ORIGIN AND METALLOGENETIC SIGNIFICANCE OF THE TERTIARY STRATONI GRANODIORITE", CHALKIDIKI N. GREECE: ISOTOPIC AND CHEMICAL EVIDENCE

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ABSTRACT

The Palaeozoic or older amphibolite grade Kerdilia formation of the Servomacedonian Massif, Northern Greece, is intruded by the 30 Ma Stratoni "granodiorite"that is spatially associated with the Madem Lakos and Mavres Petres carbonate-hosted Pb-Zn (Au,Ag) sulfide ore deposits. A study of the Nd and Sr isotope composition, the major/trace element variations and the rare earths on fresh and hydrothermally altered samples of thisTertiary pluton was undertaken and combined with existing oxygen and lead isotope data in order to determine alternatively the age of the "granodiorite" and the assompanied hydrothermal alteration, the mode of formation and the source (s) of the magma as well as its bearing to the base metal sulfide ore genesis.

Our data suggest that the Stratoni "granodiorite" was formed in a subduction - related environment by mixing of island arc type mafic liquids with small cornributions by siliceous, and isotopically more radiogenic, anatectic melts. This magma enriched in ore elements was emplaced higher in the crust and produced a skarn - replacement ore system aureole. As the system cooled ,hydrothermal circulation operated probably for a prolonged period of time (30 Ma to 24.2 Ma) reworking and recycling materials from the regioanl setting to the granodiotite and outwards to the wall rocks.

ΣΥΝΟΨΗ

Ο Παλαιοζωϊκός ή παλαιότερης ηλικίας αμφιβολιτικής φάσης σχηματισμός των Κερδυλίων της Σερβομακεδονικής Μάζας διεισδύεται στην περιοχή του χωριού Στρατωνίου από τον ομώνυμο "γρανοδιορίτη"- Ο γρανοδιορίτης αυτός, συνδέεται χωρικά με τις θειούχες μεταλλοφορίες Pb-Zn (Au, Ag) του Μαντέμ Λάκου και των Μαύρων Πετρών. Η μελέτη αυτή αναφέρεται στα ισότοπα Nd και Sr, τις μεταβολές κύριων στοιχείων και ιχνοστοιχείων καθώς και τις σπάνιες γαίες για υγιή και εξαλλοιωμένα δείγματα από το "γρανοδιορίτη". Τα στοιχεία της μελέτης αυτής συνδυάστηκαν με υπάρχοντα στοιχεία ισοτόπων οξυγόνου και μολύβδου για να απαντηθούν ερωτήματα σχετικά με την ηλικία του γρανοδιορίτη και της εξαλλοίωσης του, τον τρόπο δημιουργίας του και την πηγή προέλευσης του μάγματος όπως και τη σχέση του με την υπάρχουσα μεταλλοφορία. Τα στοιχεία μας αποδεικνύουν ότι ο Τριτογενούς ηλικίας "γρανοδιορίτης" του Στρατωνίου δημιουργήθηκε σε ένα περιβάλλον που υπήρχε διεργασία πορείας sudbuction από ανάμειξη ενός βασικής σύστασης μάγματος τύπου ηφαιστειακού τόξου (island arc type mafic magmas) με μικρή συμμετοχή περισσότερο ραδιογενούς ανατηκτικού μάγματος. Το μάγμα αυτό, εμπλουτισμένο σε στοιχεία ,ανήλθε σε υψηλότερα τμήματα

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Προέλευση και Μεταλλογενετική Σημασία του Τριτογενούς Ηλικίας "Γρανοδιορίτη" του Στρατωνίου, Χαλκιδική, Β. Ελλάδα. Ισοτοπικά και Χημικά Δεδομένα.

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του φλοιού και δημιούργησε μία άλω σ'ένα σύστημα σκαρν-αντικατάστασης. Το σύστημα αυτό καθώς εψύχετο για μια αρκετά παρατεταμένη χρονική περίοδο (30Ma μέχρι 24.2Ma) φαίνεται να δημιούργησε ένα πεδίο κυκλοφορίας ρευστών επαναδραστηριοποιώντας και ανακυκλώνοντας υλικά τόσο απο τον περιβάλλοντα χώρο προς τον γρανοδιορίτη όσο και αντίστροφα.

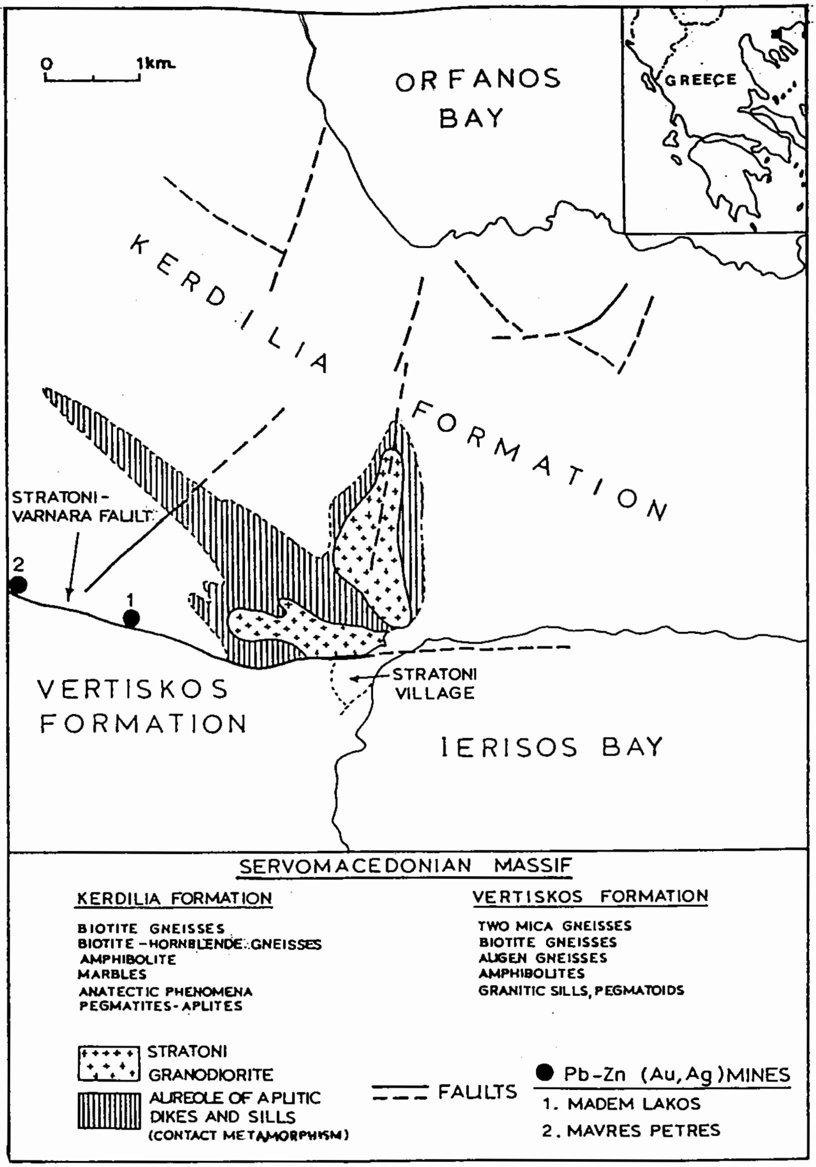

Fig. 1: Simplified location map of the Stratoni "granodiorite" (Kockel, et al. 1977).

