

Nitrogen and N-isotope variation during low-grade metamorphism of the Taiwan mountain belt

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To investigate factors affecting the evolution of nitrogen system in rocks during progressive metamorphism, unmetamorphosed to greenschist-facies pelitic samples were collected from both pelitic and (pelitic members of) psammitic rock sequences along two transects of the Taiwan mountain belt. Among all samples, greenschist-facies metapelites from the Tananao metamorphic basement of this mountain belt exhibit the most variable and depleted nitrogen content and $\delta^{15}\text{N}$ values. The observations are difficult to interpret and can only be accounted for by complicated tectonic/metamorphic history of the basement complex. On the other hand, irrespective of the different metamorphic grades, samples from the metamorphosed cover strata, which have been subjected to only one stage of metamorphism, show comparable nitrogen and N-isotope composition. The only exception is that greenschist-facies metapelites from the pelitic members of psammitic rock sequence (i.e., the G(Ps) group samples) of the cover strata are enriched in the ^{15}N isotope by at least 1‰. Taking Al content as a normalizing factor, averaged N/Al and LOI/Al show systematic decrease through progressive metamorphism. Given the non-homogeneous nature of the sedimentary protoliths, the comparable N-isotope composition among the unmetamorphosed to zeolite-facies (i.e., S-Z) group, prehnite-pumpellyite-facies (i.e., PP) group and greenschist-facies (i.e., G) group samples from pelitic rock sequences can be explained by rock devolatilization with limited nitrogen depletion (<10%). High $\delta^{15}\text{N}$ composition of the G(Ps) group samples might be mainly due to more extensive nitrogen depletion (~25%). It is suggested that during metamorphism, the pelitic rock sequence may approximate a closed system, while thick psammitic rock sequence may behave more like an open system, facilitating nitrogen depletion and N-isotope fractionation even for thin pelitic members within a thick psammitic sequence. Lithology, in addition to other factors, therefore plays a role in controlling the evolution of the nitrogen system during low-grade metamorphism. The present study implies that element transport by dehydration fluid in subduction zones may largely take place along fluid channel ways.

Keywords: nitrogen isotope, devolatilization, subduction zone, Taiwan

INTRODUCTION

In metasedimentary rocks, nitrogen is a minor component. It occurs either as ammonium substituting for potassium, in minerals such as micas and feldspars, or resides in carbonaceous material. During prograde metamorphism, some nitrogen would be released from rock into the fluid phase as a result of dehydration/decomposition of silicates or maturation of carbonaceous material. Theoretically, such nitrogen depletion processes would be accompanied by nitrogen isotope fractionation. The nitrogen content and nitrogen isotope composition of rocks would therefore be useful tracers in unraveling fluid/material transfer in subduction zones (e.g., Bebout,

1997; Bebout *et al.*, 1999a). In addition, the nitrogen depletion may also be coupled with the depletion of some mobile elements, such as Rb and Cs, because they mainly reside in K-bearing minerals (e.g., Kerrich, 1989; Busigny *et al.*, 2003).

Despite the above theoretical predictions, recent case studies on the behavior of nitrogen and nitrogen isotopes during prograde metamorphism actually showed conflicting results. In studying the Erzgebirge of the European Variscan belt and the Catalina Schist, California, Haendel *et al.* (1986), Bebout and Fogel (1992) and Mingram and Brauer (2001) demonstrated that there was indeed a significant loss of nitrogen (as well as other mobile elements) and that N-isotope fractionation accompanied devolatilization during prograde metamorphism, although Haendel *et al.* (1986) noted that the observed variations could alternatively be accounted for by primary compositional differences of protoliths. Similar trends

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with extreme nitrogen depletion and N-isotope enrichment were also reported for Archean chert and banded iron formation by Pinti *et al.* (2001). On the other hand, Busigny *et al.* (2003) and Pitcairn *et al.* (2005) showed that metamorphic rocks largely retained N-isotope composition of their protolith sediments and that there was little or no isotopic fractionation with limited devolatilization of nitrogen (or other mobile elements) during metamorphism of the Schistes Lustres nappe and the Otago/Alpine Schists. The latter conclusion actually supported the postulate that high fluxes of some trace elements in arc magmas cannot be accounted for by dehydration of metamorphic rocks during subduction. Partial melting must have played an important role (e.g., Spandler *et al.*, 2003). To understand the possible reasons for such different observations of nitrogen behavior during metamorphism is important in further utilizing this potentially important tracer to study various geological processes.

It was suggested that the apparent conflict in the behavior of nitrogen mentioned above may be a result of different geothermal gradients in different terranes, i.e., low geothermal gradients, subparallel to dehydration reactions, may not lead to N-isotope fractionation in rocks during progressive metamorphism (Busigny *et al.*, 2003). Alternatively, it may be partly due to the fact that rock units in composite terranes might have different protolith ages and experienced different metamorphic history, i.e., different *P-T-t* paths (Haendel *et al.*, 1986; Pitcairn *et al.*, 2005). It is known that nitrogen content and nitrogen isotope compositions of protolith sediments vary with geologic time (e.g., Pitcairn *et al.*, 2005; Kerrich *et al.*, 2006; and the references therein). Different protolith age and different metamorphic history may thus obscure the N-system systematics of the metamorphic rocks. To avoid such possible complications, the present study deals with the nitrogen system in Miocene–Eocene rocks from the cover strata with a simple tectonic history of a young mountain belt. The metamorphic basement of this mountain belt, with a more complicated geohistory, was also included as a comparison. In addition, pelitic rock samples were collected from both pelitic and (pelitic members of) psammitic sequences to test the possible effect of lithology on evolution of the nitrogen system.

GEOLOGICAL BACKGROUND AND SAMPLING

The Taiwan mountain belt, resulting from ongoing collision between the Eurasia and the Philippine Sea plate since the Plio–Pleistocene, is situated along the Eurasian plate margin (Fig. 1; Ho, 1986). The main part of the mountain belt consists of an Upper Paleozoic–Mesozoic basement complex (i.e., the Tananao Metamorphic Complex) and an unconformably overlying Cenozoic cover series. Whereas the basement complex has a complicated

