Petrogenesis of early paleozoic peralkaline rhyolites from the Macedo de Cavaleiros region (NE Portugal)

By M. LUISA RIBEIRO, Lisboa*

With 13 figures, 9 tables and 1 plate

Zusammenfassung


Abstract

The petrology and geochemistry of Variscan peralkaline gneisses from NE Portugal, discovered in 1962, is presented. Major and trace element data for the oversaturated sequence of the Macedo de Cavaleiros area depict some specific geochemical patterns: high Fe2O3, even higher than in the Ethiopian Main Rift, high REE concentrations and small Eu anomalies. Field and petrographical observations also suggest that liquid immiscibility has played an important petrogenetic role in the crystallization trends. The alternating pyroxene- Feldspat-hematite-rich bands observed in outcrop are interpreted as resulting from fluctuating fO2 conditions. Petrological and geochemical data show that these pantelleritic and komendinitic rocks are the end members of an alkaline-transitional basaltic sequence, by which they are overlain. An uppermost sequence of oceanic tholeiitic basalts completes the picture of an evolving rift environment, where mantle processes generate crustal thinning and eventually oceanic crust.

Résumé

L'auteur présente la pétrologie et la géochimie des gneiss varisiens peralcalins du nord-est du Portugal, découverts en 1962. Les analyses des éléments majeurs et en traces dans ces roches sousaturées montrent quelques caractéristiques spéciales comme la haute teneur en Fe2O3 (t) (supérieure même à celles de l'Ethiopian Main Rift), la haute concentration en terres rares et la faible anomalie négative de Eu. La géologie de terrain et les observations pétrographiques suggèrent aussi que l'immiscibilité entre liquides a joué un rôle pétrogéénétique important au cours de la cristallisation. Les alternances de bandes alternativement riches en pyroxène-feldspath et en hématite, observées sur les affleurements, sont interprétées comme le résultat de la fluctuations de fO2. Les données pétrologiques et géochimiques montrent que les roches pantellertiques et komendinitiques représentent les derniers termes d'une séquence du type alcalin-transitional qui les surmonte. La séquence volcanique dans le secteur de Macedo de Calvaiereiros se termine par des basaltes tholéitiques qui complètent le cadre d'une environnement d'un zone de rift dans laquelle les processus mantélique ont déterminé l'amincissement crustal et la formation d'une croûte océanique.

Краткое содержание

Приводятся петрологические и геохимические данные исследований варисских першёлочных гнейсов, распространенных в северо-восточной части Португалии, описанные впервые в 1962 году. Распределение основных и рассеянных элементов в этих перешленных породах проявляет неясные особенности, как напр.: высокое содержание Fe2O3, превышающее даже таковое в "Ethiopian Main Rift", высокое содержание Редких Земель и небольшую отрицательную аномалию европия. На основании полевых и петро графических исследований установили, что в ходе

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I. Introduction

Peralkaline silicic rocks which have molar excess of alkalies over alumina are not very common. Bowden (1974) presented a map of the sites of peralkaline magmatism in the world and its relationship with plate tectonics. Peralkaline rocks can be found in several different tectonic environments:

- epeirogenic doming and rifting as in the African occurrences;
- near or above spreading ocean ridge crests, as in Ireland and the Azores;
- at continental margins as in New-Mexico and Central Rio Grande;
- behind island arcs as in Mayor Island and New Zealand.

That author describes the different kinds of peralkaline rocks and their associated rocks in the various environments listed above which is important for correlation purposes regarding older occurrences.

Alkaline rocks in the Iberian Peninsula were first reported by MacPherson (1881) in the Vigo area (Spain) and Haavatsch (1906) in the Cevadais area (SE Portugal).

Meanwhile, many other articles have been published by other authors reporting petrographic aspects and major element geochemistry (Osann 1907; Lacroix 1916; Burri 1928; Texeira and Assunção 1956, 1958; Serralheiro 1957; Neves 1959; Assunção & Gonçalves 1970; Gonçalves 1971; Pondal 1956, 1967). Trace element data were not available, however.

Geochronological data by the Rb/Sr method (Piern et al., 1970, 1972) indicate an age of 430-440 Ma. (Upper Ordovician/Lower Silurian) for acidic magmatism in NW Galicia (including a sample from the Macedo de Cavaleiros peralkaline rhyolites). More recently Casqueries et al. (1985) have obtained 470 Ma for Almendralejo peralkaline metagranite.

However, in South Portugal there are occurrences of peralkaline volcanic rocks interbedded in Cambrian and Silurian sediments. All types are strongly deformed by the Variscan orogeny.

The relationship between these peralkaline rocks and their sources is never mentioned, perhaps because of the intensity of deformation and metamorphism and the sparsity of outcrops.

In the Macedo de Cavaleiros area, peralkaline volcanic rocks have been recently discovered by A. Ribeiro during the mapping of Eastern Trás-os-Montes.

The geology and petrography of these occurrences was described by A. Ribeiro and M. L. Ribeiro (1972) and they were tentatively correlated with the intrusive rocks of Galiñeres (FLOOR 1966).

In the lights of Coomans (1963) classical study on the trends and affinities of basaltic magmas, several young peralkaline suites have been interpreted as deriving from alkalit-transitional basaltic parental magma by fractional crystallization (see Barberi et al., 1974, and references therein).

