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CRYSTALLIZATION CONDITIONS OF THE XANTHI PLUTONIC COMPLEX (RHODOPE MASSIF, N. GREECE): GEOTHERMOMETRY AND GEOBAROMETRY

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Abstract: The Xanthi Plutonic Complex (XPC) is one of a series of Oligocene subduction-related plutonic bodies comprising an "acid" group and a "basic" group. Based on mineral compositions and assemblages of the "basic" group, the XPC is assumed to have originally crystallized at a pressure of 5.4 kbar and at a temperature of 1300°C under relatively dry conditions and oxygen fugacity (fO_2) near the NNO buffer. As the basic magma migrates to shallower levels and at a temperature of about 870°C, water content increases and oxygen fugacity moves towards the MH buffer. The increase of water content could be the result of open system evolutionary processes. The "acid" group crystallizes at an average temperature of 729°C and at a pressure of 0.7 kbar under oxidizing conditions, between the NNO and MH buffer, suggesting a possibly different origin and/or evolution for the "acid" group.

Keywords: Xanthi Plutonic Complex, Greece, geothermobarometry, crystallization conditions.

1. Introduction

Magmatic rocks and particularly granites are a common characteristic feature of orogenic belts. No matter how their melts have generated, granites of orogenic areas are significant geologic tracers and can always help in unravelling the tectonomagmatic history of such belts. Magmatic rocks are widespread in Macedonia and Thrace in northern Greece, intruding the Rhodope Massif crystalline basement.

The Oligocene to Miocene evolution of the Rhodope Massif is dominated by the presence of fault-controlled sedimentary basins with calcalkaline to high-K calc-alkaline intrusive and extrusive magmatism and volcaniclastic intercalations. Early Tertiary volcanism is widespread in the central and eastern Rhodope Massif (Innocenti et al., 1984; Eleftheriadis, 1995; Eleftheriadis and Lippolt, 1984; Christofides et al., 2001b). Granitoids of varying composition are also widespread in Rhodope Massif comprising monzonitic and granodioritic rocks and subordinate gabbro. Plutonic intrusions of mostly Oligocene age, such as Xanthi, Kavala and Vrondou, are more widespread in central and western Rhodope Massif (Kotopouli & Pe-Piper, 1989; Christofides, 1996; Christofides et al., 1998 and references therein).

It is well known that the mineral assemblages of the magmatic rocks and their compositions are strongly related to the composition of the melts and mainly to the physicochemical conditions during their crystallization. However, retrieval of pressure and temperature information can be difficult. Mineral assemblages in igneous rocks crystallize over a wide temperature interval and are not often equilibrium associations. Some mineral phases continue to react under subsolidus conditions. Nevertheless, low-variance phase assemblages still exist and can be used to estimate crystallization conditions during magma solidification.

The XPC comprises rocks with a wide range of mineral constituents (olivine, two pyroxenes, amphiboles, biotite, feldspars, iron-titanium oxides), the study of which could offer valuable information concerning the P-T conditions under which the rocks were generated. The aim of this study is to investigate the mineral assemblages of the various rock types of the XPC and to apply several published geothermobarometers, based on mineral compositions, in order to estimate its crystallization conditions.

2. Materials and Methods

Mineral analyses were carried out at the Geology Department of Manchester University, using an EDS LINK system attached to a JEOL 6400 SEM with 15 KV accelerating voltage and 3 nA probe current. Pure Co was used as an optimization element.

FeO and Fe_2O_3 values for pyroxenes and magnetite were calculated using the method of Droop (1987) and for amphiboles the method of Schumacher (Appendix 2, Leake et al., 1997). FeO and Fe_2O_3 values for biotites were determined by wet chemical method.

3. Geological setting-Petrography and Geochemistry

Geophysical data (Maltezou & Brooks, 1989; Tsokas et al., 1996) suggest that XPC is a laccolithshaped body, extending several kilometers southwards. The Complex, which is mostly undeformed and unweathered, forms an extensive contact metamorphic aureole with skarn mineralisation (Liati, 1986). The XPC (Christofides, 1977; 1989; Christofides et al., 1998; Kyriakopoulos, 1987; Koukouvelas & Pe-Piper, 1991) is in magmatic contact with gneisses, mica schists, amphibolites, calc-silicate rocks, marbles and Eocene-Oligocene sedimentary rocks of the Rhodope Massif. To the south, the XPC is in fault-contact with Neogene and Quaternary rocks. The XPC is distinguished into two main rock groups: a) the "acid" group and b) the "basic" group. The terms "acid" and "basic" do not have a strictly geochemical meaning but they are used just for the separation of the rocks into two groups.