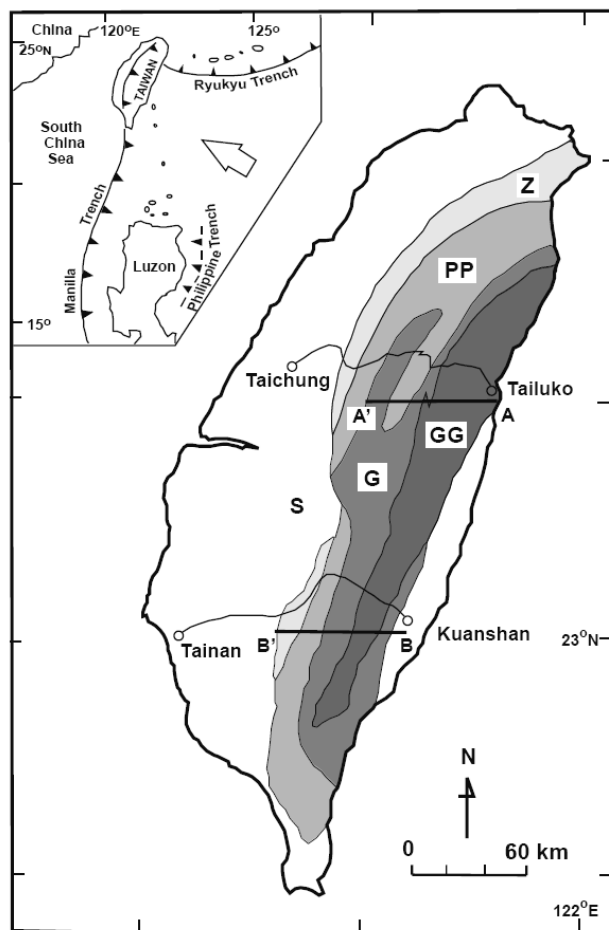


Fig. 1. Metamorphic facies map of Taiwan (after Chen *et al.*, 1983). S, unmetamorphosed sedimentary rocks; Z, zeolite facies; PP, prehnite-pumpellyite facies; G, greenschist facies; GG, polymetamorphosed greenschist facies. See text for details. Inset shows the present tectonic environment around Taiwan. Samples were collected along A–A' and B–B' transects.

metamorphic history, probably subjected to at least three stages of tectonism (Yui *et al.*, 1990), the cover strata have only been subjected to the late-Cenozoic collision metamorphism (Liou and Ernst, 1984, Yui *et al.*, 1990).

According to the metamorphic facies map (Chen *et al.*, 1983; Chen and Wang, 1995), rocks in the Taiwan mountain belt can be divided into: (1) an amphibolite facies (A) group of the pre-Tertiary basement complex; (2) a polymetamorphosed greenschist facies (GG) group of the pre-Tertiary basement complex; (3) a greenschist facies (G) group of the Tertiary cover strata; (4) a prehnite-pumpellyite facies (PP) group of the cover strata; (5) a zeolite facies (Z) group; and (6) unmetamorphosed sedimentary rocks (S) (see Fig. 1). Lithologically, the A group consists of scattered amphibolite and epidote amphibolite,

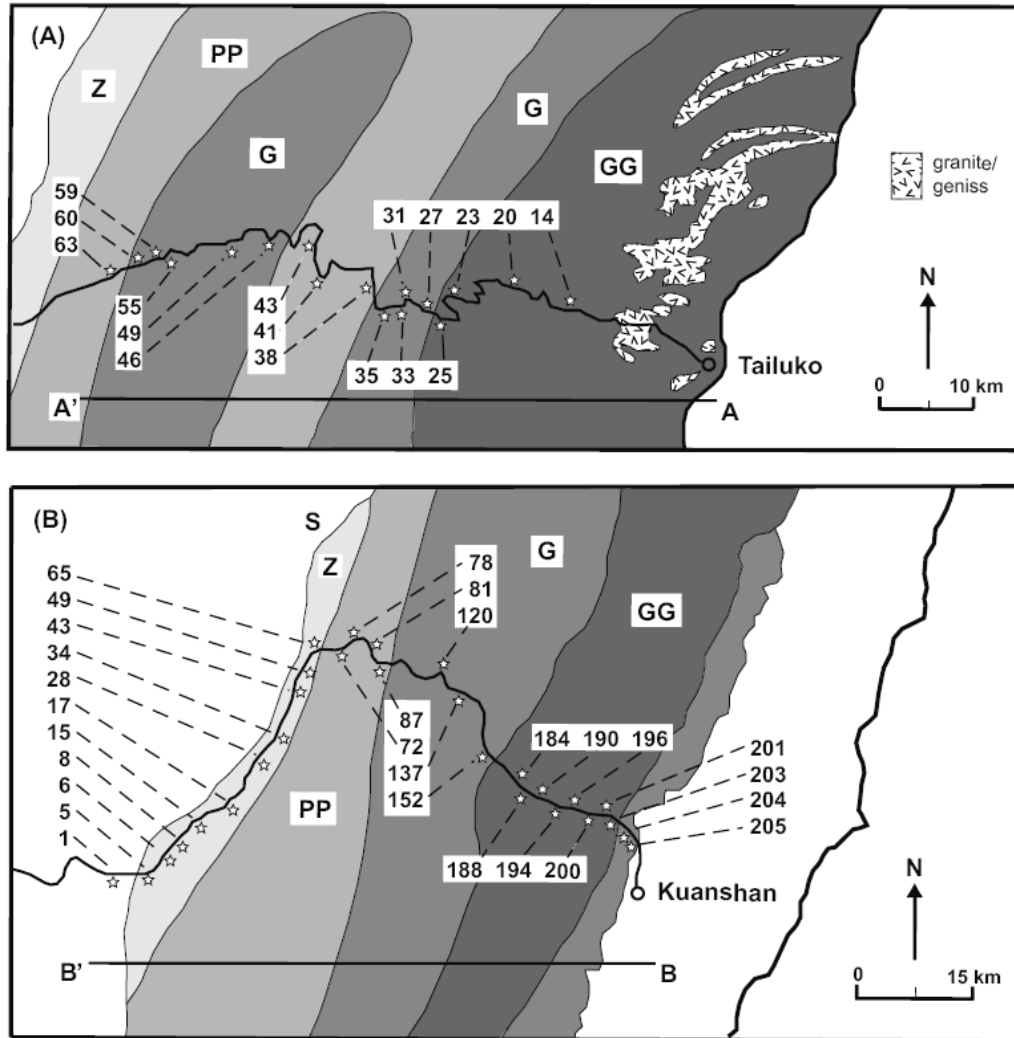


Fig. 2. Sample localities (open stars) along (A) A–A' and (B) B–B' transects. S, Z, PP, G, and GG are the same as Fig. 1. Samples 49, 55, 59 and 60 along A–A' were collected from pelitic members of thick psammitic rock sequence (i.e., the Tachien Metasandstone). All other samples are from pelitic rock sequences.

as well as granitic gneisses in the pre-Tertiary basement. The GG group is composed of marble/schist/phyllite of the Tananao Metamorphic Complex. The G and PP group mainly comprise phyllite/slate/argillite/metasandstone of the Eo–Oligocene Tachien Metasandstone/Chiayang Formation, the Eocene Pilushan Formation, and the Miocene Lushan Formation. The S and Z groups comprise shale/sandstone of the Miocene and younger formations (Ho, 1986). Based on carbon isotope fractionations between calcite and carbonaceous material, Yui (2005) showed that the temperature conditions of the Cenozoic metamorphism may be most likely lower than 500°C.

