Dichotomy of The Messada Pluton, Serbo-Macedonian Massif, Greece: From Rifting to Subduction

Charalampos Vasilatos

1Section of Economic Geology & Geochemistry, Department of Geology & Geoenvironment, National & Kapodistrian University of Athens, Zografou 15784 Athens, Greece

E-mail address: vasilatos@geol.uoa.gr

Abstract. The Messada pluton is a mafic intrusion that is located about 12 km SW of Serres town, (Macedonia Greece) that intrudes the two mica, biotite and the augen gneisses of the Vertiskos formation (Serbo-Macedonian massif). The aim of this study is to investigate, define and evaluate the geochemical characteristics of the pluton in order to determine the geotectonic environment in which the parental magma has been formed. The Mesada pluton is a mid to coarse grained intrusion presenting petrographic variety from diorite and quartz diorite to tonalite and granodiorite. The variety in petrography reflects its chemical inhomogeneity in major and trace elements. It is suggested that parts of pluton have been formed by distinctly different types of magmas originated in diverse geotectonic settings. Those parts of quartz diorite and tonalite composition, present similar geochemical characteristics, LILE/HFSE ratios and negative Nb, but no Ti anomalies in their primitive mantle normalized trace elements spider grams. They exhibit higher HFS values than those of granodioritic composition. Moreover, their ORG normalized spider grams not only suggest that they have been evolved by a common parental magma, but also present the typical characteristics of a “crust dominated” within plate pluton that may have been formed in an early stage during rifting, prior to a subsequent subduction episode. This interpretation may be in accordance with the suggestion for the Gondwanian origin of the more silicic Triassic rift related meta-granites (e.g. Arnea plutonic complex) of the Serbo-Macedonian massif. In contrary; the parts of Mesada pluton of granodioritic composition, exhibit a calc-alkaline to high K calc-alkaline magmatic suite and present higher LILE/HFSE and LREE/HREE ratios, related to a higher crustal component contribution for the magma genesis. Furthermore, their primitive mantle normalized spider grams’ present negative anomalies at Nb and Ti. These characteristics indicate that those granodioritic parts have been formed by the crystallization of a calc-alkaline magma, produced by the partial melting of lower crust, lithospheric mantle and asthenospheric mantle components, in a volcanic arc geo-tectonic setting. Their geochemical characteristics have close similarities to those of the collision related granitoids that have intruded the Serbo-Macedonian during Tertiary.

1. Introduction

The Messada pluton (Figure 1) is a mafic magmatic intrusion located at about 12 km SW of Serres town, Macedonia Greece. It intrudes the two mica, the biotite and the augen gneisses of the Vertiskos Unit (Serbo-Macedonian massif), [1].
Himmerkus et al. (2007) have defined the “Vertiskos terrane” that is composed by two lithological units (the Silurian Vertiskos Unit and the Triassic Arnea Unit), both of which were considered as exotic to the Internal Hellenides. In fact, the plutonic intrusions in the Serbo-Macedonian massif are divided into two groups according to their age, as resulted by isotopic data and geological evidences e.g. [1, 2, 3], those of Mesozoic and those of Tertiary age. The Mesozoic (Triassic to Cretaceous), plutonic rocks occur mainly in the Central and northern part of Chalkidiki peninsula while those of Tertiary age are emplaced, mainly, in the east. Kockel et al [1] had considered the Mesada pluton to be of Tertiary age, exhibiting a monzodioritic composition. We believe that the age of 231.3 ± 3.1 Ma (middle Triassic), proposed by the Himmerkus et al [3] for Mesada pluton refers to the adjacent augen gneisses formation. The aim of this study is to investigate, define and evaluate the geochemical characteristics of the Mesada pluton in order to determine the geotectonic environment in which the parental magma has been formed.

