

RB-SR WHOLE-ROCK GEOCHRONOLOGY OF GNEISSES FROM OLYMPIAS, CHALKIDIKI

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ABSTRACT

Two series of Olympias biotite-gneiss samples have yielded Rb-Sr whole-rock isochron ages of 337 ± 5 Ma (Early Carboniferous) and 113 ± 11 Ma (Early Cretaceous), respectively (errors=2s; IUGS-recommended constants used). The older age relates to the culmination of the oldest metamorphic event – amphibolite facies regional metamorphism – that affected the deeper parts of the Servomacedonian massif. This age is coupled with a very low $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio indicating that the source regions of the clastic sedimentary precursors of the biotite-gneisses comprised felsic igneous rocks of short residence time in the crust. The younger age – a reset age – corresponds to the most intensive (greenschist facies) retrograde metamorphism of the study area. The uncertainties regarding the accuracy of the isotopic ages determined, are probably related to postmetamorphic geological disturbances of the isotopic systems established during the course of the successive metamorphisms. With respect to the younger event, they may also be linked with the patchy manner that Sr reequilibration and rehomogenization was likely effected. Theoretical considerations suggest that sedimentation and sulphide ore formation at Olympias might had been accomplished by Silurian to Early Devonian times.

ΣΥΝΟΨΗ

Δύο σειρές δειγμάτων βιοτιτικών χνευσιών από την Ολυμπιάδα απέδωσαν αντιστοίχως, μετά από γεωχρονολόγηση ολικού πετρώματος με τη μέθοδο Rb-Sr, ισόχρονες ηλικίες 337 ± 5 Ma (κατώτερο Λιθάνθρακοφόρο) και 113 ± 11 Ma (κατώτερο Κρητιδικό) (σφάλματα=2s, χρησιμοποιούνται οι από το IUGS προτεινόμενες σταθερές). Η μεγαλύτερη ηλικία σχετίζεται με την κορύφωση του αρχαιότερου μεταμορφικού συμβάντος (αμφιβολιτική φάση μεταμορφώσεως) που επηρέασε τα βαθύτερα τμήματα της Σερβομακεδονικής μάζας. Η ηλικία αυτή συνοδεύεται από ένα πολύ χαμηλό αρχικό λόγο $^{87}\text{Sr}/^{86}\text{Sr}$, που υποδηλώνει ότι οι περιοχές αποκομιδής των κλαστικών ιζηματογενών πρωτολίθων των βιοτιτικών χνευσιών αποτελούντο από όξινα πυριγενή πετρώματα μικρής διάρκειας παραμονής στο φλοιό. Η νεώτερη ηλικία – αναζωπυρωμένη ηλικία – αντιστοιχεί στην πιο έντονη ανάδρομη μεταμόρφωση της περιοχής που μελετήθηκε. Τα αριθμητικά σφάλματα που συνοδεύουν τις ιστοπικές ηλικίες που προσδιορίστηκαν, ίσως συνδέονται με νεώτερες των μεταμορφώσεων γεωλογικές διαταράξεις των ιστοπικών συστημάτων που διαμορφώθηκαν στη διάρκεια των διαδοχικών μεταμορφώσεων. Όσον αφορά το νεώτερο μεταμορφικό συμβάν, το σφάλμα ηλικίας μπορεί να συσχετισθεί και με τον αποσπασματικό τρόπο με τον οποίο πιθανώς πραγματοποιήθηκε η επανομογενοποίηση και επανεξισορρόπηση του Sr. Θεωρητικές παραδοχές οδηγούν στην υπόθεση ότι η ιζηματογένεση στην Ολυμπιάδα και η δημιουργία του εκεί κοιτάσματος μεικτών θειούχων είχε ίσως ολοκληρωθεί μέσα στο χρονικό διάστημα Σιλουρίου-Κάτω Δεβονίου.

L.A. MANTZOS. Γεωχρονολόγηση ολικού πετρώματος χνευσιών της Ολυμπιάδας, Χαλκιδική, με τη μέθοδο Rb-Sr.

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1. INTRODUCTION

Olympias district is located within the eastern margins of the Servomacedonian massif (SMM) – a metamorphic belt running NW-SE through N. Greece and extending into Yugoslavia (Fig 1). It is a sequence of biotite-gneisses with intercalations of amphibolite, amphibolitic gneiss and marble, and with a plethora of leucosomes. The thickest marble horizon accommodates a slim lens of sulphide ores.

Determining the age of the SMM and of its regional upper amphibolite facies metamorphism is a long standing problem. Precambrian and late Precambrian ages, have been postulated for the SMM and the regional metamorphism, respectively (Dimitrijevic and Ciric, 1966; cit. Kockel et al, 1977). Attempts to confirm the postulated ages by radiometric dating of micas and hornblende yielded invariably younger Hercynian-Alpine ages (Kockel et al, 1977; Table 3, p.96; Papadopoulos and Kiliass, 1985) which were associated with younger metamorphic rejuvenations of the SMM.

The primary intention to determine the age of the precursor rocks of the SMM or its metamorphism remained unsolved because minerals are rather unsuitable for radiometric dating, when formation ages, or ages of the peak of high grade metamorphism are sought. As a rule, mineral ages relate to the cooling stages of a major thermal event, or to later low grade metamorphic disturbances (Jäger, 1979a). Accordingly, an Rb-Sr isotope study of the Olympias gneisses was undertaken in order to establish the geochronological framework of the Olympias country rocks with a view to: (a) provide more accurate answers regarding the metamorphic and/or the primary age of the district – the Rb-Sr method of isotopic dating being one of the most resistant clocks for measuring geological time, when applied on suites of whole-rock samples (eg Jäger, 1979a); and (b) quantify the time relationship of the at least two metamorphic events that have affected the Olympias ores and are manifested by the ore textures (Mantzios, 1989).