In the present study, pelitic rocks were collected along two highways crossing the mountain belt: the Central E–W Cross-Island Highway (A–A') and the Southern E–W

Cross-Island Highway (B–B') (Figs. 1 and 2). For all samples studied, although modal content may vary slightly, mineral compositions of pelitic samples from the same metamorphic grade are generally the same (see Table 1). It should be noted that most samples were collected from thick pelitic rock sequences, except samples C-60, C-59, C-55 and C-49 along the western part of section A–A'. The latter four samples were from thin (tens of meters) pelitic members within the Tertiary greenschist-facies thick psammitic rock sequence (i.e., the Tachien Metasandstone) and are grouped as G(Ps) to distinguish from other Tertiary G group samples. Mineral compositions, however, are similar for samples either from thick pelitic sequence or from thin pelitic members within psammitic sequence (Chen *et al.*, 1984).

Table 1. Mineral compositions of pelitic rocks of different metamorphic grades in the present study

Sample*	Mineral composition
S-group shale	smectite, kaolinite, feldspars, quartz, calcite, mixed-layer clays, and carbonaceous material
Z-group argillite	illite/smectite, kaolinite, quartz, feldspars, calcite, and carbonaceous material
PP-group phyllite/slate	chlorite-illite, kaolinite, quartz, albite, calcite, and carbonaceous material
G-group phyllite/schist	quartz, albite, white mica, chlorite, calcite, titanite, and carbonaceous material
GG-group schist	quartz, albite, white mica, biotite, chlorite, calcite, titanite, epidote, and carbonaceous material

*Samples from different metamorphic grades.

S, sedimentary rocks; Z, zeolite facies rocks; PP, prehnite-pumpellyite facies rocks; G, greenschist-facies rocks; GG, high-grade greenschist-facies basement rocks.

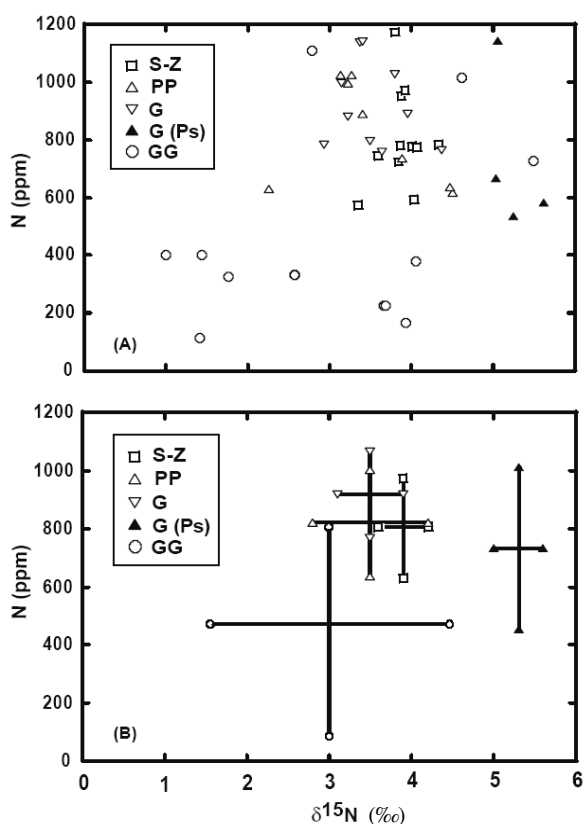


Fig. 3. (A) Nitrogen and N-isotope compositions for samples studied. (B) Averaged nitrogen and N-isotope compositions for samples of different metamorphic grades. The error bars are one standard deviation. S-Z, unmetamorphosed to zeolite-facies group samples; PP, prehnite-pumpellyite-facies group samples; G, greenschist-facies group samples collected from pelitic rock sequence; G(Ps), greenschist-facies group samples collected from psammitic rock sequence; and GG, polymetamorphosed greenschist-facies group samples from the basement complex.

ANALYTICAL METHODS

The pulverized rock samples, 50–100 mg, were analyzed for their nitrogen content and N-isotope composition in a Carlo-Erba EA 2100 elemental analyzer connected to a Thermo Finnigan Delta Plus Advantage IRMS located at the Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan. The detection limit of nitrogen measurement is $1 \mu\text{g N}$, based on a pure compound, Acetanilide (Merck) with a N content of 10.36%. In this study, the precision of nitrogen content measurement is better than $\pm 2\%$. Isotopic composition is presented in standard δ notation with respect to atmospheric nitrogen. Working standard for N isotopes is USGS 40 (L-glutamic Acid), which has a certified $\delta^{15}\text{N}$ value of -4.5‰ and with a N content of 9.52%. The long-term standard deviation of N-isotope determination for USGS 40 is better than $\pm 0.2\text{‰}$. It is noted that Brauer and Hahne (2005) reported that nitrogen content and N-isotope composition of rocks analyzed by an elemental analyzer coupled with an isotope mass spectrometer, like the one employed in this study, are sometimes lower than those derived from the conventional dissolution and distillation method (Haendel *et al.*, 1986). On the other hand, Jia (2006) reported comparable N-isotope compositions of mica from both methods. Further studies may be necessary to evaluate the different methods.

Chemical analysis on selected samples was carried out at the Department of Geology, University of Western Ontario. Major-element analyses were by X-ray fluorescence spectrometry, following the methods of Norrish and Hotton (1969). Spectral interferences were corrected for by using pre-calculated interfering factors. In general, the precision for all major-element determinations was better than 5%.

RESULTS

Nitrogen content and N-isotope composition

Nitrogen content and N-isotope composition of all samples in the present study are shown in Table 2 and

Table 2. Nitrogen content and nitrogen isotope composition of rock samples used in this study

	N (ppm)	$\delta^{15}\text{N}_{\text{air}}$ (‰)	T (°C) ⁽¹⁾	Remarks ⁽²⁾
Central Cross-Island Highway				
C-63	996	+3.2	200 < T < 300	PP
C-60	535	+5.3	341	G (Ps)
C-59	667	+5.0	~360	G (Ps)
C-55	1143 ± 55(2) ⁽³⁾	+5.1 ± 0.2(2)	~430	G (Ps)
C-49	584	+5.6	408	G (Ps)
C-46	998	+3.1	~350	G
C-43	1026	+3.3	200 < T < 300	PP
C-41	630	+2.3	200 < T < 300	PP
C-38	1025	+3.1	200 < T < 300	PP
C-35	1142	+3.4	300 < T < 350	G
C-33	1136	+3.4	300 < T < 350	G
C-31	880	+3.2	300 < T < 350	G
C-27	784	+2.9	300 < T < 350	G
C-25	400	+1.4	367	GG
C-23	400 ± 18(2)	+1.0 ± 0.2(2)	~380	GG
C-20	332	+2.6	397	GG
C-14	327	+1.8	464	GG
Southern Cross-Island Highway				
S-1	575	+3.3	<200	S-Z
S-5	725	+3.8	<200	S-Z
S-6	953	+3.9	<200	S-Z
S-8	593	+4.0	<200	S-Z
S-15	776 ± 25(2)	+4.0 ± 0.3(2)	<200	S-Z
S-17	1192	+3.8	<200	S-Z
S-28	784	+4.3	<200	S-Z
S-34	972	+3.9	<200	S-Z
S-43	779	+3.9	<200	S-Z
S-49	774	+4.1	<200	S-Z
S-65	745	+3.6	<200	S-Z
S-72	618	+4.5	200 < T < 300	PP
S-78	889	+3.4	200 < T < 300	PP
S-81	636	+4.5	200 < T < 300	PP
S-87	736 ± 10(2)	+3.9 ± 0.1(2)	200 < T < 300	PP
S-120	890	+4.0	300 < T < 350	G
S-137	758	+3.6	349	G
S-152	797	+3.5	438	G
S-184	1109	+2.8	~440	GG
S-188	1014	+4.6	~440	GG
S-190	728	+5.5	~440	GG
S-194	379	+4.1	451	GG
S-196	105 ± 1(2)	+1.4 ± 0.2(2)	406	GG
S-200	227	+3.7	410	GG
S-201	225	+3.7	430	GG
S-203	166	+3.9	404	GG
S-204	1028	+3.8	367	G
S-205	764	+4.4	300 < T < 350	G

⁽¹⁾Temperature estimates taken from Chen and Wang (1995) and Yui (2005).