Nevertheless, the petrogenesis of peralkaline silicic rocks is still poorly known and isotopic studies have revealed that other processes than fractional crystallization must be invoked to develop a petrogenetic model.

Geochemical and field evidence in the Macedo de Cavaleiros area, where the peralkaline rocks are very well exposed, shows that these result from nearby parental mafic rocks by a somewhat different process.

The present study includes the first geochemical data for pre-Hercynian peralkaline rocks of the Iberian Peninsula. It is expected that the present contribution may trigger further studies both in the petrological and the stratigraphical fields.

II. Geological setting

In recent years A. Ribeiro (1974) Bard et al. (1980) and Igleias et al. (1983) have defined the principal features of the structural unites in NW of the Iberian Peninsula. It has long been known that the tectonic and paleoerographic zones in this part of the Hercynian orogen are coincident and describe an arc (Swiss 1897/1902; Lotze 1950; Julivert et al., 1975). The oldest and most metamorphosed and deformed terrains are situated in the inner part of this orogen. Its external zones are folded with convergent vergence. The Macedo de Cavaleiros area lies on the inner part of the structure, in the Centro-Iberian zone. Nevertheless, the tectonists needed to distinguish another
petrogenesis of early paleozoic peralkaline rhyolites

fig. 1. localization of the macedo de cavaleiros area (+) in the variscan belt, after franke & engel (1986) modified. rh - rhenobercynian; st - saxothuringian; mo - moldanubian; ms - moravo-silesian; sp - south-portuguese; om - ossa morena; ci - centro iberic zone; na - north armorican; ca - centro armorican; sa - south armorican; ca - cantabrian zone; gt - galicia - trás-os-montes sub-zone

sub-zone - the w galicia - e trás-os-montes sub-zone - given the special lithological and structural characteristics of that area, fig. 1.

the main feature of the w galicia-e trás-os-montes subzone is the occurrence of a series of superimposed nappes, carried from west to east. the horizontal displacement of these nappes over the autochthonous and sub-autochthonous lower to medium paleozoic sediments, is over 200 km (see also schermerhorn and kotsch 1984).

the three principal nappes are:
1. the lowermost nappe - which represents the metasedimentary and metavolcanic centro-transmontane unit of Ordovician to Devonian age (ribere 1974);
2. the intermediate nappe - which represents the morais unit, characterized by the presence of high grade mafic/ultramafic rocks (peridotites, fassergabbros, amphibolites) belonging to an ophiolite sequence (badham et al., 1982). its age is tentatively considered variscan (ribere 1983).
3. the upper nappe - which represents the lagoa/bragança unit and consists of a high grade polymetamorphic sequence of mafic and ultramafic rocks (granulites, blastomylonitic lherzolites) overlain by a monometamorphic sequence of cambrian phyllites overlying augen gneisses which are considered precambrian in age.

the macedo de cavaleiros region lies in the lowermost nappe near the western side of the morais unit. the mapped area is bounded by the facho overthrust in the west; by the vilariça fault in the east; by the torto fault in the south and other secondary faults constitute the northern limit.

iii. lithology and stratigraphy

in the macedo de cavaleiros area different lithological types of metavolcanic and metasedimentary rocks striking roughly north-south and dipping eastward (fig. 2). from west to east the following seven lithological units occurs, representing a normal sequence, according to tectonic and sedimentary polarity criteria:

- alto de sequeira formation - the lowermost unit, consisting of phyllitic and quartz feldspathic rocks, generally with volcanic contribution. the mineralogical associations in these rocks are shown in table 1.
- facho formation - the peralkaline unit. at the base of the formation are massive rhyolitic rocks and, at the top, the banded types have also a rhyolitic composition. decimetric inclusions of mafic rocks may occur sporadically, interbedded in the upper facies.
the massive rhyolitic rocks present different facies with distinct colours, which can be seen in the field
outcrops. These colours are dependent on the mineralogical proportions of the femic components. So, riebeckite rhyolites (Fla) are dark blue; aegirine rhyolites (Fib) are green and rhyolites without sodic femic minerals (Flc) are white or pink. The riebeckitic and aegirinic facies always correspond to normal ash flow tuffs and some of them may contain some sedimentary contribution. The mineralogical associations of these facies can be seen in Table I.

However, in both massive and banded types there are a few black centimetric discontinuous layers, and clasts, mostly composed of iron oxides. Rare lenticular basic rocks interbedded in the peralkaline sequence display some characteristics of pillow lavas.

The mineralogical association is:

\[
ab + micr + bi + pheng + ep + chl + oxFe + sph + cc
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- **Carrapatas Formation** – mainly composed of low to medium grade metabasaltic rocks with two metric intercalations of rhyolitic rocks with peralkaline affinities. In this formation rare light-coloured outcrops of interme-
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Tab. 1. Qualitative mineralogical composition of facies of different formations. + - present () absent F = Fe + FeO; R = Reibekite massive type; P = Peridot massive type; G = Gabbro massive type; M = Mafic intercalations; C = Calcite; Sp = Sphene; Pl = Plagioclase; D = Diopside; C = Clinozoisite; A = Aegerine; Al = Albit; Cps = Crystalline Plagioclase; Sp = Sphene; Ph = Phenocrysts; Ph = Phlogopite; Zr = Zircon; H = Hornblende.