2 SAMPLING AND ANALYTICAL PROCEDURES

The sampling procedure was based on the following criteria: (i) the samples should be fresh (Jäger, 1979b); (ii) the samples should be as big as possible to stand a good chance to have behaved as chemically closed systems since the time of lithification, or at least regional metamorphism; and (iii) the samples should present a spread in Rb/Sr ratios, so that the slope of a potentially existing isochron might be determined more precisely. Criteria (i) and (ii) were satisfied on the basis of macroscopic and some microscopic observations. It was easy to test the samples for criterion (iii) as Rb and Sr ICPAES-data had been produced for lithochemical purposes for all the rock samples available, prior to the Rb-Sr dating.

Accordingly, of 198 samples collected from drill cores in the course of lithochemical sampling at Olympias (thanks to the access provided to drill cores by the Hellenic

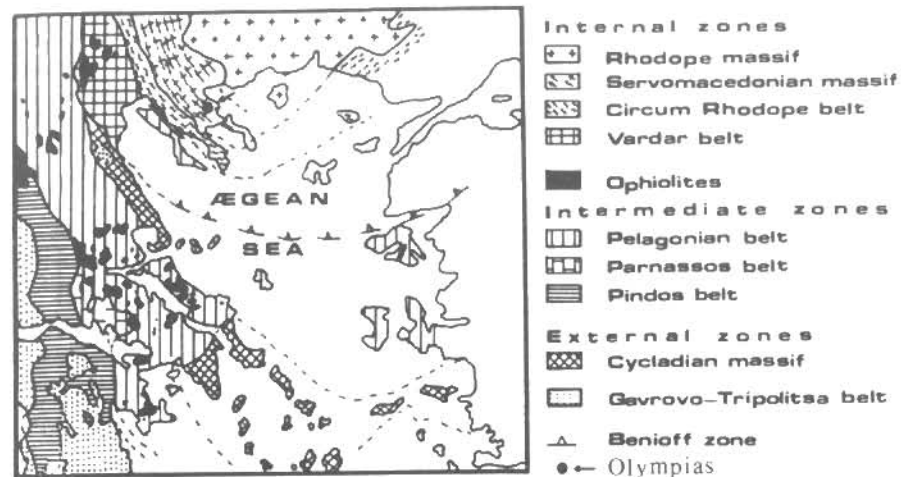


Fig 1. Geotectonic setting of Olympias district; the geotectonic sketch of the Northern Aegean region, Greece, is after Kauffmann (1976). Dashed lines represent hypothetical boundaries between belts.

Σχ. 1. Γεωτεκτονική θέση περιοχής Ολυμπιάδας: το γεωτεκτονικό σκίτσο της περιοχής Βορείου Αιγαίου, Ελλάδα, είναι του Kauffmann (1976). Οι διακεκομμένες γραμμές αντιπροσωπεύουν υποθετικά όρια μεταξύ ζωνών.

Chemical Products and Fertilizers Co, Ltd, and Dr. M. Nicolaou in particular), 18 gneiss samples, and (for comparison) 2 amphibolite and 1 amphibolitic gneiss samples, each weighing 1-2kg, were chosen for Rb-Sr dating. Of these, 19 samples derive from 12 drill cores (nos: 75, 95, 100, 102, 103, 107, 109, 111, 112, 114, 118, 134; Fig 2), covering an area of about 550x400m. The remaining 2 samples derive from the northernmost drill core (no: 69) of the study area (Fig 2). All samples, but one (GN11827) overlying the Olympias orebody by 535m, lie from 50m stratigraphically below, to 333m above the orebody.

Each rock sample was crushed in a steel jaw crusher and the whole sample was finely ground in an agate Tema mill. The atomic Rb/Sr ratios were directly determined on pressed powder pellets by a precise XRF method (Pankhurst, 1968; Pankhurst and O'Nions, 1973). Each ratio reported, is the average of 2 determinations (one for each side of the pellet). The analytical precision (in terms of 2σ) is at the range of 0.7%, on average.

Strontium was liberated from individual samples following an HF-HNO₃ attack and was isolated by means of ion exchange columns following the standard technique applied at the Isotope Unit of the British Geological Survey (BGS). The ⁸⁷Sr/⁸⁶Sr ratios were determined at the BGS on a V.G.-MM30 mass spectrometer controlled by an HP9845 computer programmed for automatic analytical control. The analytical precision is in the range 0.005-0.01% (2σ).

The regression analysis of the isotope data follows the York's (1969) procedure. The errors for individual data points, are calculated on the basis of the errors of the respective

