

REVIEW

Pathways for nitrogen cycling in Earth's crust and upper mantle: A review and new results for microporous beryl and cordierite

GRAY E. BEBOUT^{1,*}, KRIS E. LAZZERI², AND CHARLES A. GEIGER³

¹Department of Earth and Environmental Sciences, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.

²EA Engineering, Science and Technology, Inc., Layton, Utah 84041, U.S.A.

³Department of Materials Science and Physics, Section Mineralogy, Salzburg University, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria

ABSTRACT

Earth's atmosphere contains 27–30% of the planet's nitrogen and recent estimates are that about one-half that amount (11–16%) is located in the continental and oceanic crust combined. The percentage of N in the mantle is more difficult to estimate, but it is thought to be near 60%, at very low concentrations. Knowledge of the behavior of N in various fluid-melt-rock settings is key to understanding pathways for its transfer among the major solid Earth reservoirs.

Nitrogen initially bound into various organic materials is transferred into silicate minerals during burial and metamorphism, often as NH_4^+ substituting for K^+ in layer silicates (clays and micas) and feldspars. Low-grade metamorphic rocks appear to retain much of this initial organic N signature, in both concentrations and isotopic compositions, thus in some cases providing a relatively un- or little-modified record of ancient biogeochemical cycling. Devolatilization can release significant fractions of the N initially fixed in crustal rocks through organic diagenesis, during progressive metamorphism at temperatures of ~350–550 °C (depending on pressure). Loss of fractionated N during devolatilization can impart an appreciable isotopic signature on the residual rocks, producing shifts in $\delta^{15}\text{N}$ values mostly in the range of +2 to +5‰. These rocks then retain large fractions of the remaining N largely as NH_4^+ , despite further heating and ultimately partial melting, with little additional change in $\delta^{15}\text{N}$. This retention leads to the storage of relatively large amounts of N, largely as NH_4^+ , in the continental crust. Nitrogen can serve as a tracer of the mobility of organic-sedimentary components into and within the upper mantle.

This contribution focuses on our growing, but still fragmentary, knowledge of the N pathways into shallow to deep continental crustal settings and the upper mantle. We discuss the factors controlling the return of deeply subducted N to shallower reservoirs, including the atmosphere, via metamorphic devolatilization and arc magmatism. We discuss observations from natural rock suites providing tests of calculated mineral-fluid fractionation factors for N. Building on our discussion of N behavior in continental crust, we present new measurements on the N concentrations and isotopic compositions of microporous beryl and cordierite from medium- and high-grade metamorphic rocks and pegmatites, both phases containing molecular N_2 , and NH_4^+ -bearing micas coexisting with them. We suggest some avenues of investigation that could be particularly fruitful toward obtaining a better understanding of the key N reservoirs and the more important pathways for N cycling in the solid Earth.

Keywords: Nitrogen cycling, nitrogen isotopes, ammonium, microporous silicate, isotope fractionation, layer silicates, cordierite, Review article, Invited Centennial article



TABLE 2. Isotopic data for beryl and cordierite (and coexisting micas)

Sample	Beryl $\delta^{15}\text{N}_{\text{air}}$	Beryl N (ppm)	Muscovite $\delta^{15}\text{N}_{\text{air}}$	Muscovite N (ppm)	$\Delta^{15}\text{N}_{\text{mica-beryl}}$	Beryl $\delta^{15}\text{C}_{\text{VPDB}}$	Beryl C (ppm)
80192	7.9	17	9.4	80	1.5		31
23215	5.9	11	8.1	273	2.2	-8.47	48
40597	4.0	25	8.3	305	4.3		
1	3.8	18	6.7	41	2.9	28	-
80145	5.1	39	8.7	632	3.6		
Sample	Cordierite $\delta^{15}\text{N}_{\text{air}}$	Cordierite N (ppm)	Biotite $\delta^{15}\text{N}_{\text{air}}$	Biotite N (ppm)	$\Delta^{15}\text{N}_{\text{mica-crd}}$	Cordierite $\delta^{15}\text{C}_{\text{VPDB}}$	Cordierite C (ppm)
Pegmatite/partial melts							
88593	12.0	5	8.6	134	-3.4		80
80537	10.5	6	11.0	103	0.5		31
G-155a	5.1	17				-10.5	16
C006	9.0	29				-6.9	936
TUB-1	4.3	33				-13.6	195
26230	7.5	38	1.8	70	-5.7		
C004	11.4	60				-8.8	600
84264	7.4	67				-14.0	327
Mid-grade metamorphics							
Wards	16.9	8				-6.5	345
25 Geco Mine	10.4	19					
WYO-2	5.1	30				-10.8	590
118171	6.5	95				-8.4	694
Granulite facies							
X-1	4.7	41				-4.0	277
42/1A	0.9	55				-12.0	543
CL-177-1	30.0	71				-36.4	1200
TA-5	7.0	101				-13.0	221
129875	10.4	104					
I3	4.8	162	7.8	116	3.0		
26539	9.9	232	0.5	65	-9.4	-9.4	1099
VS-1	5.9	273				-6.7	1039
7114	2.9	634				-22.3	991
S. India 1	3.1	923				-16.3	408
89 V	3.6	1342					
NE86A-24b	8.6	4525				-16.5	445
Uncategorized							
CTSiM	9.0	27				-6.7	976
10398	5.5	56	5.2	48	-0.3		
43090	8.3	89	2.7	86	-5.5	-8.3	820
33294	7.5	154	4.4	25	-3.1	-9.3	614
H06	2.0	446					
106886	3.9	1457				-6.1	623

Nitrogen partitioning behavior between coexisting cordierite and biotite

Biotite in pegmatites has N concentrations of 70 to 134 ppm higher than those of the coexisting cordierites, but to varying degrees (see Fig. 9). In two of the three experiments, the $\delta^{15}\text{N}$ values (+1.8 to +11‰) of the biotites are lower than the values for cordierite from the same rock sample (Fig. 9). In the third case, the $\delta^{15}\text{N}$ values for the coexisting minerals are similar. For two granulite facies rocks, biotite has N concentrations of 65 and 116 ppm and they are lower than those of the coexisting cordierites with concentrations of 162 and 232 ppm N, respectively. For three rock samples whose origins are uncertain (“uncategorized”), cordierites have N concentrations and $\delta^{15}\text{N}$ values higher than those of coexisting biotite. Thus, the partitioning and isotopic fractionation results for N in coexisting biotite and cordierite do not show any consistent behavior and, thus, factors other than temperature must be considered.

