

Nitrogen isotope fractionations during progressive metamorphism: A case study from the Paleozoic Cooma metasedimentary complex, southeastern Australia

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Abstract

The well-studied Paleozoic Cooma metamorphic complex in southeastern Australia is characterized by a uniform siliciclastic protolith, of uniform age, with a continuous range of metamorphic grade from subgreenschist- to upper amphibolite-facies, and migmatite-grade in an annular pattern around the Cooma granodiorite. Those conditions are optimal for investigating variations of N concentrations and $\delta^{15}\text{N}$ values during progressive metamorphism. Nitrogen concentrations decrease and $\delta^{15}\text{N}$ increases with increasing metamorphic grade (sub-chlorite zone: 120 ppm N, $\delta^{15}\text{N} = 2.3\text{‰}$; chlorite zone: 110 ppm N, $\delta^{15}\text{N} = 3.0\text{‰}$; biotite and andalusite zone: 85 ppm N, $\delta^{15}\text{N} = 3.8\text{‰}$; sillimanite and migmatite zones: 40 ppm N, $\delta^{15}\text{N} = 10.7\text{‰}$). Covariation of K and N contents is consistent with N substituting for K as NH_4^+ in micas. Observed trends of increasing $\delta^{15}\text{N}$ values with decreasing nitrogen concentrations can be explained by a continuous release of nitrogen depleted in ^{15}N with progressive metamorphism, which causes an enrichment of ^{15}N in the residual nitrogen of the rock. Equilibrium models for Rayleigh distillation and batch volatilisation for data of the greenschist and amphibolite facies metasedimentary rocks can be explained by $\text{N}_2\text{-NH}_4^+$ exchange at temperatures of 300–600 °C, whereas observed large fractionations for the upper amphibolite-facies and melt products in the migmatite-grade samples may be interpreted as $\text{NH}_3\text{-NH}_4^+$ exchanges at temperature of 650–730 °C. Lower values in the highest grade zones may also stem in part from input of ^{15}N -depleted fluids from the granodiorite. The magnitude of isotope fractionation of nitrogen is about 1–2‰ during progressive metamorphism of metasedimentary rocks from sub-chlorite zone to biotite–andalusite zone, which is consistent with previous studies. Consequently, the large spread of $\delta^{15}\text{N}$ values in Archean greenschist-facies metasedimentary rocks of –6‰ to 30‰ can be accounted for by variable mixtures of mantle plume-dominated volatiles with a $\delta^{15}\text{N}$ of –5‰, and a ^{15}N -enriched marine sedimentary kerogen component inherited from a CI chondrite veneer having $\delta^{15}\text{N}$ of 30‰ to 42‰.

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1. Introduction

The nitrogen-isotope system has been used to address a number of geological questions. Included are hydrocarbon production and migration during diagenesis of organic matter (Williams et al., 1995); the redox state of the atmosphere and oceans, and its relationship to extinction

events (Rau et al., 1987; Sephton et al., 2002); the evolution of Precambrian atmosphere chemical composition and biochemical pathways (Beaumont and Robert, 1999; Pinti et al., 2001); the origin of Earth's atmosphere–hydrosphere (Javoy, 1998; Tolstikhin and Marty, 1998; Jia and Kerrich, 2004); sources of hydrothermal fluids involved in orogenic, or shear zone-hosted mesothermal-gold deposits (Jia and Kerrich, 1999, 2000; Jia et al., 2001, 2003a); nitrogen recycling processes in convergent margins (Bebout, 1997; Fischer et al., 2002; Busigny et al., 2003; Sadofsky and Bebout, 2004); and nitrogen isotope systematics of ore deposits (Kerrich et al., 2006).

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There are, however, divergent interpretations of the magnitude of nitrogen isotope fractionation due to metamorphism. This issue is critical for interpreting N-isotope data. In an early study of regionally metamorphosed diverse sedimentary rocks, Häendel et al. (1986) reported a total range of 3‰ variation from greenschist to amphibolite facies. They argued that this shift may reflect N-isotope fractionation due to metamorphism, but noted that the ^{15}N -enriched values in amphibolites were restricted to Precambrian rocks such that the range may represent in part primary isotopic differences of compositionally and chronologically diverse lithologies. In more recent studies of progressive metamorphism of sedimentary sequences of a given age, in a subduction–accretion complex (Bebout and Fogel, 1992) and regional metamorphic collisional belts (Mingram and Bräuer, 2001; Busigny et al., 2003; Pitcairn et al., 2005) isotopic shifts from little metamorphosed precursors to greenschist- and amphibolite-facies counterparts were all $<1\text{‰}$ and $\sim 3\text{‰}$, respectively.

In contrast, Beaumont and Robert (1999) reported a very large variation of $\delta^{15}\text{N}$ values ranging from -6‰ to $+30\text{‰}$ from Precambrian chemical sediments, cherts and chert-bearing banded iron formations (BIF), ranging in age from 3.5 to 0.7 Ga. They selected the most depleted values to support a model of an anoxic environment, where microorganisms using reduced forms of N (N_2 , NH_4^+), induced metabolic isotope fractionations. The enriched value of 30‰ was interpreted as due to greenschist-facies metamorphic fractionation. Pinti et al. (2001) documented $\delta^{15}\text{N}$ spanning -7‰ to 20‰ in Archean chemical sedimentary rocks from Isua belt (~ 3.8 Ga, amphibolite-facies) and the Pilbara craton (~ 3.5 to 3.2 Ga, lower greenschist-facies) using a step-heating procedure. They choose the most depleted value, released at low-temperature steps, as near primary, to propose a model where chemosynthetic bacteria generated negative shifts of ^{15}N , with an atmosphere close to the present value defined as 0‰, whereas enriched values extracted from high-temperature steps were regarded as secondary shifts by Rayleigh volatilization during metamorphism. Boyd and Philippot (1998) also report relatively ^{15}N -enriched values of 12.4‰ to 16.6‰ for the 1.0–1.5 Ga Moine amphibolite-facies siliciclastic rocks, Scotland. They suggested that the enriched values resulted from metamorphic isotope fractionation of nitrogen from precursors assumed to be $\sim 5\text{‰}$.

Previous studies of the behavior of N and N-isotopes during progressive metamorphism have not involved the complete spectrum of metamorphic grades, nor tracked the melting process. Accordingly, this paper reports the nitrogen contents and $\delta^{15}\text{N}$ values, as well as major element oxides composition, in the well-studied Paleozoic Cooma metamorphic complex. This complex is characterized by a low-pressure regional metamorphic sequence ranging from sub-greenschist slates to migmatite-grade gneisses and culminating in the Cooma granodiorite. The Cooma metamorphic complex provides a natural laboratory for examining the variations of N concentrations and $\delta^{15}\text{N}$ values during

progressive metamorphism, and melting. The N data are used to further test the Rayleigh distillation versus batch volatilization models for explaining N-isotope variation in progressively metamorphosed sedimentary rocks. This paper builds on a reconnaissance study by Jia (2004).

2. Geology of the Cooma metamorphic complex

The Ordovician Cooma Complex is centered on the township of Cooma 110 km south of Canberra, and is