Introduction

The mineralogy, geochemistry and tectonic setting of the Tertiary Stratoni "granodiorite" as well as its potential bearing to the genesis of the spatially associated carbonate-hosted Madem Lakos and Mavres Petres Pb-Zn (Au,Ag) sulfide ores have been described in various degrees of detail by Nicolaou (1960, 1964) Kalogeropoulos et al., (1989 a,b), Kalogeropoulos and Economou (1987) and Nebel (1984). As dedcribed by Nicolaou (1960) and more recently by Kalogeropoulos et al. (1989b) the Stratoni pluton collectively known as Stratoni "granodiorite" ranges in composition from quartz diorite-monzodiorite to granodiorite - adamellite and intrudes the Paleozoic (or older) amphibolite grade metamorphics of the Kerdilia Formation (Servomacedonian Massif, Kockel et al. 1977, Fig.1). The geology of the area has been described in a recent publication by Kalogeropoulos et al. (1989a) and it is not repeated here.

The primary mineralogy of the Stratoni "granodiorite" consists mainly of variable participation of quartz, microcline, plagioclase, biotite, amphibole, white mica, diopside, zircon, magnetite and pyrite. Whereas, variable degree of hydrothermal alteration produced epidote, chlorite, sericite, carbonate,

Table 1: Major and trace element analyses of unaltered and variably altered Stratoni granodiorite and marble near to their contact.

	UNALTERED						ALTERED					MARBLE		
wt %	ST2.1	10976	10978	ST1.1	4675B	4675A	ST2	ST1.0	ST1.2	ST1.3	ST1	ST4	ST4.2	ST.5
SiO_2	62.94	63.67	66.14	66.29	67.51	69.93	71.20	74.86	73.26	74.06	73.58	9.94	0.75	0.54
TiO_2	0.76	0.80	0.48	0.41	0.46	0.44	0.07	0.37	0.54	0.54	0.58	0.09	0.02	0.01
Al_2O_3	15.68	15.51	15.25	15.08	14.72	15.01	13.56	11.34	14.61	14.81	16.04	2.41	0.13	0.12
Fe_2O_3	4.91	5.11	5.05	3.72	4.49	4.33	0.69	5.41	1.86	1.65	0.85	0.69	0.14	0.13
MnO	0.09	0.12	0.12	0.05	0.04	0.07	0.09	0.01	0.02	0.02	0.01	0.07	0.02	0.01
MgO	2.24	2.51	1.93	1.20	1.72	1.77	bdl	0.60	0.59	0.65	0.74	0.74	0.61	0.44
CaO	5.56	5.38	4.99	3.16	2.96	3.13	1.98	0.16	0.22	0.23	0.24	55.80	57.54	58.43
Na_2O	3.49	3.47	3.03	2.33	2.57	2.49	1.91	bdl	bdl	bdl	bdl	bdl	bdl	bdl
K_2O	1.62	1.74	3.37	3.95	3.31	3.88	5.19	3.94	5.02	5.55	5.51	0.28	0.16	0.21
P_2O_5	0.50	0.51	0.23	0.22	0.17	0.27	0.08	0.08	0.02	0.02	0.07	0.23	0.01	0.09
Total	97.79	98.82	100.59	96.41	97.95	97.32	95.29	96.73	96.14	94.57	97.59	70.23	59.40	59.96
ppm														
Zr	208	287	153	201	242	250	<319	82	<138	163	201	25	20	20
Nb	11.67	12.9	9.85	8.55	11.1	9.7	na	na	na	na	na	na	na	na
Y	15	15	19	22	19	19	6	6	15	15	23	8	1	bdl
Rb	76.2	77.6	136	137.7	129.5	164.6	185.9	141.1	668.1	364.9	378.8	1.17	4.52	0.07
Sr	750.1	723.8	638.3	554.9	534.3	550.7	162.8	15.7	25.9	22.3	5.7	399.7	353.3	191.4
Ba	501	520	982	1268	1127	910	628	695	616	581	467	<50	<42	<26
Cs	4.5	4	8.9	5	6	3	3.7	1.2	5.2	6.6	6.7	<0.27	0.41	<0.14
Sc	9.2	10	9	8.3	8	9	1.6	6.7	9.6	8.7	8.8	1.5	0.17	0.08
Hf	5.9	6.1	4.4	4.3	4.6	4.5	2	3.7	5	4.8	5.4	0.5	<0.05	<0.05
Ta	0.5	0.7	0.8	1.2	2.1	1.9	1	1.2	1	1	1.2	0.4	<0.15	<0.15
Ga	<30	34.	<41	<29	28	29	<39	22	<20	<21	26	<23	<29	<31
V	100	115	90	95	90	95	10	75	120	105	110	<25	<20	<20
Li	7.8	5	17	7.7	17.3	11.8	3	3	2.5	2.1	6.7	0.9	0.6	0.3
Be	2.5	1.8	2.5	2.3	2.5	2.7	2.7	1.3	1.8	1.9	2.5	1.7	0.2	0.2
Br	3.2	<3.2	<2.8	<2.7	<3	<2.9	<2.3	1.2	0.7	0.8	1.2	<1.1	0.3	0.8
U	4	3	11	11	9	10	7	2.3	4.3	3.6	2.6	4.9	2.7	1.8
Th	18	22	28	37	27	31	7	8	8	9	6	1.9	0.2	0.1
Cu	<200	na	<200	<200	1240	350	na	na	73	86	na	80	67	66
Zn	338	na	81	141	72	68	187	na	28	29	na	70	9	8
Au	<0.03	0.03	<0.03	<0.03	0.04	0.04	<0.02	0.02	0.02	0.01	0.02	<0.01	<0.01	<0.01
Ag	<5.7	<6	<5.5	<5.3	<6	40	<2.5	<5	<10	<5.3	5.1	<2	<1	<1
W	<5.4	5	<4.4	2.3	835	713	2.8	19	4	4.7	26	1.3	<2.2	<2.2
As	17	10	11	5.3	6	9	15.6	8.8	32	14	6	15.2	1.8	3.6
Sb	1.2	1	2.1	1.3	1	4.4	4.4	93	75	66	30	0.8	0.3	0.4
La	58.8	69	36.8	34	36	37	11.7	26	17.7	18.5	36	9	0.7	0.6
Ce	103	124	70.7	66	69	71	21.7	43	39	38.3	67	14.3	0.97	0.69
Nd	31.5	42.4	na	23.9	na	22.7	na	17.2	17.9	na	na	na	na	na
Sm	5.5	7.7	na	5	na	4.6	na	3.1	4	na	na	na	na	na
Eu	1.37	1.67	1.02	1.09	1.16	1.08	0.34	0.28	0.55	0.54	0.69	0.28	0.03	0.02
Tb	0.49	0.67	0.61	0.53	0.53	0.38	0.22	0.32	0.37	0.42	0.38	0.29	<0.07	<0.07
Yb	1.24	1.8	2.3	2.3	2	1.8	0.34	1.1	1.6	1.25	1.46	0.53	<0.06	<0.05
Lu	0.18	0.67	0.42	0.38	0.53	0.37	<0.08	0.22	0.27	0.29	0.24	0.08	0.06	<0.01

bdl : below detection limit; na : not analysed

sphene and secondary magnetite-pyrite. Hydrothermal alteration followed "granodiorite" emplacenent and consolidation. The intrusive was dated at 30Ma by K-Ar in biotites (Papadakis, 1971, Alther et al. 1976) and recently by U/Pb in Zircons (R. Frei, person. commun.).

Application of the Debon and Le Fort (1983) classification diagrams which point to the origin of

Table 2: Chemical and isotopic data from the Stratoni "Granodiorite" and contact marbles.