2. Materials and methods
Sampling was carried out during fieldwork, taking care to include fresh rock samples from any different petrographic types of its pluton. The bulk rock chemical analyses were implemented by the X-ray Fluorescence analytical method in the Laboratory of the Department of Geology, University of Leicester, UK. The major elements analyses were performed in fussed beads while the trace elements were analysed in pressed pellets. The chemical analyses of selected samples, for the rare earth elements (REE) and for the U, Ta, Hf and Cs, were carried out by the instrumental neutron activation method (INAA) in the Institute of Nuclear Technology and Radio Safety, National Centre for Scientific Research “DEMOKRITOS” Greece.
3. Results and Discussions

The Mesada pluton is a mid to coarse grained intrusion presenting petrographic variety from diorite and quartz diorite to tonalite and granodiorite (Table 1).

The bulk rock chemical analyses are presented in Table 2. According to the classification schemes of Debon and Le Fort [4] and Villaseca et al [5], three different types are present: a metaluminus quartz diorite to diorite type (MSDR), a metaluminus tonalite to granodiorite type (MSTN) and an intermediate peraluminus granodiorite type (MSGD).

### Table 1. Mineralogical composition and petrographical classification of the samples (mineral abbreviations according to [6])

| Sample   | Symbol | Rock type | essential minerals* | accessory minerals* |
|----------|--------|-----------|---------------------|---------------------|
| MSD102   |        | Granodiorite | Pl, Kfs, Qtz, Ms, Am, Bt | Chl, Mag |
| MSD103   |        | Granodiorite | Pl, Kfs, Qtz, Ms, Am, Bt | Chl, Ttn, Hem |
| MSD104   |        | Quartz diorite | Pl, Am, Bt, Qtz | Kfs, Mag, Ep, Ttn |
| MSD105   |        | Quartz diorite | Pl, Am Bt, Qtz | Ep, Chl Mag, Ilm |
| MSD107   |        | Quartz diorite | Pl, Am Qtz | Kfs, Ms, Ep, Mag |
| MSD108   |        | Quartz diorite | Pl, Am, Bt, Qtz | Kfs, Ms, Mag, Ttn |
| MSD110   |        | Tonalite | Pl, Am, Qtz | Chl, Ms, Hem, Ttn |
| MSD111   |        | Tonalite | Pl, Am, Qtz | Chl, Kfs, Hem, Ms |
| MSD100   | +     | Augen Gneiss | Qtz, Kfs, Pl, Bt, Ms | Am, Ap, Ttn |
| MSD101   | +     | Gneiss | Pl, Kfs, Qtz, Bt | Ms, Am |

* Minerals referred in the order of their contribution to the v/v composition of each sample

Almost all the studied samples present a high K calc alkaline/shoshonitic suite according to the discrimination scheme of Hastie et al [7]. In their primitive mantle normalized trace elements spidergrams (Figure 2a, b), those parts of quartz diorite [MSDR] and tonalite [MSTN] composition, presents similar geochemical characteristics. They exhibit high LILE/HFSE ratios and negative Nb but no Ti anomalies. They have higher HFS values than those of granodioritic composition (Figure 2c). Moreover, the patterns of their ocean ridge granite (ORG) normalized spidergrams (Figure 2d) are arranged in parallel indicating a common magmatic origin and, probably, a fractional crystallization process. The most sialic sample (MSTN-type), presents enrichment throughout the series of the trace elements. Both samples present a negative slope from Rb to Yb and a negative anomaly in Ba. There is also a significant enrichment in Rb and Th elements compared to the Nb and Ta. The Ce and the Sm exhibit higher normalized values than their reciprocal adjacent elements. This selective enrichment is attributed [8] to the high contribution of a crust originated compound in the magma genesis.

Thus, it is suggested that those parts of the Mesada pluton of quartz diorite and tonalite composition have been evolved by a common parental magma. They present the typical characteristics of a crust dominated within plate pluton (WPG) described by Pearce et al [8] that may have been formed during a pre-Tertiary rifting. This interpretation may be in accordance with the suggestions for the Gondwanian origin during rifting of the more silicic, Triassic meta-granites (e.g. Arnea plutonic complex) of the Serbo-Macedonian massif [10] or during the rifting that lead to the opening of the Mesozoic Tethys [11].

