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THE MINERALOGY AND GEOCHEMISTRY OF THE STRATONI GRANODIORITE AND ITS METALLOGENETIC SIGNIFICANCE

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ABSTRACT

Mineralogical, geochemical and isotopic data have shown that the 29.6 Ma Stratoni magmatic stock is a fine to coarse-grained granodiorite of calc-alkaline affinity indicating a compressive setting. It is of hybrid nature consisting of predominantly a mantle - component with contributions from erest and has been emplaced at pressures ranging from 5 to 1 kb and a temperature near 900° C. Moreover it can be characterized as mineralized and probably metalliferous.

ΣΥΝΟΨΗ

Πειρολογικά, ΥΕωχημικά και ισοτοπικά δεδομένα έδειξαν ότι το ηλικίας 29,6 εκ. ετών μαγματικό σώμα του Στρατωνίου είναι ένας λεπτόκοκκος-αδρόκοκκος γρανοδιορίιτης, ασβεσταλκαλικού χαρακτήρα.

Η φύση του είναι υβόριδική, με συμμετοχή μανδύα και φλοιού (αλλά με κυρέαρχο το μανδυακό υλικό). Φαίνεται να έχει δημιουργηθεί σε περιβάλλον "συμπίεσης" και η τοτοθέτησή του να έγινε υπό συνθήκες πίεσης (1-5 kb) και θερμοκρασίας περίπου 900° C, και να έχει παίζει σημαντικό ρόλο σε μεταλλογενετικές διαδικασίες.

INTROUDUCTION

The last fifteen years there has been a renaissance in the study of granitic rocks due to their advances both in the interpretation of the cogmatic processes and the geotectonic settings (Chappell and White, 1974; White and Chappell, 1977; Takahashi et al., 1980; Pearce et al., 1984). The association of granites with a range of mineral deposits has also been extensively studied (Tischendorf, 1977; Beckinsale, 1979; Hildreth 1981; Eugster, 1985).

The Stratoni magnatic stock which is the subject of the present study, is located 0.5 km north of the Stratoni village (Fig. 1). This is a magnetic pluton with a surface outcrop of about 3 km², containing minor base metal sulfide mineralization in veins and disseminations and is spatially associated with the Madem Laccos and Mavres Petres carbonate-hosted Pb-Zn² (Ag, Au) sulfide orebodies (Fig. 1). The Stratoni pluton along with aplite-pegmatite dykes intrudes part of the Kerdyllia formation. The latter together with the Vertiskos formation comprise the so-called Servo-Macedonian Massif (SMM) consisting of two-mica gneisses, quartz-feldspathic gneisses and schists, hornblende-gneisses, amphibolites and marbles (Fig. 1). The metamorphic grade in the SMM rocks is that of the almandime-amphibolite facies with locally abundant anatectic phenomena. The age of the SMM is considered to be Pre-Cambrian or older (Kockel et al., 1977), whereas

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Α. ΠΕΡΛΙΚΟΣ: Ο Γρανοδιορίτης του Στρατωνίου. Η ορυκτολογία, γεωχημεία και μετΦλάκακή Βιβλισθήκη Θεδωδαστοκ^{ΔΔ-Δ}μήμα Γεωλονίας. Α.Π.Θ.

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Fig. 1. Location map of the Stratoni granodiorite (Kockel et al. 1977).

Σχ. 1. Χάρτης της περιοχής του γρανοδιορίτη του Στρατωνίου.

that of the Stratoni pluton is reported at 29.6 + 1.4 Ma, based on K-Ar dating of biotites (Alther et al, 1976).

Nicolaou (1960) considered the Stratoni magmatic stock and associated aplite-pegmatite dykes as the source of the Pb-Zn (Au,Ag) sulfide mineraliapilton in the area. This study utilizes mineralogical and geochemical data ation Stratoni intrusion in an attempt to present an up-dated version with of the ce to the source material and tectonic setting of this magmatic activity and the kind of relationship that it bears to the metallogeny of the spatially associated carbonate-hosted base sulfide ores.