Sample number	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{36}Sr$	$^{87}Sr/^{86}Sr$	$(^{87}Sr/^{86}Sr)_i$ 30Ma	$f_{Rb/Sr}$	ε_{Sr}	ε_{Sr}(30Ma)
ST2.1	76.2	750.1	.2940	.70625	.70612	2.6	20.9	19.6
10916	77.6	723.8	.3010	.70622	.70609	2.6	20.4	19.1
10978	136	638.3	.6164	.70658	.70632	6.5	25.5	22.3
ST1.1	137.7	554.9	.7179	.70649	.70618	7.7	24.3	20.5
46758	129.5	534.7	.7010	.70668	.70638	7.5	27.0	23.2
4675A	164.6	550.7	.8655	.70677	.70640	9.5	28.2	23.5
ST2	185.9	162.8	3.304	.70872	.70759	39	55.9	40.3
ST1.0	141.1	15.7	26.04	.71527	.70640	314	148.8	23.3
ST1.2	368.1	25.9	41.08	.72081	.70681	496	227.4	29.2
ST1.3	364.9	22.3	47.48	.72303	.70685	573	259	29.8
ST1	378.8	5.7	194.6	.77412	.70780	2352	984	43.2
ST5	1.17	399.7	0.008	.70710	.70709	-0.9	32.9	33.3
ST4.2	4.52	353.3	0.037	.70729	.70727	-0.6	39.6	35.9
ST4	0.066	191.40	0.001	.70741	.70740	-1.0	37.3	37.7

$$\varepsilon_{Sr}(T) = \left[\frac{(^{87}Sr/^{86}Sr)^{T}_{i}}{(^{87}Sr/^{85}Sr)^{T}_{UR}} - 1 \right] \times 10^4 \; ; \quad (^{87}Sr/^{86}Sr)^{T}_{UR} = (^{87}Sr/^{36}Sr)^{0}_{UR} - (^{87}Rb/^{86})^{0}_{UR} (\exp\lambda_{Rb}T - 1);$$

Present day reference values are $(^{87}Sr/^{86}Sr)^{0}_{UR} = 0.70478$ and $(^{87}Rb/^{86}Sr)^{0}_{UR} = 0.087$; $\lambda_{Rb} = 1.42 \times 10^{-11} yr^{-1}$. Also note that ε_{Sr} for altered "granodiorite" samples is calculated at 24.2Ma and not 30Ma (see text). Enrichment factor $f_{Rb/Sr} = \frac{(^{87}Rb/^{86}Sr)_{rock}}{0.0827} - 1$.

the common magmatic rocks suggest that the Stratoni "granodiorite" is the hybrid product of a cafemic component originating predominantly from a mantle source (or I-type) and an alumino-cafemic component of predominantly sialic meterial (or S-type) or alternatively that the latter component is a fractional product of the former. Moreover, Kalogeropoulos et al. (1989b) using a number of discriminant criteria relating the geochemistry of granitic rocks to their tectonic setting (Brown, 1981; Pearce et al, 1984) deduced a calc-alkaline affinity, and similarity to Volcanic Arc (VA) and Andean-type magmatism for the Stratoni “granodiorite”.

Neodymium and strontium isotope composition and major/trace element concentrations including rare earths were obtained for fresh and hydrothermally altered “granodiorite” samples as well as variably altered marbles from near the contact with the intrunsive complex. The purpose of this study was to determine the age of the “granodiorite” and its alteration, the mode of formation and the source(s) of the magma as well as it bearing on the base metal sulfide ore genesis.

Samples

Eleven samples were collected from the Stratoni “granodiorite” outcropping along the Stratoni-Olympias road. Moreover, three samples of marble near the contact with the granodiorite that bear variable degrees of alteration were also collected. The six granodiorite samples are practically unaltered and compositionally cover the range of the Stratoni “granodior-

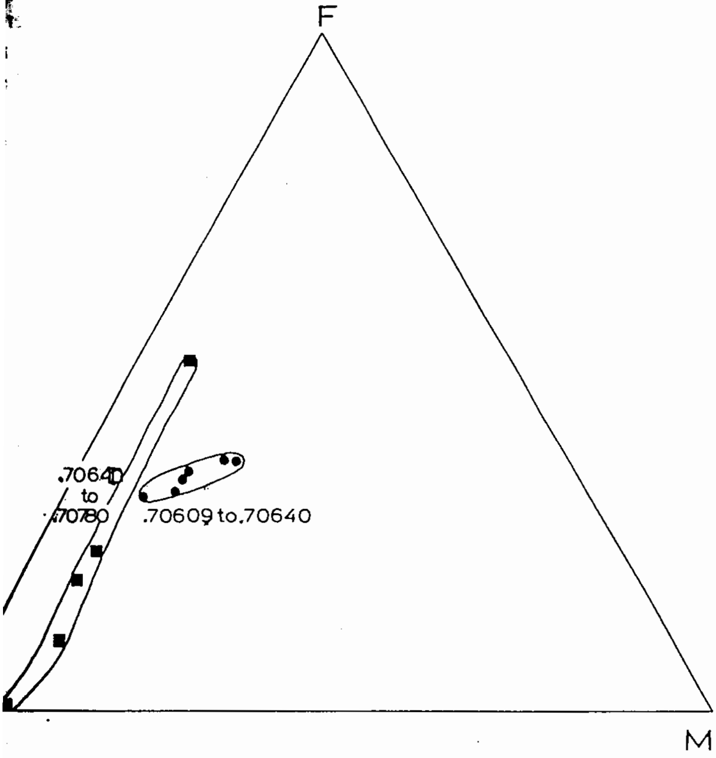

Fig. 2.: AFM ternary diagram for fresh(o) and altered ((´Y) “granodiorite” samples with corresponding initial $^{87}Sr/^{86}Sr$ ratio ranges.

Table 3: Chemical and isotopic data from the Stratoni “Granodiorite”

Sample number	Sm ppm	Nd ppm	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	$(^{143}Nd/^{144}Nd)i30Ma$	$F_{Sm/Nd}$	E_{Nd}	$E_{Nd}(30Ma)$
ST2.1	5.52	31.46	.106019	.512557	.512536	-0.5	-1.6	-1.2
10976	7.69	42.38	.109667	.512420	.512398	-0.4	-4.3	-3.9
ST1.1	5.00	23.85	.126615	.512561	.512536	-0.4	-1.5	-1.2
4675A	4.58	22.74	.121794	.512564	.512540	-0.4	-1.4	-1.2
ST1.0	3.11	17.24	.109201	.512624	.512603	-0.4	-0.3	0.1
ST1.2	4.02	17.85	.136065	.512590	.512563	-0.3	-0.9	-0.7

$$E_{Nd}(T)= \left| \frac{(^{143}Nd/^{144}Nd)^{T}_{i}}{(^{143}Sr/^{144}Sr)^{T}_{CHUR}} - 1 \right| x10^{4} ; (^{143}Nd/^{144}Nd)^{T}_{CHUR} = (^{143}Nd/^{144}Nd)^{0}_{CHUR} - (^{147}Rb/^{144}Rb)^{0}_{CHUR} (\exp\lambda_{so}T-1)$$

Present day reference values are $(^{143}Nd/^{144}Nd)^{0}_{CHUR} = 0.51264$ and $(^{147}Sm/^{144}Nd)^{0}_{CHUR} = 0.1967$

$\lambda so = 6.54 X 10^{-12yr-1}$

$$\text{Enrichment factor } F_{Rb/Sr} = \frac{(^{147}Sm/^{144}Nd)_{rock}}{0.1967} - 1$$

ite". The remaining five samples were collected along a transect normal to the alteration envelope produced by a quartz-sericite-sulfide dike which crosscuts the ingneous stock. These samples show variable degrees of phyllic hydrothermal alteration.