1. a) Riedensive rocks have also been found. Some intrusions with affinities to the Carrapatas Formation were found in the Alto de Sequeira, Facho and Alto de Casais Formations which confirms the established stratigraphy.

2. Nevertheless, in some places (near fault and thrust planes) in the southeast part of the region green-schists display markedly different mineralogical compositions. The mineralogical compositions of all these rocks are presented in Table I.

3. Alto de Casais Formation - this is another rhyolitic metavolcanic unit which becomes volcanic-sedimentary towards the base, where includes tuffites and interbedded cherts. Nevertheless, the Alto de Casais rhyolitic rocks are a rather homogeneous unit, very different from the Facho Formation, in both mineralogical and textural features. The Alto de Casais rhyolites do not contain sodic feldics. The grain size of the mineral phases is coarser than in the Facho rhyolites and magmatic relics (quartz and felspares) are frequently observed notwithstanding their strong deformation and recrystallization. The mineralogical associations present in these rhyolitic tuffs are shown in Table I.

4. Madorra Formation - a highly pelitic formation with some intercalations of green-schists and very rare interbedded centimetric layers of chertic rocks. The mineralogical associations for phyllites and green-schists are respectively in Table I. This formation has been correlated, given the facies similarities, with the «xistos borra de vinho» (red phyllites) from other parts of Trás-os-Montes.

5. Macedo de Cavaleiros Formation - a monotonous green-schist to amphibolite facies sequence of basic rocks derived from ancient basalts and tuffs. Sometimes it contains thin intercalations of phyllitic and quartz-phyllic rocks similar to those of the Madorra Formation. The mineralogical associations in metavolcanic mafic rocks are in Table I.
Valbemfeito Complex—a metagabbro series with rare and thin dikes of felsic rocks. This complex is intrusive in the Madora formation. The metagabbros present some blastomylonitic features and display mineralogical associations presented in Table I.

In the felsic rocks albite is the main mineralogic phase (85%). (The mineralogical associations are in Table I).

IV. Mineralogy of the Facho peralkaline rocks

Magmatic relict minerals in Facho rocks are very rare due to strong deformation and metamorphism. However, some relict minerals and textures still exist.

Some feldspars probably show their original shapes but not their initial chemical composition. These shapes (Pl. I) record effusive episodes.

Later albite is commonly found and unmixing textures are always present in the alkali feldspars. The compositions of these minerals (some of which are shown in Table II) may correspond to intermediate terms from an original composition. Fig. 3 shows the chemical range of alkali feldspars in comendites and pantellerites found by Garbarino & Maccioni (1968) and Nicholls & Carmichael (1969); when

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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
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<td>9.14</td>
<td>0.21</td>
<td>9.62</td>
<td>1.52</td>
<td>4.50</td>
<td>0.58</td>
<td>10.36</td>
</tr>
<tr>
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<td>5.23</td>
<td>3.22</td>
<td>15.77</td>
<td>2.11</td>
<td>14.92</td>
<td>10.13</td>
<td>15.47</td>
<td>1.12</td>
</tr>
<tr>
<td>TOTAL</td>
<td>98.46</td>
<td>99.50</td>
<td>98.41</td>
<td>98.62</td>
<td>99.12</td>
<td>99.20</td>
<td>98.86</td>
<td>97.74</td>
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</table>

Ions on the basis of 32.0 oxyg.

| A1VI| 0.026  | 0.040  | 0.001  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| T  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  |
| FeII| 0.013  | 0.003  | 0.016  | 0.388  | 0.429  | 0.037  | 0.082  | 0.043  |
| Mg  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  |
| Mn  | 0.000  | 0.000  | 0.000  | 0.000  | 0.011  | 0.000  | 0.000  | 0.000  |
| Ca  | 0.002  | 0.002  | 0.000  | 0.015  | 0.010  | 0.000  | 0.010  | 0.000  |
| Na  | 2.620  | 3.137  | 0.076  | 3.363  | 0.557  | 1.581  | 0.208  | 3.597  |
| K   | 1.189  | 0.727  | 3.766  | 0.405  | 3.600  | 2.357  | 3.850  | 0.256  |

Tab. 2. Representative compositions of alkali feldspar of peralkaline rocks.
minerals and textures still probably show their original initial chemical composition. The effusive episodes, only found and unmixed textural inter alia in the alkali feldspars. The minerals (some of which are correspondent to intermediate composition. Fig. 3 shows the feldspars in comodinicities and GARRABINO & MACCIONI & CARMICHAEL (1969); when compared with the composition of Facho rocks this opinion is strengthened.

Sodic amphiboles (Table III) are found associated with all structural surfaces including the last microshear fractures (Pl. I). They correspond mostly to riebeckite-magnesio-riebeckite amphiboles (Fig. 4). However there are two analyses of sodic amphiboles outside this range (a crossite and a magnesium-ardvedsonite) which may be relevant to the understanding of the petrogenesis of these rocks. Crossite was described 40 km west of this area (RIESE 1967; MUNHA et al. 1984) related with high-pressure metamorphism. Magnesio arvedsonite may be relat-

Fig. 3. Comparison between the chemical composition of the alkali feldspars of the Macedo de Cavaleiros peralkaline rocks and the ranges found by Nicholls & Carmichael (1969), Garbarino & Maccioni (1968) for pampellenica and komenditic rocks (see Bowden op. cit.).