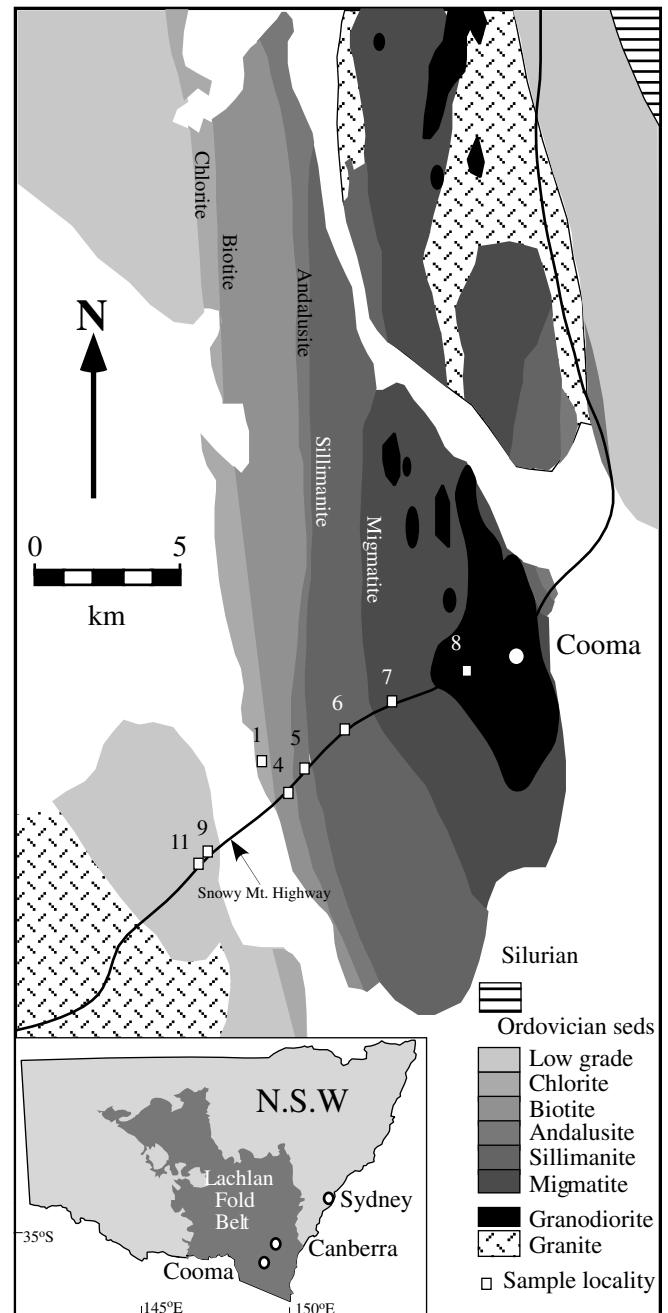


Fig. 1. Geological sketch map of the Cooma Complex (after Pidgeon and Compston, 1965; Munksgaard, 1988; Williams, 2001), showing the distribution of the principal rock types, and metamorphic isograds surrounding the complex, and sample locations.

Table 1
Characteristics of metamorphic zones for the Cooma metasedimentary complex

Zone ^a	Sample	Metamorphic grade	<i>P</i> – <i>T</i> condition ^b	Lithology	Assemblage ^c
Low-grade	C11	Sub-greenschist facies	3–4 kbar; <300 °C	Slates	qtz > alb > mus > chl
Chlorite	C1	Greenschist facies	3–4 kbar; 300 °C	Slates/phyllites	qtz > alb > mus > chl
Biotite	C4	Lower amphibolite facies	3–4 kbar; 350–500 °C	Schists	qtz > alb > mus > bio ± chl
Andalusite	C5	Lower amphibolite facies	3–4 kbar; 500–600 °C	Schists	qtz > bio > mus > crd + and
Sillimanite	C6	Upper amphibolite facies	3–4 kbar; 650–670 °C	Gneisses	qtz > kfs > bio > crd > mus + sil + and
Migmatite	C7	Upper amphibolite facies	3–4 kbar; 670–730 °C	Gneisses	qtz > kfs > bio + sil + and + mus

^a Classification of metamorphic zones were from Joplin (1942), Chappell and White (1976), and Johnson et al. (1994).

^b Metamorphic pressures and temperatures adopted from Johnson (1992) and Williams (2001).

^c Abbreviations: qtz, quartz; alb, albite; mus, muscovite; ch, chlorite; bio, biotite; and, andalusite; crd, cordierite; sil, sillimanite; kfs, k-feldspar.

one of the most intensely studied metamorphic sedimentary sequences in Australia (Fig. 1; Johnson and Vernon, 1995; Johnson, 1999; Williams, 2001; Richards and Collins, 1992, 2002). It lies in the southeastern Paleozoic Lachlan Fold Belt, part of a major orogenic belt that extended for some 20,000 km through Australia, Antarctica, and South America before breakup of the Gondwana supercontinent (Coney et al., 1990; Coney, 1992; Fergusson and Coney, 1992).

The Lachlan Fold Belt is a low-pressure metamorphic belt dominated by regional greenschist-facies metamorphism. Exposure of high-grade metamorphic rocks is limited to two north-trending belts, known as the Wagga-Omeo and Cooma metamorphic complexes respectively (Johnson and Vernon, 1995; Richards and Collins, 1992, 2002). These complexes are characterized by large domains, about 10 km wide, of low-pressure metamorphism as indicated by the presence of andalusite (300–500 MPa; Ellis and Obata, 1992; Williams, 2001). A high-temperature metamorphic aureole surrounds a small 6 × 3 km² granitic pluton called the Cooma granodiorite (Vernon et al., 2003).

The Cooma complex has a series of progressive metamorphic zones delineated, from west to east, by the presence of chlorite, biotite, andalusite, sillimanite, and migmatite, the grade increasing towards the Cooma granodiorite. In terms of metamorphic facies, the chlorite zone corresponds to subgreenschist and greenschist-facies; biotite and andalusite zones to lower amphibolite-facies; and sillimanite and migmatite zones to upper amphibolite-facies (Chappell and White, 1976; Hopwood, 1976; and references therein). The zoning is markedly asymmetric. The aureole of highest grade rocks and the enclosed Cooma granodiorite are located towards the eastern margin of the complex, with the lower grade rocks extending approximately 3 km to the east, and nearly 10 km to the west (Fig. 1).

The characteristics of mineral assemblages for different zones in the Cooma complex have been described in detail by Chappell and White (1976). In rocks of pelitic composition, they are: (1) chlorite zone in which the slates or phyllites have the mineral assemblage of quartz > albite > muscovite > chlorite; (2) biotite zone of schist or phyllites containing quartz > albite > muscovite > biotite ± chlorite; (3) andalusite zone of schists or gneisses with the mineral assemblage of quartz > biotite > muscovite >

cordierite + andalusite; (4) sillimanite zone of gneisses containing mainly quartz > K-feldspar > biotite > cordierite + muscovite + sillimanite + andalusite; and (5) migmatite zone of gneisses having the mineral assemblage of quartz > K-feldspar > biotite + sillimanite + andalusite + muscovite. The granodiorite varies from gneissic to massive and consists of quartz, K-feldspar and biotite, with andalusite, sillimanite, cordierite, and secondary muscovite (Ellis and Obata, 1992). Relative modal abundances are listed, as in previous studies, given fine-grain size in the sub-greenschist and greenschist facies pelites, and heterogeneous distribution of minerals in the upper amphibolite-facies and migmatite zones (Table 1).

The Cooma metamorphic complex consists of interbedded metapelites and metapsammities that have been metamorphosed over a range of metamorphic grades. The metasediments are compositionally and isotopically similar across metamorphic grade (Joplin, 1942; Pidgeon and Compston, 1965; McCulloch and Chappell, 1982; Munksgaard, 1988). The granodiorite is considered to be an integral part of the regional metamorphic sequence, and is interpreted to have formed by the partial melting of metasedimentary rocks similar to those surrounding it, giving similar chemical compositions of the surrounding metamorphic sequence (Pidgeon and Compston, 1965; Chappell and White, 1976; Munksgaard, 1988; Vernon et al., 2003). A detailed study of the U–Pb system of detrital zircons in the Cooma complex by Williams (2001) also shows similarities between the age at the Early Silurian populations for the low- and high-grade Cooma metasedimentary complex, and inherited zircon cores in the Cooma granodiorite; these are strong evidence for a close genetic relationship between the granodiorite and the rocks of its aureole.

3. Sampling design and analysis

To examine the behavior of nitrogen in sedimentary rocks during progressive metamorphism, compositionally equivalent metapelitic samples of the Cooma complex were collected along an approximately east–west transect extending eastwards from low-grade zone through all progressively higher zones, to migmatite and to the granodiorite (Fig. 1). Pelites were sampled given their intrinsically greater K- and N-contents than psammities. Each fresh

whole-rock sample was split into two: one part was powdered to about $<53\ \mu\text{m}$ (≤ 300 mesh) and homogenized for major-element analysis, and for whole-rock N isotope analysis after pre-concentration of N following dissolution and distillation techniques of Häendel et al. (1986). The other part was crushed, ground, and sieved to different grain fractions for mica separation, and hence for subsequent N isotope analysis. The whole-rock chemical compositions were determined by X-ray fluorescence (XRF) spectrometry at the Saskatchewan Geological Survey, Canada. Detection limits are 0.01 wt%.

The analytical techniques employed for N isotope measurement involved a Europa Scientific, high precision continuous flow-isotope ratio mass spectrometer (CF-IRMS) at the Soil Science Laboratory, University of Saskatchewan (details in Jia et al., 2003a, Appendix). Samples of 30 to 150 mg (depending on the nitrogen content of each sample) were loaded into a tin capsule in a clean room and heated at 1150 °C. Under this heating regime, nitrogen is released totally from samples, as confirmed by Boyd et al. (1993). Complete oxidation was ensured by passing the combustion products through a bed of chromium trioxide at 1000 °C using a helium carrier gas. Gases containing oxygen, nitrogen oxides and carbon dioxide were then passed through a second furnace containing copper at 600 °C where excess oxygen was absorbed, and nitrogen oxides reduced to elemental nitrogen and carbon dioxide in a trap containing “Carbosorb”. Following the method detailed by Beaumont et al. (1994), the possible isobaric interference of CO on $\delta^{15}\text{N}$ was monitored for each sample at concentrations $<0.1\%$, and this isobaric interference was ruled out by designed long-time combustion (see below).

