as compared to the initial spinel-hercynite-picrochromite solid solutions. The gradual increase in the Fe$^3+/Mg$ 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 OXGEN GEobarometry

Compositions intermediate between chromite and titanomagnetite 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-Cr₂O₃-SiO₂ (Arculus et al., 1974) illustrate in principle how both interpretations can be correct in individual circumstances. 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 subsediments cation exchange with olivine.

Studies of E. Jackson (1969) emphasized the correlation between declining T and the Mg/Mg²⁺ ratio. T. Irvine (1965) and G. Ulmer (1968) laid more stress on increase of Mg/Mg⁺⁺Fe²⁺ ratio with increasing fO₂. R. Hill & P. Roeder (1974) based on experimental work have showed that the ratio is lowered by increase in fO₂ between 10⁻³ and 10⁻⁶ atm. at 1.200°C and only at higher fO₂ does the ratio increase. According to data provided by R. Hill & P. Roeder (1974) constant fO₂ the Mg/Mg⁺⁺Fe²⁺ ratio declines steadily with falling T. The declining Mg/Mg⁺⁺Fe²⁺ 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 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 fO₂ provide a number of additional trends for the behaviour of major elements. Thus, for the Lisbon Volcanic Complex (figure 5) at constant T=1.200°C Fe²⁺/Fe³⁺+Al⁺⁺Cr and Fe²⁺/Fe³⁺+Fe⁶⁺ ratios, indicate an approximate fO₂=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 titan 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 crystalize together with chromite. At a T=1.168°C plagioclase crystallizes and below this T 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 clinopyroxene may contain up to 0.7% Cr.
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$^{2+}$, Fe$^{3+}$ and Ti of the residual liquid have increase sufficiently to cause a new spinel to precipitate: the mantles of titanomagnetite.

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 (ferrichromit) 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 appearance of the following phases:

- Aluminous chromian spinel → magnesian olivine → ferrichromite + 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 subsequent 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$^{2+}$/Fe$^{3+}$+Al+Cr and Fe$^{2+}$/Fe$^{3+}$+Fe$^{2+}$ ratios and decrease in Mg/Mg$^{2+}$ of zoned chromian spinels represent crystallization of ferrichromit 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 $f_{O_2}$.

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