# Variation in amphibole composition from the Serifos intrusive complex (Greece), under magmatic and hydrothermal alteration conditions. An application of hornblende geobarometry

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#### ABSTRACT

Microprobe analyses of amphiboles of different samples from the Serifos intrusion, including fresh to altered granodiorite, skarns, quartz diorite mafic enclaves and rhyodacite dykes, indicate that all amphiboles are calcic ( $(Ca+Na)_{g} > 1.34, Na_{g} > 0.67$ ) ranging in composition from tschermakite through Mg-hornblende to actinolite. The relatively wide compositional range of these amphiboles is controled by the *tschermakite type* and *edenite type* cation substitutions. The *tschermakite type* cation substitution is predominant in magmatic amphiboles from the unaltered granodiorite and the mafic enclaves while the *edenite type* is the main cation substitution in actinolites from the altered parts of the granodiorite.

The Al-in-hornblende barometer for calc-alkaline plutons and volcanic rocks was applied. The pressure estimates according to this geobarometer are in the range 0.33 -  $2.2 \pm 0.5$  kb.

The observed instability of hornblende as seen clearly in the mafic enclaves as well as in the dykes, indicated by its partial replacement by biotite, suggest relatively moderate H<sub>2</sub>O content and clearly water undersaturated conditions of the granodiorite system at the low e.g., 2kb, shortly before its final solidification.

## **INTRODUCTION - GEOLOGICAL SETTING**

Serifos island is part of Cyclades, located in the Southern Aegean (Fig. 1). More than one third of the island is occupied by the granitoid composite intrusion. The basement of the island is a pile of accreted metasediments, metabasites, marbles and occasional ultrabasic lenses stacked as distinct tectonic packages corresponding to variable P-T-t conditions. The intrusion produced a contact metamorphic aureole and extensive skarn and ore formations in the country rocks (SALEMINK, 1985).

The Serifos pluton represents a typical example of the upper Miocene Cyclades I-type granitoids. Most rock types comprising the granitoid are generally not per-aluminous but are hornblendic. The composition of the pluton ranges from hornblende-biotite granodiorite to biotite granite with common quartz-hornblende diorite enclaves and rhyodacite dykes, which occur near the margins of the complex. Aplite and pegmatite veins represent the most fractionating magmatic products in the pluton. Skarn ore-deposits of iron-type (MEINERT, 1992), consisting mainly of magnetite have also been developed in the contact aureole. Field relations show that the spatial development of the hydrothermal system and the development of skarn deposits in the contact aureole are controlled by the regional extensional tectonics that have been active in the Aegean since Miocene

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times (GAUTIER & BRUN, 1994).

Hydrothermal alteration of the pluton is widespread and occurs in successive stages. High temperature alteration caused bleaching along jointsfractures where hornblende disappears and biotite diminishes and recrystallises in fine-grained assemblages. At medium and low temperatures the granite in the same alteration "bleached zones", is replaced by the assemblage epidote + actinolite + chlorite + titanite  $\pm$  calcite and associated with pyrite-hematite deposition.

Amphibole is common in all the granite types of the Serifos pluton, which comprise 3-12% of the modal mineralogy of the granodiorite and up to 35% in the enclaves (STOURAITI, 1995). There is a considerable compositional variation of the amphibole. This seems to be the result of magmatic as well as of hydrothermal alteration processes. The study of the compositional variation of the amphiboles and its implication to the various petrogenetic processes (i.e. magmatic, metamorphic, hydrothermal) in the Serifos pluton are included in the present paper.

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Figure 1. Sketch map of Serifos presenting the main structural features of the intrusion (Stouraiti, 1995).

## SAMPLING AND ANALYTI-CAL METHODS

Sampling was carried out with special care to collect representative samples of all the different rock types. These include samples from the well-preserved outcrops of the fresh granite, the hydrothermally altered granite, the mafic enclaves from the intrusion, the granodiorite dykes, and granite samples from the endo-skarn zone. The mineral and bulk rock chemical analyses were made in the Department of Geology at the University of Leicester, England.

The mineral phases have been studied by polarised microscope and

analysed by an automatic electron microprobe (JXA-8600 Superprobe). The standards used were of pure elements or natural compounds.

Major element analyses of rock samples were carried out by X-ray fluorescence method using a Philips PW 1400 series spectrometer. Details on the analytical procedure, precision and accuracy on the analytical techniques are given in MARSH et al (1983). Representative major element analyses of the studied rock types from the Serifos intrusion are given in Table 1.

## PETROGRAPHY OF THE ROCK TYPES

#### Granodiorite intrusion

Serifos granitoid is a composite intrusion (Fig. 1). Two main petrological facies were observed in the field: a) the marginal, coarse-grained lineated granodiorite and minor granite, and b) the central, medium to fine-grained, faintly to non-deformed granodiorite and tonalite. There is not clear contact between the two main facies. It has an elongated, elliptical shape in a NE-SW trend and occupies more than one third of the island. The geomμήμα Γεωλογίας. Α.Π.Θ.