The size of blanks determined for mass spectrometry are typically less than $3\text{E}-10$ beam area, corresponding to approximately $0.075\ \mu\text{g N}$, when analyses of standards were $\geq 10\ \mu\text{g N}$. The sizes of samples of sedimentary rocks and mica separates were set to meet this range. The average size of the nitrogen blank is measured before each sample run. The software then corrects the $\delta^{15}\text{N}$ value of the sample for the blank contribution. To ensure reliable isotope data, each sample was run twice: the first run to measure nitrogen content; and for the second, sample weights were calculated for N contents to match the standards. Also, samples were combusted for 120 s at an oxygen supply rate of 1.17 ml O_2 per second to ensure completely combustion of larger sized mica separates, and to avoid any possible isobaric interference of CO for whole rock samples due to incomplete combustion of CO to CO_2 .

The analytical precision (1σ ; $n \geq 3$) is typically $\sim 0.3\%$ for $\delta^{15}\text{N}$. The long-term reproducibilities for international nitrogen isotope standard materials are: IAEA-N1 = $0.54 \pm 0.07\%$ ($n = 15$, accepted value 0.53%); IAEA-N2 = $20.35 \pm 0.08\%$ ($n = 10$, accepted value 20.41%); and for the internal laboratory standard material BLN.SOIL, $5.20 \pm 0.21\%$ ($n = 20$, accepted value 5.15%). Ten replicate analyses of “in house” muscovite separates of samples KAI1-1 and CD11-21-1 yield mean

$\delta^{15}\text{N}$ values of $19.4\% \pm 0.09\%$ and $3.4\% \pm 0.06\%$, respectively (Jia et al., 2003b). To evaluate the reliability of mica analyses in this study, the widely accepted dissolution and distillation techniques as described by Häendel et al. (1986), were also performed: analysis of the same muscovite (KAI1-1), in triplicate, yielded a same mean value of 19.6% ($1\sigma = 0.20\%$). Nitrogen concentrations were obtained from each sample based on system calibration using known standards. Variations in the isotopic composition of nitrogen in samples are expressed in the usual δ notation ($\%$): $\delta^{15}\text{N}_{\text{sample}} (\%) = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}} / ({}^{15}\text{N}/{}^{14}\text{N})_{\text{standard}} - 1] \times 1000$, where the standard is atmospheric N_2 .

Replicate analyses of some whole rocks show differing N-contents but similar $\delta^{15}\text{N}$. In sedimentary rocks, and metamorphosed counterparts, N is present both in detrital K-silicates and in kerogen or its metamorphic products, typically with similar $\delta^{15}\text{N}$ (Rau et al., 1987). Crushing homogenises silicates, but soft kerogen and its products may generate a “nugget” effect leading to heterogeneous distribution of N between separate aliquots of a given whole rock powder (e.g., Beaumont and Robert, 1999).

4. Results

4.1. Major element oxides

Metasedimentary rocks sampled from the six metamorphic zones of the Cooma complex are characterized by a small range of SiO_2 (56.5–61.1) wt%, TiO_2 (0.65–0.88) wt%, and Al_2O_3 (20.4–22.3) wt% contents. There is little variation of contents, or inter-element ratios, with respect to metamorphic grade (Table 2; Fig. 2). However, contents of K_2O , Na_2O , and LOI decrease by a factors of 1.3–2.0 from lowest to highest grade samples: the low-grade and chlorite zone rocks have K_2O , Na_2O , and LOI concentrations of 5.61, 0.83, and 4.92 wt%, and 5.14, 0.75, and 4.42 wt%, respectively, whereas the high-grade sillimanite and migmatite zone counterparts contain only 2.88, 0.69, and 2.69 wt%, and 2.77, 0.62, and 2.34 wt%, respectively. Consequently ratios of K and LOI to Al_2O_3 also decrease with increasing metamorphic grade (Table 2; Fig. 2).

Compositionally, the pelites are similar to data reported in previous studies of the Cooma complex (Joplin, 1942; Pidgeon and Compston, 1965; Munksgaard, 1988). The anomalously high values for MgO and low abundances of K_2O in the high-grade samples (C6 and C7) could be variation in protolith composition, but is tentatively interpreted as localized metasomatism, inasmuch as such high MgO contents were not documented in previous studies.

4.2. Nitrogen isotopes

The Cooma metasedimentary rocks show a systematic decrease in N concentration but increase in $\delta^{15}\text{N}$ with progressive metamorphism (Fig. 3). For the lowest-grade rocks, nitrogen concentrations of muscovite separates

Table 2
Whole-rock chemical compositions of the Cooma metasedimentary complex

Zone [†]	Low-grade	Chlorite	Biotite	Andalusite	Sillimanite	Migmatite
Sample	C-11	C-1	C-4	C-5	C-6	C-7
N (ppm)	120	110	86	81	43	41
SiO ₂ (wt%)	56.53	60.02	59.64	59.39	59.37	61.12
Al ₂ O ₃	21.33	20.39	20.91	20.63	22.31	21.33
TiO ₂	0.72	0.69	0.65	0.79	0.83	0.88
Fe ₂ O ₃	6.61	5.67	6.64	6.58	6.96	7.17
MnO	0.08	0.06	0.06	0.08	0.09	0.13
MgO	3.19	2.92	3.28	3.34	4.95	4.32
CaO	0.14	0.25	0.28	0.23	0.97	1.08
Na ₂ O	0.83	0.75	0.79	0.71	0.69	0.62
K ₂ O	5.61	5.14	4.49	4.29	2.88	2.77
P ₂ O ₅	0.12	0.11	0.09	0.12	0.19	0.15
LOI	4.92	4.42	3.83	3.53	2.69	2.34
Total	100.07	100.42	100.66	99.69	99.23	99.57
LOI/Al ₂ O ₃	0.23	0.22	0.18	0.17	0.12	0.11
N/K ₂ O	0.0021	0.0021	0.0019	0.0019	0.0015	0.0015
N/Al ₂ O ₃	0.0006	0.0005	0.0004	0.0004	0.0002	0.0002
SiO ₂ /Al ₂ O ₃	2.65	2.94	2.85	2.88	2.66	2.87
K ₂ O/Al ₂ O ₃	0.26	0.25	0.21	0.21	0.13	0.13
Na ₂ O/Al ₂ O ₃	0.039	0.037	0.038	0.034	0.031	0.029
Al ₂ O ₃ /TiO ₂	29.83	29.55	32.17	26.11	26.88	24.24

range from 190 to 250 ppm, and bulk rock nitrogen contents are between 90 and 120 ppm, whereas the highest-grade rocks and mica separates contain only 35 to 50 ppm and 60 to 80 ppm, respectively (Fig. 3). Nitrogen concentrations correspond to estimates of the modal proportion of muscovite in zones 1 and 2, and to muscovite and biotite in zones 3 and 4. For the six metamorphic zones from the lowest- to highest-grade rocks, N is well-correlated with K₂O content (calculated correction coefficient $r^2 = 0.996$), but no correlation with Al₂O₃ (Tables 1 and 2). This indicates that NH₄⁺ is strongly partitioned into micas, followed by K-feldspar, substituting for potassium, which is consistent with previous studies (Honma and Itihara, 1981; Cooper and Bradley, 1990; Bebout and Fogel, 1992).

The $\delta^{15}\text{N}$ values of the low-grade and chlorite zones (sub-greenschist and greenschist facies; Table 3) range from 1.7 to 2.9‰ (mean = 2.3‰, $1\sigma = 0.4\%$, $n = 13$) and 1.7‰ to 4.4‰ (mean = 3.0‰, $1\sigma = 0.7\%$, $n = 18$), respectively. There are small shifts to the biotite and andalusite zones (lower amphibolite-facies; Table 3), where respective $\delta^{15}\text{N}$ values range from 2.4‰ to 4.1‰ with a mean of 3.2‰ ($1\sigma = 0.5\%$; $n = 17$), and 2.6‰ to 5.6‰, with a mean of 3.8‰ ($1\sigma = 1.1\%$; $n = 18$). Nitrogen isotope compositions of the metasedimentary rocks increases dramatically to upper-amphibolite facies, where $\delta^{15}\text{N}$ values range from 8.9‰ to 12.5‰ with a mean of 10.4‰ ($1\sigma = 1.4\%$; $n = 11$) for the sillimanite zone and 8.9‰ to 12.7‰ with a mean of 10.7‰ ($1\sigma = 1.2\%$; $n = 12$) for the migmatite zone.