⁽²⁾Metamorphic grade of rock samples. S-Z, sedimentary to zeolite facies rocks; PP, prehnite-pumpellyite facies rocks; G, greenschist-facies rocks; GG, high-grade greenschist-facies basement rocks. Ps indicates pelitic samples from psammitic sequence. See text for details.

⁽³⁾Number of analysis.

Table 3. Average composition of samples from each metamorphic zone

	$\delta^{15}\text{N}$ (‰)	N (ppm)	(N/Al) \times 100 (molar ratio)	(K/Al) (molar ratio)	(N/K) \times 100 (molar ratio)	LOI/Al ₂ O ₃ (weight ratio)	τ (N vs. Al) ⁽⁴⁾	F ⁽⁵⁾
SZ ⁽¹⁾	3.9 \pm 0.3 ⁽²⁾ (11) ⁽³⁾	806 \pm 176 (11)	1.95	0.27 (4)	7.22 (4)	0.48 (4)	—	—
PP	3.5 \pm 0.7 (8)	820 \pm 184 (8)	1.83	0.25 (4)	7.32 (4)	0.40 (4)	-0.06	0.94
G	3.5 \pm 0.4 (10)	918 \pm 149 (10)	1.75	0.24 (4)	7.29 (4)	0.24 (4)	-0.10	0.90
G(Ps)	5.3 \pm 0.3 (4)	732 \pm 279 (4)	1.44	0.25 (4)	5.76 (4)	0.24 (4)	-0.25	0.75
GG	3.0 \pm 1.4 (12)	443 \pm 336 (12)	—	—	—	—	—	—

⁽¹⁾SZ, PP, G, GG and Ps are the same as footnote (2) in Table 2.

⁽²⁾One standard deviation.

⁽³⁾Number of analysis.

⁽⁴⁾Fraction of N loss relative to Al.

⁽⁵⁾Fraction of the initial N remaining in the rock.

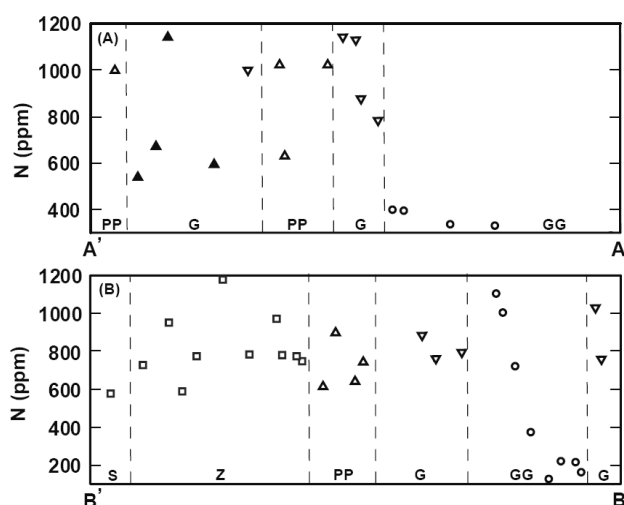


Fig. 4. Cross sections showing variations of nitrogen content along (A) A–A' and (B) B–B' transects. S, Z, PP, G, and GG are the same as Fig. 1. Symbols for samples of different metamorphic grades are the same as those in Fig. 3.

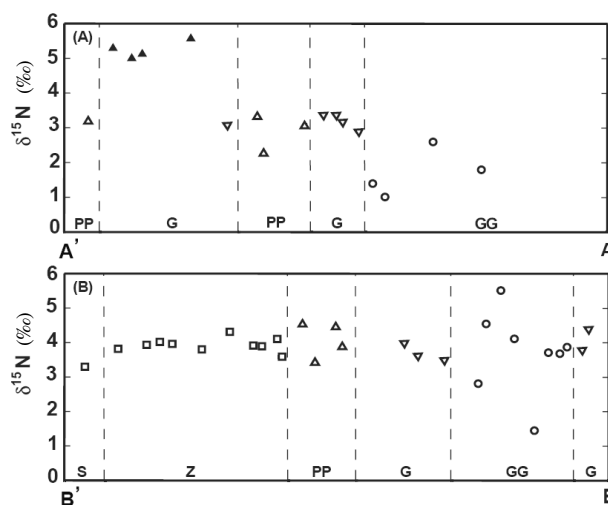


Fig. 5. Cross sections showing variations of N-isotope composition along (A) A–A' and (B) B–B' transects. S, Z, PP, G, and GG are the same as Fig. 1. Symbols for samples of different metamorphic grades are the same as those in Fig. 3. Note that the four G (Ps) samples, represented as solid triangles along A–A' transect, have high $\delta^{15}\text{N}$ -values.

Fig. 3A. Also included in Table 2 are the estimated metamorphic temperatures for each sample, derived from Chen and Wang (1995) and Yui (2005). The averaged nitrogen content and N-isotope composition of S-Z, PP, G, G(Ps) and GG group samples are listed in Table 3 and plotted in Fig. 3B. They are 806 \pm 176 ppm and +3.9 \pm 0.3‰ for eleven S-Z group samples; 820 \pm 184 ppm and +3.5 \pm 0.7‰ for eight PP group samples; 918 \pm 149 ppm and +3.5 \pm 0.4‰ for ten G group samples from pelitic rock sequences; 732 \pm 279 ppm and +5.3 \pm 0.4‰ for four G(Ps) group samples from psammitic rock sequence; and 443 \pm 336 ppm and +3.0 \pm 1.4‰ for twelve GG group samples. From these data, it is evident that the GG group samples have the most variable and also the lowest averaged nitrogen content and $\delta^{15}\text{N}$ values. The G(Ps) group sam-

ples, however, exhibit the highest $\delta^{15}\text{N}$ results. Nitrogen contents and N-isotope compositions of samples along the two transects are shown in Figs. 4 and 5, respectively.