a) The "acid" group is composed of granodiorite (Grd) which grades into monzogranite (MzGr) and occupies the largest part of the XPC. It contains plagioclase, K-feldspar, biotite hornblende and Fe-Ti oxides. Marginally it is more or less porphyritic. Granodiorite covers 75% of the Complex.

b) The "basic" group occurs in the eastern part of the Complex and is composed mainly of monzonite (Mz) with subordinate quartz monzonite, quartz monzodiorite (QMzd) and monzogabbro (Mzg). It consists of plagioclase, perthitic and nonperthitic K-feldspar, biotite, clinopyroxene, orthopyroxene, Fe-Ti oxides and locally hornblende. A small two-pyroxene-olivine gabbro (Gb) occurs at the northeastern end of the Complex (Fig. 1). Lastly, small exposures of quartz gabbro (QGb) and quartz diorite (Od), as well as monzonitic porphyry (MzP), occurring at the eastern and northeastern part of the XPC, respectively, have also been identified. Microgranular mafic enclaves of quartz diorite composition occur mainly near the margin of the granodiorite.

Silica content of the XPC ranges between 44-78 wt%. A distinction of the rocks into a gabbroicmonzonitic group, corresponding to the "basic"



group, and a granodioritic group is obvious in most element variation diagrams at about 62 wt% silica. Some of the elements e.g. Ba and Zr behave as incompatible in the first group and then become compatible dropping in the granitic group. K₂O and Rb increase with silica but with different trends, the gabbromonzonitic being steeper. ΣREE increase from gabbro to monzonite and then drop to the granodiorite. REE patterns are tightly banded. LREE are enriched and Eu anomaly is distinct negative except in cumulitic gabbro (Christofides, 1990; Christofides et al., 1998). The XPC is considered as having post-COLG characteristics (Christofides et al., 2001a). Initial ⁸⁷Sr/⁸⁶Sr ratios of 0.7045-0.7075 (Kyriakopoulos, 1987; Christofides, 1989) require an upper mantle/lower crust source material for the evolution of the Xanthi rocks.

4. Mineral Chemistry

The minerals of the XPC are extensively discussed in Christofides (1977). Here, they are only briefly described. Representative mineral analyses are given in table 1.

4.1. Olivine

Olivine is only found in the gabbro of the "basic group". Altered olivine is found in some instances in monzogabbro and monzonite. It is Mg-rich ranging in composition from Fo_{58} to Fo_{70} .

4.2. Pyroxene

Orthopyroxene and clinopyroxene, the main mafic minerals of the "basic" group, have Mg/(Mg+Fe) ratios ranging from 0.63 to 0.71 and 0.69 to 0.76, respectively, when accompanied by olivine. In orthopyroxene and clinopyroxene assemblages not accompanied by olivine, Mg/(Mg+Fe) ratios range from 0.49 to 0.61 and 0.64 to 0.75, respectively.

Octahedral Al^{3+} and Ti^{4+} (both <0.03) are relatively constant for all pyroxenes. The highest Mg/(Mg+Fe) ratio (0.71) for orthopyroxene was measured in a gabbro sample but overall pyroxene mineral chemical compositions are considered homogeneous.

4.3. Amphibole

Amphibole is present in the monzonitic rocks of the "basic" and in the rocks of the "acid" group. It appears to be homogeneous, with no apparent compositional zoning. In the IMA-approved nomenclature (Leake et al., 1997), the amphiboles are classified as magnesio-hornblendes, with the exception of the monzonitic porphyry amphiboles, which are classified as edenites. Mg/(Mg+Fe) ratios range from of 0.58 to 0.76 and Si content ranges from 6.8 to 7.6 atom per formula unit.

A positive correlation is observed between Al^{IV} and Al_{tot} (Fig. 2a), in agreement with Hammarstrom and Zen (1986), showing a systematic difference between the Al contents of the amphiboles in different rock types. The compositional variations observed in amphiboles could be the result of single or coupled substitutions. Figure 2 indicates that the possible coupled substitutions present in the amphiboles are edenite, Ti-tschermakite and simple substitution of Fe²⁺ for Mg.

4.4. Biotite

Biotite is the most common mafic mineral found in all rock types including gabbro. It is Mg-rich with a Mg/(Mg+Fe) ratio ranging from 0.49-0.76 (Fig. 3) and shows little variation in tetrahedral aluminum (2.28-2.45).

4.5. Feldspars

Plagioclase occurs in all rock types. Optically zoned crystals have a core composition of An_{53-80} in the "basic" group and An_{38-50} in the "acid" group. The overall composition of the unzoned crystals is An_{40-60} and An_{37-44} in the two groups, respectively.