The wide range of measured N concentrations and $\delta^{15}\text{N}$ values in cordierite could be attributed to differences in the temperature of crystallization, compositional heterogeneity in the protoliths (see the compilation of data for sediments in Kerrich et al. 2006), and differing magnitudes of positive isotopic shifts

in $\delta^{15}\text{N}$ resulting from lower-grade devolatilization (see Bebout and Fogel 1992; Jia 2006; Palya et al. 2011). Three additional effects that could explain the range of $\delta^{15}\text{N}$ values are: (1) the presence of some NH_4^+ in cordierite, which could result in decreased or no fractionation of N with NH_4^+ in coexisting biotite; (2) chemical disequilibrium between biotite and cordierite that could affect the N concentrations and isotopic compositions; or (3) post-crystallization or retrograde modification of the $\delta^{15}\text{N}$ values due to differential diffusive loss (i.e., preferential loss of ^{14}N). Possibility 3 must be addressed in future studies of microporous silicates and fluid-rock processes (see discussion of diffusive loss for H_2O and CO_2 in cordierite by Vry et al. 1990). Regarding the first effect, we consider the presence of significant amounts of NH_4^+ in cordierite as unlikely for crystal chemical reasons (the concentration of K, with very few exceptions, in cordierite is very low).

Nitrogen partitioning behavior between cordierite and its rock matrix for a medium-grade schist

Nitrogen concentrations and $\delta^{15}\text{N}$ values were measured for a gem-quality cordierite and its muscovite-rich matrix for one medium-grade metasedimentary schist from Connecticut,

U.S.A. (Fig. 8b). Here, quite interestingly, cordierite showed no measurable N within the experimental detection limits, whereas the muscovite-rich matrix contained 350 ppm N. Essentially all N in the schist resides as NH_4^+ in the micaceous matrix. This result is consistent with the observation that N concentrations in cordierite are highest at the highest metamorphic grades where muscovite is not present. The interpretation is that N residing in the muscovite, after its breakdown with increasing temperature, is taken up in K-feldspar and cordierite (see Palya et al. 2011).

Nitrogen partitioning behavior between coexisting beryl and muscovite

Figure 10 shows the N concentrations and $\delta^{15}\text{N}$ values for five beryl-muscovite pairs taken from four pegmatites and one metasedimentary schist (see the data in Table 2). These results show that muscovite always contains far greater amounts of N than coexisting beryl. A mean $\Delta^{15}\text{N}_{\text{musc-beryl}}$ ($\delta^{15}\text{N}_{\text{musc}} - \delta^{15}\text{N}_{\text{beryl}}$) value of +2.9 ($1\sigma = 1.1\text{‰}$) was obtained for these pairs. The direction and magnitude of this isotopic fractionation are similar to those measured for biotite-fluid inclusion pairs in a vein in metasedimentary rocks from Bastogne, Belgium (see discussion above) and predicted by the fractionation factors calculated using spectroscopic data (see Fig. 2a). Apparently, based on the limited

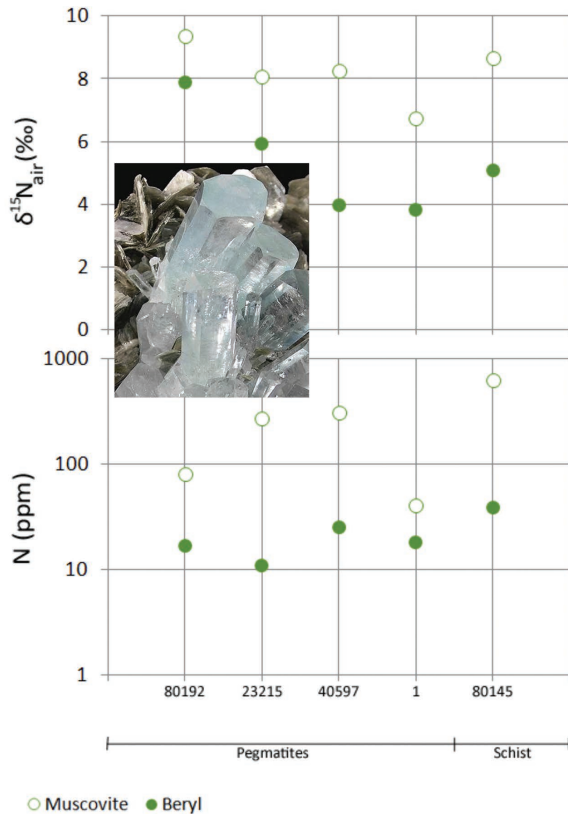


FIGURE 10. Nitrogen isotopic compositions and concentrations of coexisting beryl and muscovite from pegmatites and metamorphic schist (Table 2 and Appendix A¹; Lazzari 2012). The inset photograph of beryl in muscovite is used courtesy of Rob Lavinsky, www.iRocks.com (for photo and specimen; horizontal dimension ~8 cm). (Color online.)

data, the partitioning behavior of N and its isotopes between beryl and muscovite, compared to the case for cordierite-biotite pairs, is more systematic (Fig. 9). This could, in part, reflect (1) the presence of N_2 as the single N species in the beryl (i.e., not also NH_4^+) or (2) the more rapid cooling of pegmatites compared to most granulites. Rapid cooling would allow greater retention of N_2 incorporated during peak crystallization conditions and thus better preservation of the peak-temperature partitioning behavior.