| Sample<br>Rock-type            | SER55<br>Granodiorite | SER61<br>Altered<br>granodiorite | SER22<br>Dioritic<br>enclave | SER100<br>Ryodacitic<br>dyke | SER93-14<br>Skarn |
|--------------------------------|-----------------------|----------------------------------|------------------------------|------------------------------|-------------------|
| SiO <sub>2</sub>               | 65.50                 | 63.90                            | 59.10                        | 67.00                        | 66.70             |
| TiO                            | 0.66                  | 0.63                             | 0.62                         | 0.70                         | 0.77              |
| Al <sub>2</sub> O <sub>3</sub> | 16.70                 | 17.80                            | 16.60                        | 15.60                        | 16.10             |
| Fe <sub>2</sub> O <sub>3</sub> | 3.60                  | 2.80                             | 6.80                         | 3.10                         | 3.51              |
| MnÕ                            | 0.09                  | 0.07                             | 0.16                         | 0.09                         | 0.02              |
| MgO                            | 182                   | 2.14                             | 4.82                         | 1.70                         | 1.70              |
| CaO                            | 4.46                  | 4.50                             | 6.90                         | 4.45                         | 4.25              |
| Na <sub>2</sub> O              | 3.79                  | 4.25                             | 3.16                         | 4.13                         | 3.70              |
| K₂Ō                            | 3.04                  | 2.95                             | 2.14                         | 2.69                         | 3.24              |
| $P_2O_5$                       | 0.11                  | 0.13                             | 0.12                         | 0.11                         | 0.14              |
| LÕI                            | 0.17                  | 1.00                             | 0.76                         | 0.48                         | 0.40              |
| Total                          | 99.94                 | 100.17                           | 101.18                       | 100.05                       | 100.53            |

**TABLE 1.** Representative major element analyses of the studied rock-types from the Serifos intrusive complex.

etry and the deformation of the contact zones indicate the emplacement of a sheet-like body along a tectonically active shear zone, up-domed near its roof. Mafic enclaves of quartz diorite to tonalite composition is a common feature of the pluton but with diminishing occurrence in the central part of the intrusion.

The intrusion has a typical granitic texture with euhedral to subhedral hornblende, and subhedral plagioclase. Biotite and Mg-rich hornblende are the major mafic minerals. Biotite is formed in two generations and commonly forms big porphyroblasts (up to 1cm) overgrowing both magmatic and tectonic fabrics. K-feldspar is generally anhedral and interstitial phase, subordinate to plagioclase. Plagioclase has an intermediate composition. The accessory phases are sphene, which is more abundant than the other phases, apatite, magnetite and minor zircon; allanite occurs occasionally, in the more evolved granodiorites.

Structural data from the deformed marginal granite and the style of deformation close to the intrusive contacts indicate ductile shearing along the south contact plain (NE-SW direction) and extension in a N or NE-SW trend (STOURAITI 1995). The north-eastern margin of the pluton is more complex, exhibiting variable compositions and magma mingling of a small volume of fine grained tonalite magma pulse with quartz diorite blobs and the main granodiorite. Several generations of aplites and pegmatites crosscut the south intrusive contact and the foliation of the adjacent gneissic basement, as thin sheet-like layers shallowly dipping to the north. Besides the north contact is often cut by subvolcanic dykes mainly rhyodacitic.

#### Altered granodiorite

The pluton was strongly affected by brecciation at or near the final solidification stage (SALEMINK, 1985). Along the fractures post-magmatic, hydrothermal processes formed cm-wide bleached zones. A network of such hydrothermal veins and fractures are widespread in the whole pluton. Alteration is more intense in particular zones of fracture zones, which occur close to the margins, and the apical parts of the pluton.

The following alteration types are distinguished (STOURAITI, 1995):

1) leaching of the Fe-Mg minerals with biotite and partial replacement of hornblende by actinolite, as well as sericitisation/albitisation of plagioclase, which form the bleached zones.

2) intensively altered zones with typical assemblage epidote + actinolite + chlorite + titanite  $\pm$  calcite, with pyrite and hematite deposition in the centre of the veins. The occur locally, within the bleached zones.

3) Veins of fluorite + baryte with hematite associated with severely bleached zones and represent late stage low-T deposition.

#### Mafic enclaves

The mafic enclaves occur with increasing concentration near the margins of the pluton. Texturally they are similar to the host granodiorite, except that are finer grained and equigranular. Some enclaves have diffuse margins and show some interaction with the host granite. They occur in two varieties. One common type is the microgranular (microscopic) inclusions, which consist of aggregates mainly of hornblende with minor magnetite, plagioclase and biotite. The other type is, typical enclayes of few centimetres to over 1m diameter, oval-shaped, of quartz-diorite to tonalite composition with interstitial guartz and K-feldspar. Hornblende is the dominant mafic mineral. The modal mineralogy of the later mafic enclaves show that hornblende ranges from 20 to 35 % (STOURAITI, 1995).

## **Rhyodacite dykes**

Numerous km-long sub-volcanic dykes crosscut, in a radial mode, the borders of the intrusion and the country rocks. They range in composition from rhyolites to dacites, rhyodacites being the most common. They are fine grained with commonly porphyritic texture and often contain biotite porphyroblasts. Some of these subvolcanic veins crosscut previously developed garnet -diopside skarn at the margins of the pluton, indicating that magmatic activity continued after the pluton emplacement.

Their mineralogy is similar to the granodiorite. Study of the microscopic texture of the dykes showed that K-feldspar and guartz form spherulite intergrowths around plagioclase phenocrysts, which feature indicates magma undercooling (SHELLEY, 1993). Moreover, textural relationships

indicate replacement of hornblende by biotite. This reaction relationships have been associated in experimental studies, with subsolidus high-T replacement of the Mg-hornblende (NANEY, 1983).