The large differences in both nitrogen content and N isotope composition correspond to the significant change in chemical composition between the andalusite and sillimanite-zone rocks could imply that the protoliths of the

low- and high-grade zone rocks are not truly isochemical. For example, the protolith of the higher-grade rocks with low N content may have more chlorite (higher MgO) and less illite (lower K₂O) than the protolith of the lower-grade rocks. This difference may have affected initial N-isotope compositions. Considering that the higher MgO and lower K₂O in the high-grade samples are more likely metasomatic in origin, the low N content in the high-grade zone samples may be explained by continuous release nitrogen depleted in ¹⁵N with progressive metamorphism, which causes an enrichment of ¹⁵N in the residual nitrogen of the rocks (Häendel et al., 1986; Bebout and Fogel, 1992).

5. Discussion

5.1. Behaviour of N and major elements during progressive metamorphism

Fig. 2 shows the contents of N, LOI, and K₂O, and ratios of N, K₂O, and LOI to Al₂O₃ across the six metamorphic zones. There is a systematic decrease in the ratios of N, and LOI to Al₂O₃ and slight decrease in the K₂O to Al₂O₃ ratio with increasing grade (Table 2). However, other major oxide ratios of SiO₂ to Al₂O₃ and Al₂O₃ to TiO₂ do not decrease with increasing metamorphic grade (Fig. 2; Table 2). Loss of nitrogen, volatiles, and large ion lithophile elements is due to devolatilization during progressive metamorphism (cf., Ague, 1994, 1997).

The nitrogen isotope composition of unmetamorphosed and low-metamorphic grade Phanerozoic sedimentary rocks is generally uniform ($\delta^{15}\text{N} = 3.65 \pm 0.55\%$; $n = 217$) and primarily reflects the N-isotopic composition of organic compounds in sediments (Peters et al., 1978;

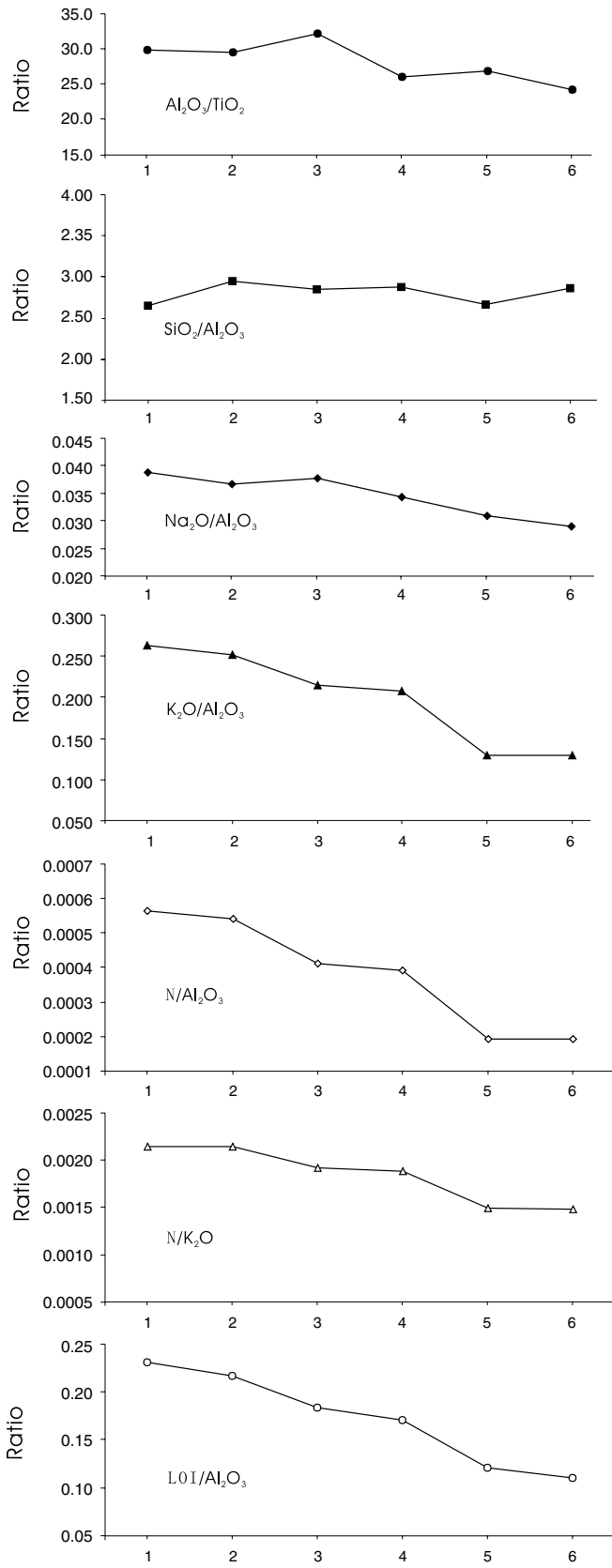


Fig. 2. Major elements and nitrogen compositions in six metasedimentary zones of the Cooma complex. 1, lowest grade zone; 2, chlorite zone; 3, biotite zone; 4, andalusite zone; 5, sillimanite zone; 6, migmatite zone. Data are in Table 2.

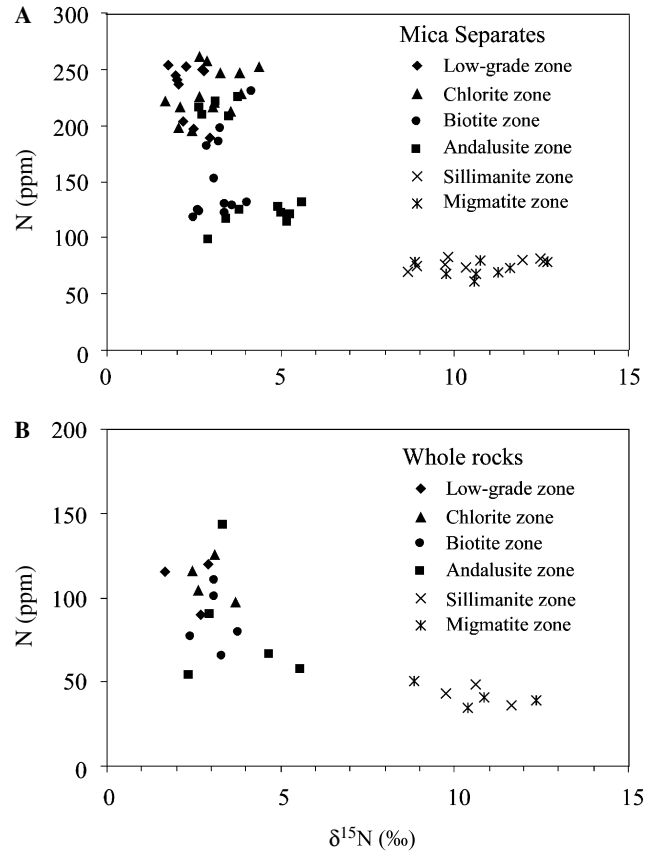


Fig. 3. Plot of N concentration vs. $\delta^{15}\text{N}$ for both mica separates (A) and whole rocks (B) in the Cooma Complex (data in Table 3).

Rau et al., 1987; Bebout and Fogel, 1992; Williams et al., 1995; Ader et al., 1998; Bebout et al., 1999; Mingram and Bräuer, 2001; Sephton et al., 2002; Sadofsky and Bebout, 2004). During diagenesis and metamorphism, N in organic compounds is progressively released; some of the N is transferred to silicates as NH_4^+ whereas some is dissolved in diagenetic fluids, with minimal isotope fractionation (Bebout and Fogel, 1992; Williams et al., 1995; Mingram and Bräuer, 2001; Jia and Kerrich, 2004; Kerrich et al., 2006).

Low-grade rocks of the Cooma complex have a mean $\delta^{15}\text{N}$ of $2.3 \pm 0.4\text{‰}$ ($n = 14$), similar to the average cited above. The mean for Cooma pelites is also consistent with $\delta^{15}\text{N}$ values of 1.9‰ for the lowest-grade rocks of the Catalina Schist (Bebout and Fogel, 1992) and 2.2‰ for the low-grade sedimentary units of the Phanerozoic Erzgebirge schist (Mingram and Bräuer, 2001).