In the Y+Nb vs. Rb discrimination diagram (Figure 3) the projection of the MSDR type samples in the field of the volcanic arc granites (VAG) despite of the fact that their ORG normalized spidergrams present WPG characteristics may be explained by the point made by Pearce [12], that in the VAG field may be projected compositions of within plate plutons (WPG) when the ratio of assimilation/fractional crystallization is extremely high or when the melt had originated exclusively from the partial melting of a crustal component (crustal melts).
| Sample | MSD102 | MSD103 | MSD104 | MSD105 | MSD107 | MSD108 | MSD110 | MSD111 | MSD100 | MSD101 |
|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| SiO₂   | 69.75  | 65.91  | 53.95  | 50.12  | 53.11  | 51.94  | 57.42  | 58.08  | 73.77  | 72.56  |
| TiO₂   | 0.67   | 0.81   | 1.5    | 1.12   | 1.74   | 1.82   | 1.82   | 2.27   | 2.11   | 0.29   |
| Al₂O₃  | 13.59  | 15.74  | 15.72  | 16.71  | 15.23  | 15.24  | 16.3   | 15.18  | 12.85  | 14.60  |
| Fe₂O₃  | 3.77   | 4.35   | 6.96   | 8.37   | 10.69  | 10.61  | 9.05   | 9.75   | 1.63   | 2.21   |
| MnO    | 0.05   | 0.05   | 0.13   | 0.16   | 0.16   | 0.19   | 0.17   | 0.17   | 0.02   | 0.05   |
| MgO    | 1.21   | 1.34   | 6.61   | 7.69   | 5.36   | 5.43   | 3.05   | 3.19   | 0.28   | 0.47   |
| CaO    | 2.47   | 2.7    | 9.68   | 10.66  | 6.84   | 7.49   | 4.53   | 5.36   | 0.7    | 0.83   |
| Na₂O   | 3.2    | 3.7    | 3.39   | 3.07   | 3.74   | 4.24   | 4.33   | 2.77   | 3.05   | 2.41   |
| K₂O    | 2.17   | 3.12   | 0.4    | 0.6    | 1.19   | 0.74   | 0.78   | 2.41   | 5.33   | 3.41   |
| P₂O₅   | 0.25   | 0.28   | 0.11   | 0.12   | 0.25   | 0.25   | 0.43   | 0.34   | 0.09   | 0.13   |
| LOI    | 2.08   | 1.62   | 1.13   | 1.34   | 1.35   | 1.33   | 1.18   | 0.54   | 0.61   | 1.67   |
| Total  | 99.21  | 99.61  | 99.58  | 99.95  | 99.68  | 99.25  | 99.51  | 99.88  | 98.61  | 98.73  |
| Nb     | 11     | 14     | 6      | 5      | 8      | 11     | 21     | 18     | 8      | 7      |
| Zr     | 190    | 223    | 73     | 93     | 165    | 175    | 275    | 313    | 133    | 93     |
| Y      | 18     | 21     | 27     | 23     | 40     | 41     | 41     | 53     | 22     | 21     |
| Sr     | 221    | 195    | 277    | 307    | 266    | 228    | 219    | 208    | 85     | 105    |
| Rb     | 84     | 99     | 17     | 22     | 44     | 19     | 27     | 80     | 96     | 106    |
| Th     | 8      | 13     | 4      | 3      | 5      | 5      | 5      | 13     | 21     | 27     |
| Zn     | 49     | 55     | 54     | 66     | 104    | 90     | 90     | 95     | 11     | 9      |