Chemical composition

Major-element compositions of 16 selected samples of the Tertiary cover strata are given in Table 4. SiO₂ and Al₂O₃ are the major components, ranging from 55.77 to 66.40% and 13.74 to 20.48%, respectively, reflecting the pelitic nature of these samples. Some chemical variations among these metasedimentary rocks are not unexpected. Generally speaking, compositional variations among samples are not large. K and Al show a slight progressive

Table 4. Chemical compositions of representative samples in the present study

Sample	S-6	S-15	S-34	S-49	S-78	S-87	C-41	C-43	S-137	S-152	C-27	C-35	C-49	C-55	C-59	C-60
SiO ₂	59.16	64.18	61.94	59.97	56.51	63.22	65.27	55.77	59.76	56.82	66.40	57.84	65.18	58.31	62.28	65.33
TiO ₂	0.83	0.82	0.76	0.83	0.58	0.75	0.83	0.90	0.80	0.86	0.72	0.82	0.71	0.69	0.67	0.81
Al ₂ O ₃	16.42	14.56	13.74	15.60	15.14	17.79	14.55	17.90	19.13	18.95	17.96	20.48	18.01	19.10	18.93	17.84
FeO	6.02	4.91	6.00	5.34	4.95	4.39	5.18	5.99	6.38	6.53	2.82	6.60	3.82	7.65	5.31	4.76
MnO	0.06	0.06	0.06	0.05	0.11	0.03	0.07	0.11	0.05	0.10	0.03	0.06	0.06	0.10	0.04	0.08
MgO	2.62	2.03	2.68	2.01	1.94	1.83	1.84	2.52	1.90	2.77	1.54	2.14	1.54	2.62	1.70	1.54
CaO	1.54	0.96	2.97	2.35	6.03	1.44	1.61	2.91	1.37	1.59	0.30	0.39	0.15	0.30	0.71	0.31
K ₂ O	4.34	3.68	2.13	3.72	2.78	4.01	3.86	4.16	4.10	4.15	4.54	3.77	4.02	3.53	4.44	4.93
Na ₂ O	1.04	1.26	0.78	0.86	1.19	1.31	1.16	1.18	1.29	1.09	2.66	1.31	0.98	0.51	1.12	0.38
P ₂ O ₅	0.12	0.12	0.11	0.12	0.10	0.14	0.11	0.15	0.13	0.20	0.09	0.16	0.20	0.17	0.12	0.22
L.O.I.	6.88	7.14	8.64	8.37	9.43	5.38	4.68	8.11	5.02	6.09	3.34	5.84	5.24	6.40	5.00	3.82
Total	99.03	99.72	99.81	99.22	98.76	100.29	99.16	99.70	99.93	99.15	100.40	99.41	99.91	99.38	100.32	100.02
	S-Z(S)*	S-Z(S)	S-Z(S)	S-Z(S)	PP(S)	PP(S)	PP(C)	PP(C)	G(S)	G(S)	G(C)	G(C)	G(C-Ps)	G(C-Ps)	G(C-Ps)	G(C-Ps)

*S-Z, PP, G, and Ps are the same as footnote (2) in Table 2.

(S) - samples collected from the Southern Cross-Island Highway, and (C) - samples collected from the Central Cross-Island Highway.

increase and LOI shows a progressive decrease for samples from S-Z, PP to G/G(Ps) groups.

DISCUSSION

Variations of the nitrogen system between units with different geohistories

Whereas the cover strata of the Taiwan mountain belt has been subjected to only one stage of metamorphism during the late Cenozoic collision tectonism, the pre-Tertiary Tananao metamorphic basement has experienced at least three stages of tectonic processes, including the late Triassic–early Jurassic subduction, the late Cretaceous subduction, and the late Cenozoic collision (Yui *et al.*, 1990). The present mineral assemblages in most basement rocks belong to the greenschist-facies metamorphic grade. A few amphibolite-facies rocks were interpreted as tectonic blocks emplaced during the Mesozoic tectonics or resulting from Mesozoic granitic intrusions (e.g., Liou, 1981). Actually, most basement rocks might have been extensively recrystallized during the late Cenozoic collision metamorphism and the Mesozoic amphibolite-facies minerals might have only been preserved as nanometer-scale mineral inclusions (Chen *et al.*, 1983; Hwang *et al.*, 2001). The estimated metamorphic temperatures listed in Table 2 are those for the late Cenozoic metamorphism.

Compared with the cover strata, rocks in the Tananao metamorphic complex show larger variations in both nitrogen content (105–1109 ppm) and N-isotope composition (+1.0 to +5.5‰) (Fig. 2). Taking samples with comparable metamorphic temperatures into consideration, some basement rocks, especially those along the A–A' section, exhibit unexpectedly low nitrogen contents (<400 ppm) and low $\delta^{15}\text{N}$ values (<2‰), compared to those G-group samples of the cover strata (N > 530 ppm and $\delta^{15}\text{N}$ > 3.0‰, see Table 2). Such differences could be simply

attributed to the different nitrogen content and N-isotope composition between sedimentary protoliths of the cover strata and the metamorphic basement, since it is known that sedimentary rocks have large ranges in nitrogen content (i.e., from <100 ppm to >15000 ppm) and N-isotope composition (i.e., from –3 to +9‰) (e.g., Holloway and Dahlgren, 2002). However, considering that some basement rocks along the B–B' section actually have comparable nitrogen content and N-isotope composition as the cover strata, the above postulate may be less likely. Alternatively, the low nitrogen content of the basement rocks may indicate that these samples have experienced higher grade metamorphism during Mesozoic tectonic events, assuming that the basement rocks have primary nitrogen and N-isotope compositions similar to the cover strata. However, the low $\delta^{15}\text{N}$ values of these samples are not consistent with this proposition, since higher metamorphic temperatures would not only cause more extensive nitrogen depletion but also lead to higher $\delta^{15}\text{N}$ composition, due to higher degrees of N-isotope fractionation. In studying the nitrogen system around contact aureole of granitic intrusions, Bebout *et al.* (1999b) suggested that low- $\delta^{15}\text{N}$ aureole-derived fluid might be responsible for those late-stage hydrothermal altered rocks with low $\delta^{15}\text{N}$ values. Mesozoic granitic intrusions are present within the Tananao basement (see Fig. 2) (Yui *et al.*, 1990). It is possible that the ^{15}N -depleted basement rocks might have resulted from reacting with low- $\delta^{15}\text{N}$ fluid derived from granitic intrusions during the Mesozoic. Unfortunately, the present granite-country rock (mostly marble along the A–A' transect) contacts are tectonic due to late Cenozoic tectonic reactivation; the original spatial relation between granitic intrusions and those samples with low $\delta^{15}\text{N}$ composition cannot be assured. Obviously, more detailed and systematic studies are needed to yield proper interpretations. In addition to that, the situation may be even more complicated by the facts that the nitrogen system may be