## Skarn

Extensive Ca-Fe-Mg exo-skarns and minor endoskarns, associated with large Fe-deposits (magnetite, hematite) and minor Cu, Pb-Zn and Ba mineralisation, occur in the metamorphic aureole, within a zone of about 0.5-1 km (SALEMINK, 1985). Generally the contact metasomatic formations developed predominately in the Si-containing country rocks close to the intrusive contact. Occasionally they occur in the coarse-grained granodiorite, along fractures. These are high-T endoskarn deposits and consist of pyroxene+garnet and magnetite-pyrite ore. The primary hornblende is diminished in the metasomatised granodiorite within the endo-skarn zones.

# MINERAL CHEMISTRY OF THE AMPHIB-OLES

Detailed optical microscopy of all the rock samples was carried out in order to determine the main textural characteristics of the amphiboles, such as magmatic zonation, and replacements due to post magmatic alteration. Chemical analyses of the different types of amphiboles were performed by electron microprobe and they were processed using the computer program MINPET 2.02. The basic formula used for the recalculation of oxides to cations allows for 23 oxygens and excludes Ca, Na, K from the sum of cations (13 cations overall). According to LEAKE's (1978) classification, the analysed amphiboles are calcic with (Ca+Na)<sub>8</sub>>1.5 and (Na+K)<sub>4</sub><0.5. The results, which are presented below, are grouped according to the rock type.

## Granodiorite

Amphibole occurs either in subhedral to euhedral isolated grains or forming aggregates with minor magnetite. It is pleochroic (green to brown) showing common twinning and core-to-rim compositional zonation. Representative chemical Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.

| ADLE 2. Representative chemical analyses of amphiboles from the Senios granoulonte |           |        |        |        |        |        |        |           |           |
|--|-----------|--------|--------|--------|--------|--------|--------|-----------|-----------|
| Sample   | SER24a    | SER540 | SER54p | SER55c | SER63c | SER63j | SER63d | SER92-11b | Ser92-11a |
|  | (altered) | (core) | (rim)  |        |        |        |        | (core)    | (rim)     |
| SiO2   | 53.42     | 49.90  | 4527   | 47.07  | 53.90  | 45.17  | 52.23  | 42.43     | 47.50     |
| TiO,   | 0.09      | 0.92   | 1.55   | 1.55   | 0.30   | 1.63   | 0.39   | 2.18      | 1.03      |
| $Al_2O_3$  | 2.00      | 5.19   | 8.70   | 7.03   | 3.16   | 8.58   | 3.66   | 10.32     | 6.04      |
| FeO  | 7.52      | 13.05  | 15.83  | 14.93  | 10.38  | 12.26  | 10.81  | 14.83     | 13.91     |
| Cr <sub>2</sub> 0 <sub>3</sub><br>MnO  | 0.00      | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00   | 0.00      | 0.00      |
| MnÕ  | 0.06      | 0.31   | 0.36   | 0.33   | 0.22   | 0.28   | 0.19   | 0.43      | 0.48      |
| MgO  | 18.86     | 13.77  | 11.28  | 12.67  | 16.72  | 14.73  | 16.20  | 11.26     | 13.49     |
| Ca0  | 14.01     | 12.22  | 11.84  | 12.07  | 12.53  | 1182   | 12.54  | 11.32     | 11.45     |
| Na <sub>2</sub> 0  | 0.52      | 1.02   | 1.56   | 1.23   | 0.63   | 1.73   | 0.88   | 2.02      | 124       |
| K,ō ∣  | 0.27      | 0.48   | 0.76   | 0.71   | 0.21   | 0.53   | 0.27   | 0.69      | 0.45      |
| Total  | 96.75     | 96.86  | 97.15  | 97.59  | 98.05  | 96.73  | 97.17  | 95.48     | 95.59     |
|  |           | _      |        |        |        |        |        |           |           |
| TSi  | 7.691     | 7.338  | 6.761  | 6.940  | 7.646  | 6.602  | 7.529  | 6.431     | 7.054     |
| TAI  | 0.309     | 0.662  | 1.239  | 1.060  | 0.354  | 1.398  | 0.471  | 1.569     | 0.946     |
| Sum_T  | 8.000     | 8.000  | 8.000  | 8.000  | 8.000  | 8.000  | 8.000  | 8.000     | 8.000     |
| CAI  | 0.030     | 0.236  | 0.292  | 0.161  | 0.174  | 0.078  | 0.150  | 0273      | 0.110     |
| CCr  | 0.000     | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000     | 0.000     |
| CFe3   | 0.000     | 0.000  | 0213   | 0.256  | 0.095  | 0.671  | 0.067  | 0.396     | 0.519     |
| CTi  | 0.010     | 0.102  | 0.174  | 0.172  | 0.032  | 0.179  | 0.042  | 0.249     | 0.115     |
| CMg  | 4.048     | 3.019  | 2.512  | 2.785  | 3.536  | 3209   | 3.481  | 2.544     | 2.987     |
| CFe2   | 0.905     | 1.605  | 1.764  | 1.585  | 1.136  | 0.828  | 1.236  | 1.483     | 1.208     |
| CMn  | 0.007     | 0.039  | 0.046  | 0.041  | 0.026  | 0.035  | 0.023  | 0.055     | 0.060     |
| CCa  | 0.000     | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000     | 0.000     |
| Sum_C  | 5.000     | 5.000  | 5.000  | 5.000  | 5.000  | 5.000  | 5.000  | 5.000     | 5.000     |
| BCa  | 2.000     | 1.925  | 1.895  | 1.907  | 1.904  | 1.851  | 1.937  | 1.838     | 1.822     |
| BNa  | 0.000     | 0.075  | 0.105  | 0.093  | 0.096  | 0.149  | 0.063  | 0.162     | 0.178     |
| Sum_B  | 2.000     | 2.000  | 2.000  | 2.000  | 2.000  | 2.000  | 2.000  | 2.000     | 2.000     |
| ACa  | 0.161     | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000     | 0.000     |
| ANa  | 0.145     | 0.216  | 0.346  | 0.258  | 0.078  | 0.341  | 0.183  | 0.432     | 0.179     |
| 4K   | 0.050     | 0.090  | 0.145  | 0.134  | 0.038  | 0.099  | 0.050  | 0.133     | 0.085     |
| Sum_A  | 0.356     | 0.306  | 0.491  | 0.392  | 0.116  | 0.440  | 0.232  | 0.565     | 0.264     |