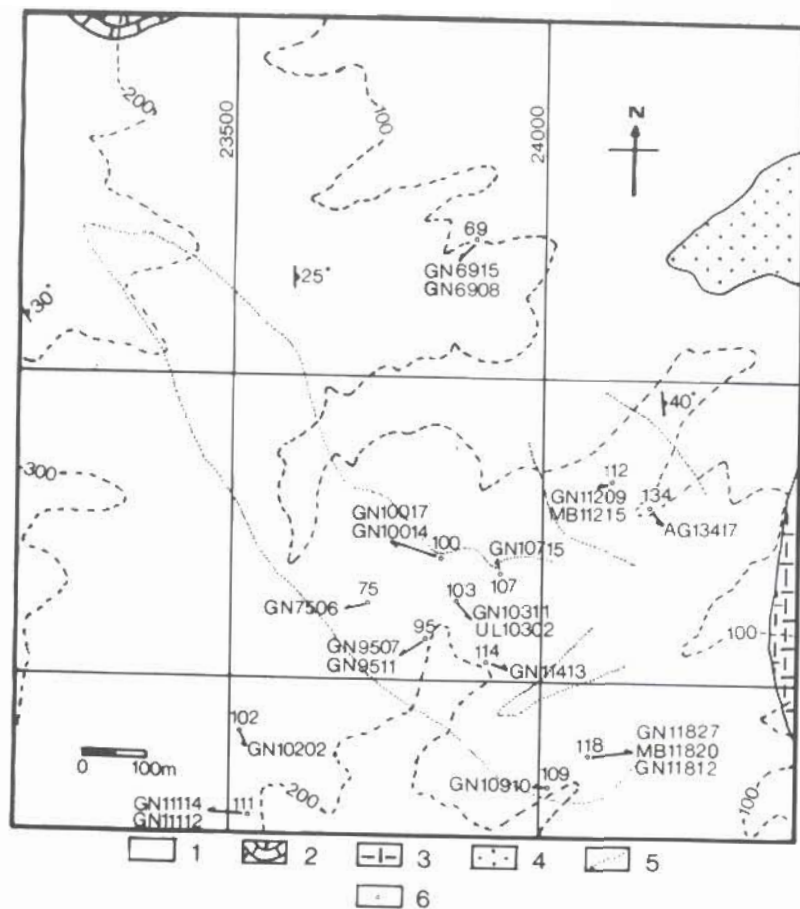


Fig 2. Sampling positions for the rock units analyzed in the context of the Rb-Sr isotope study. Key: 1= biotite-gneiss with amphibolitic gneiss, amphibolite and marble intercalations, and swarms of leucosomes; 2= marble; 3= biotite-hornblende-gneiss; 4= undivided Pleistocene deposits; 5= planar section of the Olympus orebody, projected onto the topographic surface; 6= drillholes from which core samples were collected. (Modified from Nicolaou and Kokonis, 1980).

Σχ. 2. Θέσεις δειγματοληψίας των πετρωμάτων που αναλύθηκαν στα πλαίσια της ισοτοπικής μελέτης Rb-Sr. Κλείδα: 1= βιοτιτικός χνεύσιος με ενδιαστρώσεις αμφιβολιτικού χνεύσιου, αμφιβολίτη και λεπτών οριζόντων μαρμάρου, και με μια αβήθονια λευκοσωμάτων, 2= μάρμαρο, 3= βιοτιτικός-αμφιβολιτικός χνεύσιος, 4= αδιαίρετες Πλειστοκαινείς αποθέσεις, 5= προβολή του κοιτάσματος της Ολυμπιάδας στην τοπογραφική επιφάνεια, 6= χεωτρήσεις απ' όπου συνελλέγησαν τα δείγματα πυρήνος. (Τροποποιημένο σχέδιο του χάρτη των Nicolaou and Kokonis, 1980).

$^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, presented in Table 1. Age and initial ratio (IR) errors are quoted at the 2s confidence level. The IUGS-recommended constants are applied (Steiger and Jäger, 1977).

Analytical data for major and trace elements were produced by XRF for 15 samples and by ICPAES for all of the samples used for the Rb-Sr study (Mantzios, 1989).

3. ISOTOPIC AND GEOCHEMICAL RESULTS

The Rb, Sr, $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data are listed in Table 1. The total Rb-Sr isotope data are graphically presented on the Rb-Sr evolution diagram in Fig 3.

The 2 amphibolites and the amphibolitic gneiss are characterized by similar Rb-Sr isotope features. Each of them has a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.705 and a low $^{87}\text{Rb}/^{86}\text{Sr}$ ratio in the range 0.36-0.60. The scatter of the gneiss isotope data precludes the drawing of a single isochron line. Instead, two Sr evolutionary trends, labelled a1 and a2 in Fig 3, are recognizable.

Table 1. Rubidium and Sr contents, $(\text{Rb}/\text{Sr})_{\text{at}}$ ratios, and Rb-Sr isotope data for gneisses, amphibolites and an amphibolitic gneiss from Olympus

Sample	Rb μg/g	Sr μg/g	$(\text{Rb}/\text{Sr})_{\text{at}}$	$^{87}\text{Rb}/^{86}\text{Sr}$	P %	$^{87}\text{Sr}/^{86}\text{Sr}$	P %
GN 6915 ¹	112	1,686	0.06781	0.1913	0.50	0.70537	0.005
GN10014 ¹	125	141	0.67263	1.8994	0.99	0.71373	0.007
GN10202 ¹	133	123	1.10380	3.1188	0.50	0.71940	0.007
GN10715 ¹	110	122	0.92886	2.6202	0.50	0.71627	0.008
GN11413 ¹	126	229	0.56278	1.5891	0.50	0.71211	0.006
GN11827 ¹	114	150	0.78435	2.2153	0.50	0.71450	0.010
UL10302 ¹	127	138	0.94393	2.6665	0.91	0.71721	0.010
GN 6908 ²	99	228	0.44327	1.2517	0.50	0.71222	0.005
GN 7506 ²	117	308	0.39062	1.1028	1.49	0.71145	0.005
GN 9507 ²	73	349	0.21285	0.6265	1.50	0.71090	0.005
GN 9511 ²	89	308	0.29493	0.8326	0.50	0.71125	0.006
GN10017 ²	96	186	0.53055	1.4982	0.50	0.71125	0.006
GN10311 ²	130	151	0.87806	2.4797	0.50	0.71382	0.010
GN10910 ²	77	228	0.34663	0.9785	1.27	0.71122	0.005
GN11112 ²	99	224	0.45156	1.2751	0.50	0.71183	0.005
GN11114 ²	118	265	0.45703	1.2903	1.11	0.71208	0.005
GN11209 ²	100	266	0.38505	1.0869	0.50	0.71111	0.005
GN11812 ²	129	153	0.86016	2.4292	0.50	0.71369	0.006
AG13417	22	171	0.12911	0.3643	0.95	0.70509	0.005
MB11820	25	142	0.18080	0.5102	0.92	0.70545	0.007
MB11215	54	262	0.21267	0.6001	0.55	0.70504	0.006