Analytical Techniques

Most major and trace element analyses were carried out using conventional XRF techniques, whereas the rare earth elements were analysed by instrumental neutron activation analysis (INAA). All these analyses were also determined independendly by isotope dilution at the Scottish Universities Research Reactor Centre (S.U.R.R.C) giving results in excellent agreement with those obtained from INAA. Sr and Nd isotopic analyses were carried out at S.U.R.R.C. following the procedure described by O'Niond et al. (1977). All isotopic analyses were made in a fully automated V.G. Isomass 54E mass spectrometer and the data are corrected for machine discrimination using ^{88}Sr/^{86}Sr=8.37521 and ^{146}Nd/^{144}Nd=0.7219. The average ^{87}Sr/^{86}Sr for NBS987 during the cource of the analyses was o.710275± 7 (26 mean) N=79). The average ^{143}Nd/^{144}Nd of BCR-1 and GSP-1 at the time of the present work were 0.512633±12 (2σmean, N=5) and 0.511383±12 (2σ mean, N=2), respectively. The major and trace element analyses are all summarized in Table 1. The Rb-Sr and Sm-Nd isotope data are presented in Tables 2 and 3, respectively. The lead and oxygen isotope data of the Stratoni "granodiorite" utilized in

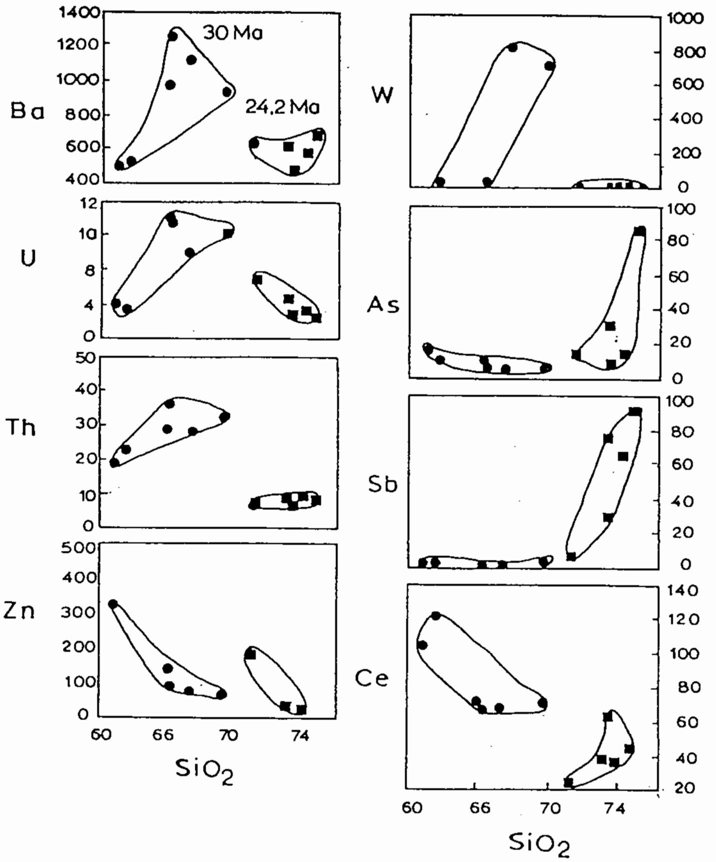

Fig. 3: Selected trace element concentrations in ppm versus SiO_2 in weight percent for the fresh and the altered "granodiorite" samples. Symbols as in Fig. 2.

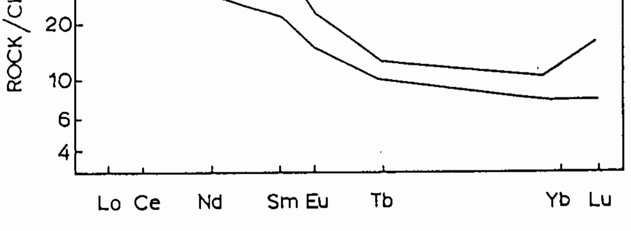

Fig. 4: Chondrite-normalized REE patterns band for the fresh Stratoni "granodiorite" samples.

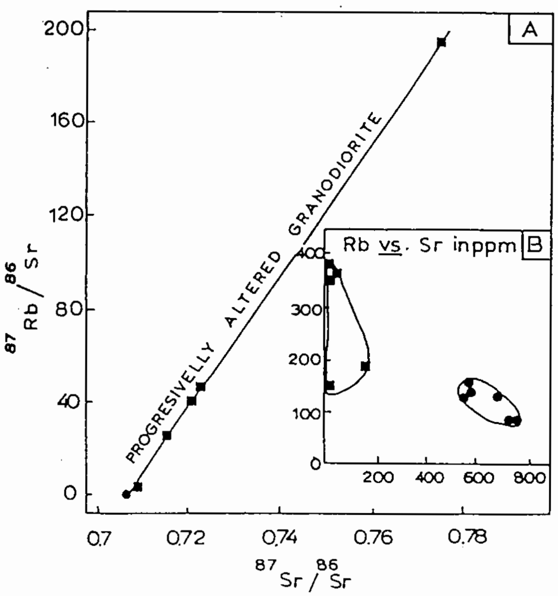

Fig. 5: Plots of Rb-Sr isotope data (A) and Rb-Sr concentration data (B) for fresh and altered "granodiorite" samples. Symbols as in Fig. 2.

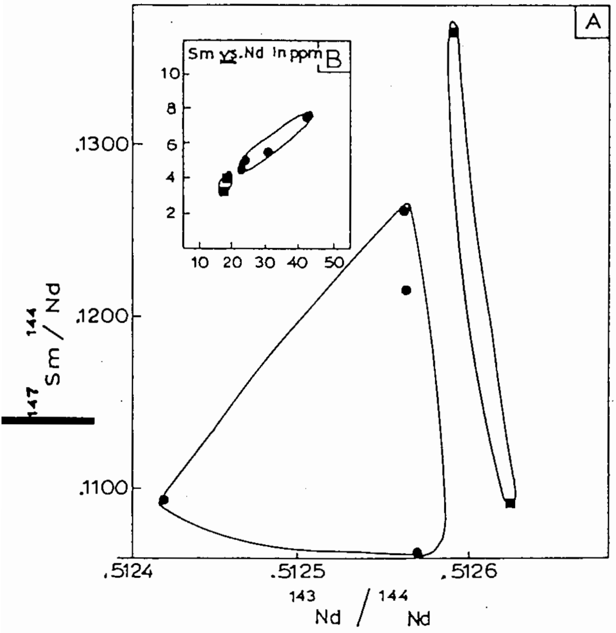

Fig. 6: Plots of Sm-Nd isotope data (A) and Sm-Nd concentration data (B) for fresh and altered "granodiorite" samples. Symbols as in Fig. 2.

this study are from other sources and as do not correspond to any of our samples they are treated independently.