| Ba     | 512    | 751    | 118    | 386    | 604    | 290    | 261    | 679    | 518    | 850    |
| La     | 17     | 32     | 5      | 3      | 16     | 26     | 23     | 30     | 24     |        |
| Ce     | 40     | 64     | 26     | 15     | 41     | 43     | 45     | 78     | 65     | 75     |
| Nd     | 23     | 35     | 19     | 16     | 29     | 31     | 16     | 24     | 34     | 28     |
| Ga     | 16     | 18     | 19     | 15     | 19     | 18     | 21     | 23     | 13     | 16     |
| Ni     | 5      | 5      | 55     | 79     | 23     | 17     | 3      | 10     | bdl    | 2      |
| Sc     | 9      | 9      | 49     | 34     | 35     | 36     | 26     | 31     | 2      | 9      |
| V      | 72     | 72     | 239    | 173    | 211    | 234    | 198    | 203    | 23     | 42     |
| Cr     | 16     | 20     | 63     | 273    | 161    | 145    | 44     | 43     | 8      | 15     |
| Co     | 45     | 39     | 40     | 45     | 45     | 40     | 46     | 58     | 39     | 46     |
| Cu     | 16     | 18     | 19     | 15     | 19     | 18     | 21     | 23     | 13     | 16     |
| La     | 22     | 40     | 10     | 6      | 30     | 44     |        |        |        |        |
| Ce     | 43     | 76     | 23     | 15     | 62     | 96     |        |        |        |        |
| Sm     | 4.3    | 6.5    | 3.9    | 2.9    | 7.8    | 9.3    |        |        |        |        |
| Eu     | 1.1    | 1.4    | 1.4    | 1.1    | 1.9    | 2.0    |        |        |        |        |
| Tb     | 0.5    | 0.5    | 0.6    | 0.5    | 1.8    | 1.7    |        |        |        |        |
| Yb     | 1.8    | 2.2    | 2.4    | 2.0    | 4.0    | 5.7    |        |        |        |        |
| Lu     | 0.2    | 0.3    | 0.3    | 0.2    | 0.6    | 0.8    |        |        |        |        |
| U      | 2.3    | 2.1    | 1.6    | 0.0    | 2.3    | 2.7    |        |        |        |        |
| Ta     | 1.5    | 1.4    | 0.6    | 0.3    | 1.8    | 1.2    |        |        |        |        |
| Hf     | 5.2    | 6.1    | 2.0    | 1.9    | 6.7    | 8.8    |        |        |        |        |
| Cs     | 1.0    | 1.4    | 0.0    | 0.0    | 0.4    | 1.6    |        |        |        |        |
Figure 2. Trace elements spidergrams from Mesada pluton: a. primitive mantle normalized (after Sun and McDonough, [9]), MSDR samples, b. primitive mantle normalized MSTN samples, c. primitive mantle normalized MSGD samples, d. Ocean ridge granite (ORG) normalized plots (after Pearce et al. [8]) of representative MSTN (upper) and MSDR (lower) samples.