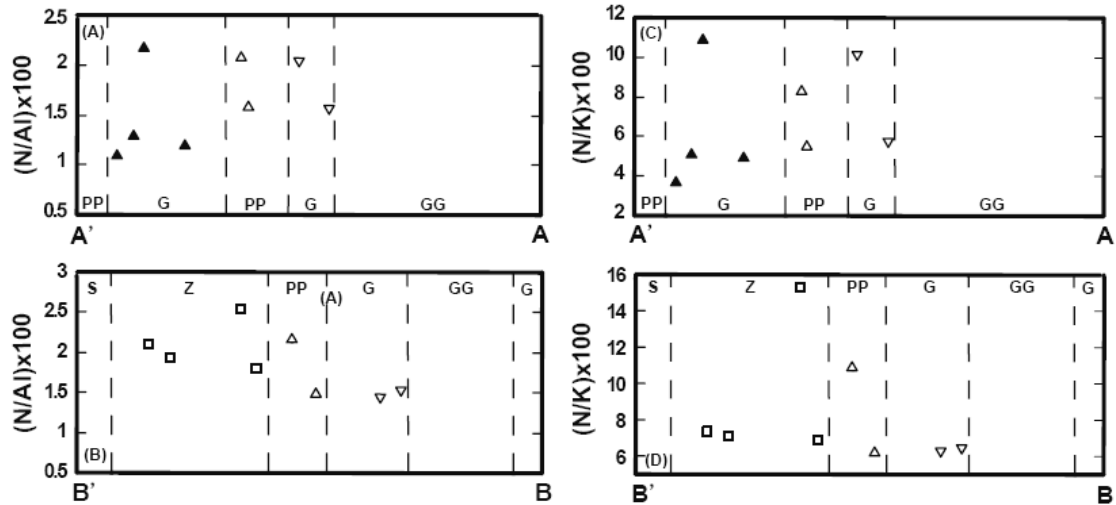


Fig. 6. Cross sections showing variations of N/AI (molar) ratio along (A) $A-A'$ and (B) $B-B'$ transects, and N/K (molar) ratio along (C) $A-A'$ and (D) $B-B'$ transects. S, Z, PP, G and GG are the same as Fig. 1. Symbols for samples of different metamorphic grades are the same as those in Fig. 3.

easily disturbed by retrograde metamorphic overprinting (Bos *et al.*, 1988) and that the Tananao basement has been subjected to at least three stages of metamorphism (Yui *et al.*, 1990). Although it is difficult to have a confirmed and satisfactory explanation, the present data certainly demonstrate the complexity in data comparisons/interpretations when dealing with rock units of different geohistory. The basement rocks are therefore excluded from the following discussion.

Evolution of the nitrogen system of the Tertiary cover strata

Isotopic variations due to metamorphism Irrespective of the different metamorphic grades, all samples from the cover strata have comparable nitrogen contents and N-isotope compositions, with the exception that the G(Ps) group pelitic samples have higher $\delta^{15}N$ values (Fig. 3). Note that the estimated metamorphic temperatures for the G(Ps) group samples (341–430°C, Table 2) are comparable to those of the G group samples (300–438°C, Table 2). One possible explanation for the observed difference is that the protoliths of the G(Ps) samples have heavy N-isotope compositions. However, the G(Ps) group samples were collected from thin pelitic layers within a thick psammitic sequence, i.e., the Tachien Metasandstone. It has been suggested that this Metasandstone is continent-derived sediments deposited in an early-rifting, slowly-subsiding, half-graben trough on the outer shelf along the south-east Chinese continental margin during the Eocene (Teng, 1992). For other G group samples in the present study, their protoliths were also continent-derived

sediments, deposited at the continental shelf/slope during the Eocene. Given the same sediment source/sedimentation age and proximity of sedimentations, the primary N composition is comparable at least for the G and the G(Ps) group samples.

It is also noted that Lehmann *et al.* (2002), based on incubation experiments, showed that oxic or anoxic environments may have different effects on the N-isotope variation of organic matter during early diagenesis. For example, in anoxic incubation experiments, $\delta^{15}N$ of organic matter decreases continuously by about 3‰. On the other hand, in oxic incubation experiments, the $\delta^{15}N$ of organic matter would increase by 3‰ before decreasing to the initial value. Although final steady state cannot be ensured for these experiments, the study indicated that organic matter in psammitic and pelitic rocks might evolve differently, due to different oxidation states (even if the organic matter originally has comparable N-isotope compositions). However, one should note that all samples collected in the present study are pelitic in nature, with similar mineral assemblages. Considering the impermeable nature of the pelitic rocks, the early diagenetic environments for these samples (even for the G(Ps) group pelitic samples from the psammitic rock sequence) should not be so different, leading to substantial N-isotope differentiation. If these arguments hold, it is suggested that the observed difference in N-isotope composition between the G and G(Ps) group samples would most probably have resulted from metamorphism.

Nitrogen devolatilization: Lithologic control To investigate compositional variations of a rock sequence through

progressive metamorphism, it may not be meaningful to compare the chemical compositions of samples, because not only rock composition but also rock volume changes during metamorphism. Because of this, it is a common practice to use the content of an immobile element as a normalizing factor to monitor the possible changes of other elements (e.g., Gresens, 1967; Ague, 1991). In the present case, Al is assumed to be immobile during low-grade metamorphism. The N/Al ratio along the B–B' transect shows a systematic decrease from the Z to the G group samples, although such a trend is not evident along A–A' transect (Figs. 6A and B). Considering the limited number of samples for chemical analysis in this study, and the heterogeneous nature of sedimentary rocks, the results may not be unexpected. Systematics, however, might be better revealed by the averaged data. Table 3 shows that averaged N/Al and LOI/Al ratios, and to a lesser extent K/Al ratio, do show a systematic decrease from S–Z to G group samples. Specifically, the averaged molar ratio of (N/Al) × 100 decreases from 1.95 for the S–Z group samples, through 1.83 for the PP group samples, to 1.75/1.44 for the G/G(Ps) group samples. These systematics may in turn imply that the two assumptions of the above comparisons may be justifiable, i.e., (1) these Miocene–Eocene metapelites from the cover strata of the Taiwan mountain belt might have comparable protolith compositions; and (2) Al was largely immobile during metamorphism. The present data therefore demonstrate that although nitrogen content decreases continuously during progressive metamorphism of the cover strata of the Taiwan mountain belt, N-isotope composition remain largely unchanged (around +3.5 to +3.9‰), except that the G(Ps) group samples exhibit distinctly high $\delta^{15}\text{N}$ values (+5.3 ± 0.3‰).

To quantitatively evaluate the extent of nitrogen loss during metamorphism, the mass change values can be calculated (after Ague, 1991) as:

$$\tau = [(C_{\text{Al}}^0/C_{\text{Al}}')/(C_{\text{N}}^0/C_{\text{N}}') - 1] \times 100$$

where τ is the percentage change of nitrogen relative to aluminum and C^0 and C' are the concentrations of element in the initial and final states, respectively. The calculated results are shown in Table 3. In average, compared with the S–Z group samples, the nitrogen loss is 6% for the PP group samples, 10% for the G group samples, and 25% for the G(Ps) group samples.