ABLE 2. Representative chemical analyses of amphiboles from the Serifos granodiorite

nalyses of amphiboles from fresh as well as alred granodiorite samples are given in Table 2. slight increase in Si with decrease in Al, Fe, Ti, hile Mg and Ca increase express the chemical ariation from core to rim. The chemical evoluon cause the compositional variation from Mgornblende to actinolitic hornblende in the rim (magatic fractionation). Amphibole with high chermakite content core, evolving to actinolitic

hornblende was identified only in one sample from the central granodiorite intrusion (SER92-11a,b). Rarely occurs the reverse variation that is starting from actinolitic-hornblende core evolving to Mg-hornblende composition in the rim (SER54o, SER54p). Such compositional variation in amphiboles is associated with bleached zones where hydrothermal alteration cause the replacement of Mg-hornblende by actinolitic hornblende. Finally



**Figure 2.** A. Classification of amphiboles from fresh granodiorite (=), altered granodiorite (o), partly altered granodiorite SER63 (u) and skarn (<) of the Serifos intrusion. B. SumA+CAI+CFe3+CTi versus TAI plot, presenting the combination of tschermakite type and edenite type cation substitutions in the above amphiboles.

there is no differentiation in amphibole composition from the outer intrusion with those in the central intrusion.

In amphiboles from altered samples, actino- actinolitic hornblende ar Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.

lite replaces Mg-hornblende starting either from the edges or the centre of the crystal. In the bleached zones actinolite is predominant and primary hornblende is extinct. Actinolites from the thoroughly altered granite in the endo-skarn zone (Table 5), are very poor in Al, Ti and alkalies and enriched in Mg, compared to actinolites replacing hornblendes in the slightly altered granite.

The compositional variation in amphiboles of both the fresh and the altered granodiorite is the result of combination of tschermakite type and edenite type cation substitutions (Fig. 2A-B). The observed progression from tschermakitic hornblende to Mg-hornblende, which is predominant in amphiboles of the unaltered granodiorite, marks the tschermakite type (HELZ, 1973) substitution (AIAI <=> MgSi in the C and T sites). The parallel increase in Na, K in A site and Aliv, with decreasing Si indicates edenite substitution. Na,K<sup>A</sup> + Aliv <=> [ ]<sup>A</sup> + Si<sup>iv</sup>. It has been found that such an increase is directly dependent on temperature (HELZ, 1973). It was found that in amphiboles from the altered parts of the granodiorite edenite type is the main cation substitution.

#### Mafic enclaves

Hornblendes in the quartz diorite and tonalite enclaves often form aggregates, together with magnetite. Mg-hornblende and tschermakitic hornblende (Fig. 3A) are the two varieties identified (Table 3). Concentric compositional zoning is pronounced in these amphiboles. Detailed analyses on the compositional profile of these zones show systematic variation from core to rim. One type of variation show increasing silica from core to rim, with parallel decrease in Al, Fe, Ti, and increase in Mg. The observed compositional variation corresponds to *tschermakite type*, while *edenite type* cation substitution is subordinate (Fig. 3B).

#### Rhyodacite dykes

Representative chemical analyses of amphiboles from the rhyodacite dykes are given in Table 4. Mg-hornblende (SER100a) which evolve to actinolitic hornblende and actinolite (SER100h), Τμήμα Γεωλογίας. Α.Π.Θ.