Fig. 4. Plot of sodic amphiboles of peralkaline rocks according to Leake's (1978) classification of amphiboles.

<table>
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<tr>
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<th>rsm172.4</th>
<th>rsm174.2</th>
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<td>3.84</td>
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<tr>
<td>TiO2</td>
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<td>0.14</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>Fe2O3</td>
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<td>24.26</td>
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<tr>
<td>MgO</td>
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<td>10.13</td>
<td>2.62</td>
<td>8.65</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.42</td>
<td>0.73</td>
<td>0.28</td>
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<tr>
<td>CoO</td>
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<td>1.21</td>
<td>1.56</td>
<td>1.87</td>
</tr>
<tr>
<td>Na2O</td>
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<td>7.13</td>
<td>4.71</td>
<td>8.44</td>
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<tr>
<td>K2O</td>
<td>0.56</td>
<td>0.41</td>
<td>0.01</td>
<td>0.13</td>
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<tr>
<td>Cr2O3</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TOTAL</td>
<td>96.25</td>
<td>95.55</td>
<td>95.56</td>
<td>95.77</td>
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</table>

13 CATIONS EXCEPT CA NA K

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<td>TiO2</td>
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<td>0.05</td>
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</tr>
<tr>
<td>Cr</td>
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<td>0.00</td>
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<td>Co</td>
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</tr>
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<td>Ca</td>
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<td>0.20</td>
<td>0.27</td>
</tr>
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<td>1,609</td>
<td>1,416</td>
<td>1,730</td>
</tr>
<tr>
<td>Na (A)</td>
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<td>0.02</td>
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</tr>
<tr>
<td>K</td>
<td>0.11</td>
<td>0.07</td>
<td>0.05</td>
<td>0.02</td>
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Tab. 3. Representative compositions of alkali amphiboles of the Facho peralkaline rocks.

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<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Mg</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Al</td>
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<td>0.010</td>
<td>0.010</td>
<td>0.010</td>
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<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>Fe</td>
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<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
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<tr>
<td>Mn</td>
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<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>Mg</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>Fe</td>
<td>0.030</td>
<td>0.030</td>
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<td>0.030</td>
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<tr>
<td>Mn</td>
<td>0.030</td>
<td>0.030</td>
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<td>0.030</td>
</tr>
<tr>
<td>Co</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>Na</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>K</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Tab. 4. Representative compositions of alkali pyroxenes of the Facho peralkaline rocks.
Fig. 5. Plot of alkali pyroxenes in terms of (Na+K), Mg and (Fe\textsuperscript{3+}+Mn).

ted with magmatic or postmagmatic parageneses of these rocks.

Sodiic pyroxenes usually are very small and always display deformation textures. Their chemical compositions (Table IV) project as two groups the Aegirine-Augite field (Fig. 5). The most magnesian pyroxenes are probably more closely related with magmatic parageneses and the other less magnesian group are related with metamorphic events.

Biotite is another mineral present in the Facho Formation. It has green colour in the aegirine-dominant volcanics and brown colour in the other types. It is always a metamorphic mineral. The analyses (Table V) show how it is dependent on the rock composition and the effect of the low alumina rock content on the biotite composition.

Garnet rarely occurs, it is found especially in the FeC group and it is also related with metamorphic events. The garnets studied are mainly andradite (Table VI). Also magnetite and sphene display textures related with metamorphic events. However, zircon and allanite, as relict minerals of magmatic paragenesis, are frequently present in the peralkaline rocks. Both may attain sizes of about 0.5 mm but usually are smaller. Frequently they are broken and deformed. Allanite sometimes displays a zoned structure (Pl. I).

V. Structure

As shown above, the Macedo de Cavaleiros area lies in the lowermost of the stacked nappe of the Galicia – Trás-os-Montes subzone. The Facho thrust is the contact surface between this highest centrotransmontan nappe and the lower centro-transmontan units.

The southeast part of the area is bound by the Torto Fault, an important structure contemporaneous with the overthrusting (Ribeiro et al., in press).
Petrogenesis of early paleozoic peralkaline rhyolites.

The other faults, in the East Vilarica Fault and in the North of the mapped area, seem to have less affected the internal structure of the rocks. However, the degree of deformation in all facies is very strong, as evidenced in both field outcrops and thin sections.

On the basis of field evidence it was possible to distinguish three phases of deformation:
- The first phase was the most important and it was responsible for the main features of the present structure. At the macroscopic scale it produced recumbent folds and overthrusts. The folds at the outcrop scale are expressed as shear folds. There is a strong preferred orientation along the cinematic axis-3 of these folds. The cleavage associated with the first phase is a planar-linear or planar structure transposing the bedding and the lineations are usually alignments.
- The second phase produced more open and asymmetric folds (not isoclinal folds) with vergence to the E. Its cleavage is a strain-slip-cleavage with smaller dips than the first cleavage. In the outcrops some facies (especially the banded peralkaline rhyolites) show spectacular interference structures of the two main phases of deformation. Related with these phases of deformation are also the Facho overthrust and the Torto fault.