K-feldspar ranges in composition from Or_{56} to Or_{87} , and in a few cases includes a celsian component that reaches 2.35wt%. In the monzonitic samples from the "basic" group a perthitic K-feldspar has been recognized. These perthitic feldspars consist of intergrowths of alkali feldspar and albitic plagioclase. In most cases they are mesoperthites, i.e. with wormy intergrowths of a Na-rich phase the composition of which is An ~30 (An₂₆₋₄₄) and a K-rich phase (host K-feldspar) having Or_{62-75} (Fig. 4). They have been interpreted to be original ternary feldspars that have subsequently exsolved (Fuhrman et al., 1988; Papadopoulou et al., 2005).

4.6. Fe-Ti oxides

Magnetite is the predominant Fe-Ti oxide in all rock samples. Ilmenite is found as single crystals and also as thin lamellae in magnetite. The TiO₂ content of magnetite varies (up to 9.5 wt%) while MnO is rather constant (0.5 wt%). Ilmenite composition ranges from 0.89 to 0.96 x_{ilm} with varying MnO content (0.8-3 wt%).

| | Olivine | | | | | | | | | | |
|------------------|---------|--------|--------|--------|--|--|--|--|--|--|--|
| Rock group | | Bas | ic | | | | | | | | |
| Sample | Gb | Gb | Gb | Gb | | | | | | | |
| SiO ₂ | 37,67 | 36,20 | 36,41 | 37,08 | | | | | | | |
| FeO | 29,09 | 34,25 | 34,41 | 29,81 | | | | | | | |
| MnO | 0,52 | 0,90 | 0,67 | 0,43 | | | | | | | |
| MgO | 33,47 | 28,91 | 29,25 | 32,67 | | | | | | | |
| CaO | | | | 0,12 | | | | | | | |
| Total | 100,75 | 100,25 | 100,75 | 100,11 | | | | | | | |

Table 1. Representative mineral analyses of the XPC.