| Sample                         | SER22f | SER22j | SER22I | SER30 (core) | SER30 (rim)   | SER93-2d |
|--------------------------------|--------|--------|--------|--------------|---------------|----------|
| SiO,                           | 46.13  | 48.75  | 46.79  | 44.48        | 48.13         | 43.76    |
| TiO                            | 1.20   | 0.76   | 0.91   | 1.69         | 0.99          | 2.36     |
| Al <sub>2</sub> O <sub>3</sub> | 7.74   | 5.60   | 7.59   | 9.22         | 6.59          | 11.91    |
| FeO                            | 15.10  | 14.18  | 13.66  | 15.49        | 13.70         | 10.11    |
| $Cr_2O_3$                      | 0.00   | 0.00   | 0.00   | 0.00         | 0.00          | 0.04     |
| MnÔ                            | 0.51   | 0.55   | 0.48   | 0.26         | 0.28          | 0.09     |
| MgO                            | 12.34  | 13.67  | 13.43  | 12.23        | 14.25         | 16.14    |
| Ca0                            | 11.76  | 11.98  | 11.88  | 11.43        | 11.59         | 11.76    |
| Na,0                           | 1.40   | 0.94   | 1.36   | 158          | 1.20          | 2.02     |
| K,Ô                            | 0.72   | 0.47   | 0.49   | 0.79         | 0.56          | 0.59     |
| Total                          | 96.90  | 96.90  | 96.59  | 97.17        | 97 <i>2</i> 9 | 98.78    |
|                                |        |        |        |              | 0.005         | 6 1 7 1  |
| TSi                            | 6.845  | 7.151  | 6.891  | 6.570        | 6.985         | 6.171    |
| TAI                            | 1.155  | 0.849  | 1.109  | 1.430        | 1.015         | 1.829    |
| Sum_T                          | 8.000  | 8.000  | 8.000  | 8.000        | 8.000         | 8.000    |
| CAI                            | 0.198  | 0.119  | 0.208  | 0.173        | 0.112         | 0.149    |
| CCr                            | 0.000  | 0.000  | 0.000  | 0.000        | 0.000         | 0.004    |
| CFe3                           | 0.410  | 0.441  | 0.469  | 0.662        | 0.640         | 0.963    |
| CTi                            | 0.134  | 0.084  | 0.101  | 0.188        | 0.108         | 0.250    |
| CMg                            | 2.730  | 2.989  | 2.949  | 2.693        | 3.083         | 3.393    |
| CFe2                           | 1.464  | 1.299  | 1.213  | 1.251        | 1.023         | 0.230    |
| CMn                            | 0.064  | 0.068  | 0.060  | 0.033        | 0.034         | 0.011    |
| CCa                            | 0.000  | 0.000  | 0.000  | 0.000        | 0.000         | 0.000    |
| Sum_C                          | 5.000  | 5.000  | 5.000  | 5.000        | 5.000         | 5.000    |
| BCa                            | 1.870  | 1.883  | 1.875  | 1.809        | 1.802         | 1.777    |
| BNa                            | 0.130  | 0.117  | 0.125  | 0.191        | 0.198         | 0.223    |
| Sum_B                          | 2.000  | 2.000  | 2.000  | 2.000        | 2.000         | 2.000    |
| ACa                            | 0.000  | 0.000  | 0.000  | 0.000        | 0.000         | 0.000    |
| ANa                            | 0.273  | 0.150  | 0.263  | 0.261        | 0.141         | 0.329    |
| AK                             | 0.136  | 0.088  | 0.092  | 0.149        | 0.104         | 0.106    |
| Sum_A                          | 0.409  | 0.238  | 0.355  | 0.410        | 0.245         | 0.435    |

TABLE 3. Representative chemical analyses of amphiboles from the Serifos mafic enclaves

after replacement of hornblende, are the amphiboles observed in the dykes (Fig. 4A). Reverse compositional variation is also noticed in some hornblende grains, having Act-hornblende core (SER100c) and Mg-hornblende rim (SER100d).

Actinolitic rims on zoned Mg-hornblendes, and the existence of primary actinolite in the subvolcanic dykes with lower Ti and Ai<sup>V</sup>, could be an indication of an increase in oxygen fugasity, due to higher water contents at the late magmatic stages or a decrease in temperature as the crystallisation proceeds from Mg-hornblende composition to actinolite amphibole (HELZ, 1973; HAMMARSTROM & ZEN, 1986).

In some cases random actinolite formation at the expense of primary hornblende, is attributed to hydrothermal alteration.

As it is shown in Fig. 4B, in the fresh amphiboles only a minor substitution of tschermakite type occur, while in the hydrothermal actinolites, edenite



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**Figure 3.** A. Classification of amphiboles of mafic enclaves from the Serifos intrusion. B. SumA+CAI+CFe3+CTi versus TAI plot, presenting the combination of *tschermakite type* and *edenite type* cation substitutions in the above amphiboles.

type substitution, similar to that found in the amphiboles from the altered granodiorite, predominates.

**Figure 4.** A. Classification of amphiboles from rhyodacite dykes of the Serifos intrusion. B. SumA+CAI+CFe3+CTi versus TAI plot, presenting the combination of *tschermakite type* and *edenite type* cation substitutions in the above amphiboles.

# HORNBLENDE GEOBAROMETRY

The Al-in-hornblende barometer has been proven to be useful empirical geobarometer for