It has been suggested that nitrogen released from rock sequences during progressive metamorphism is generally in the form of N_2 or NH_3 (e.g., Haendel *et al.*, 1986). N-isotope fractionation between N_2 and ammonium or between NH_3 and ammonium would lead to $\delta^{15}\text{N}$ enrichment in the rock. N-isotope fractionations among these nitrogen species were calculated by Hanschmann (1981);

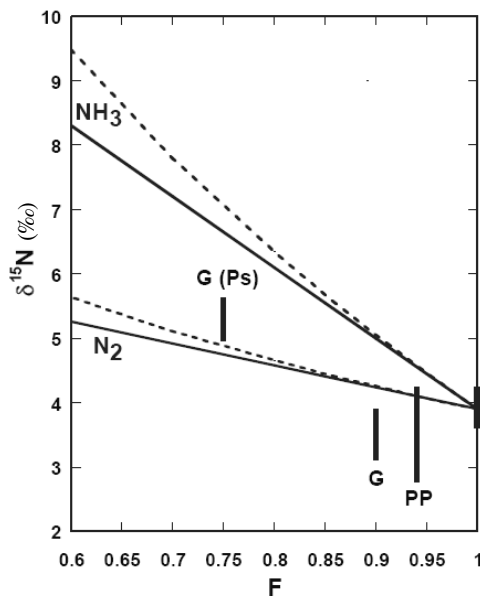


Fig. 7. Model calculations for N-isotope variation during batch (solid line) and Rayleigh (dashed line) devolatilization. Temperature condition is assumed to be 350°C. $\Delta^{15}\text{N}(\text{N}_2\text{--NH}_4^+)$ and $\Delta^{15}\text{N}(\text{NH}_3\text{--NH}_4^+)$ are -3.4‰ and -11.0‰ , respectively. Averaged N-isotope compositions of samples with different metamorphic grades from cover strata in the present study, along with respective F values (i.e., fraction of the initial N remaining in the rock) (see Table 3), are also shown for comparison. The averaged N-isotope composition of S–Z group samples, i.e., $+3.9 \pm 0.3\text{‰}$, is taken as the initial point. PP, prehnite-pumpellyite-facies group samples; G, greenschist-facies group samples collected from pelitic rock sequence; G(Ps), greenschist-facies group samples collected from pelitic members of psammitic rock sequence.

the results of those calculations for temperatures of 327–927°C are tabulated in Haendel *et al.* (1986). At 350°C, $\Delta^{15}\text{N}(\text{N}_2\text{--NH}_4^+)$ and $\Delta^{15}\text{N}(\text{NH}_3\text{--NH}_4^+)$ are about -3.4‰ and -11.0‰ , respectively.

The effect of nitrogen loss on the N-isotope composition can be quantitatively modeled as (1) batch devolatilization, where all released fluids are in equilibrium with the rock in a closed system, and (2) Rayleigh distillation, where each small aliquot of released volatile is immediately removed from the rock in an open system (see Valley, 1986). The modeling results at 350°C and the data in the present study are shown in Fig. 7. Given the inhomogeneous N-isotope composition of the sedimentary rock sequence, the overlapping N-isotopic compositions for the S–Z group samples, the PP group samples and the G group samples can be explained by either batch or Rayleigh distillation of the $\text{N}_2\text{--NH}_4^+$ system due to limited nitrogen loss (<10%). On the other hand, the

distinctly high $\delta^{15}\text{N}$ data for the G(Ps) group samples would be a result of higher extent of nitrogen loss (~25%) due, more probably, to Rayleigh distillation of the N_2 – NH_4^+ system.

In recent studies of progressive metamorphism of sedimentary sequences of a given age in subduction (Bebout and Fogel, 1992) or collision (Mingram and Brauer, 2001) complexes, the maximum N-isotope shift from little-metamorphosed protoliths to greenschist- and amphibolite-facies counterparts was in general ~1‰ and ~2‰, respectively. In studying granitic contact aureoles (Jia, 2006; Bebout *et al.*, 1999b), N-isotope shift in country rocks is also low (<1‰) in chlorite and biotite zone and may reach to 3–8‰ at the contact. Mica/K-feldspar decomposition may be the major mechanism to account for large N-isotope enrichment in high grade metamorphic rocks. On the other hand, despite variations, systematic N-isotope compositional variation with metamorphic grade was not observed for the Schistes Lustres complex (Western Alps) ($\delta^{15}\text{N} = +2.6$ to $+4.8$ ‰; Busigny *et al.*, 2003) and the Otago and Alpine Schists (New Zealand) ($\delta^{15}\text{N} = +0.2$ to $+7.0$ ‰; Pitcairn *et al.*, 2005). Busigny *et al.* (2003) attributed this lack of covariance to no (or little) N devolatilization occurring in sediments which metamorphosed along low geothermal gradients.

As a comparison, in the present study, the G group (i.e., greenschist-facies) samples show little N-isotope variation from the S-Z/PP group samples. In contrast, the G(Ps) group samples are enriched in ^{15}N by more than 1‰. The difference is distinct. As shown in Fig. 7, the enrichment in ^{15}N for the G(Ps) group samples is associated with a higher extent of nitrogen loss. The temperature conditions for both the G group and the G(Ps) group samples are comparable (see Table 2) and therefore should not be contributory. The present on-land geothermal gradient, as well as the geothermal gradient on sea floor to the south of Taiwan along the Manila trench, are variable but largely higher than 20–30°C/km (Chi and Donald, 2008). Although the geothermal gradient may vary in space and in time along subduction/collision zones, it seems improbable that the geothermal gradient is the major factor causing the observed difference in N-isotope variations, since all greenschist-facies metamorphic rocks from the cover strata of the Taiwan mountain belt might have experienced similar *P-T* paths, approximately synchronously, during Plio–Pleistocene collision metamorphism.

One noticeable difference between the G group and the G(Ps) group samples is that, despite both groups of samples being pelitic, the G(Ps) group samples with high $\delta^{15}\text{N}$ values were collected from the pelitic members of a psammitic sequence (i.e., from the Tachien Metasandstone) and G group samples were collected from pelitic sequences. The Tachien Metasandstone, with a total

thickness of 2700 meters, is composed of medium to coarse grained quartzite with thin intercalated metapelite (Chen, 1977). Numerous cross-cutting quartz veins, with thickness up to 0.5 m, testify that fluid activity occurred during metamorphism. It is possible that element release processes may be different between thick competent psammitic rock sequences and incompetent pelitic rock sequences. In the latter case, the process is approximated by closed-system batch devolatilization. In the former case, it is better described as an open-system Rayleigh distillation, facilitating fluid/element transfer even for the thin pelitic members within the psammitic sequence. Lithology therefore plays a role in the evolution of the nitrogen system, at least during low-grade progressive metamorphism. It should, however, be pointed out that the devolatilization model given in Fig. 7 is rather simple. It may not completely and precisely describe the real situation, which could be more complicated and may even involve open-system isotopic exchange. Further studies are obviously needed.