Major and trace elements

Major and trace element variations in the Stratoni intrusive complex have been dedcribed relative to $Si0_2$ variation (Kalogeropoulos, et al., 1989b). The salient features of the variations in the major and their geochemically associated trace elements also highlighted by R-mode factor analysis have been assigned by Kalogeropoulos et al. (1989b) to the combined effects of petrogenetic processes (fractional crystallization and/or mixing and the hydrothermal alteration). Our present data are in support of their conclusions. K_20+Na_20(A), Fe0 Total (F), and Mg0(M) normalized to 100% for fresh and variably altered samples given in Table 1 are plotted on a standard AFM petrological diagram in Fig. 2. Two discrete fields become apparent that correspond to the fresh and the altered Stratoni "granodiorite" samples. The range of initial $^{87}Sr/^{86}Sr$ (Sri) for each field is also indicated on Fig.2. The concomitance of the phyllic alteration with the radiogenic addition of strontium are features emerging from this figure. Certain selected trace elements, namely Ba, U, Th, Zn, W, As, Sb, and Ce (representing REE) are plotted against SiO_2 for the fresh and the alltered "granodiorite" samples on Fig. 4. The two discrete fields that are apparent in Figure 2, and correspond to fresh and altered groups are also depicted in Figure 3. The variation of the elements shown in Figure 1 relative to SiO_2 (i.e. positive for Ba, U.Th, W and negative for Zn, Ce (REE)) within the former group is compatible with variations resulting from petrogenetic processes alone (i.e. magma mixing and/or fractional crystallization). The concetrations of all the elements, except Ce for the fresh "granodiorite" samples (Fig. 3) are higher than the corresponding Clark values (Wedepohl, 1969) implying their enrichment in the original magma. This, combined with the enrichment of the same elements in the host marbles (Kalogeropoulos, et al., 1989), and a well-developed aureole present as a skarn-replacement ore system suggest that this alteration in the host rocks most likely have proceeded during the emplacement and consolidation of the Stratoni "granodiorite". Ba, U, Th, W, Ce and probably Zn in the altered group are depleted relative to their average concentraions in the fresh group, whereas the opposite holds true for As, Sb, and SiO_2 (Fig.3). These data suggest that the 24.2Ma (see proper section) hydrothermal event leached from, and introduced to, the "granodiorite" the former and the latter elements, respectively. This late hydrothermal fluid when discharged from the intrusive complex outwards into pertinent sites (e.g. faults, marbles, gneisses) is expected to have caused changes variably superimposed on earlier mineralizations and alterations.

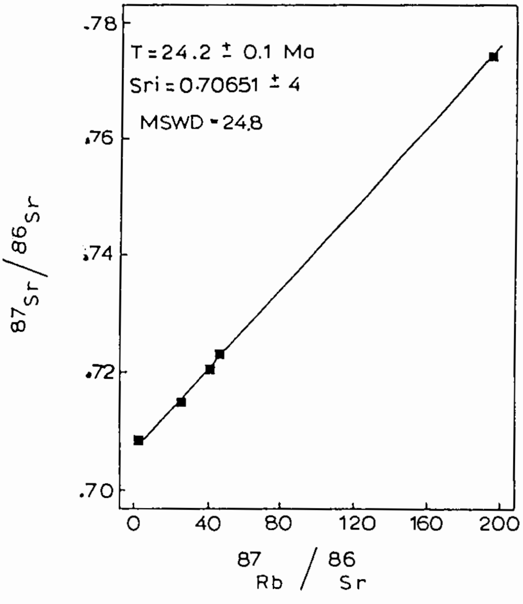

Fig. 7: Rb-Sr evolution diagram for the altered "granodiorite" samples.

Rare Earth Elements (REE)

The REE abundances of the Stratoni "granodiorite" are characterized by highly fractionated REE pattern and light REE (LREE) enrichments (Fig.4) Moreover, a weakly developed negative Eu anomaly (Fig. 4). and a negative correlation between REE and SiO_2 concentrations (Table 1 and Fig. 3) can also be observed. The weak Eu anomaly suggests that plagioclase was not a significant fractionated phase, whereas the latter is a correlation not uncommon in granitic rocks (Hill et al., 1981) for which not general solution has yet been provided to explain it. The data presented above are identical with that of Mesozoic and Tertiary granites from the Western United States which are interpreted to have formed by mixing between mantle and crustal components. (Farmer and DePaolo, 1984) in subduction-related processes.

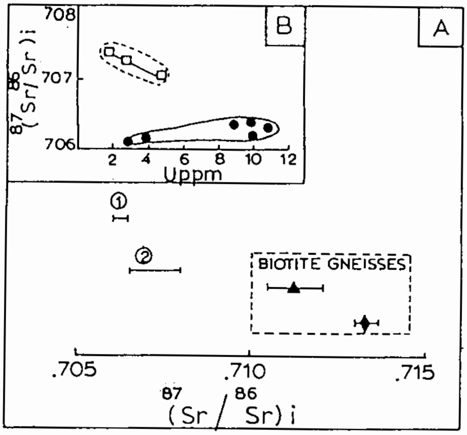

Fig. 8: Initial $^{87}Sr/^{86}Sr$ ranges for fresh(1) and altered (2) "granodiorite" and means ± 1σ for two groups of Kerdilia biotite gnesses at 30 Ma (Mantzos, 1990) are shown in A. Initial $^{87}Sr/^{86}Sr$ versus U in the fresh "granodiorite" samples and marbles at 30 Ma (open squares) with the latter exhibiting increasing degree of alteration with increasing uranium concentration (Kalogeropoulos, et al., 1989c).

In addition, Kalogeropoulos et al. (1990) in a primordial mantle normalized HYG element plot for the Stratoni intrusives observed the decoupling of LFS and HFS elements and the Ta-Nb through which are taken as indicative of arc-related magmatic suites (Wood et al., 1980; 1981; Saunders et al., 1980; 1981).

Rb-Sr and Sm-Nd systematics

Rubidium versus strontium and samarium versus neudymium with their corresponnding isotopic values for unaltered and altered Stratoni "granodiorite"

Table 4: Ranges of lead isotope ratios for rocks and ores from the Kerdylia Formation. The values in parentheses are those corrected for in situ radioactive decay.

Rock type	Sample type No of analyses	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Source
Stratoni Intrusives	Plagioclase	18.857 (18,835)	15.691 (15.690)	38.994 (38.981)	Nebel (1989)
	3 Feldspars and 1 Whole rock	18.827 to 18.888	15.666 to 15.672	38.916 to 38.977	Frei (1990) (pers.com.)
Kerdylia Form Anatexite	Whole rock n = 3	18.809 to 18.830	15.670 to 15.676	38.909 to 39.022	
Kerdylia Form Biot/Musc. Gneiss	Whole rock n = 8	18.657 to 18.995	15.631 to 15.690	38.757 to 39.019	
E. Chalkidiki Carbonate-hosted Pb-Zn (Au,Ag) **Sulfide** ores	Ore galena n = 18	18.736 to 18.825	15.620 to 15.691	38.770 to 39.003	Kalogeropoulos et al. (1990)

samples (Tables 1,2 and 3) are plotted on Figures 5 and 6. Two discrete fields related to unaltered and altered samples become apparent in both cases. The altered samples are variably enriched in radiogenic strontium and neodymium implying mobility of these elements during alteration. This mobility is more pronounced for strontium, whereas for neodymium is extremely low. The latter observation implies that "granodiorite" accessory mineral phases that host rare earth elements (e.g. sphene etc.) were relatively stable during hydrothemal alteration or that the solubility of neodymium was extremely low in the hydrothermal fluids that produced the phyllic allteration.