MINERALOGY - MINERAL CHEMISTRY

The Stratoni pluton is a fine to coarse grained allotriomorphic.inequigranular stock, with a mineralogy consisting mainly of quartz, microcline, plagioclase and biotite. K-mica, aphibole, pyroxene, epidote, sphene, calcite, magnetite and pyrite occur as accessories. The microcline shows cross hatched twinning, microperthitic exsolution of albite and comprises nearly 20 percent of the volume of the total feldspar. Microprobe analyses give feldspar compositions in the range of Or 88-92 (Table 1). Plagioclasse occurs as coarse -and finer- grained varieties that show limited chemical zoning. compositions are in the range of An 37-47 (Table 1). The latter plagioclase variety shows the highest degree of alteration to sericite, illustrated in Figure 2c. Biotite shows variable degree of alteration to chlorite (Fig. 2a and b). Microprobe analyses, given in Table 1, indicate, that they are typical biotites, which contain appreciable amounts of TiO2. On the basis of their high TiO: content, they are considered to be of primary origin (magmatic). Actinolitic amphibole was observed in a small number of samples. Its composition is given in Table 1, together with that of a rarely seen diopside, which displays alteration to actinolite. Chlorites are the result of hydrothermal alteration of both biotite and amphibole. The microprobe analyses are summarized in Table I and their classification falls in the pycnochlorite to ripidolite field (Fig.3a). Sphene occurs as small anhedral to subhedral grains. Scattered grains of magnetite and pyrite are also present.

The rock generally displays variable degrees of hydrothermal alteration. Feldspars are altered to an association of sericite and carbonate. Biotite and amphibole are altered to chlorite, sphene and opaque minerals.

GEOCHEMISTRY

The chemical data on major and trace elements for twenty two samples of the Stratoni pluton, are given in Table 2. The samples with codes 4a, 4b, 4c and 4e were analysed by XRF at Southampton University. The results from samples N1,N2 and N3 (Nicolaou, 1960) were also used here. All the other samples were analysed for major elements (except TiO,) and Cu, Pb, Zn, Ba, Cr. Rb. Li. by AA and for Ti, Rb, Y, Sr, Nb, Zr by XRF at the analytical laboratories of the Institute of Geology and Mineral Exploration (Gerouki et al., 1988).

CLASSIFICATION

Based on the classification scheme of Debon and Le Fort (1983), the Stratoni pluton shows a variable composition ranging from quartz dioritemonzodiorite to granodiorite-adamellite (Fig.3b). The classification that results from Figure 3b is sensitive to the alteration of feldspars, which



Fig. 2. Photomicrographs of the Stratoni granodiorite.

- a. Partially chloritized biotite (Bi) and chlorite (Chl) derived from alteration of mafic minerals in a quartz-feldspar groundmass. The opaque is magnetite (Mt).
- b. Biotite (Bi) almost completely chloritized (Chl). Groundmass as in a.
- c. A euhedral plagioclase grain (P1) with minimal sericitization set in a quartzfeldspar groundmass.
- d. A euhedral plagioclase grain (P1) with advanced sericitization. Groundmass as in c.
- Σχ. 2. Φωτογραφίες μιπροσποπίου από τον γρανοδυθρύτη του Σιρ**ατωνίου** α. Βιοτύτης (Bi) μεριπώς χλωριτιωμένος παι χλωρύτης (Chl) προερχόμενος από εξ**θ**^λ⁼ λούωση φεμιπών ορυπτών μέσα σε χαλαζο-αστριούχο μάζα. Τα αδιαφανή εύναι μαγνή τύτης (Mt).
- β. Βιοτίτης (Bi) σχεδόν τελείως χλωριτιωμένος
- γ. Ιδιόμορφος κρύσταλλος πλαγιοκλάστου (P1) μερικώς σερικιτιωμένος μέσα σε χάλαξα αστριούχο μάζα.
- δ) Ιδιόμορφος πρύσταλλος πλωγιοπλάστου (Ρ1) με έντονη σεριπιτίωση. Μάζα ίδια με το γ.



- Fig. 3a. : Composition of chlorites from the Strutoni granodiorite. The nomenclature is from Hey (1954).
- Σχ. 3α. : Σύσταση χλωριτών του γρανοδιορίτη του Στρατωνίου. Η ονοματολογία είναι από του Hey (1954).