Nitrogen host One interesting point to note is that, relative to Al, nitrogen depletion is more pronounced than potassium for the G(Ps) group samples than for the G group samples (see Table 3). Since all samples have comparable mineral compositions, this difference indicates that the observed N depletion might not be related to K depletion only. This suggestion can be specifically exemplified by the N/K ratio. The averaged $(\text{N/K}) \times 100$ molar ratio for the G(Ps) group samples (i.e., 5.76) is distinctly lower than those of other group samples (i.e., 7.22–7.32) (Table 3), although the variation of N/K ratio of samples along the two transects is not so distinct, due to the abnormally high N content in the G(Ps) sample C-55 (Figs. 6C and D). It was noted that nitrogen depletion during low grade progressive metamorphism may not necessarily result solely from dehydration of silicates, and that maturation of carbonaceous material may also play a role (Pitcairn *et al.*, 2005). Unfortunately, the N-isotope fractionation mechanism during maturation of carbonaceous material in metamorphic rocks is not yet clear. In studying the organic nitrogen from contact metamorphic rocks, Ader *et al.* (2006) found that, despite significant nitrogen depletion, the averaged N-isotope composition of carbonaceous (organic) material remains largely unchanged during anchi-/epi-metamorphism up to semi-graphite stage (corresponding to amphibolite facies conditions). This observation was explained by assuming that, in the presence of water, the external reaction front progresses until nitrogen mineralization is complete, before progressing towards the interior part of the carbonaceous material (Ader *et al.*, 2006). If this scenario of batch loss of organic nitrogen is correct, the effect of maturation of carbonaceous material on the N-isotope variation observed in the present study would depend on

the amount of organic nitrogen released and the N-isotope composition of the carbonaceous material. Such an effect is difficult to evaluate quantitatively, although the content of carbonaceous material in rocks is rather low ($\ll 1\%$). It should be noted that the uncertainty of this effect would not affect the above conclusion about lithology control on the evolution of nitrogen system during progressive metamorphism.

Implications for element transfer during subduction It is well-known that subduction zone volcanics are enriched in some large ion lithophile elements (LILE) such as Ba, K, Rb, Cs, Sr, relative to the high field strength elements (HFSE) such as Ti, Hf, Nb, Zr, which are geochemical characteristics of continental crust (e.g., Gill, 1981). Such characteristics are generally believed to have resulted from the superimposition of subduction components on the magma source region or the mantle wedge above the subduction zone. It has been suggested that addition of subduction components was through either a fluid phase (e.g., Tatsumi, 1989) or melts (e.g., Nicholls and Ringwood, 1973; Wyllie, 1984) derived from the descending slab. Recent studies by Busigny *et al.* (2003), Chalot-Prat *et al.* (2003), Spandler *et al.* (2003, 2004) and Pitcairn *et al.* (2005) showed that devolatilization associated with subduction-collision metamorphism does not lead to significant chemical alteration of the rocks, implying that fluid release from subducting materials and subduction component enrichment in magma source region/mantle wedge might be de-coupled. Based on theoretical and experimental constraints, Manning (2004) also suggested that subduction-zone fluids might be surprisingly dilute. On the other hand, significant removal of trace elements during subduction metamorphism was also documented by Bebout *et al.* (1999a), Breeding *et al.* (2004) and John *et al.* (2004), which favor the scenario of magma-source metasomatism by dehydrated fluids at subduction zones.

Based on the nitrogen system, the present study shows that element behavior may be different during devolatilization, if lithology is an issue. Whereas the relative depletion of LOI content is similar for greenschist-facies metapelites from both the psammitic sequence and the pelitic sequence, nitrogen depletion is more pronounced for those pelitic samples from the psammitic sequence (Table 3). Significant ^{15}N enrichment is also evident for greenschist-facies metapelites from the psammitic sequence (Fig. 7). Obviously, mobile elements are more easily fractionated and carried away by the fluid phase if the whole system is more open and if the devolatilization process is close to Rayleigh behavior. Although this conclusion is derived from a consideration of low-grade metamorphic rocks, it may be applicable to high-grade metamorphic processes as well. For higher grade metamorphic rocks, the permeability of the rock sequence must be even lower. Devolatilization in such an

environment would conform to closed system behavior, with element mobility and isotopic fractionation being highly restricted. It has been clearly demonstrated by stable isotope studies that most eclogite-facies veins were locally sourced (Nadeau *et al.*, 1993); this can, at least partially, explain the observations given by Busigny *et al.* (2003), Chalot-Prat *et al.* (2003), Spandler *et al.* (2003, 2004) and Pitcairn *et al.* (2005) mentioned above. However, the situation would be drastically different along fluid channel ways, where the integrated fluid/rock ratio would be high. In this case, element (and isotope) distributions would be more effectively fractionated through Rayleigh-type devolatilization. The Catalina Schist and the Syros subduction complex studied by Bebout *et al.* (1999a) and Breeding *et al.* (2004), respectively, may be good examples, being megashear mélange zones acting as fluid channel ways. Whether dehydration fluid can in effect metasomatize the magma source region in subduction zones may therefore depend, at least partly, on whether the fluid derives from large fluid channel ways within the subduction complex.

CONCLUSIONS

The Taiwan mountain belt consists mainly of two tectonic units: the pre-Tertiary Tananao metamorphic basement complex and the Cenozoic cover strata. Whereas the latter has only been subjected to late Cenozoic collision metamorphism, the former has experienced at least three stages of tectonism/metamorphism. Pelitic rock samples were collected along two transects of this mountain belt, to investigate possible factors affecting the evolution of nitrogen systematics in rocks during progressive metamorphism.

The nitrogen content and N-isotope composition for twelve greenschist-facies metapelites from the basement complex are 443 ± 336 ppm and $3.0 \pm 1.4\%$, respectively. Corresponding values for cover strata are: 806 ± 176 ppm and $3.9 \pm 0.3\%$ for eleven S-Z group samples; 820 ± 184 ppm and $3.5 \pm 0.7\%$ for eight PP group samples; 918 ± 149 ppm and $3.5 \pm 0.4\%$ for ten G group samples from pelitic rock sequences; and 732 ± 279 ppm and $5.3 \pm 0.4\%$ for four G(Ps) group samples from pelitic members of psammitic rock sequence.

Compared with the cover strata, the variable and depleted nitrogen content and $\delta^{15}\text{N}$ composition of the basement rocks can only be accounted for by complicated tectonic/metamorphic history. It certainly shows that special caution is necessary in studying evolution of the nitrogen system of metamorphic complexes with different tectonometamorphic units.

Taking Al as an immobile element during low-grade metamorphism, nitrogen was systematically depleted from the S-Z, PP, G to G(Ps) group samples of the cover strata.

The comparable N-isotope composition of the S-Z, PP and G group samples can be accounted for by limited nitrogen depletion (<10%), as well as inhomogeneous N-isotope composition of the protolith. The higher $\delta^{15}\text{N}$ values of the G(Ps) group samples might be due to a greater extent of nitrogen depletion (~25%). The different degrees of nitrogen depletion may result from the different lithologies of rock sequences from which the pelitic rock samples were collected. Thick psammitic rock sequence may approximate an open system, in which element depletion is easier and N-isotope fractionation follows Rayleigh distillation during low-grade metamorphism, while pelitic rock sequence may behave more like a closed system.

If lithology is an important issue to consider during metamorphic dehydration, element transport during subduction devolatilization processes may most likely be limited to within fluid channel ways. For high-grade metamorphic rocks, permeability of the rock sequence would be extremely low and element mobility would be highly restricted.

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