### Table 5: Representative compositions of biotite in Facho peralkaline rocks.

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<tr>
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<th>btm702.1</th>
<th>btm702.2</th>
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<td>5102</td>
<td>36.28</td>
<td>38.46</td>
<td>37.73</td>
<td>38.03</td>
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<tr>
<td>41203</td>
<td>10.28</td>
<td>9.86</td>
<td>9.83</td>
<td>10.43</td>
</tr>
<tr>
<td>4102</td>
<td>2.47</td>
<td>2.33</td>
<td>1.78</td>
<td>1.90</td>
</tr>
<tr>
<td>FeO</td>
<td>29.23</td>
<td>28.36</td>
<td>28.04</td>
<td>29.53</td>
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<tr>
<td>MgO</td>
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<td>5.65</td>
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<tr>
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<td>0.01</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Na2O</td>
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<td>0.13</td>
<td>0.07</td>
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<tr>
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<td>8.86</td>
<td>9.08</td>
<td>8.82</td>
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Ions on the basis of 22 cations

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<th>3.005</th>
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<td>0.000</td>
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<td>Ti</td>
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### Table 6: Representative compositions of garnets in Facho peralkaline rocks.

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<td>MnO</td>
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</tr>
<tr>
<td>K2O</td>
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Ions on the basis of oxines

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<td>alm</td>
<td>3.06</td>
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</table>

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...
In this section the cleavage style of this phase is always recognizable. Also, some minerals like stilpnomelane are related exclusively to the second phase of deformation. Albite porphyroblasts is also mostly related with this phase.

- The third phase is not very important in the area. It developed small concentric folds, with crenulation and kinks, more visible in the Alto de Caisais rhyolitic unit. The main effect of this 3rd phase event in the area was to obscure the evidence of the two primitive phases.

VI. Metamorphism

The metamorphism in the W-Galicia/E-Trás-os-Montes subzone is very different from the other parts of Centro-Iberian zone.

The main feature of the Centro-Iberian zone metamorphism is the low P/T gradient which was enough to partially melt enormous amounts of sediments in the lower and medium parts of the crust for extensive areas. That melt ascended to the upper part of the crust, as several various sized granitic batholiths, producing also local thermal gradients, which sometimes intercept one another.

These batholiths are occasionally associated with basic rocks, and there is no concensus regarding the role of these rocks on the origin and evolution of the magmatism and metamorphism of the Variscan chain. (Could these rocks have produced enough heat to initiate melting? or would they have enhanced the Variscan gradient everywhere they were emplaced?)

The granitic rocks began to arrive at the upper crust between the first and the second phases of deformation but the climax of granitic magmatism in the Centro-Iberian zone appears to be closely related with the third phase of deformation.

In the W-Galicia/E-Trás-os-Montes subzone, the granitic batholiths are very rare, specially where the nappe units are thicker. The metamorphic isograds are frequently inverted. Blueschist metamorphism has been reported from several places (Neiva 1948; Ribeiro 1976; Ribeiro et al., 1982; Munha et al., 1984; Schmerhorn & Kotsch (1984); Ibaragiuch & Grines (1981)) associated with the lowermost nappe.

In the upper nappe the history of the metamorphism is much more complex: granulitic and eclogitic rocks are also associated with medium and high grade polymetamorphic mafic rocks which in turn were also intruded by other basic monometamorphic ones at the intermediate nappe; at the top of the pile, the low to medium grade metamorphic sequence is not continuous with the underlying very high grade sequence.

However, in the lowermost nappe and the subautochthonous Paleozoic sediments of the W-Galicia/E-Trás-on-Montes subzone the metamorphic regime of the first and second phases seems to be different from that of the third phase.

Blueschist metamorphism was contemporaneous with the two initial phases which are related with overthrusting. When the third phase took place, the nappe were already in their present positions, where they attained the general metamorphic gradient of the Centro-Iberian zone.

In the area mapped the contact metamorphism of the Romeu granite (situated 1 km to the West) stops at the Facho overthrust.

On the W side of this structure, the pelitic schists have andalusite porphyroblasts and on the E side, the peralkaline and other metasedimentary rocks of the area under study seem not to be affected by the Romeu granite thermal gradient. This must signify that contact metamorphism predates the latest movement along the Facho overthrust, possibly in extensional regime by gravity spreading.

Table I shows the main mineralogical associations in the several facies of different formations of the Macedo de Cavaleiros area.

The metamorphic facies of the rocks are the most sensitive to the metamorphism. Their mineralogical associations show a gradual increase in modal hornblende contents from the Northwest to the Southeast. As commonly observed in other areas, there is a transitional zone between greenschists and amphibolites making it impossible to draw an isograd. Thus, the studied zone may be considered an intermediate greenstone – amphibolite metamorphic facies zone in which the younger formations are more metamorphic than those at the bottom.

However some outcrops in the central and southeast parts of the area show specific mineralogical associations and textures. The rocks are sometimes banded with internal comb and fassiclar structures. Some of their features resemble those of skarns.