The results of the present study indicating loss of nitrogen accompanied by increase in $\delta^{15}\text{N}$ during progressive metamorphism in the Cooma complex (Figs. 2 and 3) agree well with other studies of Phanerozoic metasedimentary sequences. The mean $\delta^{15}\text{N}$ values of lower amphibolite-facies (3.2‰ in biotite zone and 3.8‰ for andalusite zone) rocks are also compatible with the reports of Bebout and Fogel (1992) and Mingram and Bräuer (2001). However, the higher-grade (upper amphibolite-facies) sillimanite

Table 3
Nitrogen concentration and $\delta^{15}\text{N}_{\text{air}}$ of mica separates and whole rock samples in the Cooma complex

Zone	Sample	N (ppm)	$\delta^{15}\text{N}_{\text{air}}$ (‰)
Low-grade			
<i>Mica separates (mean $\pm 1\sigma$)</i>		232 \pm 25	2.3 \pm 0.4
	C11m-1	254	1.7
	C11m-2	245	2.0
	C11m-4	237	2.0
	C11m-6	248	2.8
	C11m-7	189	2.9
	C11m-9	197	2.5
	C11m-10	252	2.3
	C11m-12	203	2.2
	C11m-15	241	2.0
	C11m-17	250	2.8
<i>Whole rocks (mean $\pm 1\sigma$)</i>		120 \pm 4	2.0 \pm 0.7
	C11w-2	120	2.9
	C11w-6	118	2.7
	C11w-7	125	1.7
<i>Mica separates + whole rocks (mean $\pm 1\sigma$)</i>			2.3 \pm 0.5
Chlorite			
<i>Mica separates (mean $\pm 1\sigma$)</i>		228 \pm 21	3.0 \pm 0.7
	C1m-2	245	3.3
	C1m-3	228	3.8
	C1m-5	194	2.4
	C1m-6	196	2.1
	C1m-8	257	2.9
	C1m-10	212	3.6
	C1m-11	216	3.0
	C1m-13	260	2.7
	C1m-14	251	4.4
	C1m-15	216	2.1
	C1m-16	221	1.7
	C1m-18	246	3.8
	C1m-19	219	3.1
	C1m-21	225	2.6
<i>Whole rocks (mean $\pm 1\sigma$)</i>		110 \pm 12	2.9 \pm 0.6
	C1w-8	125	3.1
	C1w-11	104	2.6
	C1w-12	97	3.6
	C1w-14	115	2.4
<i>Mica separates + whole rocks (mean $\pm 1\sigma$)</i>			3.0 \pm 0.7
Biotite			
<i>Mica separates (mean $\pm 1\sigma$)</i>		153 \pm 37	3.2 \pm 0.5
	C4m-2	198	3.2
	C4m-3	186	3.2
	C4m-4	119	2.4
	C4m-6	153	3.1
	C4m-7	130	3.5
	C4m-9	123	3.3
	C4b-10	131	3.3
	C4b-11	124	2.6
	C4b-12	132	4.0
	C4b-14	126	2.6
	C4b-16	183	2.8
	C4b-17	231	4.1
<i>Whole rocks (mean $\pm 1\sigma$)</i>		86 \pm 18	3.1 \pm 0.5
	C4M-2	101	3.1
	C4M4	65	3.3
	C4M11	76	2.4
	C4M17	110	3.1
	C4M9	79	3.8
<i>Mica separates + whole rocks (mean $\pm 1\sigma$)</i>			3.2 \pm 0.5
Andalusite			
<i>Mica separates (mean $\pm 1\sigma$)</i>		156 \pm 50	3.9 \pm 1.1
	C5m-1	116	3.3

Table 3 (continued)

Zone	Sample	N (ppm)	$\delta^{15}\text{N}_{\text{air}}$ (‰)
	C5m-2	97	2.8
	C5m-8	127	4.9
	C5m-9	114	5.1
	C5b-14	208	3.4
	C5m-16	131	5.5
	C5m-17	120	5.2
	C5b-21	224	3.7
	C5b-23	209	2.7
	C5m-24	122	4.9
	C5b-29	215	2.6
	C5m-31	124	3.7
	C5b-33	220	3.0
<i>Whole rocks (mean $\pm 1\sigma$)</i>		81 \pm 37	3.8 \pm 1.2
	C5w-8	66	4.7
	C5w-21	90	2.9
	C5w-16	57	5.6
	C5w-24	143	3.3
	C5w-29	54	2.6
<i>Mica separates + whole rocks (mean $\pm 1\sigma$)</i>			3.8 \pm 1.1
Sillimanite			
<i>Mica separates (mean $\pm 1\sigma$)</i>		76 \pm 4	10.5 \pm 1.6
	C6b-06	74	8.9
	C6b-07	73	10.3
	C6b-09	81	12.4
	C6b-11	82	9.8
	C6b-12	76	9.7
	C6b-13	69	8.6
	C6b-15	80	11.9
	C6b-16	77	12.5
<i>Whole rocks (mean $\pm 1\sigma$)</i>		43 \pm 6	10.4 \pm 1.5
	C6w-13	36	11.7
	C6w-15	43	9.8
	C6w-07	48	10.7
<i>Mica separates + whole rocks (mean $\pm 1\sigma$)</i>			10.4 \pm 1.4
Migmatite			
<i>Mica separates (mean $\pm 1\sigma$)</i>		72 \pm 6	10.8 \pm 1.2
	C7b-2	68	9.8
	C7b-3	68	11.3
	C7b-5	73	11.6
	C7b-6	77	8.9
	C7b-8	61	10.6
	C7b-10	67	10.6
	C7b-12	78	12.7
	C7b-13	79	10.8
<i>Whole rocks (mean $\pm 1\sigma$)</i>		41 \pm 7	10.6 \pm 1.5
	C7w-3	50	8.9
	C7w-6	40	10.9
	C7w-12	39	12.4
	C7w-10	34	10.4
<i>Mica separates + whole rocks (mean $\pm 1\sigma$)</i>			10.7 \pm 1.2

and migmatite-zone rocks, which have average $\delta^{15}\text{N}$ values of 10.4‰ and 10.7‰ respectively, are much higher than the value of 7.7‰ for amphibolite gneiss unit of the Erzgebirge schist (Mingram and Bräuer, 2001). The trend of increasing $\delta^{15}\text{N}$ with decreasing nitrogen concentrations may be explained by a continuous release of N, preferentially ^{14}N , due to devolatilization reactions occurred during progressive metamorphism. This process causes an enrichment of ^{15}N in residual N of the rock (Figs. 2 and 3; Häendel

Table 4
Results of mass balance estimates using equation of [Ague \(1991\)](#) for calculation of N loss in the Cooma metasedimentary zones^a

	τ_{Al}^N (%)	τ_{Ti}^N (%)	F^b	τ_{Al}^K (%)	τ_{Ti}^K (%)	F^c
Chlorite zone	−4.1	−5.0	0.96–0.95	−4.2	−21.1	0.79–0.96
Biotite zone	−26.9	−21.2	0.79–0.73	−18.4	−7.7	0.82–0.92
Andalusite zone	−30.2	−38.9	0.70–0.61	−21.0	−30.8	0.69–0.79
Sillimanite zone	−65.7	−69.1	0.34–0.31	−51.0	−55.8	0.44–0.49
Magmatite zone	−65.8	−72.2	0.34–0.28	−50.6	−59.9	0.40–0.49

^a Calculation on N and K loss relative to reference elements (Al and Ti).

^b Fraction of the initial N remaining in the rock after devolatilization.

^c Fraction of the initial K remaining in the rock after devolatilization.

et al., 1986; [Bebout and Fogel, 1992](#); [Mingram and Bräuer, 2001](#)).

5.2. Constraints on nitrogen loss and isotope fractionation

5.2.1. Estimate of nitrogen loss

Assessments of compositional changes in sedimentary rocks during progressive metamorphism and devolatilization (e.g., [Ague, 1994, 1997](#)) are complicated due to the large degree of variability in protolith compositions and in some cases age ([Häendel et al., 1986](#); [Moss et al., 1995](#); [Bebout et al., 1999](#)). The Cooma metasedimentary rocks (metapelites) may provide optimum conditions to allow the examination of N loss during metamorphism, given that: (1) the low- and high-grade metamorphic zone rocks have similar protolith composition of metapelites, and age, as confirmed previously by [Munksgaard \(1988\)](#) and [Williams \(2001\)](#); (2) the systematic decreases of K_2O and Na_2 and volatiles relative to Al_2O_3 and TiO_2 in progressively metamorphosed zones as evidenced in this study; and (3) there is no subsequent deformational or metamorphic overprint.