P: precision(2s); at: atomic; GN, UL: gneiss; AG: amphibolitic gneiss; MB: amphibolite; 1: "older"-gneiss; 2: "younger"-gneiss; $^{87}\text{Rb}/^{86}\text{Sr}=0.27835(^{87}\text{Sr}/^{86}\text{Sr}+9.4318)(\text{Rb}/\text{Sr})_{\text{at}}$

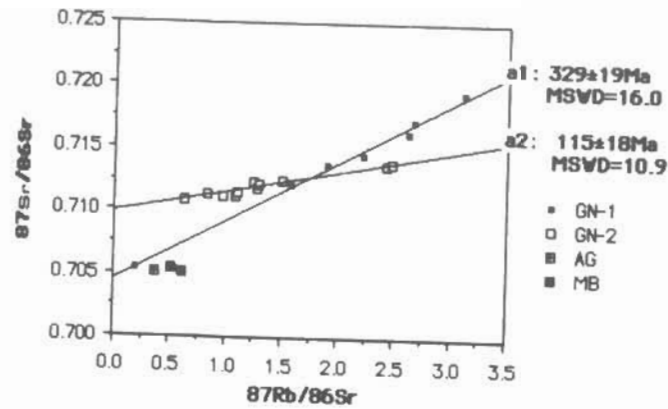


Fig 3. Rb-Sr evolution diagram for gneisses, amphibolites and an amphibolitic gneiss from Olympias. Key: GN-1= "older"-gneiss; GN-2= "younger"-gneiss; AG= amphibolitic gneiss; MB= amphibolite; a1= "Older"-gneisses Sr evolutionary trend (slope=0.00469±0.00003, IR=0.70451±0.00014, age=329±19Ma); a2= "Younger"-gneisses Sr evolutionary trend (slope=0.00163±0.00004, intercept=0.70980±0.00011, age=115±18Ma).

Σχ. 3. Διάγραμμα εξέλιξης του Rb-Sr γνευσίων, αμφιβολιτών και ενός αμφιβολιτικού γνευσίου της Ολυμπιάδας. Κλείδα: GN-1= "παλαιότεροι"-γνεύσιοι, GN-2= "νεώτεροι"-γνεύσιοι; AG= αμφιβολιτικός γνεύσιος, MB= αμφιβολίτης, a1= εξελικτική τάση του Sr των "παλαιότερων"-γνευσίων (κλίση = 0.00469±0.00003, IR = 0.70451±0.00014, ηλικία = 329±19Ma); a2= εξελικτική τάση του Sr των "νεωτέρων"-γνευσίων (κλίση= 0.00163±0.00004, IR=0.70980±0.00011, ηλικία=115±18Ma).

Trend a1 is defined by 7 biotite-gneisses distinguished in Table 1 by the superscript 1 attached to their sample numbers. For simplicity, these 7 gneisses will be referred to below, as "older"-gneisses. The regression line that describes trend a1 (Fig 3), yields an age of 329±19Ma, an IR=0.70451, and has a Mean Square of Weighted Deviates (MSWD; Brooks et al, 1972) of 16.0. This MSWD is higher than 2.5, which is the upper limit for an acceptable isochron relationship (Brooks et al, 1972). Accordingly, the scatter of the "older"-gneisses about their regression line cannot relate to experimental error alone, but manifests some geological disturbance. Excluding 2 samples (GN10715, GN11827), lying furthest from the regression line, the remaining ones form a very good 5 point isochron (Fig 4), with a low MSWD=1.1. This isochron yields a whole rock apparent age of 337±5Ma and an IR=0.70448.

The trend a2 is defined by 11 biotite-gneisses distinguished in Table 1, by the superscript 2 attached to their sample numbers. For simplicity, these 11 gneisses will be referred to in the following, as "younger"-gneisses. The regression line that corresponds to trend a2 (Fig 3), gives an age of 115±18 Ma, an IR=0.70980 and has a MSWD=10.9 indicating geological disturbance. Disturbance that is substantiated by the fact that nine of the "younger"-gneisses are from within 15m from leucosomes (distance measured along drillcore). Excluding 2 samples (GN6908, GN11209), lying closer to leucosomes (4-6m) than any other

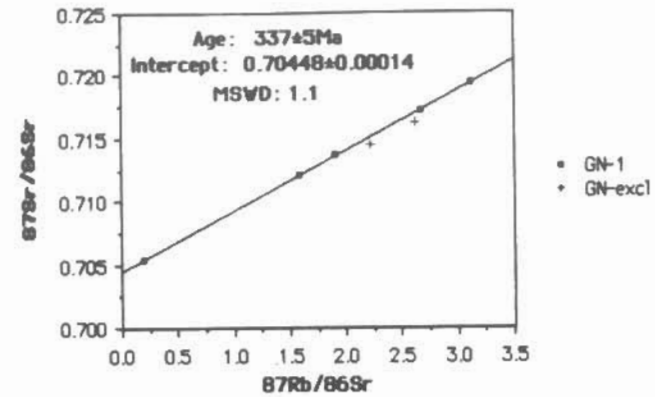


Fig 4. Rb-Sr evolution diagram for the "older"-gneisses. Key: GN-1="older"-gneiss; GN-excl="older"-gneiss excluded from the isochron calculation; slope of the isochron: 0.00480±0.00004 (the other parameters of the isochron are shown in the diagram).