Carbon concentrations and $\delta^{13}\text{C}$ values of cordierite and beryl

Figure 11a shows a plot of N and C concentrations for various cordierites and a single beryl sample (see also Table 2). The two elements show a rough positive correlation. Figure 11b shows a plot of C concentrations and $\delta^{13}\text{C}_{\text{VPDB}}$ values. The various samples have roughly similar $\delta^{13}\text{C}$ values with a mean = -9.8‰ ($1\sigma = 3.5\text{‰}$), with the exception of two cordierites outliers from granulites having $\delta^{13}\text{C}$ values of -36.4 and -22.3‰ . For the range of rocks types studied here, pegmatite cordierites tend to have lower C concentrations. Cordierites from granulites and

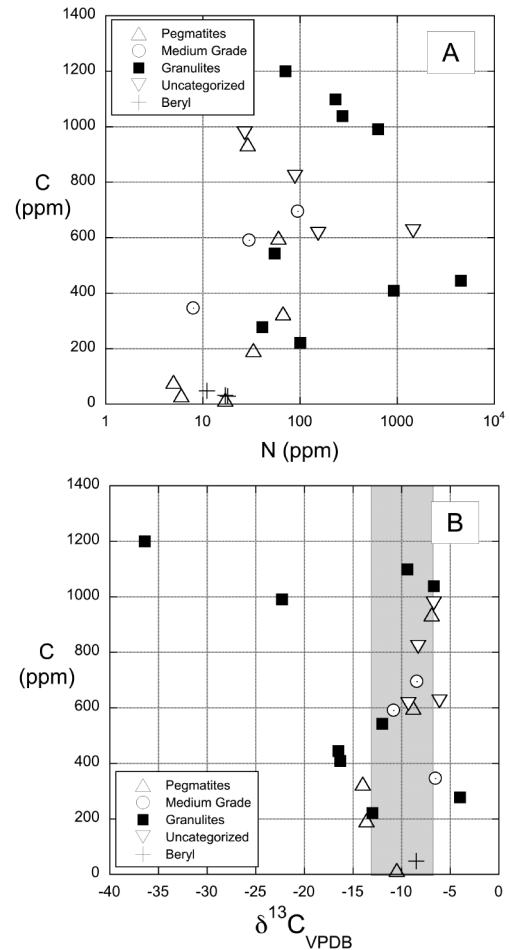


FIGURE 11. C and N concentrations and $\delta^{13}\text{C}$ values for the cordierites and beryl analyzed in this study. (a) N vs. C concentrations. Cordierites from the granulite facies tend to show the highest N concentrations and those from pegmatites the lowest, as is also the case for beryl. (b) Carbon concentration vs. $\delta^{13}\text{C}$ showing the relatively narrow range of isotopic compositions and the wide range in C concentrations.

medium-grade metapelites (and the uncategorized cordierites) have, in general, similar concentrations of C, but the most C-rich samples (i.e., 990 to 1200 ppm C) come from granulites (there is considerable overlap among the data for medium grade, granulite, and uncategorized cordierites). These observations for C concentrations and $\delta^{13}\text{C}$ values are consistent with those made by Vry et al. (1990) in their isotopic investigation of cordierite. Beryl, unlike cordierite, contains very little C, with only one sample containing amounts sufficient for an analysis of $\delta^{13}\text{C}$.

How important are microporous silicates and tourmaline for storage of nitrogen in continental crust?

Cordierite can be a volumetrically significant rock-forming mineral in metapelitic rocks. It is stable over a wide range of temperatures and at low to moderate pressures corresponding to upper to middle levels of the continental crust (e.g., Schreyer 1965; Kalt et al. 1998; White et al. 2003; Palya et al. 2011). Tourmaline, which may also contain appreciable amounts of N (e.g., Wunder et al. 2015), occurs in metapelitic rocks over a broader range of *P* and *T*, even in UHP rocks that experienced pressures of up to ~3.0 GPa (Bebout and Nakamura 2003; see the summary by Marschall et al. 2009; van Hinsberg et al. 2011). However, its modal abundance is limited in both metamorphic and igneous rocks, therefore it is unlikely to play a role as a major sink in the crust and for the deep-Earth N cycle. Tourmaline and beryl in larger amounts can occur in pegmatites (London and Evensen 2002), but pegmatites are unlikely to act as significant N reservoirs due to their relative scarcity. Summarizing, cordierite could be a notable sink for N in shallow- to mid-levels of the continental crust.

CONCLUSIONS AND OUTLOOK

Fluxes of N among the oceanic and continental crust, mantle, oceans, and atmosphere largely determine the abundance and the isotopic composition of N in all of these reservoirs. Models of modern and ancient volatile cycling on Earth are highly dependent on understanding the nature of these fluxes (Javoy 1997; Tolstikhin and Marty 1998; Zhang and Zindler 1993). Biological processes play a key role in affecting the concentrations and behavior of N in the solid Earth. Nitrogen in the oceans and atmosphere can be incorporated (via biological processes) into mineral phases, some of which are carried into the deep Earth (via burial and subduction). Nitrogen can thus be an effective tracer in the study of the transfer of sedimentary and organic components into and within the crust and upper mantle. In this article, we present some important observations regarding this hydrosphere-crust-upper mantle transfer, based on the studies to date, and we suggest several areas needing attention.

- NH_4^+ can replace K^+ via a solid solution mechanism in some K-bearing rock-forming silicate minerals, especially layer silicates (clays and micas) and feldspar. This substitution is so prevalent that an estimate of N subduction-input fluxes can be based on knowledge of the rates of K subduction (see Busigny et al. 2003, 2011; Busigny and Bebout 2013). Recent research suggests that cordierite and tourmaline can also serve as reservoirs for N, with concentrations roughly similar to those of coexisting micas. Cordierite could be a

significant phase for the storage of molecular N_2 in shallow- to mid-levels of the continental crust.