For estimating the extent of N loss, the mass change values were calculated following the equation of [Ague \(1991\)](#):

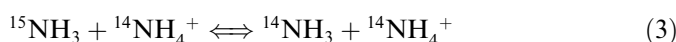
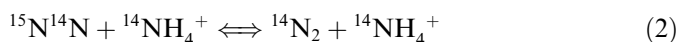
$$\tau_i^j \equiv [(C_i^0/C_i^f)(C_j^f/C_j^0) - 1] \times 100 \quad (1)$$

where τ_i^j are the percentage changes in masses of individual mobile species j relative to immobile reference species i ; C_i^0 and C_i^f are the concentrations of immobile reference species i in the initial and final states; and C_j^0 and C_j^f are the concentrations of the mobile species j in the initial and final states.

The composition of the low-grade zone is assumed to be approximately the initial protolith composition of the Cooma metapelites, and from uniform interelement ratios that Al_2O_3 and TiO_2 behaved isochemically ([Fig. 3](#)). The calculated mass changes of nitrogen, relative to the reference elements Al and Ti, in progressive metamorphic zones are given in [Table 4](#). For comparison, the loss of potassium relative to Al and Ti was also estimated. These results show a similar behavior between N and K, reflecting a partial loss of N probably largely from dehydration of K-micas during progressive metamorphism, in keeping with coherent loss of K and N in the Catalina metamorphic complex ([Bebout and Fogel, 1992](#)).

5.2.2. Nitrogen isotope fractionation

During progressive metamorphism resulting in progressive loss of N and other volatile and mobile elements, the form of released nitrogen may be molecular nitrogen (N_2) or ammonia (NH_3), given that both species have been documented in fluid inclusions in hydrothermal systems ([Bottrell et al., 1988](#); [Krohn et al., 1993](#); [Yardley et al., 1993](#); [de Ronde et al., 1992](#); [Mariner et al., 2003](#)). Accordingly, the enrichment of ^{15}N may be caused by isotope exchange reactions between silicate-hosted ammonium and either volatile molecular nitrogen or ammonia. According to [Scalan \(1957\)](#), the reactions are:



The fractionation factors for these exchange reactions were calculated by [Hanschmann \(1981\)](#), and the results of those calculations for temperatures of 327–927 °C are tabulated by [Häendel et al. \(1986\)](#). Using stepwise heating experiments on a phyllite, [Häendel et al. \(1986\)](#) showed that the fractionation factors for $^{14}NH_4^+/N_2$ are temperature dependent, and are consistent with those calculated by ([Scalan, 1957](#)) and [Hanschmann \(1981\)](#). Based on the fractionation factors of [Hanschmann \(1981\)](#), the calculated isotope fractionations ($\Delta^{15}N_{fluid-rock}$) between fluid and rock ($\Delta^{15}N_{fluid-rock} = \delta^{15}N_{fluid} - \delta^{15}N_{rock}$) in the Cooma metasedimentary rocks would range from approximately −3.8‰ to −2.2‰ for (N_2 release) the exchange reaction (2), and from −11.4‰ to −6.7‰ for (NH_3 release) in exchange reaction (3) at temperatures of 327 to 727 °C.

The $\delta^{15}N$ shift due to loss of N during progressive metamorphism of the Cooma metasedimentary rocks can be evaluated using models of: (1) Batch volatilization where all evolved fluid equilibrates with the rock, and the changes of the isotopic ratio of the rock will depend on whether the fluid preferentially partitions the light or heavy isotope in a closed system; and (2) Rayleigh distillation in which successive small aliquots of volatile that are released are immediately removed from the rock in an open system (see [Valley, 1986](#) for a review, and discussion by [Bebout and Fogel, 1992](#)). Isotopic fractionation arising from batch devolatilization is described by the equation:

$$\delta^{15}\text{N}_f = \delta^{15}\text{N}_i - (1 - F)1000 \ln \alpha \quad (4)$$

and the fractionation following the Rayleigh distillation process is described as:

$$\delta^{15}\text{N}_f = \delta^{15}\text{N}_i + 1000(F^{\alpha-1} - 1) \quad (5)$$

where $\delta^{15}\text{N}_i$ and $\delta^{15}\text{N}_f$ are the initial and final isotopic compositions of the rock; F is the fraction of nitrogen that remains in the rock after devolatilization reactions; and α is the fractionation factor (fluid-rock) for N_2 - $^{14}\text{NH}_4^+$ and NH_3 - $^{14}\text{NH}_4^+$.

Fig. 4 shows rock $\delta^{15}\text{N}$ evolution due to batch volatilization and Rayleigh distillation processes for both N_2 - $^{14}\text{NH}_4^+$ and NH_3 - $^{14}\text{NH}_4^+$ exchanges based on the calculated fractionation factors of Hanschmann (1981) for temperatures from 327 to 727 °C. Estimated F values are given in Table 4. For the biotite and andalusite zones, estimated F values range from 0.73 to 0.79 and 0.61 to 0.70, respectively, corresponding to $\delta^{15}\text{N}$ values ranging from 2.4‰ to 4.1‰ and 2.6‰ to 5.5‰ (Table 3). The observed shifts in N content and isotopic composition in the Cooma metasedimentary complex (see boxes on Figs. 4A and B) can be explained either a batch volatilisation model or Rayleigh distillation model each involving both N_2 - $^{14}\text{NH}_4^+$ and NH_3 - $^{14}\text{NH}_4^+$ exchanges at 350–600 °C, but are more compatible with the calculated lines and curves for the N_2 - $^{14}\text{NH}_4^+$ exchange. High N loss (F values of 0.34–0.28) accompanied the pronounced $\delta^{15}\text{N}$ shifts from 8.9‰ to 12.7‰ for the sillimanite and migmatite zones can also be explained by either batch volatilization model or Rayleigh distillation, but involving only NH_3 - $^{14}\text{NH}_4^+$ exchange at >600–730 °C (Figs. 4A and B; Table 3). Regional and contact metamorphism, in reality, involve some combination of continuous loss (within zones) and batch loss (between zones), but the approximation of Rayleigh distillation is generally made (Valley, 1986).

5.2.3. Volatile phase isotope fractionation

These calculations are consistent with the volatile phases involved in isotope fractionation changing from more N_2 -dominated releases for the biotite and andalusite zones (350–600 °C), to NH_3 -dominated release for the sillimanite and migmatite zones (>600–730 °C). This process is not well-understood as pointed out in previous studies (e.g., Häendel et al., 1986; Bebout and Fogel, 1992; Mingram and Bräuer, 2001). On the basis of an experimental study using stepwise heating of phyllite, Häendel et al. (1986) found that both molecular nitrogen and ammonia were released in the temperatures of 400–700 °C, but they emphasized that the isotope exchange took place mainly between ammonium and molecular nitrogen. Stability relation experiments on ammonium silicates observed by Hallam and Eugster (1976) suggest that ammonium-bearing muscovite is stable at less than 600 °C, but at greater temperatures of metamorphism

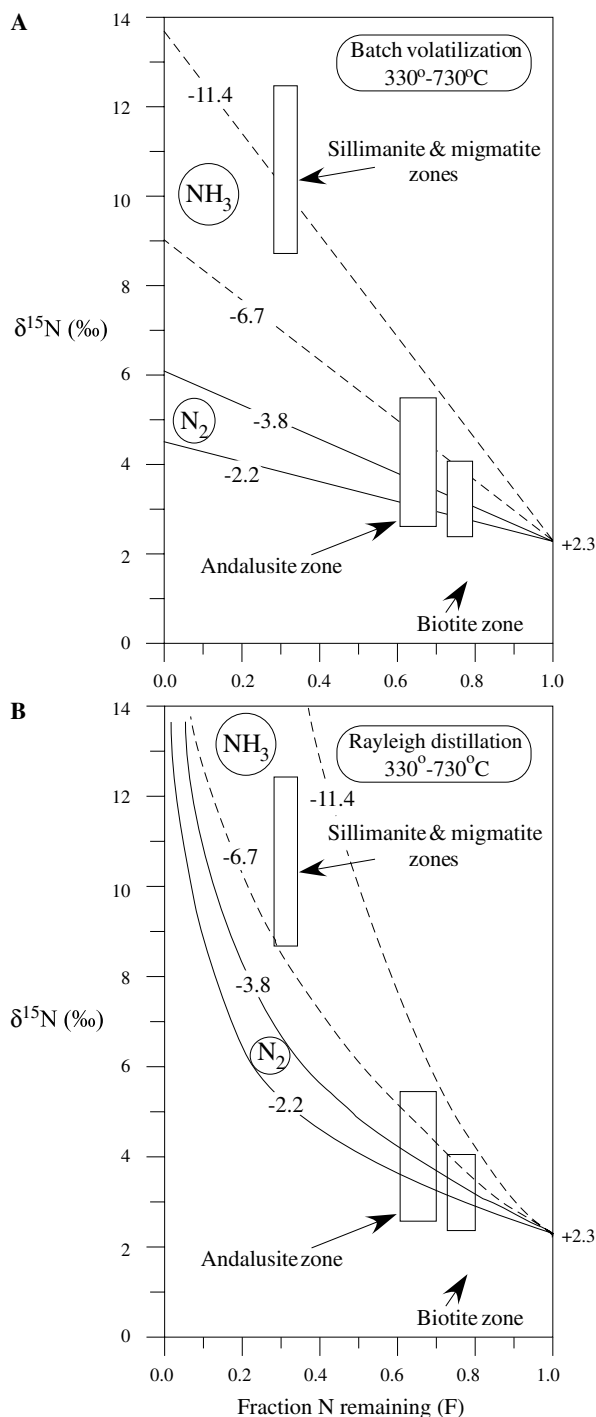
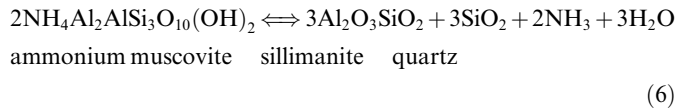