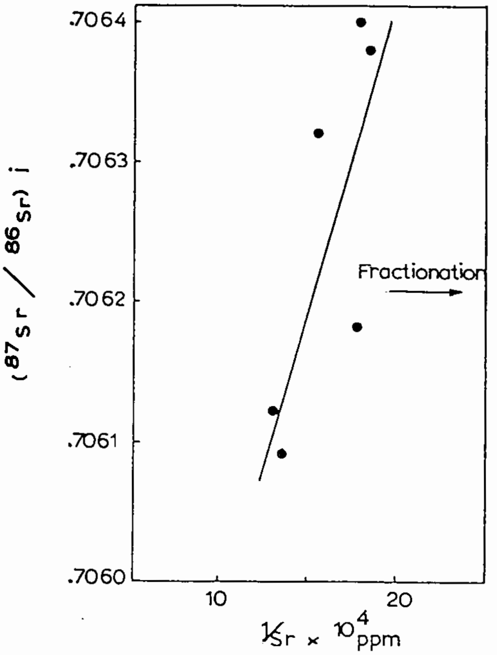

Fig. 9: Linear correlation between initial $^{87}Sr/^{86}Sr$ versus 1/Sr for the fresh Stratoni "granodiorite".

Regression of the Pb-Sr whole-rock data for the fresh "granodiorite" samples is poor, yield low Sri=0.7059 and no reliable isochrone (e.g. =60Ma as compared to reliable 30Ma, U/Pb in zircons; R.Frei, person. commun.). On the contrary, similar regression for the altered group (Fig. 7) yield T=24.2 ±0.1 Ma, Sri=070651±0.00004, MSWD=24.8 (n=5). Identical age has been obtained for the quartz-sericite-sulfide (phyllic) alteration in the granodiorite by A. Gild (person. commun.) employing the K-Ar method in sericite separates. This age is interpreted as the age of the phyllic alteration that follows emplacement and consolidation of the Stratoni intrusive suite (30 Ma). Hydrothermal alterations of intermediate ages during the cooling of the system may possibly be revealed when more detailed studies are undertaken.

Initial strontium isotope data for fresh (#1) and altered (#2) "granodiorite" samples and for Kerdylia formation biotite gneisses (Mantzos, 1990) at 30Ma are plotted on Figure 8A. Moreover, Figure 8B is a plot of the 30 Ma strontium isotopes for variably altered marble samples from

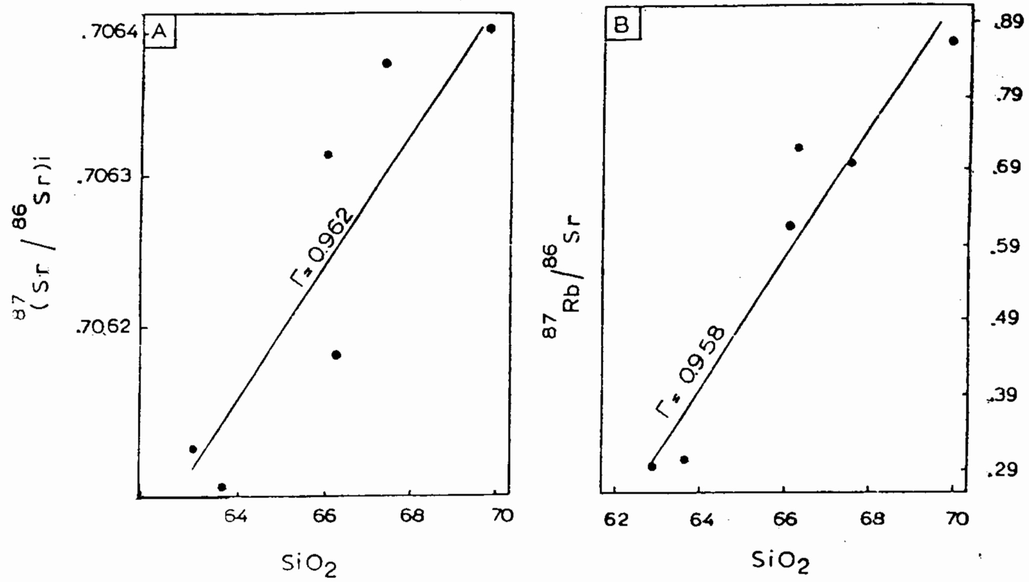

Fig. 10: Correlation between initial ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr with SiO$_2$(Wt%).

near the contact with the Stratoni intrusives and the fresh "granodiorite" samples versus their uranium concentration taken as an index of alteration degree for the marbles (Kalogeropoulos et al., 1989c). The data of Figure 8A suggest that the hydrothermal fluids that produced the phyllic alteration during the 24.2Ma hydrothermal event have most likely picked up strontium and rubidium from the biotite gneisses as well. The trend depicted for the marbles in Figure 8B is a strong evidence that strontium and uranium mobility was from the "granodiorite" outward into the marble wall rock regardless of the original source of the fluid. The widespread uranium enrichements in the host marbles (Kalogeropoulos et al., 1989c) and by extent the depletions in their initial strontium isotope values rather than radiogenic additions by the late fluids have most likely been caused by interaction of the 30Ma intrusive complex with the host marble rather than with the localized fracture-controlled 24.2Ma hydrothermal event.

Evidence of Mixing/Sources of magma

In tectonic settings dominated by orogenic magmatism fractional crystallization and/or various schemes of mixing might be called upon to account for granite genesis.

Closed-system fractional crystallization can be ruled out as a major process of the variation observed in the Stratoni intrusive complex (also, Kalogeropoulos, et al., 1990) on the basis of the following evidence.

(i) Faure et al. (1974) showed that if two components of differing strontium concentration and differing ^{87}Sr/^{86}Sr values are mixed in varying proportions, ^{87}Sr/^{86}Sr values and strontium concentration in any mixture can be related hyperbolically by the equation (^{87}Sr/^{86}Sr) $M=A+B/(Sr)_M$. where the subscript M refers to these values in the mixture, and A and B are functions of the concentrations and isotopic compositions of the two components. This hyperbolic relation can be treated as the equation of straight line in the slope-intercept form of coordinates of (^{87}Sr/^{86}Sr)M and $1/(Sr)_M$, where A is the intercept and B is the slope of the line:

(^{87}Sr/^{86}Sr)$=A+B(1/(Sr)_M)$. A plot of the Stratoni intrusive is shown in Figure 9. The best fit line of the specimens that lie along the limiting trends in Figure 9 is $(^{87}Sr/^{86}Sr)_M=0.705532+4.39866X10^{-1}$ $(1/(Sr)_M)$. This straight line relationship indicates that these samples are compatible with being related by mixing two components with deffering strontium. concentrations and $^{87}Sr/^{86}Sr$ values. One component with lower strontium and higher $^{87}Sr/^{86}Sr$ and a second component with higher strontium and lower $^{87}Sr/^{86}Sr$, corresponding most likely to crust - and mantle-like components, respectively.

(ii) Mixing (or contamination) of a mafic component with continental crust is expected to yield igneous products with positive correlations between $^{87}Sr/^{86}Sr$ ratios, $^{87}Rb/^{86}Sr$ ratios and and SiO_2 (Bailey et al, 1987). These relationships were found to be the case for the fresh Stratoni specimens as shown in Figures 10A and 10B.

(iii) The significant range of the strontium (this study) and oxygen (7.8 to 11.6; A. Gild, pers. commun.) isotope values contrary to the well established constancy and small shift, respectively, produced by simple closed-system crystallization of mafic magmas. Moreover, there is no evidence for any pristine, purely mantle-derived component at Stratoni. This point is clearly supported by the striking deviation of observed ($^{87}Sr/^{86}Sr$) i and $\delta^{18}O$ values from their recognized mantle values (-0.702-0.703 and 5.5-6.0, respectively).