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2

8.0

7.5

7.0

TSi

6.5

6.0

В

5.5

| Sample                         | SER100a        | SER100k        | SER100<br>(core) | SER100<br>(rim) | SER100f<br>(altered) | SER100g        | SER100h        |
|--------------------------------|----------------|----------------|------------------|-----------------|----------------------|----------------|----------------|
| SiO <sub>2</sub>               | 48.30          | 50.17          | 52.56            | 46.86           | 53.39                | 53.93          | 54.22          |
| TiO2                           | 1.50           | 1.02           | 022              | 1.99            | 0.24                 | 0.18           | 0.13           |
| Al <sub>2</sub> O <sub>3</sub> | 6.42           | 5.49           | 3.26             | 828             | 2.99                 | 2.41           | 2.52           |
| FeO                            | 11.86          | 12.51          | 13.47            | 12.22           | 11.05                | 10.72          | 10.75          |
| Cr <sub>2</sub> O <sub>3</sub> | 0.01           | 0.01           | 0.04             | 0.02            | 0.03                 | 0.01           | 0.02           |
| MhÔ                            | 0.18           | 0.26           | 0.16             | 023             | 0.12                 | 0.16           | 0.19           |
| MgO                            | 15.20          | 15.70          | 15.80            | 14.97           | 17.39                | 17.47          | 1721           |
| Ca0                            | 12.11          | 11.96          | 12.64            | 11.5            | 12.84                | 12.58          | 12.56          |
| Na <sub>2</sub> O              | 1.57           | 1.46           | 0.68             | 2.03            | 0.72                 | 0.56           | 0.56           |
| K,Ď                            | 0.52           | 0.35           | 0.30             | 0.45            | 021                  | 0.24           | 0.18           |
| Total                          | 97.67          | 98.93          | 99.13            | 98.55           | 98.98                | 98.26          | 98.34          |
| TSi                            | 6.998          | 7.128          | 7.463            | 6.705           | 7.513                | 7.616          | 7.652          |
| TAI                            | 0.998<br>1.002 | 7.128<br>0.872 | 7.463<br>0.537   | 6.705<br>1.295  | 0.487                | 0.384          | 0.348          |
| Sum_T                          | 8.000          | 0.872<br>8.000 | 8.000            | 8.000           | 0.487<br>8.000       | 0.304<br>8.000 | 0.548<br>8.000 |
| CAI                            | 0.093          | .0.047         | 0.009            | 0.100           | 0.008                | 0.000          | 0.000          |
| CCr                            | 0.093          | 0.047          | 0.003            | 0.002           | 0.003                | 0.001          | 0.002          |
| CFe3                           | 0.284          | 0.499          | 0.389            | 0.593           | 0.318                | 0.325          | 0.262          |
| CTi                            | 0.163          | 0.499          | 0.023            | 0.335           | 0.025                | 0.019          | 0.014          |
| CMg                            | 3.283          | 3.325          | 3.345            | 3.193           | 3.648                | 3.678          | 3.621          |
| CFe2                           | 1.153          | 0.987          | 1211             | 0.869           | 0.982                | 0.941          | 1.007          |
| CMn                            | 0.022          | 0.031          | 0.019            | 0.028           | 0.014                | 0.019          | 0.023          |
| CCa                            | 0.000          | 0.000          | 0.000            | 0.000           | 0.000                | 0.000          | 0.000          |
| Sum_C                          | 5.000          | 5.000          | 5.000            | 5.000           | 5.000                | 5.000          | 5.000          |
| BCa                            | 1.880          | 1.821          | 1.923            | 1.763           | 1.936                | 1.903          | 1.899          |
| BNa                            | 0.120          | 0.179          | 0.077            | 0.237           | 0.064                | 0.097          | 0.101          |
| Sum_B                          | 2.000          | 2.000          | 2.000            | 2.000           | 2.000                | 2.000          | 2.000          |
| ACa                            | 0.000          | 0.000          | 0.000            | 0.000           | 0.000                | 0.000          | 0.000          |
| ANa                            | 0.321          | 0.223          | 0.110            | 0.326           | 0.132                | 0.057          | 0.053          |
| AK                             | 0.096          | 0.063          | 0.054            | 0.082           | 0.038                | 0.043          | 0.032          |
| Sum_A                          | 0.417          | 0.286          | 0.165            | 0.408           | 0.170                | 0.100          | 0.085          |

TABLE 4. Representative chemical analyses of amphiboles from the Serifos rhyodacite dykes.

calc-alkaline plutons and volcanic rocks (HAMMARSTROM & ZEN, 1986). The premise of this barometer is the assumption that the temperature of hornblende equilibration was in the vicinity of the solidus and therefore approximately constant. This is because below about 2 kb the temperature of final crystallisation increases rapidly with drop in pressure (HOLLISTER et al., 1987). Because the applicability of the barometer depends strongly on the P-T sets selected for the calibration of the Al-in-hornblende system in the different studies, it is selected a calibration set similar to the crystallisation conditions of Serifos granodiorite. JOHNSON & RUTHERFORD (1989), experimental calibration is considered more applicable for the Serifos pluton, since the study is