Figure 3. Y+Nb vs. Rb discrimination diagram [12] for the tectonic interpretation of Mesada pluton (symbol legend in Table 1).

In contrary, those parts of the Mesada pluton of MSGD type, exhibit a calc-alkaline to high K calc-alkaline magmatic suite and present higher LILE/HFSE and LREE/HREE ratios (Figure 2d). This is probably related to a higher crustal component contribution in the magma formation. Furthermore, their primitive mantle normalized spidergrams present negative anomalies at Nb and Ti. These
characteristics indicate that those parts have originated by the crystallization of a calc-alkaline magma, produced by the partial melting of lower crust, lithospheric mantle and asthenospheric mantle components, in a volcanic arc geotectonic setting [8, 12]. Their geochemical characteristics have close similarities to those of the collision related granitoids that have intruded into the Serbo-Macedonian massif during Tertiary [13].

4. Conclusions
The aim of this study was to investigate and evaluate the geochemical characteristics of the pluton in order to determine the geotectonic environment in which its parental magma has been formed. Our results suggest that different parts of the Mesada pluton have been formed by distinctly different types of magmas originated in diverse geotectonic settings. Those parts of quartz diorite and tonalite composition, have been evolved by a common parental magma, and present the typical characteristics of a “crust dominated” within plate pluton, that may have been formed in an early stage during rifting (Triassic?), prior to a subsequent subduction (orogenic) episode in Tertiary. In contrary; the parts of granodioritic composition have been formed by the crystallization of a calc-alkaline magma, produced by the partial melting of lower crust, lithospheric mantle and asthenospheric mantle components, during plate collision in a volcanic arc geotectonic setting. Their geochemical characteristics have close similarities to those of the collision related granitoids that have intruded the Serbo-Macedonian during Tertiary.

Acknowledgement(s)
The N.C.S.R. “DEMOKRITOS”, Greece, provided the radiation and analytical facilities for the instrumental neutron activation analyses. National and Kapodistrian University of Athens is acknowledged for supporting the implementation and funding the presentation this work.

References
[1] Kockel, F., Mollat, H., Antoniadis, P., Ioannides, K., 1979. Geological map of Greece: Sochos sheet, Scale 1:50000. Institute of Geological and Mining Research, Greece
[2] Poli, G., Ghristofides, G., Soldatos, T., Koroneso, A., 2008. Early Triassic Granitic Magmatism (Arnea and Kerkini Granitic Complexes) in the Vertiskos Unit (Serbo-Macedonian Massif, North-Eastern Greece) and its significance in the Geodynamic Evolution of the area. Acta Vulcanologica, 20 (1/2): 1000-1024
[3] Himmerkus, F., Reischmann, T., Kostopoulos, D., 2009. Triassic rift-related meta-granites in the Internal Hellenides, Greece. Geol. Mag. 146 (2): 252–265
[4] Debon, F., Le Fort, P., 1983. A chemical–mineralogical classification of common plutonic rocks and associations. Transactions of the Royal Society of Edinburgh, Earth Sciences, 73: 135–149
[5] Villaseca, C., Barbero, L., Herreros, V., 1998. A re-examination of the typology of peraluminous granite types in intracontinental orogenic belts. Transactions of the Royal Society of Edinburgh, Earth Sciences, 89: 113–119
[6] Whitney L.D., Evans, W.B., 2010. Abbreviations for names of rock-forming minerals. American Mineralogist, 95: 185–187
[7] Hastie, A.R., Kerr, A.C., Pearce, J.A., Mitchell, S.F., 2007. Classification of altered volcanic island arc rocks using immobile trace elements: development of the Th Co discrimination diagram. Journal of Petrology, 48: 2341–2357
[8] Pearce, J.A., Harris, N.B.W., Tindle, A.G., 1984. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. J. Petrol., 25: 956-983
[9] Sun, S.S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In: Magmatism in the ocean basins. A.D. Saunders, and M.J. Norry, (eds), Geological Society of London, 42: 313-345
[10] Himmerkus, F., Anders, B., Reischmann, T., Kostopoulos, D., 2007. Gondwana-derived
terranes in the northern Hellenides. Geological Society of America Memoirs, 200: 379-390

[11] Antić, M., Peytcheva, I., von Quadt, A., Kounov, A., Trivić, B., Serafimovski, T., Tasev, G., Gerdjikov, I., Wetzel, A., 2015. Pre-Alpine evolution of a segment of the North-Gondwanan margin: Geochronological and geochemical evidence from the central Serbo-Macedonian Massif. Gondwana Research

[12] Pearce, J.A., 1996. Sources and Settings of Granitic Rocks. Episodes, 19 (4): 120-125

[13] Vasilatos, C., 2013. A comparative study in the geochemistry of the trace and the rare earth elements in tertiary granites in Central Macedonia, related or not, with known mineralization - Definition of the geotectonic environment for the granites’ genesis. PhD Thesis, Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Greece, 502p