Σχ. 4. Διάγραμμα εξέλιξης του Rb-Sr των "παλαιότερων"-γνευσίων. Κλείδα: GN-1= "παλαιότεροι"-γνεύσιοι, GN-excl= "παλαιότεροι"-γνεύσιοι εξαιρεθέντες του υπολογισμού της ισοχρόνου, κλίση της ισοχρόνου: 0.00480±0.00004 (οι άλλες παράμετροι της ισοχρόνου δίνονται στο διάγραμμα).

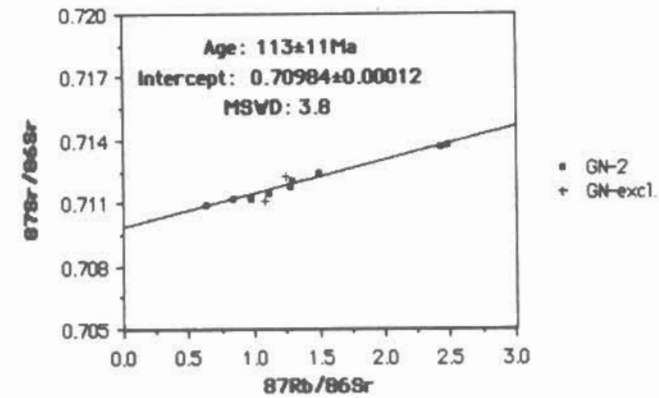


Fig 5. Rb-Sr evolution diagram for the "younger"-gneisses. Key: GN-2= "younger"-gneiss; GN-excl= "younger"-gneiss excluded from the isochron calculation; slope of the isochron: 0.00161±0.00004 (the other parameters of the isochron are shown in the diagram).

Σχ. 5. Διάγραμμα εξέλιξης του Rb-Sr των "νεωτέρων"-γνευσίων. Κλείδα: GN-1= "νεώτεροι"-γνεύσιοι, GN-excl= "νεώτεροι"-γνεύσιοι εξαιρεθέντες του υπολογισμού της ισοχρόνου, κλίση της ισοχρόνου: 0.00161±0.00004 (οι άλλες παράμετροι της ισοχρόνου δίνονται στο διάγραμμα).

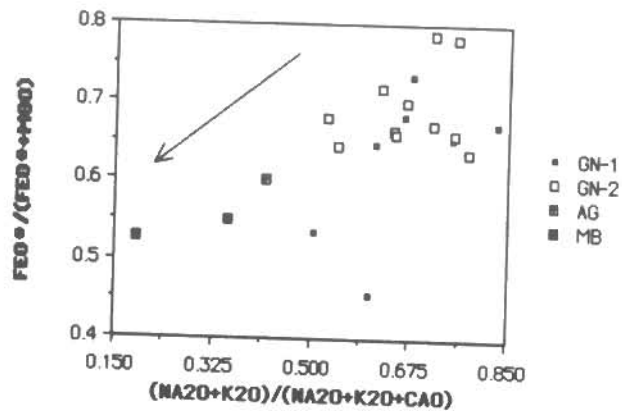


Fig 6. $(\text{Na}_2\text{O}+\text{K}_2\text{O})/(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO})$ vs $\text{FeO}^*/(\text{FeO}^*+\text{MgO})$ diagram for the samples utilized in the Rb-Sr isotope study. Key: GN-1, GN-2, AG and MB as in Fig 2; $\text{FeO}^*=\text{FeO}+0.899\text{Fe}_2\text{O}_3$; the arrow illustrates a trend of increasingly mafic composition.

Σχ. 6. Διάγραμμα $(\text{Na}_2\text{O}+\text{K}_2\text{O})/(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO})$ έναντι $\text{FeO}^*/(\text{FeO}^*+\text{MgO})$ των δειγμάτων που χρησιμοποιήθηκαν στην ισοτοπική μελέτη Rb-Sr. Κλειδα: GN-1, GN-2, AG και MB όπως στο Σχ. 2, $\text{FeO}^*=\text{FeO}+0.899\text{Fe}_2\text{O}_3$, το βέλος απεικονίζει αυξητική τάση βασικής σύστασης.

gneiss sample analyzed, the remaining ones define a relatively good 9 point isochron (Fig 5) – strictly speaking an errorchron – with a moderate MSWD=3.8. The new isochron yields a likely reset whole-rock age of 113 ± 11 and an $\text{IR}=0.70984$.

The reasons why the gneisses analyzed constitute two isotopically distinct rock groups yielding discordant ages are rather unclear. Bell and Blenkinsop (1978), consider that more felsic rocks are more susceptible to open-system behaviour with respect to Rb and Sr, than less felsic ones. As a result, the former are more prone to Rb-Sr age resetting, than the latter. In order to examine whether the isotopic differences between the "older"-gneisses and the "younger"-gneisses are a function of bulk chemistry, all samples utilized in the Rb-Sr study were plotted in a Felsic index vs Mafic index diagram (Fig 6); where: sensus Best (1982; p.50), Felsic-index = $(\text{Na}_2\text{O}+\text{K}_2\text{O})/(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO})$, Mafic-index = $\text{FeO}^*/(\text{FeO}^*+\text{MgO})$, FeO^* being the total Fe expressed as FeO. Nevertheless, no consistent differences regarding the bulk chemistry of the two gneiss groups were observed. It is noteworthy, however, that the 2 relatively more felsic and the 2 relatively more mafic gneisses are "younger"-gneisses and "older"-gneisses, respectively (Fig 6).