- Fig. 3b. : Classification of the Stratoni magmatic stock according to Debon and Le Fort (1983).
- Σχ. 3β. : Ταξινόμηση του μαγματικού σώματος του Στρατωνίου σύμφωνα με τους Debon και Le Fort (1983).

Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.

Table 1. Composition of plagioclase, K. feldspar, biotite, chlorite, amphibole and pyroxene of the Stratoni granodiorite.

Πίν. 1. Χημική σύσταση πλαγιοκλάστου, καλιούχου αστρίου, βιοτίτη, χλωρίτη, αμφι βολου και πυροξένου του γρανοδιορίτη του Στρατωνίου.

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31203	25.6	2.9	25.9-28.3	1à.3	6.4	17.8-19.9	14.8	2.3	13.4-14.4	18.5	1.1	17.3-17.6	3.5	2.6	3.7-4.9	4 17
FeQ							14.7	0.8	13.8-15.9	19.5	8.7	13.4-20.7	11.0	8.5	18.5-11.7	6.0.4
76g (C							13.9	6.5	13.2-14.0	19.3	1.5	18.2-13.9	16.2	ð.1	16.1-15.3	14.95
1102							5.6	0.1	4.8- 5.2	0.1	-	8.85-3.87	0.8	8.3	8.4-1.1	3.33
1.0							0.3	0.1	8.2-8.3	0.4	ð.1	8.21-8.51	9.5	0.1	A 3- 2 L	3 67
CaO	8.9	9.9	7.7-10.7	3.1	-	0.05-0.10	21	-	3 1-3 17	0, 1	-	8.05-8.07	12.1	0.4	11.9-12.5	23.17
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Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.

δειγμάτων από του γρανοδιορίτη του Στρατωνίου

of the Stratoni granodiorite samples.

Chenical analyses Xhpumés avalugeus

Table 2. Ruv. 2. was variably evidenced in our samples (Fig. 2c and 2d). The variable degree of such alteration pools the samples towards adamellite. Eventhough, when samples that both microscopically and chemically (Hughes, 1982) show prominent potassic alteration are excluded from the plot, the above trend is still valid. Since granodiorite is the most frequently occurring variety, the studied rocks hereafter will be referred to as the Stratoni granodiorite. The wide compositional spectrum of the Stratoni granodiorite most likely implies a complex magmatic regime in which mantle-and crust-derived components probably interacted.

SOURCE MATERIAL (PRECURSOR)

Debon and Le Fort (1983) provide a number of classification diagrams pointing also to the origin of common magmatic associations. Figure 4a clearly shows the metaluminous and peraluminous nature of the Stratoni granodiorite as well as a compositional trend spanning from cafemic through alumino-cafemic to aluminous types (Fig.4b). Since, the latter type is represented by samples that display the most prominent alteration they are considered not to bear any significance as to the precursors of the Stratoni granodiorite. However, samples without or with a slight evidence of alteration plot in the fields of the alumino-cafemic and cafemic types. This picture is further enhanced from the application of the criteria used to distinguish I - and S-type granitoids (Chappell and White 1974; White and Chappell 1977; Beckinscale, 1979). It may therefore be concluded that the Stratoni granodiorite is the hybrid product of two components : a cafemic component originating predominantly from a mantle source (or I-type) and an alumino-cafemic component of predominantly sialic material or S-type. Alternatively the latter component is a fractional product of the former,

TECTONIC SETTING

Brown (1981) and Pearce et al. (1984) have published a number of discriminant criteria for relating the geochemistry of granitic rocks to their geotectonic settings. Brown (1981) uses the diagram SiO. versus log CaO/. Na_0+K_0 to discriminate between calc-alkaline and alkalic suites which in turn suggest compressional and extensional regimes respectively. Our data (Fig.5a) indicate a calc-alkaline affinity for the Stratoni stock, which can be interpreted as suggesting compressional setting. In the diagrams of Figure 5b and that of Figure 5c the Stratoni granodiorite plots in the Volcanic Arc (VAG) field, and shows similarity with an Andean-type magmatism.