The most characteristic mineralogical associations are: ± cpx + andesine ± horn ± gross/hydrogross ± prehnite ± ox(Fe) ± sph ± cc.

The field and chronological relations between these rocks and the three main phases of deformation show that they were generated after overthrusting but closely related with the thrust and fault planes. Ribeiro et al., (1982) and Munha et al. (1984) pointed out the importance of fluids produced by dehydration reactions in the underthrust to the metamorphic process. These fluids from Centro-Iberian rocks
rocks may be responsible for those exotic mineralogical associations (and textures) which are located near the shear planes and which developed after the cessation of the shearing forces.

VIII. Geochemistry of Facho peralkaline rhyolites

Table VII shows the average and range chemical compositions of the massive volcanic rocks of the Facho Formation and their range.

The geochemical data on the Facho rhyolites and the Alto de Casais calcalkaline rhyolitic series (M. L. Ribeiro, unpublished data) are plotted together to compare the main differences between peralkaline and normal rhyolites (Fig. 6). In spite of their similar averages in Si and K, the Facho rhyolites have small differences in Na (positive) and Al (negative) and large differences in Fe and Mn (positive) and P (negative), so we can say that peralkaline Facho rocks are not very rich in alkali contents but only poor in alumina.

For the trace elements the more significant differences are:

- Sn, La, Ce, Ta, Nb, Nd, Hf, Zr, Ga, Y, Zn (positive);
- Sc, Cu, W, Pb, Ba, Rb (negative)

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<th>MgO</th>
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</table>

Tab. 7. Average and range in major and trace elements of the rhyolitic volcanic rocks of the Facho Formation. (The analyses were performed at Inst. für Mineralogie, FU, Berlin, using a Phillips PW 1402 X-ray florescence spectrometer calibrated against international standards of appropriate composition).
High contents in incompatible elements are always found in this type of rocks, whereas the high Fe₂O₃ content of the Facho peralkaline rocks (averages of 9.25; 8.03; 6.19, respectively for riebeckite, aegirine and no sodic femic rhyolites) are rare (see Noble & Haftty (1969); Bowden (1971); Bailey & MacDonald (1970); Gibson (1970); Barbery et al. (1974).

According with Shand’s definition, peralkaline rocks are those with molecular excess of alkalies over alumina. In the Facho Formation, and in spite of the mobility of the alkalies during metamorphism and alteration process, (albite porphyroblastesis is always present, see A. Ribiero & M. L. Ribiero 1972; Floor 1966), the greatest part of the rhyolites have an aegirine index of more than one, Fig. 7.

Lacroix (1927) distinguished two types of peralkaline rhyolites on the basis of their femic normative contents:

- Pantellerites (femcs > 12.5%) and Comendites (femcs < 12.5%). So, according to Lacroix’s classification, the massive riebeckite and aegirine rhyolites are almost pantellerites and other massive rhyolites are comendites (Table VIII).

Petrographic and field studies have distinguished some different facies in Facho Formation which also display some special geochemical features.

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>(SiO₂, CaO, %)</th>
<th>(V, Cr, Ni, Cu, W, Pb, ppm)</th>
<th>(Fe₂O₃, MgO, K₂O, TiO₂, %)</th>
<th>(Zn, Ga, Y, Zr, Nb, Sn, Hf, Ta, Th, U, La, Ce, Nd, ppm)</th>
<th>(max. Na₂O%)</th>
<th>Fels (max. Sc, Co, Sr, Ba, ppm)</th>
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<tbody>
<tr>
<td>Fla &lt; Flb</td>
<td>&lt; Flb &lt; Fcl</td>
<td>&gt; massive volc. (SiO₂, K₂O, %)</td>
<td>&lt; massive volc. (Na₂O%)</td>
<td></td>
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</tbody>
</table>

These differences are not very easy to explain by a normal differentiation process. The mobility of the alkalies, evidenced by their scatter in diagrams for the Facho rocks, do not allow study of the variation of other oxides and elements as a consequence of the increase in peralkalinity.

Ce content was used as a simple indicator of rock differentiation, given its maximal range in the Facho rhyolites as well as its very small Kd (Dce << 1). The incompatible elements (Y, Zr, Nb, La) show a positive correlation with Ce contents (Fig. 8) which means that melt fractionation has operated.

Two analyses of rare-earth elements of peralkaline
Fig. 7. Diagram showing SiO₂ versus Agpaitic Index in the Facho Formation.

Facho’s rocks (Fla) are plotted in Fig. 9 together with two analyses of Alto de Casais rhyolites. Facho peralkaline rocks display a progressive enrichment in REE from Lu to La with small negative Eu anomalies which are very different from those of the Alto de Casais rhyolites (negative slope in middle REE contents and larger Eu anomalies). The peralkaline Facho patterns are also different from those of some peralkaline granites listed in the literature (see Bowden & Whitley 1974).

Geochemical diagrams do not show sharp differences among lithofacies, but massive riebeckite and aegirine types always stand out among the most differentiated rocks.