4. AGE AND INITIAL RATIO (IR) INTERPRETATIONS

4.1. ISOTOPIC AGES

4.1.1. "OLDER"-GNEISSES

The gneisses defining the 5 point isochron are spread over 347m of the local lithostratigraphic column (585m, when all the "older"-gneisses are considered). This demonstrates that at 337Ma the "older"-gneisses were part of a geological system which: (a) embraced a very significant part of the Olympias lithostratigraphy, and (b) was homogeneous with respect to Sr isotope compositions, being characterized by a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70448. Since then, the above system remained virtually closed with regard to Rb and Sr.

The $337\pm 5\text{Ma}$ isochron age determined may reflect either the formation age of the protoliths of the gneisses, or a later metamorphic event. The former possibility should probably be rejected in view of the clastic sedimentary character of the precursors of the gneisses (Dimitriadis, 1974; Mantzos, 1989).

Clastic sediments comprise allogenic materials which are transported to basins of sedimentation as detrital particles. The Sr isotope composition of the allogenic materials is a function of their ages and Rb/Sr ratios and is not significantly modified during transport and deposition in the basins of sedimentation (Faure, 1977; p.132). Following deposition, detrital matter does not equilibrate isotopically with Sr in seawater (Dasch, 1969). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of clastic sediments preserve, therefore, a record of the provenance of the sediments. Had homogeneous $^{87}\text{Sr}/^{86}\text{Sr}$ ratios been a primary feature of the clastic protoliths of the Olympias gneisses, the protoliths should comprise the weathering products of an isotopically homogeneous source region. However, such a concept would be geologically unrealistic particularly on account of (a) the thickness of the sedimentary sequence involved; and (b) the possibility that the source region of the clastic protoliths not only consisted of felsic rocks of variable composition (as the geochemical composition of the gneisses indicates; Fig 6) and accordingly of rocks of probably differing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, but also might include mafic rocks.

It follows that, at $337\pm 5\text{Ma}$ the "older"-gneisses were not characterized by an inherently uniform Sr isotope ratio, but this was developed with the aid of metamorphic processes which led to large scale Sr redistribution and Sr isotope homogenization. Intense metamorphism, probably created a suitable environment for the operation of the above processes, producing metamorphic fluids and anatectic melts promoting Sr isotope exchange reactions, throughout the study area.

Accordingly, the $337\pm 5\text{Ma}$ date, likely denotes the age of a high grade regional

4.1.2. "YOUNGER"-GNEISSES

The "younger"-gneisses and the "older"-gneisses deriving from the same parts of the study area, are equally affected by the 337 ± 11 Ma metamorphic event. Despite that, the former define a distinct 9 point isochron yielding a reset age of 113 ± 11 Ma and an $IR=0.70984$. Accordingly, a 113 ± 11 Ma old dynamothermal event overprinting the 337 ± 5 Ma old metamorphic event, is envisaged.

In the course of the 113 ± 11 Ma event, the "younger"-gneisses were subjected to open-system behaviour with respect to Sr which was redistributed and isotopically rehomogenized. At the completion of this dynamothermal event the "younger"-gneisses attained a uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70984. Since then, accumulation of radiogenic ^{87}Sr resumed and the 113 ± 11 Ma isochron developed.

The dynamothermal event advocated, probably represents moderately intensive retrograde metamorphism. Regarding country rocks, the evidence for metamorphic retrogression in the study area is limited, being confined to the occasional chloritization of hornblende – on the contrary, such evidence is very prominent in the Vertiskos formation (Dimitriadis, 1974). Conversely, the ore textures of the Olympias sulphides provide significant evidence for metamorphic retrogression (Mantzou, 1989). Evidently, the resetting of the Rb-Sr clock, in parts of the study area, is the more important geochemical indication for metamorphic retrogression. This does not undermine the validity of the reset isochron as a metamorphic event is not rarely manifested through its effects on isotopic systems alone (Jäger, 1979a).

In the case of the 337Ma metamorphic event, metamorphic fluids and anatectic melts were deemed responsible for the pervasive Sr homogenization inferred. On the contrary, in the rocks showing the 113Ma event, Sr homogenization agents identical, in nature and/or volume, to those related to the 337Ma event cannot be envisaged. Had such agents been operative they would have led to large scale Sr rehomogenization completely erasing the isotopic evidence for the 337Ma event. Also, they would have facilitated extensive retrograde mineralogical changes within the gneisses. Thus, metamorphic fluids of a limited volume, acting on the country rocks in a rather patchy manner, constitute more plausible media for the small scale Sr rehomogenization.

Nine of the 11 "younger"-gneisses lie within 15m from leucosomes, the 2 more isotopically disturbed ones (those excluded from the calculation of the reset isochron) lying within 6m from leucosomes. The leucosomes constitute geochemical inhomogeneities within the relatively more mafic Olympias lithostratigraphy. Geochemical inhomogeneities can enhance Rb, Sr exchange (Jäger, 1979a). Accordingly, rock units in the vicinity of leucosomes are, possibly, more susceptible to Sr homogenization. Moreover, the predominantly discordant leucosomes of the study area are frequently related to structural discontinuities. Such discontinuities generally promote an open-system behaviour for the rocks they crosscut (Field and Raheim, 1979). Discontinuities the leucosomes had already followed or even created, have

possibly facilitated the preferential circulation of the metamorphic fluids through those parts of the local lithostratigraphy which embrace "younger"-gneisses, preferentially promoting the rehomogenization of their Sr.