- Low-temperature devolatilization of organic matter, and the concomitant crystallization of clay minerals such as illite, permit the retention of this initially organic N as NH_4^+ , apparently with little isotopic fractionation. Although whole-rock C/N ratios of very low-grade metamorphosed sediments can retain biogeochemical information, kerogen itself (the reduced C reservoir) contains very little N. Most of the initially organic N is transferred into and housed in clays and low-grade metamorphic micas (and in some cases, authigenic feldspars; Svensen et al. 2008).
- Considerable loss of N from minerals to fluids can occur at low to medium metamorphic grades, depending upon the prograde *P-T* path the rocks experience (see Bebout and Fogel 1992; Busigny et al. 2013; Li and Keppler 2014). In many cases, the isotopic shifts associated with this loss point to a N_2 - NH_4^+ exchange mechanism. Li et al. (2009) proposed, however, the possibility of kinetically controlled NH_3 - NH_4^+ exchange. In relatively “cool” subduction zone settings, sedimentary rocks can retain a large fraction of their original N contents to great depths, perhaps even the depths beneath volcanic fronts (see Busigny et al. 2003; Bebout et al. 2013a). Experimental phase equilibrium studies document the stability of mica (e.g., phengite), the key N mineral reservoir, to great depths in most subduction zones (Schmidt and Poli 2014).
- Further investigation of the concentrations, isotope compositions, and fluxes of N into and within the continental crust is badly needed (see the discussion by Johnson and Goldblatt 2015). The estimated average concentration of 56 ppm for this reservoir is based on a very small number of analyses (see Wedepohl 1995; Bach et al. 1999; Palya et al. 2011; Rudnick and Gao 2014). It goes without saying that further work on the concentrations and isotopic compositions of N in the mantle is needed, as the mantle could contain ~60% of the Earth’s N (Table 1; see the discussions by Cartigny and Marty 2013; cf. Johnson and Goldblatt 2015).
- The rates and mechanisms by which N diffuses in key minerals such as the micas, alkali feldspars, clinopyroxenes, and microporous silicates are poorly understood (see Watson and Cherniak 2014). Closure temperatures for the retention of N in these phases are not known, complicating the assessment of N isotope behavior at high geologic temperatures.
- All research done thus far on N in silicate systems has been on either whole-rock samples or mineral separates. It will be important to develop microanalytical methods for analyzing N concentrations and $\delta^{15}\text{N}$ at scales allowing consideration of intramineral heterogeneity (see the first analyses on cordierite using the ion microprobe by Hervig et al. 2014).
- Finally, we stress the need for experimental calibration of N isotope fractionation in silicate fluid-mineral systems. This is required to understand and resolve the differences among the various calculated fractionation factors.

ACKNOWLEDGMENTS

Funding from the National Science Foundation (most recently, EAR-0711355) supported the N isotope work conducted at Lehigh University. C.A.G. is supported by the Austrian Science Fund (FWF) through grant P25597-N20. We thank George Harlow and Jamie Newman, at the American Museum of Natural History (New York), for assisting in the acquisition of some specimens. The cordierite samples investigated in this and the degassing study (Geiger et al. in preparation) were supplied by several colleagues and here Julie Vry (Victoria University of Wellington, New Zealand) deserves special thanks. Thanks also go to Long Li, who prepared the size splits of the beryl sample used in the tests of the release during heating. Comments by Daniele Pinti and an anonymous reviewer improved the manuscript.