(iv) The plot of the Stratoni samples between mantle and an assumed old crust on the E_{Nd} vs E_{Sr} diagmam (Fig. 11A) and along the least-square mixing hyperbola deduced by Juteau et al. (1986) for Tertiary circum-Mediterranean granites (Fig. 11B) provide a strong evidence for a mixing system. One end member must lie in the realm of "mantle" and island arc basalts (higher E_{Nd} or initial $^{143}Nd/^{144}Nd$ ratio and lower E_{Sr} and initial $^{87}Sr/^{86}Sr$ ratios). The determination of the other end member (Lower E_{Nd} or initial $^{143}Nd/^{144}Nd$ ratio and high E_{Sr} or initial $^{87}Sr/^{86}Sr$ ratios) is more subjective but the general deduction is that this will be a continental crustal meterial.

Although mixing as a process for the formation of the Stratoni intrusives is clearly documented,the accurate identification of the two end member components and how the mixing process takes place need further elaboration.

As described by Farmer and Depaolo (1983), the E_{Nd} and E_{Sr} of young granites can be used to infer their source regions if the isotopic compositions of potential mantle and crustal sources are known. Despite the lack of such data from the Kerdilia metamorphic terrain, the relatively high E_{Nd} values suggest that the Stratoni intrusives were mostly originated from mantle-derived material with minor contributions from crust components and the low E_{Sr} (<- +60) values indicate that the crustal component had low E_{Sr} (i.e. probably deep in the crust; Farmer and Depaolo, 1984). However, Juteau et all. (1986) on the basis of the lack of any distinct variation beitween the isotopic composition of either Sr or Nd with the Sm/Nd concentration ratios in some Tertiary circum-Mediterranean granites (i.e. Greece, northern Italy and northern Africa) suggest that the mafic component requires a crustal-like $^{147}Sm/^{144}Nd$ value (i.e. 0.09 to 0.12). As the 30Ma Stratoni "granodiorite" shares the above features it is reasonable to accept the validity of the argument for our case as well. The constraint put forward above, rules out MORB- and most OIB-type sources for DM component and supports the involvement of island Arc Basalts which are commonly LREE-enriched relative to other magma types.

As the amphibolites in the Kerfylia formation metamorphics are subalkaline basalts/basalltic-andesites of tholeitic affinity with MORB-characteristics (Fournaraki, 1981, Kalogeropoulos et al., 1990) Lerge scale anatexis of such a component in the Kerdylia composite terrain can be discarded. Consequently, intrusion of island arc type mafic magmas into the Kerdilia formation and mixing with anatectic crustal melts can be considered as the most likely mechanism for the formation of the Stratoni intrusives. The identification of the mixing process (e.g. simple mixing, ACF (De Paolo, 1980)) that would explain our data for Stratoni quantitatively best needs chemical and isotopic data from the various Kerdilia metamorphic rocks which are unfortunately lacking at present.

Moreover, the fresh "granodiorite" samples are characterised by enrichments in a number of ore

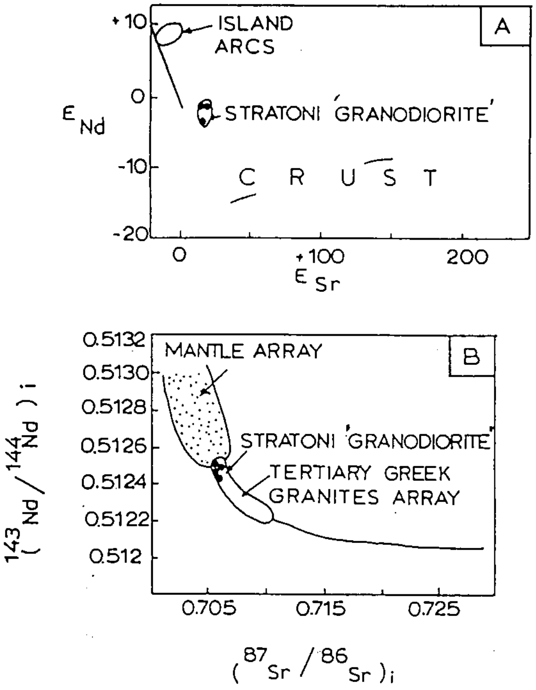

Fig. 11: The E_{Nd} versus E_{Sr} (A) and ($^{143}Nd/^{144}Nd$)i versus ($^{87}Sr/^{86}Sr$)i (B) for the Stratoni "granodiorite". The remaining data in (A) are from Farmer and DePaolo (1984), whereas the mixing hyperbola in B and the rest of the data are from Juteau, et al. (1986).

elements relative to their corresponding Clark values, a feature assigned to the initial magmas (see proper section) which classifies the Stratoni pluton to metalliferous granites. Farmer and DePaolo (1984; 1987) state that the formation of economic base metal deposits in association with a given granite is not dependent on the source region (e.g. proportion of mantle versus crustal metarial incorporated into the magma), since in many cases ore producing and barren plutons have identical isotopic composition. This urged them to suggest that other factors such as mecharism and/or depth of magma emplacement must control ore genesis. However, the "specialized" nature of the ore-related granites when assigned to the initial magma cannot be discarded as an additional prerequisite for economic ore concentrations.

Lead isotopes

The ranges of the lead isotope ratios for the 30Ma stratoni "granodiorite" the Kerdilia formation anatexites and biotite/muscovite gneisses, and the catbonate-hosted Pb-Zn (Au, Ag) sulfide mineralizations of the eastern Chalkidiki Peninsula are summarized in Table 4. All the data without previous correction for the in situ decay of uranium and thorium, but one, are plotted in Figures 12A and 12B. A measure at this correction is obtained from one sample of the 30Ma Stratoni "granodiorite" (fig. 12A and 12B). Similar shifts are expected in the gneisses and the anatexites as they bear comparable concentrations in uranium and thorium (umpubl. Data) and smaller in the ore leads. Due to the fact that the lead isotope data originate from different sources and were not determined on our samples no correlation with our present neodymium and strontium isotope data was attempted.

The lead isotope ratios, but one, were determined at Eth-Zurich using a Finnigan MAT 261 mass spectrometer. Fractionation effects were corrected which accounted for 0.13% per mass unit according to the measurements of the NBS SRM981 lead. The reproducibility of the standard is + 0.05% for the ^{206}Pb ad $^{207}Pb/^{204}Pb$ ratios and +0.1% for the $^{208}Pb/^{204}Pb$ ratio at 1 sigma level (Cumming et al. 1987; Koppel and Schroll, 1988).

All the data plotted in Figures 12A and 12B have high μ values typical of envolved crust-derived materials (Doe and Zartman, 1979) which are expected to mask any mantle contribution. Moreover, apart from the elongated isotopic field occupied by samples of the gneisses the remaining show tight, mutually overlapping yet distinct distributions.

The elongated isotopic field of the gneisses can be interpreted in several ways. One and most likely possibility is that it reflects the influence of the high grade metamorphism and the hydrothermal alteratiion processes. Consequently, the initial fingerprints of the gneisses have been obliterated. In fact, Amov (1990, written commun.) in a study of the feldspar leads from Rhodopian metamorphic rocks found that soluble lead is more radiogenic than the lead in the crystal lattice of the feldspars and assigned this feature to late contamination processes. Therefore, in this interpretation the gneiss mples having the lowest isotope ratios would be closer to gneisses which are less disturbed by secndary contaminations. This end of the isotopic field of the gneisses despite it is represented by a mall number of samples and more analyses are needed (primarily feldspars) could be taken as epresenting the evolved lead isotopic ratios of the gneisses. These isotopic ratios are distinctly differnt from those of the ores (Figs 12A and 12B).