Fig. 4. Batch volatilization (A) and Rayleigh distillation (B) models for both N_2 - NH_4^+ (straight lines and curves) and NH_3 - NH_4^+ (dashed straight lines and curves) exchanges using fractionation factors from Hanschmann (1981) for temperatures range of 350–730 °C. Boxes indicate the calculated range of N loss and isotope shift of biotite, andalusite, sillimanite, and magmatite zone rocks. The observed shifts in concentration and isotope composition in biotite and andalusite zones are compatible with batch volatilization and Rayleigh distillation involving both N_2 - NH_4^+ and NH_3 - NH_4^+ exchanges, whereas these observed shifts in sillimanite and magmatite zones are compatible with batch volatilization and Rayleigh distillation involving only NH_3 - NH_4^+ exchange.

NH_3 will be predominantly released by decomposition and dehydration:



Bebout and Fogel (1992) analyzed the N concentrations and isotopic compositions of the Catalina metasedimentary rocks. They show a general decrease in N content and a corresponding increase in $\delta^{15}\text{N}$ with increasing metamorphic devolatilization, from 100 to 1000 ppm N with $\delta^{15}\text{N}$ values of 1.0–3.1‰ in the lowest-grade rocks (300 °C) to 30–250 ppm N with $\delta^{15}\text{N}$ values of 3.6–5.3‰ for the high-grade amphibolite-facies equivalents (600 °C). The shifts in N concentration and isotope composition can be explained by N_2 – NH_4^+ fractionation over the temperature range of 350–600 °C in a batch volatilisation or Rayleigh distillation process. However, they also pointed out that exchange involving NH_3 and NH_4^+ with a less efficient equilibration of fluid and rock during volatile loss cannot be entirely discounted. Bos et al. (1988) suggested that N_2 would be easily liberated during retrograde decomposition of ammonium (NH_4^+)-bearing biotite to chlorite or white mica.

In another recent study of the N-isotope compositions of the Erzgebirge metasedimentary rocks, Germany, Mingram and Bräuer (2001) indicate that isotope exchange reaction due to metamorphism varies from NH_3 release in the low-grade garnet phyllites (9 kbar/470 °C), to N_2 release for the amphibolite-facies mica schists (12 kbar/550 °C), and again back to NH_3 release from the granulite-facies gneisses (12 kbar/730 °C).

More complex processes may have operated in the Cooma complex. For example, it is possible that the high $\delta^{15}\text{N}$ values of the sillimanite and magmatite-zone rocks could be some combination of a positive shift from release of N as NH_3 during progressive metamorphism, and the influx of N-bearing fluids derived from the adjacent granodiorite. These scenarios are difficult to test.

5.2.4. Magnitude of isotope fractionation

Nitrogen isotope fractionations during progressive metamorphism of sediments to conditions of high pressure (P) and high geothermal gradient (ca. 15–20 °C/km; Bebout and Fogel, 1992; Mingram and Bräuer, 2001), and high and ultrahigh pressure (P) with low geothermal gradient (ca. 8 °C/km; Busigny et al., 2003; Pitcairn et al., 2005) have been previously studied (Fig. 5). According to Bebout and Fogel (1992), the Catalina schists are terrigenous sediments subducted at depths of 15 to 45 km in an accretionary complex, which experienced relatively high temperature conditions (300–750 °C and 0.5–1.1 GPa), resulting in a drastic devolatilization of N and other volatile elements with increasing metamorphism. Based on $\delta^{15}\text{N}$ of 1.9 ± 0.6 ‰ in low-grade rocks and 4.3 ± 0.8 ‰ for high-grade amphibolite

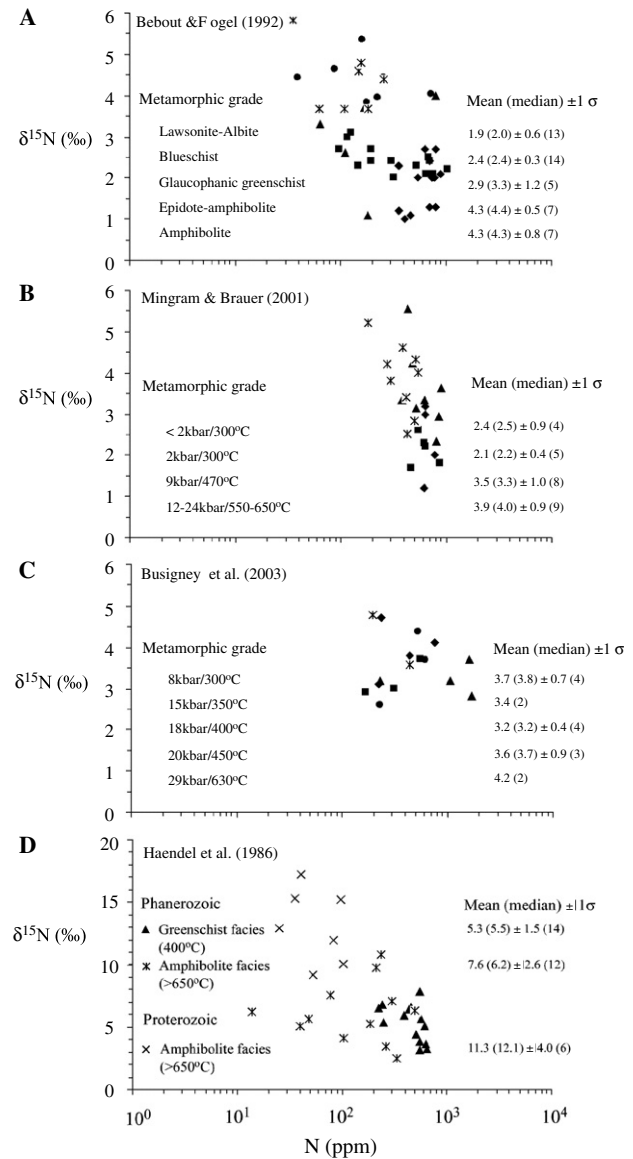


Fig. 5. $\delta^{15}\text{N}$ vs. N content for progressively metamorphosed sedimentary rocks. Values on the right-hand side are mean (and median) $\delta^{15}\text{N}$ plus one standard deviation, and numbers in parentheses are the number of samples. Data sources: (A) Bebout and Fogel (1992), (B) Mingram and Bräuer (2001), (C) Busigny et al. (2003), and (D) Häendel et al. (1986).

facies counterparts, they calculated fluid-rock N-isotope fractionations of -1.5 ± 1 ‰ with the Rayleigh distillation equation.

Nitrogen isotopic analyses of Erzgebirge Schists (metasediments) also indicate that N can be devolatilized with increasing metamorphism at 300–550 °C and 0.2–1.2 GPa, showing $\delta^{15}\text{N}$ of 2.2 ± 0.6 ‰ in low-grade units and 3.9 ± 0.9 ‰ in high-grade counterparts, indicating small $\delta^{15}\text{N}$ shifts of 1 to 2‰ from the low-grade rocks to amphibolite facies (Fig. 5; Mingram and Bräuer, 2001).

Nitrogen behaviour of metasedimentary rocks during metamorphism in a cold slab with high- to ultrahigh- P environment has recently been investigated by Busigny et al. (2003) and Pitcairn et al. (2005). The Schistes

Lustrés complex (metasediments), Western Alps, subducted to depths from shallow level to 90 km before obduction, had undergone progressive metamorphism at pressure and temperature conditions from <0.17 GPa and <300 °C to 0.8–2.9 GPa and 300–650 °C (Busigny et al., 2003). $\delta^{15}\text{N}$ values of metasedimentary rocks are between 2.6‰ and 4.8‰, showing no systematic isotopic shifts with increasing metamorphic grade (Fig. 5). According to Pitcairn et al. (2005), the $\delta^{15}\text{N}$ value of the Otago and Alpine Schists range from 0.2‰ to 7.0‰, having no systematic variations with metamorphic grade. They indicate that these schists had undergone progressive metamorphism ranging from prehnite–pumpellyite- to upper greenschist-facies conditions, to a maximum temperature and pressure of 450 °C and 0.8–1.0 GPa (Fig. 5).