The proposed mechanism of Sr rehomogenization, in connection with the thickness of the metamorphic sequence affected, would be more compatible with the presence of more than one systems of metamorphic fluids, each operating in different parts of the sequence. However, as the above mechanism produced a reasonable isochron, the fluids involved were likely of the same age, acted in an analogous manner, and were compositionally similar. The absence of integral fluid uniformity is reflected by the reset isochron MSWD, which is not as low as required by a perfectly fit isochron, resulting as aforementioned in a relatively high age error of 11Ma (=9.7%) more pertinent to an errorchron.

4.2. STRONTIUM ISOTOPE COMPOSITION OF THE AMPHIBOLITES AND THE AMPHIBOLITIC GNEISS, AND IMPLICATIONS REGARDING IRs

The amphibolites, despite lying about 195m stratigraphically apart, present almost identical and very low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios averaging 0.70525. This confirms the mafic igneous parentage and the upper mantle derivation proposed for the amphibolites by Fournarakis (1981) and Mantzou (1989). For the sake of argument, the current geological opinion considering these amphibolites as late Precambrian will be accepted. Upper mantle material of such an age has probably an IR in the range 0.7036-0.7062 (Faure, 1977; p.113: terrestrial Sr evolutionary trends). Conversely, the amphibolite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios set an upper limit to the amphibolite IR which, therefore, probably lies in the range 0.7036-0.705. Apparently, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the amphibolites has changed very little since the time their precursors formed.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the amphibolitic gneiss is almost within analytical error from the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of one of the amphibolites (Table 1). It may be of significance that the stratigraphic distance between the two rocks is only 7m. The mutual Rb-Sr isotopic resemblance of these rocks may be explained by the Olympias amphibolitic gneisses representing metamorphic products of lithologies which resulted from clastic sediment and mafic magma mixtures as advocated by Mantzou (1989). The clastic sediment component was minor - attaining the isotopic features of the mafic magma component upon mixing - and/or deficient in ^{87}Sr . Metamorphic differentiation led to the appearance of the amphibolitic gneiss as alternating layers of hornblende-plagioclase and quartz-plagioclase.

4.3. INITIAL RATIO IMPLICATIONS REGARDING SR EVOLUTION

4.3.1. "OLDER"-GNEISSES IR

The "older"-gneisses have a very low $IR=0.70448$ which is similar to the $^{87}\text{Sr}/^{86}\text{Sr}$

ratios of the amphibolites and the amphibolitic gneiss. Moreover, the "older"-gneiss IR lies in the range 0.7037-0.7063, which is the field representing Sr evolution in the upper mantle, at $\approx 337\text{Ma}$ (Faure, 1977; p.113: terrestrial Sr evolutionary trends).

The foregoing suggest that Sr isotope equilibration between the protoliths of the gneisses and of the amphibolites may have been accomplished during the course of the 337Ma event. It also follows that the precursors of the gneisses had not significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the protoliths of the amphibolites. If they had, either the "older"-gneiss IR would be of a crustal rather than upper mantle signature, or the amphibolites would contain crustal Sr.

The following scenario attempts to explain the reasons for crustal materials, like the probably clastic sedimentary protoliths of the gneisses, containing upper mantle Sr.

The source region of the predecessors of the gneisses comprised felsic igneous rocks, differentiation products of upper mantle magmas. These felsic rocks were of a very short residence time in the crust. As a result, they preserved a primary Sr isotope composition characteristic of their upper mantle provenance (Moorbath, 1977). Sediments derived from such crustal regions shortly after the formation of the felsic rocks have depositional $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7051$ (McDermott and Hawkesworth, 1990). Accordingly, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the predecessors of the gneisses probably reflected those of the felsic igneous rocks. If the aforementioned source region included mafic igneous rocks of low $^{87}\text{Sr}/^{86}\text{Sr}$ values, more upper mantle Sr was donated to the protoliths of the gneisses. Alternatively, or additionally, the precursors of the gneisses were possibly enriched in upper mantle Sr, during the course of mafic igneous activity contemporaneous to, or succeeding their formation.

A functional relationship between the protoliths of the gneisses and rocks which are of short residence time in the crust and bear upper mantle Sr, is not the single precondition for the former to furnish low $^{87}\text{Sr}/^{86}\text{Sr}$ values. Equally necessarily, the time elapsed since the formation of the protoliths of the gneisses and until their Sr was homogenized has to be rather short; otherwise, the protoliths considered would have developed significant ^{87}Sr amounts through ^{87}Rb decay - which they have not.

4.3.2. "YOUNGER"-GNEISSES IR

The "younger"-gneisses were part of the geological system which underwent Sr homogenization in the course of the $337 \pm 5\text{Ma}$ metamorphic event. Hence, at $337 \pm 5\text{Ma}$, these gneisses were characterized by a uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratio equal to the IR of the "older"-gneisses. Since then and until the culmination of the retrograde metamorphism advocated, ie within $\approx 224\text{Ma}$, the "younger"-gneisses developed a weighted average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.70984 - implying a $^{87}\text{Sr}/^{86}\text{Sr}$ increase of about $0.239 \times 10^{-4}/\text{Ma}$. Following the Sr rehomogenization which coupled the metamorphic retrogression, the 0.70984 value became the reset IR of the "younger"-gneisses.