REFERENCES CITED

- Ader, M., Boudou, J.-P., Javoy, M., Goffé, B., and Daniels, E. (1998) Isotope study on organic nitrogen of Westphalian anthracites from the Western Middle field of Pennsylvania (U.S.A.) and from the Bramsche Massif (Germany). *Organic Geochemistry*, 29, 315–328.
- Ader, M., Cartigny, P., Boudou, J.P., Oh, J.H., Petit, E., and Javoy, M. (2006) Nitrogen isotopic evolution of carbonaceous matter during metamorphism: Methodology and preliminary results. *Chemical Geology*, 232, 152–169.
- Andersen, T., Austrheim, H., and Burke, E.A.J. (1990) Fluid inclusions in granulites and eclogites from the Bergen Arcs, Caledonides of Western Norway. *Mineralogical Magazine*, 54, 145–158.
- Andersen, T., Austrheim, H., Burke, E.A., and Elvevold, S. (1993) N₂ and CO₂ in deep crustal fluids: Evidence from the Caledonides of Norway. *Chemical Geology*, 108, 113–132.
- Armbruster, T. (1985) Ar, N₂ and CO₂ in the structural cavities of cordierite, an optical and X-ray single crystal study. *Physics and Chemistry of Minerals*, 12, 233–245.
- (1986) Role of Na in the structure of low-cordierite: A single-crystal X-ray study. *American Mineralogist*, 71, 746–757.
- Bach, W., Naumann, D., and Erzinger, J. (1999) A helium, argon, and nitrogen record of the upper continental crust (KTB drill holes, Oberpfalz, Germany): implications for crustal degassing. *Chemical Geology*, 160, 81–101.
- Bakker, R.M., and Jansen, J.B.H. (1993) Calculated fluid evolution path versus fluid inclusion data in the COHN system as exemplified by metamorphic rocks from Rogaland, southwest Norway. *Journal of Metamorphic Geology*, 11, 357–370.
- Barker, D.S. (1964) Ammonium in alkali feldspar. *American Mineralogist*, 49, 851–858.
- Bebout, G.E. (1997) Nitrogen isotope tracers of high-temperature fluid-rock interactions: case study of the Catalina Schist, California. *Earth and Planetary Science Letters*, 151, 77–90.
- (2007) Metamorphic chemical geodynamics of subduction zones. *Earth and Planetary Science Letters*, 260, 373–393.
- Bebout, G.E., and Barton, M.D. (1993) Metasomatism during subduction: products and possible paths in the Catalina Schist, California. *Chemical Geology*, 108, 61–92.
- Bebout, G.E., and Fogel, M.L. (1992) Nitrogen-isotope compositions of metasedimentary rocks in the Catalina Schist, California—Implications for metamorphic devolatilization history. *Geochimica et Cosmochimica Acta*, 56, 2839–2849.
- Bebout, G.E., and Nakamura, E. (2003) Record in metamorphic tourmalines of subduction zone devolatilization and boron cycling. *Geology*, 31, 407–410.
- Bebout, G.E., and Sadofsky, S.J. (2004) $\delta^{15}\text{N}$ analyses of ammonium-rich silicate minerals by sealed-tube extractions and dual inlet, viscous-flow mass spectrometry. In P. de Groot, Ed., *Handbook of Stable Isotope Techniques*, p. 348–360. Elsevier, Amsterdam.
- Bebout, G.E., Cooper, D.C., Bradley, A.D., and Sadofsky, S.J. (1999a) Nitrogen-isotope record of fluid rock interactions in the Skiddaw Aureole and granite, English Lake District. *American Mineralogist*, 84, 1495–1505.
- Bebout, G.E., Ryan, J.G., Leeman, W.P., and Bebout, A.E. (1999b) Fractionation of trace elements by subduction-zone metamorphism—effect of convergent-margin thermal evolution. *Earth and Planetary Science Letters*, 171, 63–81.
- Bebout, G.E., Idleman, B.D., Li, L., and Hilkert, A. (2007) Isotope-ratio-monitoring gas chromatography methods for high-precision isotopic analysis of nanomole quantities of silicate nitrogen. *Chemical Geology*, 240, 1–10.
- Bebout, G.E., Agard, P., Kobayashi, K., Moriguti, T., and Nakamura, E. (2013a) Devolatilization history and trace element mobility in deeply subducted sedimentary rocks: Evidence from Western Alps HP/UHP suites. *Chemical Geology*, 342, 1–20.
- Bebout, G.E., Fogel, M.L., and Cartigny, P. (2013b) Nitrogen: Highly volatile yet surprisingly compatible. *Elements*, 9, 333–338.
- Bebout, G.E., Banerjee, N.R., Izawa, M.R.M., Lazzari, K.E., Kobayashi, K., and Nakamura, E. (2015) Enrichment of sedimentary/organic nitrogen in altered terrestrial glassy basaltic rocks: Possible implications for astrobiology. *Astrobiology Science Conference*, Chicago, June, 2015.
- Beinlich, A., Klemd, R., John, T., and Gao, J. (2010) Trace-element mobilization during Ca-metasomatism along a major fluid conduit: Eclogitization of blueschist as a consequence of fluid-rock interaction. *Geochimica et Cosmochimica Acta*, 74, 1892–1922.
- Bobos, I., and Eberl, D.D. (2013) Thickness distributions and evolution of growth mechanisms of NH₄-illite from the fossil hydrothermal system of Harghita Băi, Eastern Carpathians, Romania. *Clays and Clay Minerals*, 61, 375–391.
- Bos, A., Duit, W., van Der Eerden, M.J., and Jansen, B. (1988) Nitrogen storage in biotite: An experimental study of the ammonium and potassium partitioning between 1 M-phlogopite and vapour at 2 kb. *Geochimica et Cosmochimica Acta*, 52, 1275–1283.
- Bottrell, S.H., Carr, L.P., and Dubessy, J. (1988) A nitrogen-rich metamorphic fluid and coexisting minerals in slates from North Wales. *Mineralogical Magazine*, 52, 451–457.
- Boudou, J.-P., Schimmelmann, A., Ader, M., Mastalerz, M., Sebilo, M., and Gengembre, L. (2008) Organic nitrogen chemistry during low-grade metamorphism. *Geochimica et Cosmochimica Acta*, 72, 1199–1221.
- Boyd, S.R. (1997) Determination of the ammonium content of potassic rocks by capacitance manometry: a prelude to the calibration of FTIR microscopes. *Chemical Geology*, 137, 57–66.
- (2001) Nitrogen in future biosphere studies. *Chemical Geology*, 176, 1–30.
- Boyd, S.R., Hall, A., and Pillinger, C.T. (1993) The measurement of $\delta^{15}\text{N}$ in crustal rocks by static vacuum mass spectrometry: Application to the origin of the ammonium in the Cornubian batholith, southwest England. *Geochimica et Cosmochimica Acta*, 57, 1339–1347.
- Bräuer, K., and Hahne, K. (2005) Methodical aspects of the ^{15}N -analysis of Precambrian and Palaeozoic sediments rich in organic matter. *Chemical Geology*, 218, 361–368.
- Bul'bak, T.A., and Shvedenkov, G.Y. (2005) Experimental study on incorporation of C-H-O-N fluid components in Mg-cordierite. *European Journal of Mineralogy*, 17, 829–838.
- Busigny, V., and Bebout, G.E. (2013) Nitrogen in the silicate Earth: Speciation and isotopic behavior during mineral–fluid interactions. *Elements*, 9, 353–358.
- Busigny, V., Cartigny, P., Philippot, P., Ader, M., and Javoy, M. (2003) Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe (western Alps, Europe). *Earth and Planetary Science Letters*, 215, 27–42.
- Busigny, V., Cartigny, P., Philippot, P., and Javoy, M. (2004) Quantitative analysis of ammonium in biotite using infrared spectroscopy. *American Mineralogist*, 89, 1625–1630.
- Busigny, V., Ader, M., and Cartigny, P. (2005a) Quantification and isotopic analysis of nitrogen in rocks at the ppm level using tube combustion technique: A prelude to the study of altered oceanic crust. *Chemical Geology*, 223, 249–258.
- Busigny, V., Laverne, C., and Bonifacie, M. (2005b) Nitrogen content and isotopic composition of oceanic crust at a superfast spreading ridge: A profile in altered basalts from ODP Site 1256, Leg 206. *Geochemistry, Geophysics, Geosystems*, 6, <http://dx.doi.org/10.1029/2005GC001020>.
- Busigny, V., Cartigny, P., and Philippot, P. (2011) Nitrogen isotopes in ophiolitic metagabbros: A reevaluation of modern nitrogen fluxes in subduction zones and implication for the early Earth atmosphere. *Geochimica et Cosmochimica Acta*, 75, 7502–7521.
- Cartigny, P. (2005) Stable isotopes and the origin of diamond. *Elements*, 1, 79–84.
- Cartigny, P., and Marty, B. (2013) Nitrogen isotopes and mantle geodynamics: The emergence of life and the atmosphere-crust-mantle connection. *Elements*, 9, 359–366.
- Cartigny, P., De Corte, K., Shatsky, V.S., Ader, M., De Paep, P., Sobolev, N.V., and Javoy, M. (2001) The origin and formation of metamorphic microdiamonds from the Kokchetav massif, Kazakhstan: a nitrogen and carbon isotopic study. *Chemical Geology*, 176, 265–281.
- Cartigny, P., Busigny, V., and Rudnick, R. (2013) Re-investigating the nitrogen budget in the upper continental crust. *Goldschmidt Conference Abstracts*, p. 835.
- Clarke, D.B. (1995) Cordierite in felsic igneous rocks: A synthesis. *Mineralogical Magazine*, 59, 311–325.
- Cockell, C.S., van Calsteren, P., Mosselmans, J.F.W., Franchi, I.A., Gilmour, I., Kelly, L., Olsson-Francis, K., Johnson, D., and the J24 Shipboard Scientific Party (2010) Microbial endolithic colonization and the geochemical environment in young seafloor basalts. *Chemical Geology*, 279, 17–30.
- Collins, N.C., Bebout, G.E., Angiboust, S., Agard, P., Scambelluri, M., Crispini, L., and John, T. (2015) Subduction zone metamorphic pathway for deep carbon cycling: II. Evidence from HP/UHP metabasaltic rocks and ophiocarbons. *Chemical Geology*, 412, 132–150.
- Cook-Kollars, J., Bebout, G.E., Collins, N.C., Angiboust, S., and Agard, P. (2014) Subduction zone metamorphic pathway for deep carbon cycling: I. Evidence from HP/UHP metasedimentary rocks, Italian Alps. *Chemical Geology*, 386, 31–48.
- Damon, P.E., and Kulp, J.L. (1958) Excess helium and argon in beryl and other minerals. *American Mineralogist*, 43, 433–459.
- Darimont, A., Burke, E., and Touret, J. (1988) Nitrogen-rich metamorphic fluids in Devonian metasediments from Bastogne, Belgium. *Bulletin Mineralogie*, 111, 321–330.
- Dobrzynetskaya, L.F., Wirth, R., Yang, J., Hutcheon, I.D., Weber, P.K., and Green, H.W. (2009) High pressure highly reduced nitrides and oxides from chromitite of a Tibetan ophiolite. *Proceedings of the National Academy of Sciences*, 106, 19233–19238.
- Duit, W., Jansen, J.B.H., van Breeman, A., and Bos, A. (1986) Ammonium micas in metamorphic rocks as exemplified by Dome de l'Agout (France). *American Journal of Science*, 286, 702–732.
- Elkins, L.J., Fischer, T.P., Hilton, D.R., Sharp, Z.D., McKnight, S., and Walker, J. (2006) Tracing nitrogen in volcanic and geothermal volatiles from the Nicaraguan volcanic front. *Geochimica et Cosmochimica Acta*, 70, 5215–5235.
- Erd, R.C., White, D.E., Fahey, J.J., and Lee, D.E. (1964) Buddingtonite, an ammonium feldspar with zeolitic water. *American Mineralogist*, 49, 831–850.
- Eugster, H.P., and Munoz, J. (1966) Ammonium micas: possible sources of atmospheric ammonia and nitrogen. *Science*, 151, 683–686.