DEPTH AND TEMPERATURE OF EMPLACEMENT

An estimate of pressure range can be deduced by plotting the Stratoni granodiorite whole-rock composition on a normative Q-Ab-Or plot (Fig. 6). Data of Figure 6 indicates that its crystallization took place in a stagewise manner at a pressure range from 5 kb to about 1 kb. This was followed by pegmatite formation and probably the development of an ore-forming system. These points are discussed further in a later section dealing with petrogenesis and the metallogenetic implications. Experimental data (Burnham, 1979) at pressures around 3.5 kb, for an average hornblende-biotite granodiorite, such as the Stratoni igneous stock, indicate that this magma was emplaced at an average temperature near $900^{\circ}c$.





Χ. 49, β / Πήγή προέλευσης του γρανοδιορίτη του Στρατωνίου. (Κατά Debon και Le Fort, 1983).

Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.





- Fig. 5b : Discriminant diagrams for deducing the tectonic setting of the Stratoni granodicrite. (Diagrams after Pearce et al.,
- Σχ. 5β : Διαγράμματα καθορισμού γεωτεπτονικού περιβάλλουτος του γρανοδιορίτη του Στρατωνίου. Kara Pearce et al., 1984).



- Fig. 5c : Normalized geochemical patterns of the Stratoni granodiorite and Chile volcanic arc granites (VAG) in relation to the ocean ridge granite (ORG) (After Pearce et al 1984).
- 5γ : Κανονικοποιημένο γεωχημικό διάγραμμα του γρανοδιορίτη του Στρατω-Σχ. νίου και γρανιτών από το ηφαιστειακό τόξο της Χιλής (VAG) σε σχέση με την σύσταση γρανώτη ωκεάνειας τάχης (ORG) (Μαρμακή Βηβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ. 1984).



- Fig. 6 : Q-Ab-Or plot for normative compositions from the Stratoni granodiorite. (After Tuttle and Bowen, 1958).
- Σχ. 6 : Προβολή των συστάσεων κατά norm. του γρανοδιορίτη του Στρατωνίου στο διάγραμμα Q-Ab-Or. (Κατά Tuttle and Bowen, 1958).

MAJOR AND TRACE ELEMENT VARIATIONS

The SiO₂ content of 22 samples from the Stratoni granodiorite ranges from 59 to 69 weight percent corresponding to intermediate and felsic compositions (Table 2). The Harker variation diagrams for TiO₂, Al₂O₃, FeO, MgO, MnO, CaO, Na₂O and P₂O, despite some scatter, they show near-linear trends, with negative correlations with SiO₂ (Fig.7a). K₂O increases with increasing SiO₂ and displays an exactly opposite distribution to that of Na₂O (Fig.7a).

Trace element patterns although not as regular as those of the major elements show both positive and negative correlations (Fig.7b). The trends for most trace elements indicate that their behaviour was controlled mainly by geochemical processes similar to those that controlled the major elements. The broad scattering together with some deviations from the general trends are probably due to later hydrothermal processes. It should be noted that Pb and Ba tend to be correlatable to SiO. and K. (i.e. K-feldspar). A detailed picture of significant interlationships among the analysed elements is given by the correlation matrix shown in Table 3a.

STATISTICAL TREATMENT OF DATA

Factor Analysis

The statistical technique of R-mode factor analysis provides the means of combining the chemical data into a smaller number of correlated variables (factors) and it is only useful if the components can be related to geochemical processes. The programme available in Davis (1973) was used for the calculations. The results of the five-factor model for the Stratoni grano diorite are given in Table 3b.

Communalities for each variable, are shown in Table 3b from which it can be seen, that the model accounts quite well for the variance of all elements. Together the five factors explain 89% of the combined variance. Factor 1, which accounts for 29% of the variance, has high loadings for all the components except Fe.O.,FeO, MnO and Na.O, with the loadings of SiO , K_O and Rb being opposite to the remaining oxides. Factor 2, accounts for 25% of the variance and along with the factor 1, indicates the dilution of the mafic minerals by quartz, K-feldspar and associated trace elements and the carbonate/K-mica alteration mainly at the expense of plagioclase. Factor 3, which explains 16% of the variance shows the competition of both Cu and Zn against Sr. Since the latter is mainly tied to plagioclase feldspars, this factor suggests, that two distinct processes namely alteration and petrogenesis, contribute to the variation explained by this factor. Factor 4, accounts for 12 0 of the variance and has loadings for FeO and CaO, opposite to those of Al_O , Fe O and Pb, signifying processes similar to those indicated by Factor 3. Factor 5, explains only 9% of the variance and indicates the opposing behaviour of MnO and Nb, Zr. A graphical representation of the correlated variables is shown on quasi-enrichment-depletion diagrams, constructed from the factor loadings of each of the five factors (Fig.8a-e).