| Orthopyroxene | | | | | Clinopyroxene | | | | | | | |
|---------------|---|---|--|--|--|---|--|---|--|--|--|--|
| | Basi | c | | Rock group | | Basic | | | | | | |
| Mz | QMzd | MzP | Gb | Sample | Mz | QMzd | Gb | MzP | Mzg | Qd | | |
| 52,24 | 53,66 | 51,94 | 53,52 | SiO ₂ | 51,29 | 51,76 | 51,83 | 51,88 | 51,91 | 53,21 | | |
| | | 0,18 | 0,27 | TiO ₂ | 0,98 | 0,68 | 0,62 | 0,73 | 0,92 | | | |
| 0,77 | 0,60 | 0,32 | 0,94 | Al_2O_3 | 3,29 | 2,25 | 2,25 | 2,67 | 1,95 | 0,62 | | |
| 24,67 | 20,96 | 27,79 | 20,98 | FeO | 9,17 | 9,31 | 9,55 | 8,92 | 10,75 | 7,97 | | |
| 0,66 | 0,82 | 1,4 | 0,73 | MnO | 0,25 | 0,30 | 0,31 | 0,00 | 0,43 | 0,67 | | |
| 19,30 | 22,99 | 17,21 | 22,17 | MgO | 14,32 | 13,80 | 13,76 | 13,88 | 13,91 | 13,98 | | |
| 1,55 | 1,51 | 0,97 | 1,52 | CaO | 20,38 | 20,99 | 21,78 | 21,42 | 20,65 | 23,11 | | |
| 0,39 | | | | Na ₂ O | 0,53 | 0,36 | 0,35 | 0,55 | | | | |
| 99,58 | 100,55 | 99,81 | 100,12 | Total | 100,21 | 99,45 | 100,45 | 100,06 | 100,52 | 99,56 | | |
| | Orth <u>Mz</u> 52,24 0,77 24,67 0,66 19,30 1,55 0,39 99,58 | Orthopyroxene Basi Mz QMzd 52,24 53,66 0,77 0,60 24,67 20,96 0,66 0,82 19,30 22,99 1,55 1,51 0,39 99,58 | Orthopyroxene Basic Mz QMzd MzP 52,24 53,66 51,94 0,18 0,17 0,60 0,32 24,67 20,96 27,79 0,66 0,82 1,4 19,30 22,99 17,21 1,55 1,51 0,97 0,39 99,58 100,55 99,81 | Orthopyroxene Basic Mz QMzd MzP Gb 52,24 53,66 51,94 53,52 0,18 0,27 0,77 0,60 0,32 0,94 24,67 20,96 27,79 20,98 0,66 0,82 1,4 0,73 19,30 22,99 17,21 22,17 1,55 1,51 0,97 1,52 0,39 99,58 100,55 99,81 100,12 | Mz QMzd MzP Gb Sample 52,24 53,66 51,94 53,52 SiO2 0,18 0,27 TiO2 0,18 0,27 0,77 0,60 0,32 0,94 Al2O3 24,67 20,96 27,79 20,98 FeO 0,66 0,82 1,4 0,73 MnO 19,30 22,99 17,21 22,17 MgO 1,55 1,51 0,97 1,52 CaO 0,39 Na2O Na2O 99,58 100,55 99,81 100,12 Total | Mz Mze Rock group 52,24 53,66 51,94 53,52 SiO ₂ 51,29 0,18 0,27 TiO ₂ 0,98 0,77 0,60 0,32 0,94 Al ₂ O ₃ 3,29 24,67 20,96 27,79 20,98 FeO 9,17 0,66 0,82 1,4 0,73 MnO 0,25 19,30 22,99 17,21 22,17 MgO 14,32 1,55 1,51 0,97 1,52 CaO 20,38 0,39 Na ₂ O 0,53 99,58 100,55 99,81 100,12 Total 100,21 | $\begin{tabular}{ c c c c c c } \hline Orthopyroxene & Clinopy \\ \hline \hline Basic & Rock group \\ \hline \hline Mz & QMzd & MzP & Gb \\ \hline 52,24 & 53,66 & 51,94 & 53,52 \\ \hline 52,24 & 53,66 & 51,94 & 53,52 \\ \hline 0,18 & 0,27 & TiO_2 & 0,98 & 0,68 \\ \hline 0,77 & 0,60 & 0,32 & 0,94 & Al_2O_3 & 3,29 & 2,25 \\ \hline 24,67 & 20,96 & 27,79 & 20,98 & FeO & 9,17 & 9,31 \\ \hline 0,66 & 0,82 & 1,4 & 0,73 & MnO & 0,25 & 0,30 \\ \hline 19,30 & 22,99 & 17,21 & 22,17 & MgO & 14,32 & 13,80 \\ \hline 1,55 & 1,51 & 0,97 & 1,52 & CaO & 20,38 & 20,99 \\ \hline 0,39 & Na_2O & 0,53 & 0,36 \\ \hline 99,58 & 100,55 & 99,81 & 100,12 & Total & 100,21 & 99,45 \\ \hline \end{tabular}$ | Orthopyroxene Rock group Basic Rock group Basic Basic Basic Basic Basic Rock group Basic <th< th=""><th>Orthopyroxene Rock group Basic Basic Sample Mz QMzd MzP Gb Sample Mz QMzd Gb Sample Mz QMzd Gb Sample Mz QMzd Gb MzP 52,24 53,66 51,94 53,52 SiO2 51,29 51,76 51,83 51,88 0,77 0,60 0,32 0,94 Al2O3 3,29 2,25 2,25 2,67 24,67 20,96 27,79 20,98 FeO 9,17 9,31 9,55 8,92 0,66 0,82 1,4 0,73 MnO 0,25 0,30 0,31 0,00 19,30 22,99 17,21 22,17 MgO 14,32 13,80 13,76 13,88 1,55 1,51 0,97 1,52 CaO 20,38 20,99 21,78 21,42 0,39 V Na2O 0,53 0,36 0,35 0,55 99,58 <t< th=""><th>Orthopyroxene Rock group Basic Mz QMzd MzP Gb Sample Mz QMzd Gb Mzg 52,24 53,66 51,94 53,52 SiO2 51,29 51,76 51,83 51,88 51,91 0,18 0,27 TiO2 0,98 0,68 0,62 0,73 0,92 0,77 0,60 0,32 0,94 Al₂O₃ 3,29 2,25 2,25 2,67 1,95 24,67 20,96 27,79 20,98 FeO 9,17 9,31 9,55 8,92 10,75 0,66 0,82 1,4 0,73 MnO 0,25 0,30 0,31 0,00 0,43 19,30 22,99 17,21 22,17 MgO 14,32 13,80 13,76 13,88 13,91 1,55 1,51 0,97 1,52 CaO 20,38 20,99 21,78 21,42 20,65 0,39 Na₂O</th></t<></th></th<> | Orthopyroxene Rock group Basic Basic Sample Mz QMzd MzP Gb Sample Mz QMzd Gb Sample Mz QMzd Gb Sample Mz QMzd Gb MzP 52,24 53,66 51,94 53,52 SiO2 51,29 51,76 51,83 51,88 0,77 0,60 0,32 0,94 Al2O3 3,29 2,25 2,25 2,67 24,67 20,96 27,79 20,98 FeO 9,17 9,31 9,55 8,92 0,66 0,82 1,4 0,73 MnO 0,25 0,30 0,31 0,00 19,30 22,99 17,21 22,17 MgO 14,32 13,80 13,76 13,88 1,55 1,51 0,97 1,52 CaO 20,38 20,99 21,78 21,42 0,39 V Na2O 0,53 0,36 0,35 0,55 99,58 <t< th=""><th>Orthopyroxene Rock group Basic Mz QMzd MzP Gb Sample Mz QMzd Gb Mzg 52,24 53,66 51,94 53,52 SiO2 51,29 51,76 51,83 51,88 51,91 0,18 0,27 TiO2 0,98 0,68 0,62 0,73 0,92 0,77 0,60 0,32 0,94 Al₂O₃ 3,29 2,25 2,25 2,67 1,95 24,67 20,96 27,79 20,98 FeO 9,17 9,31 9,55 8,92 10,75 0,66 0,82 1,4 0,73 MnO 0,25 0,30 0,31 0,00 0,43 19,30 22,99 17,21 22,17 MgO 14,32 13,80 13,76 13,88 13,91 1,55 1,51 0,97 1,52 CaO 20,38 20,99 21,78 21,42 20,65 0,39 Na₂O</th></t<> | Orthopyroxene Rock group Basic Mz QMzd MzP Gb Sample Mz QMzd Gb Mzg 52,24 53,66 51,94 53,52 SiO2 51,29 51,76 51,83 51,88 51,91 0,18 0,27 TiO2 0,98 0,68 0,62 0,73 0,92 0,77 0,60 0,32 0,94 Al ₂ O ₃ 3,29 2,25 2,25 2,67 1,95 24,67 20,96 27,79 20,98 FeO 9,17 9,31 9,55 8,92 10,75 0,66 0,82 1,4 0,73 MnO 0,25 0,30 0,31 0,00 0,43 19,30 22,99 17,21 22,17 MgO 14,32 13,80 13,76 13,88 13,91 1,55 1,51 0,97 1,52 CaO 20,38 20,99 21,78 21,42 20,65 0,39 Na ₂ O | | |