- Facq, S., Daniel, I., Montagnac, G., Cardon, H., and Sverjensky, D.A. (2014) In situ Raman study and thermodynamic model of aqueous carbonate speciation in equilibrium with aragonite under subduction zone conditions. *Geochimica et Cosmochimica Acta*, 132, 375–390.
- Fischer, T. (2008) Fluxes of volatiles (H₂O, CO₂, N₂, Cl, F) from arc volcanoes. *Geochemical Journal*, 42, 21–38.
- Galloway, J.N. (2003) The global nitrogen cycle. In *Treatise on Geochemistry*, chapter 8.12, p. 557–583. Elsevier, Amsterdam.
- Goldblatt, C., Claire, M.W., Lenton, T.M., Matthews, A.J., Watson, A.J., and Zahnle, K.J. (2009) Nitrogen enhanced greenhouse warming on early Earth. *Nature Geoscience*, 2, 891–896.
- Grove, M., and Bebout, G.E. (1995) Cretaceous tectonic evolution of coastal southern California: insights from the Catalina Schist. *Tectonics*, 14, 1290–1308.
- Haendel, D., Mühle, K., Nitzsche, H., Stiehl, G., and Wand, U. (1986) Isotopic variations of the fixed nitrogen in metamorphic rocks. *Geochimica et Cosmochimica Acta*, 50, 749–758.
- Halama, R., Bebout, G.E., John, T., and Schenk, V. (2010) Nitrogen recycling in subducted oceanic lithosphere: the record in high- and ultrahigh-pressure metabasaltic rocks. *Geochimica et Cosmochimica Acta*, 74, 1636–1652.
- Halama, R., Bebout, G.E., John, T., and Scambelluri, M. (2012) Nitrogen recycling in subducted mantle rocks and implications for the global nitrogen cycle. *International Journal of Earth Sciences*, <http://dx.doi.org/10.1007/s00531-012-0782-3>.
- Halama, R., Bebout, G., John, T., Magna, T., and Seitz, M. (2009) Behavior of nitrogen and its isotopes during high-pressure fluid-driven metasomatic processes: A case study from the Tian Shan, China. Invited paper, Abstracts of the 19th Goldschmidt Conference, Davos, Switzerland.
- Hall, A. (1999) Ammonium in granites and its petrogenetic significance. *Earth-Science Reviews*, 45, 145–165.
- Hall, A., Pereira, M.D., and Bea, F. (1996) The abundance of ammonium in the granites of central Spain, and the behaviour of the ammonium ion during anatexis and fractional crystallization. *Mineralogy and Petrology*, 56, 105–123.
- Hanschmann, G. (1981) Berechnung von Isotopieeffekten auf quantenchemischer Grundlage am Beispiel stickstoffhaltiger Moleküle. *ZFI-Mitteilungen*, 41, 19–39.
- Hashizume, K., and Marty, B. (2005) Nitrogen isotopic analyses at the sub-picometer level using an ultra-low blank laser extraction technique. In P. de Groot, Ed., *Handbook of Stable Isotope Analytical Techniques*. Elsevier, Amsterdam.
- Heinrich, E.W. (1950) Cordierite in pegmatite near Micanite, Colorado. *American Mineralogist*, 35, 173–184.
- Hervig, R.L., Fudge, C., and Navrotsky, A. (2014) Analyzing nitrogen in cordierites and other phases by SIMS. *Goldschmidt Conference abstract 982*.
- Higashi, S. (1982) Tobelitte, a new ammonium dioctahedral mica. *Mineralogical Journal*, 11, 138–146.
- Hilton, D.R., Fischer, T.P., and Marty, B. (2002) Noble gases and volatile recycling at subduction zones. *Reviews in Mineralogy and Geochemistry*, 47, 319–370.
- Holloway, J.M., and Dahlgren, R.A. (2002) Nitrogen in rock: Occurrences and biogeochemical implications. *Global Biogeochemical Cycles*, 16, <http://dx.doi.org/10.1029/2002GB001862>.
- Honma, H., and Itihara, Y. (1981) Distribution of ammonium in minerals of metamorphic and granitic rocks. *Geochimica et Cosmochimica Acta*, 45, 983–988.
- Javoy, M. (1997) The major volatile elements of the Earth: their origin, behavior, and fate. *Geophysical Research Letters*, 24, 177–180.
- Jenden, P.D., Kaplan, I.R., Poreda, R.J., and Craig, H. (1988) Origin of nitrogen-rich natural gases in the California Great Valley: Evidence from helium, carbon, and nitrogen isotope ratios. *Geochimica et Cosmochimica Acta*, 52, 851–861.
- Jia, Y.F. (2006) Nitrogen isotope fractionations during progressive metamorphism: A case study from the Paleozoic Cooma metasedimentary complex, southeastern Australia. *Geochimica et Cosmochimica Acta*, 70, 5201–5214.
- Jia, Y., Kerrich, R., and Goldfarb, R. (2003) Metamorphic origin of ore-forming fluids for orogenic gold-bearing quartz vein systems in the North American Cordillera: Constraints from a reconnaissance study of $\delta^{15}\text{N}$, δD , and $\delta^{18}\text{O}$. *Economic Geology*, 98, 109–123.
- John, T., Gussone, N., Podladchikov, Y.Y., Bebout, G.E., Dohmen, R., Halama, R., Klemd, R., Magna, T., and Seitz, M. (2012) Pulsed long-distance fluid flow through subducting slabs feeds volcanic arcs. *Nature Geoscience*, <http://dx.doi.org/10.1038/NGEO1482>.
- Johnson, B., and Goldblatt, C. (2015) The nitrogen budget of Earth. *Earth-Science Reviews*, 148, 150–173, <http://dx.doi.org/10.1016/j.earscirev.2015.05.006>.
- Junge, F., Seltmann, R., and Stiehl, G. (1989) Nitrogen isotope characteristics of breccias, granitoids, and greisens from eastern Erzgebirge tin ore deposits (Sadisdorf: Altenberg). *GDR. Proceedings of the 5th Working Meeting, Isotopes in Nature*, Leipzig, September, p. 321–332.
- Kalt, A., Altherr, R., and Ludwig, T. (1998) Contact metamorphism in pelitic rocks on the island of Kos (Greece, Eastern Aegean Sea): a test for the Na-in-cordierite thermometer. *Journal of Petrology*, 39, 663–688.
- Kerrich, R., Jia, Y., Manikyamba, C., and Naqvi, S.M. (2006) Secular variations of N-isotopes in terrestrial reservoirs and ore deposits. In S.E. Kesler and H. Ohmoto, Eds., *Evolution of Early Earth's Atmosphere, Hydrosphere, and Biosphere—Constraints from ore deposits*. Geological Society of America Memoir, 198, 81–104.
- Kolesov, B.A., and Geiger, C.A. (2000) Cordierite II: The role of CO₂ and H₂O. *American Mineralogist*, 85, 1265–1274.
- Kreuln, R., and Schuling, R.D. (1982) N₂-CH₄-CO₂ fluids during formation of the Dome de l'Agout, France. *Geochimica et Cosmochimica Acta*, 46, 193–203.