<table>
<thead>
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<th></th>
<th>FiP</th>
<th>FiB</th>
<th>TiO₂</th>
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| Tab. 8. CPIW Norms of rhyolitic Facho rocks. (Fe₂O₃, FeO by wet analyses. The high oxidation stage of the samples and also the relatively low Na₂O content inhibit the presence of NS. (+ pantellerites; - comendites)).
VIII. Relationships between peralkaline and mafic rocks of Macedo de Cavaleiros

Mafic rocks in the Macedo de Cavaleiros area are divided according to their geochemical features into two groups (Ribeiro M. L., unpublished):
- Carrapatas Group, composed of the basaltic rocks of the Carrapatas metabasalts and the metadiabases intruded in Alto de Sequeira, Facho and Alto de Casais formations.
- Macedo Group, composed of mafic rocks of the Macedo de Cavaleiros and Valbemfeito formations.

These Groups display different initial contents of incompatible elements (Nb, Y, REE, etc.) and distinct Y/Nb, Ti/V, Nb/Y/Zr/P_2O_5, ratios (Figs. 10, 11).

The geochemical characteristics of the Carrapatas Group correspond to an alkaline-transitional basaltic series, on a continental intraplate setting. The Macedo Group corresponds to tholeiitic basaltic series of Transitional MORB type (La/Sm_N = > - 98 < 1.08, Sun & Nesbitt 1979).

The incompatible elements ratios (Nb/Zr; Y/Zr; La/Zr; La/Ce; La/Nb) for the Facho peralkaline series are similar to those of the Carrapatas Group and very different from those of the Macedo Group (Fig. 12).

Moreover, the geochemical data confirm the field relationships between Carrapatas and Facho Forma-
Petrogenesis of early paleozoic peralkaline rhyolites

Fig. 9. Plot of chondrite-normalized (Masuda et al., 1973) REE abundances for selected rhyolitic rocks of the Macedo de Cavaleiros area.

However, the behaviour of TiO$_2$, P$_2$O$_5$, and Ba is different from that described for the above elements (Fig. 13). Ba has usually the same behaviour as K: its content increases continuously in the mafic melt. In the felsic melt its contribution to K-feldspar (which is fractionating at this stage) becomes more and more important, decreasing the Ba content in the melt. P$_2$O$_5$ and TiO$_2$ display a very different behaviour. Both oxides increase continuously in the Carrapatas Group but they were fractionated before the peralkaline residuum were attained. However if the drastic fall of P$_2$O$_5$ content in the melt may be explained by apatite fractionation, a similar process cannot be invoked for TiO$_2$, because it is usually fractionated in iron-titanium oxides, and the iron content remains high in peralkaline Facho rocks. Iron-titanium oxide formation is a function of oxygen fugacities, alkali concentration and temperature decrease (Paul & Douglas 1965, in Hess 1977).

The normal trend in a magmatic series is Po$_4$ decay, but the net result of all the above conditions may be a different trend. Webster & Bright (1961) and Carmichael & Nicholls (1967) have demonstrated that different solid solutions of Ti-Fe may coexist. Phases of α and w series equilibrate, at similar oxygen fugacities, to α and β phases, and it is the Fe/Ti ratio or the fO$_2$ that determines the presence or abundance of an w phase – if the oxygen fugacity is high or the Fe/Ti ratio is low, an α phase may precipitate. In both cases there will be more fractionation in TiO$_2$ than in Fe oxides. The especially high alkali content of the Facho rhyolites has been an important factor in determining the iron oxidation stage, and consequently the TiO$_2$ decay.

IX. Petrogenetic discussion

Peralkaline rocks cannot understood through the «Petrogenetic Residua System», Ne-Ks-Qz, (HAMILTON & MacKenzie 1965) but the analysis of this system is very important in its study. There, the «thermal barrier» that separates both termal
throughs — «granite minimum» and «nepheline syenite minimum» — does not permit any undersaturated melt to shift to the oversaturated fields of the diagram, or vice versa.

Some peralkaline melts found in this system have been attributed to the «plagioclase effect» defined by Bowen (1945) — plagioclase crystallization inhibits albite crystallization, increasing the Na₂O/Al₂O₃ ratio and the molar excess of the alkalies over Al₂O₃. Some comendites associated with calc-alkaline series may have resulted in this way (Carmichael & Mackenzie 1963).

Field evidence in the Macedo de Cavaleiros region shows that the «plagioclase effect» has operated — as can be seen in the plagioclase cumulates (Pl. 1) of some small batholiths of the Carrapatas Group which is spatially and geochemically related with the peralkaline rhyolites. The very low Ca and Sr contents in the peralkaline rocks may confirm this Mafic rocks included in the Pacho Formation also have low Sr contents, indicating that plagioclase fractionation began in the basaltic liquid compositions.

Peralkaline rocks, besides, their molar excess of alkalies over alumine, also contain an enormous...
For the two mafic groups of the Macedo de Cavaleiros region the effect has operated – as in plagioclase cumulates (Pl. I) of the Carrapatas Group which is closely related with the peralkaline rocks (low Ca and Sr contents in comparison) and confirm this Mafic rocks fractionation also have low Sr contents and plagioclase fractionation products.

The mafic liquids, their molar excess of FeO, 8-14% to contain an enormous amount of FeO, which may induce acmite crystallization. For this reason Bailey & Schairer (1966) have considered the so-called peralkaline residua system. Na$_2$O-Al$_2$O$_3$-Fe$_2$O$_3$-SiO$_2$.