| | | Biotite | | | Amphibole | | | | | | | |
|--------------------------------|-------|---------|-------|-------|--------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Rock group | Acid | | Basic | | Rock group | Ac | id | Basic | | | | |
| Sample | Grd | QMzd | MzP | Mzg | Sample | Grd | MzGr | Mz | QMzd | MzP | Qd | QGb |
| SiO ₂ | 36,85 | 37,82 | 37,69 | 37,22 | SiO ₂ | 50,02 | 51,56 | 49,37 | 48,71 | 46,23 | 49,02 | 48,78 |
| TiO ₂ | 4,91 | 4,36 | 4,83 | 6,61 | TiO ₂ | 0,88 | 0,48 | 0,64 | 0,64 | 1,61 | 1,19 | 1,5 |
| Al ₂ O ₃ | 13,46 | 13,34 | 13,26 | 13,02 | Al ₂ O ₃ | 4,57 | 3,77 | 5,23 | 5,12 | 6,83 | 5,64 | 5,96 |
| Fe ₂ O ₃ | 3,63 | 1,36 | 4,99 | 3,11 | FeO | 12,84 | 12,05 | 14,20 | 15,15 | 13,82 | 12,66 | 12,18 |
| FeO | 14,79 | 15,52 | 13,65 | 18,46 | MnO | 0,74 | 0,86 | 0,50 | 0,40 | 0,29 | 0,47 | 0,49 |
| MnO | 0,53 | 0,21 | 0,32 | | MgO | 15,17 | 15,5 | 14,66 | 13,67 | 13,54 | 14,90 | 15,13 |
| MgO | 12,39 | 13,92 | 12,93 | 10,01 | CaO | 11,87 | 12,07 | 11,45 | 11,21 | 11,44 | 11,94 | 11,63 |
| CaO | | 0,17 | 0,20 | 0,22 | Na ₂ O | 1,17 | 0,68 | 1,42 | 1,31 | 1,80 | 0,97 | 0,98 |
| Na ₂ O | 0,31 | 0,29 | 0,31 | 0,31 | K ₂ O | 0,43 | 0,29 | 0,59 | 0,62 | 1,25 | 0,54 | 0,51 |
| K ₂ O | 9,36 | 9,39 | 9,37 | 9,44 | Total | 97,69 | 97,26 | 98,05 | 96,82 | 96,80 | 97,33 | 97,16 |
| Total | 96,23 | 96,38 | 97,55 | 98,40 | | | • | | | | | |