- Kreuln, R., van Breeman, A., and Duit, W. (1982) Nitrogen and carbon isotopes in metamorphic fluids from the Dome de l'Agout, France. *Proceedings of the 5th International Conference for Geochronology, Cosmochronology, and Isotope Geology*, p. 191.
- Krohn, M.D., Kendall, C., Evans, J.R., and Fries, T.L. (1993) Relations of ammonium minerals at several hydrothermal systems in the western U.S. *Journal of Volcanology and Geothermal Research*, 4, 401–413.
- Krooss, B.M., Friberg, L., Gensterblum, Y., Hollenstein, J., Prinz, D., and Littke, R. (2005) Investigation of the pyrolytic liberation of molecular nitrogen from Paleozoic sedimentary rocks. *International Journal of Earth Sciences*, 94, 1023–1038.
- Lazzeri, K.E. (2012) Storage of nitrogen in silicate minerals and glasses. M.S. thesis, Lehigh University, 76 pp.
- Lepezin, G.G., Bul'bak, T.A., Sokol, E.V., and Shvedenkov, G.Y. (1999) Fluid components in cordierites and their significance for metamorphic petrology. *Russian Geology and Geophysics*, 40, 99–116.
- Li, Y., and Keppler, H. (2014) Nitrogen speciation in mantle and crustal fluids. *Geochimica et Cosmochimica Acta*, 129, 13–32.
- Li, L., Bebout, G.E., and Idleman, B.D. (2007) Nitrogen concentration and $\delta^{15}\text{N}$ of altered oceanic crust obtained on ODP Legs 129 and 185: Insights into alteration-related nitrogen enrichment and the nitrogen subduction budget. *Geochimica et Cosmochimica Acta*, 71, 2344–2360.
- Li, L., Cartigny, P., and Ader, M. (2009) Kinetic nitrogen isotope fractionation associated with thermal decomposition of NH₃: Experimental results and potential applications to trace the origin of N₂ in natural gas and hydrothermal systems. *Geochimica et Cosmochimica Acta*, 73, 6282–6297.
- Li, L., Zheng, Y.-F., Cartigny, P., and Li, J. (2014) Anomalous nitrogen isotopes in ultrahigh-pressure metamorphic rocks from the Sulu orogenic belt: Effect of abiogenic nitrogen reduction during fluid-rock interaction. *Earth and Planetary Science Letters*, 403, 67–78.
- Libourel, G., Marty, B., and Humbert, F. (2003) Nitrogen solubility in basaltic melt. Part I. Effect of oxygen fugacity. *Geochimica et Cosmochimica Acta*, 67, 4123–4135.
- London, D., and Evensen, J.M. (2002) Beryllium in silicic magmas and the origin of beryl-bearing pegmatites. *Reviews in Mineralogy and Geochemistry*, 50, 445–486.
- Mariotti, A. (1984) Natural ¹⁵N abundance measurements and atmospheric nitrogen standard calibration. *Nature*, 311, 251–252.
- Marschall, H.R., Korsakov, A.V., Luvizotto, G.L., Nasdala, L., and Ludwig, T. (2009) On the occurrence and boron isotopic composition of tourmaline in (ultra)high-pressure metamorphic rocks. *Journal of the Geological Society, London*, 177, 811–823.
- Mashkovtsev, R.I., and Solntsev, V.P. (2002) Channel constituents in synthetic beryl: ammonium. *Physics and Chemistry of Minerals*, 29, 65–71.
- Mikhail, S., and Sverjensky, D.A. (2014) Nitrogen speciation in upper mantle fluids and the origin of Earth's nitrogen-rich atmosphere. *Nature Geoscience*, 7, <http://dx.doi.org/10.1038/NGEO2271>.
- Mingram, B., and Bräuer, K. (2001) Ammonium concentration and nitrogen isotope composition in metasedimentary rocks from different tectonometamorphic units of the European Variscan Belt. *Geochimica et Cosmochimica Acta*, 65, 273–287.
- Mingram, B., Hoth, P., Luders, V., and Harlov, D. (2005) The significance of fixed ammonium in Palaeozoic sediments for the generation of nitrogen-rich natural gases in the North German Basin. *International Journal of Earth Sciences*, 94, 1010–1022.
- Mitchell, E.C., Fischer, T.P., Hilton, D.R., Hauri, E.H., Shaw, A.M., de Moor, J.M., Sharp, Z.D., and Kazahaya, K. (2010) Nitrogen sources and recycling at subduction zones: insights from the Izu–Bonin–Mariana arc. *Geochemistry, Geophysics, Geosystems*, 11(2), [doi.org/10.1029/2009GC002783](http://dx.doi.org/10.1029/2009GC002783).
- Moine, B., Guillot, C., and Gibert, F. (1994) Controls on the composition of nitrogen-rich fluids originating from reaction with graphite and ammonium-bearing biotite. *Geochimica et Cosmochimica Acta*, 58, 5503–5523.
- Müller, E.P., May, F., and Stiehl, G. (1976) Zur Isotopengeochemie des Stickstoffs und zur Genese stickstoffreicher Erdgase. *Zeitschrift für Angewandte Geologie*, 22, 319–324.
- Mysen, B., and Fogel, M.L. (2010) Nitrogen and hydrogen isotope compositions and solubility in silicate melts in equilibrium with reduced (N+H)-bearing fluids at high pressure and temperature: Effects of melt structure. *American Mineralogist*, 95, 987–999.
- Ortega, L., Vendel, E., and Beny, C. (1991) C-O-H-N fluid inclusions associated with gold-stibnite mineralization in low-grade metamorphic rocks, Mari Rosa mine, Cáceres, Spain. *Mineralogical Magazine*, 55, 235–247.
- Palya, A.P., Buick, I.S., and Bebout, G.E. (2011) Storage and mobility of nitrogen in the continental crust: Evidence from partially melted metasedimentary rocks, Mt. Stafford, Australia. *Chemical Geology*, 281, 211–226.
- Pan, D., Spanu, L., Harrison, B., Sverjensky, D.A., and Galli, G. (2013) Dielectric properties of water under extreme conditions and transport of carbonates in the deep Earth. *Proceedings of the National Academy of Sciences*, 110, 6646–6650.
- Petts, D.C., Chacko, T., Stachel, T., Stern, R.A., and Heaman, L.M. (2015) A nitrogen isotope fractionation factor between diamond and its parental fluid derived from detailed SIMS analysis of a gem diamond and theoretical calculations. *Chemical Geology*, 410, 188–200.
- Philipot, P., Busigny, V., Scambelluri, M., and Cartigny, P. (2007) Oxygen and nitrogen isotopes as tracers of fluid activities in serpentinites and metasediments during