The anatexite samples are more radiogenic than their respective lead isotope ratios in the gneisses Figs. 12A and 12B). These features clearly indicate that late magmatization proceeded under open ystem conditions for at least uranium and thorium most likely producing a candidate for the crystal omponent of the Stratoni intrusives. The island arc type mafic component indicated by neodymiumtrondium isotapic data could be barely envisaged also in Figures 12A and 12B.

As deduced from Figures 12A and 12B the ore leads can be considered as quite homogeneous mixtures of various sources such as granitc, "metamorphic" and probably mantle. The mixtures may e products for either one of the following two main processes:

(1) The syngenetic, that was subsequently modified by metamorphism, anatexis and the Tertiary gneous activity, and

(2) The typical magmatic-hydrothermal ore-forming process.

Despite that the fromer process cannot be easily discarded by inspecting the pertiment data, Figures 12A and 12B, however the following point, render this possibility highly unlikely.

(i) If syngenetic Paleozoic (Mantzos, 1990) ore and rock leads are shifted forward to Tertiary, the field of the envolved ore leads is expected to be significantly retarded relative to that of the rock leads. This feature would be the consequence of the lower uranium/thorium concentrations in the former, compared to the latter group. Assuming, that the processes subsequent to deposition have equally affected both the rocks and the ores their evolved distinct difference is not expected to have changed. Our data, on the contrary highlight the opposite relationship between the gneisses and the ores, thus placing discredit to the validity of the former case for the sulfide ore genesis.

(ii) Nebel (1990) in his study of the sulfide ores at Madem Lakos concluded that the isotopic composition of the galenas cannot be older than Mesozoic. This conclusion together with the premise that the ore is modified syngenetic drived him to the inference that the rocks should also be Mesozoic. Concurrenlty, Mantzos (1990) based on the Rb-Sr isotopic data of the neighboring Kerdylia gneisses and on theoretical considerations arrived at on Ordovisian/Silurian age for these rocks. Cross- evaluation of the above conclusions invalidates the syngenetic ore-forming process.

(iii) The overlap of the oxygen isotope ranges, in both the ore-forming fluid and the Stratoni intrusives (Kalogeropoulos et al., 1990; Gild, A., pers. commun.)

(iv) The low pressure (<1kb) and high temperature (300^0- 400^0 C) conditions for the formation of the bulk of the sulfide ores as deduced from fluid inclusions data on quartz, intimately associated with the ores which are distinctly different from the P/T conditions that prevailed during the regional amphobolite grade at metamorphism (Kalogeropoulos, et al. 1990).

As the lead isotopic ratios of the ores are quite uniform on a rather large scale and are levelled at the local average of the crustal lead an efficient transport and/or reequilibration mechanism are required in our opinion. This observation implies a large scale circulation of fluid during melting of the crust and the magma generation/emlacement processes. Such an environment of the ore genesis is in line with the magmatic-hydrothermal circulating ore-forming process as it explains our observations and data better (Kalogeropoulos, et al. 1990).

Summary and conclusions

The major, trace and rare earth, element data of the 30Ma Stratoni "granodiorite" combined with

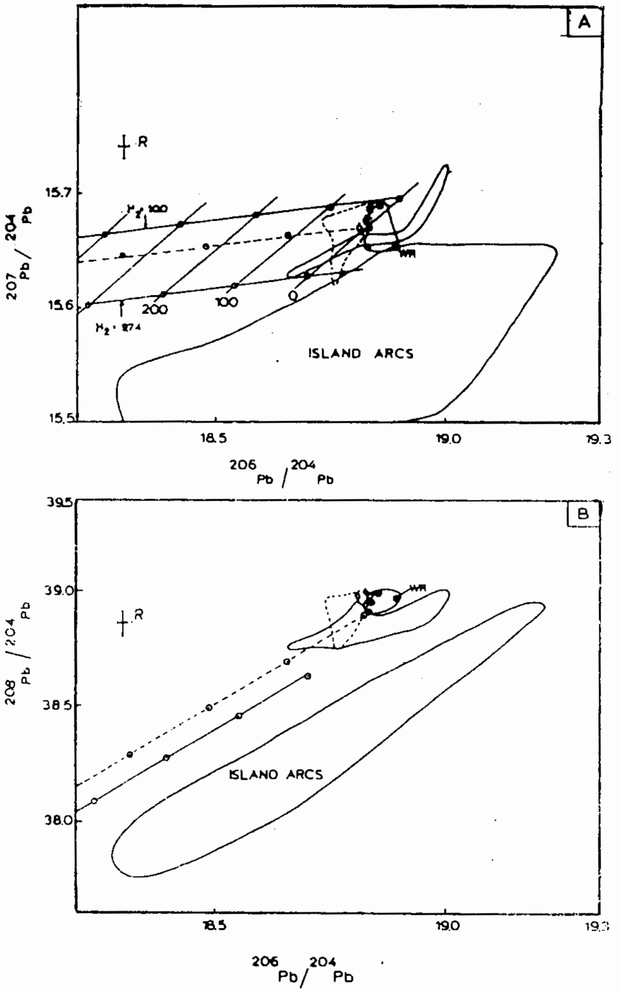

Fig.12: ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb (A) and ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb (B) diagram. Solid lead evolution curves in A are according to Stacey and Kramers (1975). The broken lead evolution line is according to Cumming and Richards (1975). R, denotes reproducibility. Elongated field is for biotite gneisses, solid circles are data from Stratoni "granodiorite" feldspars (three data points), whole rock (WR) and the open circile is the corrected value for in situ radioactive decay. Open rombs are anatexite and broken line outlines the ore galena leads. Generalized field for island arcs are from Oversby and Ewart, 1972: Church, 1976: Meijer, 1976: Kay, et la, 1978.

the presence of andesite (Nebel, 1989), and calcalkaline lamprophyre dikes (Nikolaou, 1960: Kalogeropoulos et al., 1990), suggest that this Tertiary complex that intrudes the amphibolite grade metamorphic Kerdilia Formation was formed in a subduction-related setting. Nd-Sr isotope data, oxygen and probably lead indicate that the Stratoni "granodiorite" was produced by mixing primarily of Island-arc type mafic liquids with small contributions by siliceous, and isotopically more radiogenic, anatectic melts (see also Jutaeu et al. 1986). The magma mixture that produced the Stratoni "granodiorite" is characterized by enrichments in a number of ore elements relative to the corresponding Clark values, thus classifying it to the "specialized" granites.

The Stratoni "granodiorite" during emplacement and consolidation produced an aureole which is represented by a skarn-replacement ore system and the associated alterations.

This ore system on the basis of lead, oxygen isotope, and fluid inclusions, data fits better to epigenetic rather than to syngenetic-remobilized processes. At the early stages of this intrusive event, materials and heat were transferred primarily from the "granodiorite" outward to the wall rocks. The late (24.2 Ma) hydrothermal fluids that produced the phylically altered "granodiorite" acquired their more radiogenetic nature as regards the studied isotopes via interaction most likely with the isotopically evolved Kerdilia gneisses. The origin of these late fluids is currently under investigation (A. Gild, pers. commun.) whereas the nature of hydrothermal activity operating between 30Ma and 24.2Ma as the intrusive system cooled is expected to be revealed by our on-going more detailed studies.

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