| | P | lagioclase | | | K-feldspar | | | | | |
|--------------------------------|-------|------------|-------|-------|--------------------------------|-------|-------|--------|-------|--|
| Rock group | Acid | | Basic | | Rock group | Acid | | Basic | | |
| Sample | Grd | MzP | Gb | Mz | Sample | Grd | MzP | Gb | Mz | |
| SiO ₂ | 57,14 | 55,18 | 55,30 | 58,22 | SiO ₂ | 64,13 | 64,85 | 65,72 | 64,66 | |
| Al ₂ O ₃ | 26,29 | 28,14 | 28,14 | 25,65 | TiO ₂ | [| 0,23 | 0,41 | 0,34 | |
| FeO | 0,28 | 0,34 | | | Al ₂ O ₃ | 18,99 | 19,12 | 19,07 | 18,76 | |
| CaO | 9,01 | 11,23 | 11,46 | 8,36 | FeO | 0,17 | | | | |
| Na ₂ O | 6,13 | 4,91 | 4,64 | 6,68 | CaO | 0,15 | 1,11 | 0,31 | 0,22 | |
| K_2O | 0,25 | 0,33 | 0,45 | 0,25 | Na ₂ O | 1,34 | 4,17 | 2,80 | 2,53 | |
| Total | 99,10 | 100,13 | 99,99 | 99,15 | K ₂ O | 14,32 | 9,59 | 12,30 | 12,80 | |
| | | | | | BaO | 0,57 | | | | |
| | | | | | Total | 99,67 | 99,06 | 100,60 | 99,32 | |

| | Magnetite | | | | | | Ilmenite | | | | | |
|--------------------------------|-----------|------|------|------|------------------|-------|----------|-------|-------|--|--|--|
| Rock group | | Basi | c | | Rock group | | Bas | sic | | | | |
| Sample | QMzd | Mz | MzP | Gb | Sample | QMzd | Mz | MzP | Gb | | | |
| SiO ₂ | 0,31 | 0,45 | 0,25 | 0,88 | SiO ₂ | 0,29 | 0,17 | 0,20 | 0,74 | | | |
| TiO ₂ | 0,34 | 0,71 | 2,61 | 4,30 | TiO ₂ | 49,15 | 49,93 | 50,28 | 49,58 | | | |
| Al ₂ O ₃ | 0,49 | 0,66 | 1,01 | 2,87 | Al_2O_3 | | | | 0,47 | | | |



Fig. 2. Fig. 2. a) Relationship between Al^{IV} and Al_{tot} in amphiboles of the studied pluton; b-c) diagrams showing coupled ion substitutions in amphiboles, b) edenite, c) Ti-tschermakite; d) simple Fe^{2+} -Mg substitution. $\circ=$ "acid" group, $\blacksquare =$ "basic" group.



Fig. 3. Nomenclature of biotites of the XPC according to Deer et al. (1962). Symbols as in fig. 2.



Fig. 4. Wormy intergrowth of Na-rich plagioclase and K-feldspar having originally ternary compositions. Under crossed polars. Horizontal dimension is 0.5 mm.

5. Intensive parameters

Mineral chemical data were used to constrain the crystallization conditions of the XPC, i.e. pressure, temperature, f_{O_2} and f_{H_2O} .

5.1. Pressure

Pressure estimates were made using the clinopyroxene and the Al-in-amphibole geobarometer. According to Nimis (1999), pressure is the main physical variable that controls the chemical behaviour of clinopyroxene in a magmatic environment. The pressure of crystallization of the Complex was calculated assuming a mean temperature of 1000°C, as discussed later. The highest pressures have been calculated for the porphyritic monzonite and quartz monzodiorite, probably representing a lower crystallization level for these two rock types and/or a different crystallization history. We consider that the pluton started to consolidate at a pressure of 5.8 kbar.

Several studies (e.g. Hammarstrom & Zen, 1986; Hollister et al., 1987; Johnson & Rutherford, 1989; Schmidt, 1992; Anderson & Smith, 1995) revealed that Al content of hornblende varies linearly with pressure of crystallization. However, pressure estimates may be affected by ion substitutions in hornblende, oxygen fugacity and fluid composition.

Anderson & Smith (1995) argue that temperature and f_{O_2} can greatly affect the Al content in amphibole and suggest a ratio of Fe³⁺/(Fe³⁺+Fe²⁺)>0.25 (or 0.20, as suggested by Schmidt, 1992) and, subsequently, Fe_{tot}/(Fe_{tot}+Mg) ratios in the range of 0.40-0.65 for amphiboles used for barometry.

Although MzP shows the highest pressure of crystallization, as calculated by the barometer of Schmidt (1992), it is not taken into account, as amphiboles of this rock type, fail to meet the above criteria. Negative values obtained by the Anderson & Smith (1995) geobarometer are attributed to the same reason.