Discrimination between Stratoni vs.Sithonia-Ierissos granodiorites

Discrimination between the younger Stratoni stock and the older Ierissos and Sithonia granodiorites (45.6 - 54.5 m.y), (Christofides et al,1985) was obtained, with the application of the discriminant analysis technique.



granodiorite. TOU YPAVO άιαγράμματα μεταβολής πων πυρύων στοιχεύων παι ιχνοστοιχεύων διορύτη του Στρατωνίου. the Stratoni HO. element variation diagnams and trace Major •• ... 90 A 7a . 7a, Fig. ΣX.

Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.



Fig. 8f. Frequency distribution of discriminant scores for Stratoni granodiorite as compared to those for Sithonia-Ierissos granodiorites.

Σχ. 8στ. Συχνότητα χατανομής των τυμών διαπρισης των μαγματιχών σωμάτων Στρατωνίου χαι Σιθωνίας-Γερισσού. Table 3a. Correlation matrix of geochemical data or the Stratoni granodiorite.

μέν. 3α. Συντελεστής συσχέτισης γεωχημικών δεδομένων του γρανοδιορίτη του Στρατω-

Si02	1102	A1:33	Fe203	٢٤٦	MaQ	M;0	CaO	N#20	1:20	ĥb	Y	Sr	Nb		Ç u	Pb	ln	Ð
1.00	-3.43	-0.60	-0.73		-0.63	-0.84	-0.66			6.49								
	1.60			0.40		0.63			-0.73									-0.6
		00.1	0.54		0,50			-0.51		1	0.81					0.49		0,8
			1.00			0.40			-0.49	-0.42				0.45		0.44		
				1.00		0.52										-0.62	0.43	
					1.00	0.61	0.93				0.49		-0.45					0.4
						1.00	0.67			-0.51								
							1.00		-0.52			0.42						
								1.00	-0.72	-0.75	-0.67							-0.1
									1.00	0.93		-0.40		-0.42				
										1.00				-0.44				Ú.4
											1.00							0.9
												1.00	0.40	0.45	-0.47		-0.77	
													1.00	0.49				
														1.00				
															1.00		0.42	
																1.00		
																	1.09	
																		1.
																		-

Table 3b. Factor analysis of geochemical data of the Stratoni granodiorite.

Πέν. 3β. Ανάλυση παραγόντων γεωχημικών δεδομένων του γρανοδιορύτη του Στραιωνίου.

Variables			factor3		Factor5	Contunality
Si02		0.44				0.93
1102	-0.78	0.51				0.93
A1203		-0.78		-0.42		0.95
Fe203	-1).43			-0.57		0.78
FeD	-0.45			0.83		0.95
KaO	-0.47	-0.56				0.92
Kago	-0.93				0.53	0.97
Ca9	-0.63	-0.45		0.43		0.92
8:20	-0.59	0.74				0.95
120	0.51					0.95
85	0.84					0.95
Y		-0.92				0.85
Sr			0.67		-0.86	0.95
12					-0.74	0,84
le						0.81
Cu			-0.72	-0.90		0.63
Pb						0.67
Zn			-0.87			0.83
8.a		-0,9ċ				0.75
Variation (22.9	24.5	15.6	11.5	8.7	

#GIE: Orides and elements with factor locdings 0.4 are coulted.

Ψηφιακή Βιβλιοθήκη "Θεόφραστος" - Τμήμα Γεωλογίας. Α.Π.Θ.

Ex. 8a-ε. למנטטעבטיגאל טנמיסמשעמדם בא-

πλουτισμού/ελάττωσης του γρανοδιορίτη

του Στρατωνίου.

This multivariate statistical technique, is increasingly used, for distinguishing predefined groups of data (Davis 1973, Kalogeropoulos, 1985) and provides a very good discrimination between the two groups of granodiorites referred to above (Fig.8f). It should be noted that no significant sulfide mineralization is known as yet to be spatially and probably genetically related to the latter magmatic stocks.