| Sample     SER93-14a     SER93-14       SiO2     54.01     54.35       TiO2     0.03     0.01       Al2O3     1.95     1.62       FeO     10.55     10.87       Cr2O3     0.01     0.02       MrO     0.10     0.09       MgO     17.16     16.77       CaO     13.03     13.24       Na2O     0.26     0.23       K2O     0.09     0.07       Total     97.19     97.27       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
|---|-----------|--|--|--|--|--|--|
| $\begin{array}{c cccc} {\rm TiO}_2^2 & 0.03 & 0.01 \\ {\rm Al}_2{\rm O}_3 & 1.95 & 1.62 \\ {\rm FeO} & 10.55 & 10.87 \\ {\rm Cr}_2{\rm O}_3 & 0.01 & 0.02 \\ {\rm MrO} & 0.10 & 0.09 \\ {\rm MgO} & 17.16 & 16.77 \\ {\rm CaO} & 13.03 & 13.24 \\ {\rm Na}_2{\rm O} & 0.26 & 0.23 \\ {\rm K}_2{\rm O} & 0.09 & 0.07 \\ {\rm Total} & 97.19 & 97.27 \\ \hline \\ \hline \\ {\rm TSi} & 7.730 & 7.812 \\ {\rm TAI} & 0.270 & 0.188 \\ {\rm Sum}_{-}{\rm T} & 8.000 & 8.000 \\ {\rm CAI} & 0.059 & 0.086 \\ {\rm CCr} & 0.001 & 0.002 \\ {\rm CFe3} & 0.118 & 0.000 \\ {\rm CTi} & 0.003 & 0.001 \\ {\rm CMg} & 3.662 & 3.593 \\ {\rm CFe2} & 1.145 & 1.307 \\ {\rm CMn} & 0.012 & 0.011 \\ {\rm CCa} & 0.000 & 0.000 \\ \hline \end{array}$ | SER93-14b |  |  |  |  |  |  |
| $\begin{array}{c cccc} Al_2O_3 & 1.95 & 1.62 \\ FeO & 10.55 & 10.87 \\ Cr_2O_3 & 0.01 & 0.02 \\ MrO & 0.10 & 0.09 \\ MgO & 17.16 & 16.77 \\ CaO & 13.03 & 13.24 \\ Na_2O & 0.26 & 0.23 \\ K_2O & 0.09 & 0.07 \\ Total & 97.19 & 97.27 \\ \hline \\ \hline \\ TSi & 7.730 & 7.812 \\ TAI & 0.270 & 0.188 \\ Sum_T & 8.000 & 8.000 \\ CAI & 0.059 & 0.086 \\ CCr & 0.001 & 0.002 \\ CFe3 & 0.118 & 0.000 \\ CTi & 0.003 & 0.001 \\ CMg & 3.662 & 3.593 \\ CFe2 & 1.145 & 1.307 \\ CMn & 0.012 & 0.011 \\ CCa & 0.000 & 0.000 \\ \end{array}$  |           |  |  |  |  |  |  |
| $\begin{array}{c cccc} Al_2O_3 & 1.95 & 1.62 \\ FeO & 10.55 & 10.87 \\ Cr_2O_3 & 0.01 & 0.02 \\ MrO & 0.10 & 0.09 \\ MgO & 17.16 & 16.77 \\ CaO & 13.03 & 13.24 \\ Na_2O & 0.26 & 0.23 \\ K_2O & 0.09 & 0.07 \\ Total & 97.19 & 97.27 \\ \hline \\ \hline \\ TSi & 7.730 & 7.812 \\ TAI & 0.270 & 0.188 \\ Sum_T & 8.000 & 8.000 \\ CAI & 0.059 & 0.086 \\ CCr & 0.001 & 0.002 \\ CFe3 & 0.118 & 0.000 \\ CTi & 0.003 & 0.001 \\ CMg & 3.662 & 3.593 \\ CFe2 & 1.145 & 1.307 \\ CMn & 0.012 & 0.011 \\ CCa & 0.000 & 0.000 \\ \end{array}$  |           |  |  |  |  |  |  |
| FeO     10.55     10.87       Cr <sub>2</sub> O <sub>3</sub> 0.01     0.02       MrO     0.10     0.09       MgO     17.16     16.77       CaO     13.03     13.24       Na <sub>2</sub> O     0.26     0.23       K <sub>2</sub> O     0.09     0.07       Total     97.19     97.27       TSi     7.730       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| MnO     0.10     0.09       MgO     17.16     16.77       CaO     13.03     13.24       Na_O     0.26     0.23       K_O     0.09     0.07       Total     97.19     97.27       TSi     7.730     7.812       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
| MnO     0.10     0.09       MgO     17.16     16.77       CaO     13.03     13.24       Na <sub>2</sub> O     0.26     0.23       K <sub>2</sub> O     0.09     0.07       Total     97.19     97.27       TSi     7.730     7.812       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
| CaO     13.03     13.24       Na2O     0.26     0.23       K2O     0.09     0.07       Total     97.19     97.27       TSi     7.730     7.812       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
| Na2O     0.26     0.23       K2O     0.09     0.07       Total     97.19     97.27       TSi     7.730     7.812       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
| K2Ô     0.09     0.07       Total     97.19     97.27       TSi     7.730     7.812       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| Total     97.19     97.27       TSi     7.730     7.812       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| Total     97.19     97.27       TSi     7.730     7.812       TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| TAI     0.270     0.188       Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| Sum_T     8.000     8.000       CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| CAI     0.059     0.086       CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| CCr     0.001     0.002       CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| CFe3     0.118     0.000       CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| CTi     0.003     0.001       CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
| CMg     3.662     3.593       CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
| CFe2     1.145     1.307       CMn     0.012     0.011       CCa     0.000     0.000  |           |  |  |  |  |  |  |
| CMn     0.012     0.011       CCa     0.000     0.000   |           |  |  |  |  |  |  |
| CCa 0.000 0.000   |           |  |  |  |  |  |  |
|   |           |  |  |  |  |  |  |
| Sum_C 5.000 5.000   |           |  |  |  |  |  |  |
|   |           |  |  |  |  |  |  |
| BCa 1.998 2.000   |           |  |  |  |  |  |  |
| BNa 0.002 0.000   |           |  |  |  |  |  |  |
| Sum_B 2.000 2.000   |           |  |  |  |  |  |  |
| ACa 0.000 0.039   |           |  |  |  |  |  |  |
| ANa 0.070 0.064   |           |  |  |  |  |  |  |
| AK 0.016 0.013  |           |  |  |  |  |  |  |
| Sum_A 0.087 0.116   |           |  |  |  |  |  |  |

**TABLE 5.** Chemical analyses of amphiboles from the Serifos skarns.

based on a similar composition system with P=1.5 kb and  $T=720^{\circ}$ C. Indication for estimating emplacement depth of a pluton is the metamorphic assemblage in the contact aureole. Formation depths of the irregular-shaped andradite-pyroxene-magnetite skarn suggest formation depths of 3-3.5 km (SALEMINK, 1985).

Figure 5 presents the variation of AI tot in

amphiboles from the Serifos pluton *vs.* pressure, according to the selected equation of JOHNSON & RUTHERFORD (1989). The selected amphiboles which were used for the geobarometer calculation correspond to rim compositions of fresh and fairly homogeneous hornblende crystals from the granodiorite intrusion. The pressure is estimated from the following equation::  $P = -3.46(\pm 0.24) +$ 4.23 ( $\pm 0.13$ ) (Al<sup>T</sup>), and r<sup>2</sup> = 0.99.