As a result, we accept a pressure of 1.8 kbar for the "basic" group and 0.7 for the "acid" group, the latter being supported by the extensive contact metamorphism. For the "basic" group, pressure values are lower than those calculated from clinopyroxenes. They probably reflect the level at which hornblende crystallizes rather than the pluton itself. Average pressure estimates are given in table 2 for the "basic" and "acid" group.

| Table 2. Pressur | e estimates for | the XPC | 2. |
|------------------|-----------------|---------|-------|
| Clinopyroxene | geobarometer | (Nimis | 1999) |

| | | Basic | | | | | | | | |
|----------|-----|-------|-----|------|------|-----|--|--|--|--|
| P (kbar) | Mz | Mzg | Qd | QMzd | MzP | Gb | | | | |
| min | 3,3 | 3,3 | 3,5 | 7,1 | 5,8 | 2,3 | | | | |
| max | 4,5 | 5,8 | 3,5 | 11,4 | 14,2 | 5,4 | | | | |
| average | 4,1 | 4,5 | 3,5 | 9,2 | 10,0 | 3,8 | | | | |

Al-in-amphibole geobarometer

| 1992) | | | | | | |
|-------|----------------------------------|-----------------------------------|---|--|---|--|
| A | cid | | | | | |
| Grd | MzGr | Mz | QMzd | MzP | Qd | QGb |
| 0,7 | 0,1 | 1,3 | 1,2 | 2,5 | 1,6 | 1,8 |
| | 1992) A Grd 0,7 | Igg2) Acid Grd MzGr 0,7 0,1 | Igg2 Acid Grd MzGr Mz 0,7 0,1 1,3 | Acid Mz M | Ig92) Acid Basic Grd MzGr Mz QMzd MzP 0,7 0,1 1,3 1,2 2,5 | Ig92) Acid Basic Grd MzGr Mz QMzd MzP Qd 0,7 0,1 1,3 1,2 2,5 1,6 |

| Anderson & Smith (1995) | | | | | | | | | |
|-------------------------|-----|------|------------------------|------|------|------|-----|--|--|
| | A | cid | Basic | | | | | | |
| P (kbar) | Grd | MzGr | $\mathbf{M}\mathbf{z}$ | QMzd | MzP | Qd | QGb | | |
| average | 0,5 | 0,2 | 0,8 | 0,8 | -1,6 | -3,6 | 0,4 | | |

5.2. Temperature

In magmatic rocks, mineral phases crystallize in a wide range of temperature values and it is rather uncertain if they have reached equilibration during magma consolidation. Many minerals continue to equilibrate under subsolidus conditions or exhibit zonation indicating continuous reaction with the melt. In order to determine the crystallization conditions of a pluton it is necessary to use different geothermometers (Anderson, 1996).

Temperature estimates in the present study are based on the QUIIF program (Quartz + Ulvospinel = Ilmenite + Fayalite equilibrium abbreviated as QUIIF) applications to the olivine-pyroxene, twopyroxene and magnetite-ilmenite assemblages (Frost & Lindsley, 1992; Lindsley & Frost, 1992), the hornblende-plagioclase geothermometer of Holland & Blundy (1994) and the two-feldspar geothermometer of Fuhrman & Lindsley (1988), modified by Kroll et al. (1993).

Table 3 summarizes the results of crystallization temperatures. Application of the QUIIF program to the olivine-pyroxene and the two-pyroxene assemblages found in the "basic" group, yield maximum temperatures of 1300 and 1000°C (\pm 40°C), respectively (average temperatures 1000° and 868°C). The two-oxide thermometer provides a wide range of temperatures from 428-824°C, possibly reflecting re-equilibration during cooling and a maximum temperature of 916°C calculated from ilmenite lamellae in magnetite.

Table 3. Temperature estimates for the XPC.

| | · · · · · · · | | | | | | | | |
|-----------|---|--|--|--|--|--|--|--|--|
| Olivine+(| Olivine+Orthopyroxene+Clinopyroxene (Lindsley & Frost 1992) | | | | | | | | |
| | Basic | | | | | | | | |
| T (°C) | Gb | | | | | | | | |
| min | 841 | | | | | | | | |
| max | 1306 | | | | | | | | |
| average | 999 | | | | | | | | |
| | | | | | | | | | |

Orthopyroxene+Clinopyroxene (Lindsley & Frost 1992)

| Basic | | | | | | | | |
|-------|--------------------------|--|--|--|--|--|--|--|
| Mz | QMzd | MzP | Gb | | | | | |
| 613 | 608 | 676 | 670 | | | | | |
| 1020 | 723 | 837 | 1008 | | | | | |
| 868 | 667 | 751 | 791 | | | | | |
| | Mz 613 1020 868 | Mz QMzd 613 608 1020 723 868 667 | Mz QMzd MzP 613 608 676 1020 723 837 868 667 751 | | | | | |

Amphibole+Plagioclase (Holland & Blundy 1994)

| | Ac | id | | | | | |
|---------|-----|------|-----|------|-----|-----|-----|
| T (°C) | Grd | MzGr | Mz | QMzd | MzP | Qd | QGb |
| min | 693 | 710 | 726 | 728 | 834 | 924 | 741 |
| max | 769 | 710 | 745 | 768 | 954 | 924 | 741 |
| average | 729 | 710 | 735 | 756 | 881 | 924 | 741 |

Magnetite+Ilmenite (Lindsley & Frost 1992)

| | Basic | | |
|---------|-------|---------|-----|
| T (°C) | QMzd | Mz MzP | Gb |
| average | 864 | 666 604 | 741 |

The plagioclase-amphibole geothermometer yields an average temperature of 729°C and 878°C for the "acid" and "basic" group, respectively. The latter agrees with the average temperature calculated with the two-pyroxene geothermometer.