Bebout et al. (1999) have studied the N-isotope record of fluid-rock interactions in the Skiddaw aureole and granite, England Lake District. They show that there are systematic changes of N concentration and N-isotopic composition in the aureole from 849 ± 44 ppm and 3.6 ± 0.4 ‰ at distances >2.5 km (Outer zone: andalusite slates) from the contact, through 840 ± 119 ppm and 4.0 ± 0.6 ‰ at distance 1.0–2.5 km (Intermediate zone: cordierite–andalusite slates), to 382 ± 162 ppm and 6.3 ± 1.3 ‰ (Inner zone: cordierite hornfels) at ≤ 1.0 km from the contact. These results indicate small $\delta^{15}\text{N}$ shifts of 2.7‰ from the low-grade rocks to amphibolite facies. Magnitudes and directions of shifts are comparable in this study, albeit with lower N concentrations, which are variable in siliciclastic rocks (cf. Bebout et al., 1999).

Consequently, the nitrogen isotope composition shifts of 1–2‰ obtained from the low- P and high- T Cooma metasedimentary rocks in this study during progressive metamorphism to lower amphibolite-facies are consistent with those under conditions of either high- P and high thermal gradients, or high- P and low thermal gradient. The Schistes Lustrés metasediments, Western Alps, showing no $\delta^{15}\text{N}$ shifts with increasing metamorphism may reflect more closed-system volatile behaviour in an ultrahigh- P and low thermal gradient regime, compared to extensive devolatilization of the Catalina schist (Bebout and Fogel, 1992), the Erzgebirge terrane (Mingram and Bräuer, 2001), and the Cooma complex (Figs. 3 and 5).

The larger shifts of 7–10‰ for the sillimanite- and migmatite-zone rocks in this study are interpreted as due to the highest-grade metamorphism and melt conditions leading to larger release of $^{14}\text{NH}_3$ to the fluids. This result is consistent with shifts of ~ 7 ‰ from sedimentary precursors having a global mean of 3.6‰ to peraluminous, S-type granites of the Cornubian batholith, southwest England, characterized by $\delta^{15}\text{N}$ of 8.4–10.2‰ (Boyd et al., 1993). It is also consistent with late Archean tonalites of -5 to 5‰, that are likely melts of basaltic slabs in a convergent margin with mantle-like $\delta^{15}\text{N}$ of ~ -5 ‰ (Jia and Kerrich, 2000; Cartigny and Ader, 2003; Cartigny, 2005).

6. Conclusions and implications

The Paleozoic Cooma metasedimentary complex is characterized by a uniform siliciclastic protolith, containing a range of metamorphic grade from sub-greenschist- to upper amphibolite-facies and migmatite-grade zones. As such, the complex represents an ideal area for the investigation of the magnitude of nitrogen isotope fractionation during progressive metamorphic processes. The N contents and isotopic compositions of both mica separates and bulk metasedimentary rocks show a systematic evolution with increasing metamorphic conditions. The lowest-grade metasedimentary rocks in the Cooma complex having $\delta^{15}\text{N}$ of 2.3 ± 0.5 ‰ are compatible with that of Phanerozoic and Recent unmetamorphosed seafloor sedimentary equivalents. Shifts of 1–2‰ for progressively metamorphosed (at low- P and high- T) sedimentary rocks up to amphibolite facies are consistent with other studies of high- P and high thermal gradient sedimentary rocks metamorphosed to high P – T conditions. The results are consistent with Rayleigh distillation and/or batch devolatilization process involving mainly N_2 – NH_4^+ exchange processes. Significant $\delta^{15}\text{N}$ shifts of 7–10‰ for the upper amphibolite-facies and migmatite-grade metasedimentary rocks and melt products suggest a larger isotope fractionation involving NH_3 – NH_4^+ exchange processes.

Reduction in N and K_2O concentrations accompanies decrease in LOI content in the Cooma metasedimentary rocks, in keeping with progressive partitioning of N and K into H_2O -rich fluids produced by devolatilization reactions primarily involving breakdown of chlorite and mica. The N-isotope system may provide a valuable means for evaluating behavior of mobile elements during metamorphic devolatilization under open- or closed system conditions.

Numerous well-controlled studies document N-isotope fractionation of 1‰ at greenschist-facies to 3‰ at amphibolite-facies during progressive metamorphism of sedimentary rocks under a variety of P – T – t conditions and geodynamic settings. This convergence implies a need to re-evaluate earlier interpretations of shifts of 36 to 27‰ accompanying metamorphism. Beaumont and Robert (1999) reported a range of $\delta^{15}\text{N}$ from -6 ‰ to 30‰ for Precambrian cherts and banded iron formations (BIF), all at greenschist-facies; the most depleted values were interpreted as primary signatures, whereas the most enriched were considered metamorphic shifts, although all rocks analyzed were metamorphosed at greenschist-facies or lower grade. Pinti et al. (2001) reported a range of -7 ‰ to 20‰ for ~ 3.8 Ga amphibolite-facies sedimentary rocks from Isua belt, Greenland having multiple tectonometamorphic overprints, and ~ 3.5 – 3.2 Ga lower greenschist-facies rocks, from the Pilbara craton. Data for the two sample suites overlap. These authors modeled the 27‰ shift in terms of metamorphism, also selecting the most depleted value as

primary. The large Rayleigh fractionation calculated by Pinti et al. (2001) stems from primary values of -7‰ , Rayleigh devolatilization using fractionation factors of Hanschmann (1981), and no constraint on the fraction of residual nitrogen in the rocks. Modelling was on a mix of data from 3.8 Ga amphibolite-facies chert-BIF, that had undergone multiple metamorphic-deformational events and 3.5–3.2 Ga greenschist-facies cherts.

Given constraints of $\sim 1\text{‰}$ on N-isotope shifts to lower grade metamorphism, Jia and co-workers proposed alternatively that enriched ^{15}N values reported by Beaumont and Robert (1999), Pinti et al. (2001), and their own Precambrian data, were largely primary. Collectively, data on sedimentary rocks record a trend from the Neoproterozoic (~ 2.7 Ga, $15.4 \pm 1.7\text{‰}$; $n = 29$), through the Paleoproterozoic ($10.8 \pm 1.1\text{‰}$; $n = 11$), to the Phanerozoic ($3.6 \pm 0.5\text{‰}$; $n = 217$). Micas in post peak-metamorphic hydrothermal deposits, precipitated from fluids generated by regional metamorphism of sedimentary-volcanic sequences show the same secular trend (data and sources summarized in (Jia and Kerrich, 2004; Kerrich et al., 2006). The spatial and temporal association of Precambrian chert and BIF with volcanic sequences erupted from mantle plumes has been used as evidence for a hydrothermal origin of these sediments (Bailey et al., 1998; Isley and Abbott, 1999; Condie et al., 2001). The mantle has a $\delta^{15}\text{N}$ estimated at -5‰ (Cartigny and Ader, 2003; Cartigny, 2005, and references therein). Kramers (2003) has shown that the volatile inventory of Earth is consistent with CI chondrites, Ne excepted. CI chondrites are characterized by $\delta^{15}\text{N} +30\text{‰}$ to $+42\text{‰}$ (Kerridge, 1985, and references therein). Consequently, the large spread of $\delta^{15}\text{N}$ values in Archean metasedimentary rocks can be accounted for by variable mixtures of mantle plume-dominated volatiles, and a ^{15}N -enriched marine sedimentary kerogen component inherited from a CI chondrite veneer (Jia and Kerrich, 2004; Kerrich et al., 2006).

Boyd and Philippot (1998) reported N contents of 140–472 ppm, and $\delta^{15}\text{N}$ of 12.4–14‰, for amphibolite-facies metasedimentary rocks of the Moine group, Scotland. They interpreted the “enriched” values to result from progressive metamorphism of a protolith assumed to be comparable to the Phanerozoic average of 3.6‰. No data for lower grade Moine counterparts was acquired. Given a Proterozoic age of the Moine group, and constraints on N-isotope shifts to amphibolite-facies, these enriched values mesh with the observed secular trend, as originally proposed for ^{15}N -enriched Proterozoic metasedimentary rocks of the Ezergebirge by Häendel et al. (1986).

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