The relationships in this system can be seen in the Jancke projection of acmite on the SiO$_2$; Na$_2$O; Al$_2$O$_3$ plane. There, the acmite-plagioclase-sodium disilicate plane would be the saturation plane, if incongruent melting of acmite and albite solid solution had not taken place.

When the reaction hematite + liq → acmite is not completely achieved, iron oxide is removed and undersaturated liquids may cross the saturation barrier to the oversaturated part of the peralkaline residua system.

The enormous range of Fe$_2$O$_3$% contents in the studied samples (1.7-11.7%) and the presence of aegirine-augite and aegirine, suggest that both conditions – equilibrium crystallization and hematite fractionation – have taken place. Hematite fractionation in the Facho Formation can frequently be observed. Its high concentration in some outcrops more often suggests immiscibility. Doubtless Fe$_2$O$_3$% fractionation frequently corresponds to well defined time steps, more consonant with liquid immiscibility than with fractional crystallization.

Conditions of increasing oxygen fugacity favour liquid immiscibility (Naslund 1976, in Shood 1981) and Eu abundances in the Facho peralkaline rocks (very small negative anomaly) suggest that oxygen fugacity was high. Hess (1977) pointed out that Al$_2$O$_3$ and FeO contents are very important in determining the size of the field in liquid immiscibility of silicate melts. The immiscibility fields increase in
Fig. 12. Relationships between Facho rhyolites and the two mafic Groups of Macedo de Cavaleiros region. Facho rhyolites and Carrapatas Group have the same ratios in incompatible elements which are different from those the Macedo Groups. (Δ- Carrapatas Gr. and peralkaline interbedded rocks; ○ – Macedo Gr.; □ – Fla; + – Flb; ◊ – Flc; ● – FII; ▲ – interbedded mafic rocks in Facho Formation.

high-Al₂O₃ and low-SiO₂ melts and in low-Al₂O₃, high-FeO melts. The two types of melts correspond respectively to the Facho and Carrapatas volcanic series.

Table IX shows marked similarities between the compositions of two coexisting immiscible liquids obtained from experimental data (Hsii 1977) and two analyses of Facho samples, indicating that peralkaline rocks of the Macedo de Cavaleiros area may have resulted by liquid immiscibility of an initial less siliceous and more iron rich melt.

The initial high alkali content of the parental Carrapatas mafic series makes it unnecessary to appeal to volatile transfer so frequently called upon in peralkaline petrogenic models. However some kind of volatile transfer may have occurred as deduced from stratigraphic realtionships. These show that there was an enrichment of the upper portions of the magma reservoir in the constituents of the «petrogenetic peralkaline residua system».

It is now possible to summarize the process by which the special composition of the alkaline-transi-
Petrogenesis of early paleozoic peralkaline rhyolites

The petrologic region. Facho rhyolites are those in the Macedo Groups. (FL: - FLH; - FLH, • - interbeds.

The petrologic region. Facho rhyolites are those in the Macedo Groups. (FL: - FLH; - FLH, • - interbeds.

Fig. 13. Ba, P₂O₅, TiO₂ versus Zr plots of the Mafic Grs. and Facho rocks. symbols as in Fig. 12.

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<td></td>
<td>M. 147</td>
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<td>Oxides</td>
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<tr>
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<td>FeO</td>
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<tr>
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<td>CaO</td>
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<td>Na₂O</td>
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<tr>
<td>P₂O₅</td>
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Tab. 9. Composition of coexisting immiscible liquids

- Decrease of the Al content in the alkali-transitional basaltic magma by the enormous amounts of plagioclase fractionation. (The melt became more iron, silica, and alkali-rich).
- Subsequent increase of the Fe³⁺/Fe²⁺, ratio favoured by higher alkali content. A first iron fractionation takes place and TiO₂ content, drops.
- New increase in SiO₂ and alkali contents. The special composition thus obtained and the oxy-

- Interbeds.

- Interbeds.
Pl. 1 – Some petrographic aspects of minerals in the Facho rhyolites. A – Relict feldspar porphyroclast; LP. B – Riebeckite oriented in all structural planes; LP. C – Zoned allanite; LP. D – Cumulates of the Carrapatas Form.
gen fugacity promoted liquid immiscibility with hematite precipitation.

Finally, fluctuations in $\text{PO}_2$ contents (with lowering or increasing of alkalies content) caused an alternation of acmite-feldspar and hematite rich bands.

Final remarks

Geochemical data confirm the stratigraphic relationships established by field methods. Peralkaline silicic rocks are the end member of the alkali-transitional series of Carapatos Group by which they are overlain. Fractional crystalization and liquid immiscibility were the principal process responsible for the development of the peralkaline trend.

The fact that peralkaline rhylotic rocks predates their alkali-transitional mafic rocks indicates that they were sited in an area of attenuated silicic crust. Further more, the alkali-transitional basaltic magmas can have been produced after crustal separation has occurred.

The presence of the uppermost tholeitic MORB-type series of the Macedo de Cavaleiros Group confirms that a low pressure magmatic regime environment was reached with the production of ocean crust.

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