5. DISCUSSION-CONCLUSIONS

The Rb-Sr isotope study disclosed that a high grade metamorphism of the Olympias gneisses culminated in the Early Carboniferous, at about 337Ma. The 337Ma date is the oldest radiometric age reported from the SMM, until now. Because this date is coupled with a very low IR, it is unlikely that: (a) long time elapsed between rock genesis and metamorphism and (b) another metamorphic event preceded the 337Ma one. Thus, the 337Ma high grade metamorphism is probably the oldest metamorphic event affecting the deeper parts of the SMM, corresponding to the amphibolite facies regional metamorphism of the study area. Consequently, the "conventional" view regarding the age of the older regional metamorphism of the SMM as late Precambrian (e.g. Kockel et al, 1977), should rather be abandoned. The new findings also suggest that the hiatus between the regional metamorphism and the formation of the circum Rhodope belt is in the likely range of 50-60Ma, instead of the about 300Ma indicated by the older concepts.

The Rb-Sr isotope data have also indicated that the study area has been affected by a retrograde metamorphic event of moderate intensity, at about 113Ma (Early Cretaceous). This event is younger than the Early Jurassic (180Ma) greenschist facies retrograde metamorphism of the SMM, recognized by Kockel et al (1977). However, it corresponds well: (a) to a younger (113Ma!) greenschist facies metamorphism reported by the same authors (1/100,000 map of the Halkidiki, and accompanying explanatory memoir); and (b) to a Cretaceous upper greenschist facies retrograde metamorphic event (overprinting an amphibolite facies regional metamorphism), recognized by Papadopoulos and Kilias (1985) at mountain Vertiskos north of Lake Volvi (30-40km NW of Olympias district) - average Rb-Sr, K-Ar ages obtained from white micas, biotites and hornblends: about 115Ma. Accordingly, the reset age determined is, with an uncertainty of 11Ma, the age of the more intensive retrograde greenschist facies metamorphism affecting the deeper regions of the SMM.

The uncertainties regarding the accuracy of the isotopic ages determined, are probably related to postmetamorphic geological disturbances of the isotopic systems established during the course of the successive metamorphisms of the deeper parts of the SMM. They may also be linked with the patchy manner that Sr reequilibration was effected during the younger metamorphic event.

A significant deduction emanating from the study of IRs is that the clastic sedimentary precursors of the gneisses, enclosed a dominant Sr component of upper mantle provenance. This has been interpreted as indicating that the source regions of the aforementioned precursors comprised felsic igneous rocks of short residence time in the crust and, possibly, some mafic igneous rocks. Furthermore, mafic igneous matter may have been injected into the protoliths of the gneisses, in situ. Source regions and petrogenetic processes, such as those implied, are compatible with tectonic settings related to continental rift basins, active continental margins, marginal basins, continental arcs, or even a combination of these

environments. The petrological environment and the geochemistry of the local metamorphic rocks in connection with their Pb isotope composition rather favour the marginal basin option (Mantzou, 1989).

Having established the gneiss forming event as 337 ± 5 Ma old, it may be attempted to infer a rough estimate of the sedimentation age at Olympias, firstly on the basis of the pressure conditions prevailing during metamorphism, and considerations regarding the local sedimentation rate (SR); and secondly on account of the IRs determined and the local rate of radiogenic ^{37}Sr production.

At Olympias the regional metamorphism reached a pressure of 3.5Kb (Dimitriadis, 1974). The effective pressure is a function of the load of the overlying rocks. Provided that the predecessors of the gneisses were of a low density – as is normally the case with clastic rocks – pressure increased with depth at a rate of about 250b/km (Winkler, 1979; p.18). Accordingly, assuming that the original stratigraphic sequence had not been significantly disturbed through e.g. multiple folding, a 3.5Kb metamorphic pressure corresponds to a sedimentary rock cover as thick as 14km (Winkler, 1979: Fig 7.4). According to Schwab (1976), fore-arc, back-arc (marginal sea) and rift basins are characterized by average SRs of 0.12-0.17m/1,000a. Conversely, Kennett (1982; p.464) advocates SRs of 0.10m/1,000a and occasionally over 0.20-0.30m/1,000a, at inland seas. Assuming that a reasonable approximation of the SR at Olympias would possibly be at the range of 0.10-0.20m/1,000a (potentially closer to the upper end of the range) the foregoing indicate that sedimentation had possibly been accomplished 140-70Ma prior to the culmination of the regional metamorphism, ie at around 480-410Ma. As a result of the requirement for a short time interval between sedimentation and regional metamorphism (section 4.3.1), a sedimentation age closer to 410Ma is a more acceptable estimate – faster SRs and/or extensive folding of the area would point towards the possibility of an even younger sedimentation age. Such an age also complies with the concept, that metamorphism generally occurred shortly after sedimentation, on the European continent (Jäger, 1979b).

A younger sedimentation age is further supported by calculations involving the rate of $^{87}\text{Sr}/^{86}\text{Sr}$ increase in the time span between the two metamorphic events. Accepting that since sedimentation the above rate ($=0.239 \times 10^{-4}/\text{Ma}$; section 4.3.2) remained more or less constant, and that the IR of the precursors of the gneisses could not have been lower than 0.7036 – even in case these precursors were as old as 1Ma (Faure, 1977; p.113: terrestrial Sr evolutionary trends) –, the time elapsed since sedimentation and until the culmination of the regional metamorphism is $(0.70448 - 0.7036)/(0.239 \times 10^{-4}/\text{Ma}) = 37\text{Ma}$, where 0.70448 is the "older"-gneisses IR. Accordingly, sedimentation could be as young as 374Ma (Early Devonian).

Having suggested that the Olympias sulphide deposit has formed syngenetically (Mantzou, 1989), it is possible that its age is Silurian to Early Devonian. The high grade metamorphic features of the ore have been developed in response to the Early Carboniferous

amphibolite facies metamorphism, whereas its lower grade metamorphic characteristics are likely a manifestation of the Early Cretaceous metamorphic retrogression.

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