PETROGENESIS AND METALLOGENETIC IMPLICATIONS

On the basis of geophysical data (Kyriakidis, 1984) Stratoni granodiorite is a surficial expression of a probably larger magnatic stock at depth extending from the Stratoni towards the Olympias village in the north (Fig. 1). This granodiorite is spatially associated with significant Pb-Zn (Au, Ag) sulfide ore deposits. Magmatism, tectonic activity and mineralization show a close link in space,time and probably genesis. This is evidenced by the abundant presence of monomictic and polymict breccias consisting of various combinations of carbonates including rhodochrosite, pegmatites,quartz and mineralization as fragments and matrix (Kalogeropoulos et al.,1987). The following discussion is pertinent to the above mentioned association.

Crystallization of magmas of granedioritic composition at high pressures (>4 kb; Eugster, 1985) such as those indicated by parts of the Stratoni granodiorite (Fig.6) suggests that such magma types were initially water saturated (>3.3wt # H 0). However, there is evidence that crystallization took place over a range of pressures spanning from greater than 5 kb to as low as about 1.0 with a clear potassic trend (Fig.6). This suggests a stagewise solidification at various depths, most likely during tectonic uplift and/or concomitant faulting. Such a process, would release water and associated ore metals to the fluid phase as a result of decompression, which would also aid further ascend of magma to higher crustal levels. Whether or not waters of other origin, participate at various stages of the magmatic -hydrothermal evolution through convection and their relative contribution to the ore-forming process, through water-rock interaction, are tasks, that are currently under investigation by utilizing combined fluid inclusion and stable isotope data. However, experimental work indicates that only aluminous and water - saturated granites are capable of producing hydrothermal fluids, which would contain significant amounts of ore metals (Urabe, 1985 and 1987). The partitioning of ore metals into the fluid phase is enhanced by increased salinities (Holland, 1972; Urabe, 1985). Such properties are seen in the Stratoni granodiorite as well as in the Pb-Zn (Au,Ag) sulfide mineralization (Kilias, 1987; pers.commun.).

Since, the isotopic signature of the lead from the spatially associated sulfide ore, is homogeneous and identical to that of the nearby Skouries porphyry Cu (Au) deposit and of hybrid nature and taking into consideration that the Stratoni granodiorite is comprised of mantle- and crust-devired components it could be concluded that the source of lead and consequently that of zinc is of similar origin. These metals were most likely released into the ore-forming fluid through the process referred to above and further by water-rock interaction. A convective hydrothermal system is expected to be sustained and enhanced by the decay of radioactive elements (i.e. U, Th, K). These elements show elevated concentrations in the Stratoni granodiorite (Table 2).

EXPLORATION SIGNIFICANCE OF THE STRATONI GRANODIORITE

Variations of K, Rb and Sr have been shown to be useful in the exploration for granite-related mineral deposits (Govett, 1983). In porphyry granites there is a trend of increasing K and Rb from barren to metalliferous rocks in any particular region but the level of concentration varies between regions (Govett, 1983). Figure 8a, b and Table 3a shows the positive correlation between Rb and K and the negative of Sr as to the former elements. The samples with the highest values in these two elements are the most altered and also enriched in base metals. The same conclusion can he drawn from the data of figure 8a, b when combined with the data of Table 2. Since, mineralization in the Stratoni granodiorite took place after its consolidation, as it occurs in the form of veins and disseminations with concomitant potassic and carbonate alteration, we may assign this granodiorite to mineralized granites according to the definition given by Plant et al. (1985). However, with the data available, it can not be stated whether or not this granodiorite is or has been metalliferous as well. These data suggest that the Stratoni magmatic stock, a manifestation probably of a larger pluton at depth, was evolved through pegmatite-aplite to a metalliferous hydrothermal stage or/and just acted as a heat engine for driving a metalliferous hydrothermal convection cell. In all cases however the presence of such type of a magmatic complex provides a guide for exploration of Pb-Zn (Au,Ag) sulfide ores in regions that bear geotectonic setting similar to that of the Kerdyllia formation.

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242