The advantage of this experimental calibration is that it minimises the error to less than  $\pm 0.5$  kb at the low pressure end. The pressure determinations for the Serifos intrusion vary significantly as for the mafic enclaves range from 1.0 to 2.2 kb whereas for the granodiorite from 0.33 to 1.7 kb. According to field relations (STOURAITI, 1995), it is likely that the pluton contains successive injections of melt that came up and crystallise at different depths. Under such conditions a wide pressure range of 2.0 kb would be expected.

## **DISCUSSION - CONCLUSIONS**

The majority of the studied amphiboles exhibit compositional zoning. This is the result of different cation substitutions that take place (HELZ, 1973) under varying physical-chemical conditions. This compositional zoning is more pronounced in the mafic enclaves. The Mg/Mg+Fe<sup>+2</sup> ratio of tschermakites in the enclaves is comparable with Mg-rich hornblendes from gabbros and andesites (DEER et al., 1966).

The mafic enclaves contain the common Mghornblende, which is similar in composition with the main granodiorite hornblende however it tends to be more Mg-rich. Granodiorite hornblendes display generally lower Mg/Mg+Fe<sup>+2</sup> ratio, relative to the enclaves, due to higher Fe<sup>+2</sup> content. Moreover it is noticed that the Fe<sup>+3</sup> /Fe<sup>+2</sup> ratio is increased in the mafic enclaves and the subvolcanic dykes (up to 0.5 a.p.f.u), similar to hornblende composition from the recent andesitic lavas on the flanks of the Aegean Arc (MITROPOULOS & TARNEY, 1992). In the tschermakite variety, Ti as Turing Esuboring A D Q



Figure 5. Al tot in hornblende as a function of pressure. Lines for all calibrations are shown for reference. Pressure for Serifos amphiboles were calculated according to JOHNSON & RUTHERFORD (1989) experimental calibration. (S: SCHMIDT (1992); J&R: JOHNSON & RUTHER-FORD (1989); H&Z: HAMMARSTROM & ZEN (1986)).

well as Al<sup>w</sup> have a positive correlation with T and a negative correlation with oxygen fugacity. The elevated content of Ti- and Al<sub>w</sub> relative to the other more evolved amphiboles, suggest crystallisation from a higher temperature mafic magma.

Finally the observed instability of hornblende as seen clearly in the mafic enclaves as well as in the dykes, indicated by the partial replacement by biotite, suggest relatively moderate  $H_2O$  content and clearly water undersaturated conditions of the granodiorite system at the low e.g., 2kb, shortly before its final solidification.

#### REFERENCES

- DEER W.A., HOWIE R.A. & ZUSSMAN J. (1966). An introduction to the rock forming minerals. Longman, London, 528 pp.
- GAUTIER P. & BRUN J.-P. (1994). Crustal-scale geometry and kinematics of late-orogenic extension in the central Aegean (Cyclades and Evvia Island). Tectonophysics, **238**, 399-424.
- HAMMARSTROM J.M. & ZEN E-an (1986). Aluminium in hornblende: an empirical igneous geobarometer. American Mineralogist, **71**, 1297-1313.

- HELZ R.T. (1973). Phase relations of basalts in their melting range at  $PH_2O = 5$  kb as a function of oxygen fugacity. Part I. Mafic phases. *Journal of Petrology*, **14**, 249-302.
- HOLLISTER L.S., GRISSOM G.C., PETERS E.K., STOWELL H.H. & GISSON V.B. (1987). Confirmation of the empirical correlation of AI in hornblende with pressure of solidification of calc- alkaline plutons. American Mineralogist, 72, 231-239.
- JOHNSON M.C. & RUTHERFORD M.J. (1989).Experimental calibration of the aluminum-in-hornblende geobarometer with application to Long Valley caldera (California) volcanic rocks. Geology, 17, 837-841.
- LEAKE B.E. (1978). Nomenclature of amphiboles. Canadian Mineralogist, **16**, 501-520.
- MARSH, N.G., TARNEY, J. & HENDRY, G.L (1983). Trace element geochemistry of basalts from Hole 504B, Panama Basin, DSDP Legs 69 and 70. Init. Rept. DSDP, **69**, 747-764.
- MEINERT L. (1992). Skarns and skarn deposits. Geoscience Canada, **19**, 145-162.
- MITROPOULOS P. & TARNEY J. (1992). Significance of mineralogical composition variations in the Aegean island arc. Journal of Volcanology and Geothermal Research, **51**, 283-303.

- NANEY M.T. (1983). Phase equilibria of rock-forming ferromagnesian silicates in granitic systems. American Journal of Science, 283, 993-1033.
- SALEMINK J. (1985). Skarn and ore formation at Serifos, Greece, as a consequence of granodiorite intrusion. Geol. Ultraiectina, 40, 1-232.
- SCHMIDT, M.W. (1992). Amphibole composition in tonalite as function of pressure: an experimental calibration of the Al-in-hornblende barometer.

Contribution to Mineralogy and Petrology, **110**, 304-310.

- SHELLEY D. (1993). Igneous and metamorphic rocks under the microscope. Chapman & Hall, London.
- STOURAITI C. (1995). Geochemistry and petrogenesis of the Serifos granite, in relation to other Aegean granitoids, Greece. Ph. D. Thesis (unpbl.), Univ. of Leicester, 239 pp.