The two-feldspar geothermometry application provides temperatures ranging from 830-880°C for the mesoperthite feldspars found in the monzonitic rocks of the "basic" group and an average temperature of 580°C for the feldspar pairs found in the "acid" group. The former are in good agreement with the average temperatures calculated with the two-pyroxene geothermometer, while the latter are considerably lower than those calculated by the hornblende-plagioclase geothermometer, possibly indicating subsolidus re-equilibration.

5.3. Oxygen fugacity

Oxygen fugacity calculated by the QUIIF program for magnetite and ilmenite bearing assemblages shows a wide variation in the "basic" group, from 1.6 to -1.3 DFMQ log f_{0_2} in the gabbroic rocks and 0.2 to 4.0 DFMQ log f_{0_2} in the monzonitic rocks, reflecting more oxidizing conditions. Increase of oxygen fugacity causes crystallization of magnetite and Mg-enrichment of amphibole and pyroxenes (Cornejo & Mahood, 1997).

According to Wones & Eugster (1965) Mg-rich biotites suggest crystallization at relatively oxidizing conditions. As seen in figure 5, biotites crystallize above the NNO buffer. Under the same conditions Fe^{2+} is more readily oxidized than Mn and this leads to Mn enrichment in ilmenite. Indeed, ilmenite has Mn content up to 4wt%.



Fig. 5. Plot of biotites of the XPC on the triangular diagram $Fe^{3+}-Fe^{2+}-Mg$ of Wones & Eugster (1965). 1. $Fe_3O_4-Fe_2O_3$ (MH), 2. Ni-NiO (NNO), 3. SiO_2- $Fe_2SiO_4-Fe_3O_4$ (QFM). Symbols as in fig. 2.

5.4. Water fugacity

An estimation of the water content during final crystallization can be made using the biotitesanidine-titanomagnetite geobarometer (Wones & Eugster, 1965). Using temperatures and oxygen fugacity calculations from coexisting Fe-Ti oxides, values of $f_{\rm H_2O}$ span a wide range from 0.2 to 2.5 kbar in the "basic" group, probably reflecting disequilibrium among biotite, K-feldspar and Fe-Ti oxides.

Textural relations compared with experimental studies on similar compositions (Naney, 1983) can give qualitative information on water content of the XPC. Biotite crystallizes under rather dry conditions (0.5-5% wt H₂O) while the presence of hornblende requires a minimum of approximately 4 %wt H₂O in a granodioritic system at 2 kbar and f_{0_2} between NNO and MH buffers. In the "basic" group, amphibole is absent from most of the mineral assemblages and its crystallization follows that of biotite. These observations suggest low water content during the early stages of crystallization, below 4 wt%. In a later crystallization stage water content increases, due very probably to open system evolutionary processes, leading to amphibole crystallization.

6. Discussion

Estimation of the crystallization conditions of a pluton can provide evidence concerning its evolution history. From this study, it is evidenced that the XPC originally crystallized at a pressure of 5.8 kbar and at a maximum temperature of 1300°C under relatively dry conditions and f_{O_2} near the NNO buffer. This temperature probably reflects the initial crystallization of the gabbroic magma immediately after its emplacement. At a later stage of crystallization and at an average temperature of about 870°C, water content increases (above 4%wt) leading to the crystallization of amphibole, the disappearance of olivine and the formation of mesoperthites, which follow the exsolution of initial ternary feldspar. The increase of water content could allow the magma to reach shallower emplacement levels, which probably is reflected in the lower pressures calculated by the Al-inhornblende barometer. Oxygen fugacity increases towards the MH buffer as indicated by the Fe³⁺ content of biotite and the composition of the Fe-Ti oxides. The increase of water content could be the result of open system evolutionary processes.

The "acid" group crystallizes at an average temperature of 729°C and at a pressure of 0.7 kbar under oxidizing conditions, between the NNO and MH buffer. Temperatures, and mainly pressures, are significantly lower than those of the "basic" group, suggesting possibly a different origin and/or evolution of the "acid" group.

Lower temperatures (400-600°C) obtained for individual plagioclase and K-feldspar pairs and Fe-Ti oxides confirm that these minerals are affected by subsolidus re-equilibration.

These results seem to be in agreement with the geochemical characteristics of the Complex (work in progress).

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