- subduction. *Mineralogy and Petrology*, 91, 11–24.
- Pinti, D.L., Hashizume, K., Orberger, B., Gallien, J.-P., Cloquet, C., and Massault, M. (2007) Biogenic nitrogen and carbon in Fe-Mn-oxyhydroxides from an Archean chert, Marble Bar, Western Australia. *Geochemistry, Geophysics, Geosystems*, 8, <http://dx.doi.org/10.1029/2006GC001394>.
- Pitcairn, I.K., Teagle, D.A.H., Kerrich, R., Craw, D., and Brewer, T.S. (2005) The behavior of nitrogen and nitrogen isotopes during metamorphism and mineralization: Evidence from the Otago and Alpine Schists, New Zealand. *Earth and Planetary Science Letters*, 233, 229–246.
- Plessen, B., Harlov, D.E., Henry, D., and Guidotti, C.V. (2010) Ammonium loss and nitrogen isotopic fractionation in biotite as a function of metamorphic grade in metapelites from western Maine, USA. *Geochimica et Cosmochimica Acta*, 74, 4759–4771.
- Pöter, B., Gottschalk, M., and Heinrich, W. (2004) Experimental determination of the ammonium partitioning among muscovite, K-feldspar, and aqueous chloride solutions. *Lithos*, 74, 67–90.
- Richet, P., Bottinga, Y., and Javoy, M. (1977) A review of hydrogen, carbon, nitrogen, oxygen, sulphur and chlorine stable isotope fractionation among gaseous molecules. *Annual Review of Earth and Planetary Sciences*, 5, 65–110.
- Roskosz, M., Mysen, B., and Cody, G.D. (2006) Dual speciation of nitrogen in silicate melts at high pressure and temperature: An experimental study. *Geochimica et Cosmochimica Acta*, 70, 2902–2918.
- Roskosz, M., Bouhifd, M., Jephcoat, A., Marty, B., and Mysen, B. (2013) Nitrogen solubility in molten metal and silicate at high pressure and temperature. *Geochimica et Cosmochimica Acta*, 121, 15–28.
- Rudnick, R.L., and Gao, A. (2014) Composition of the continental crust. In H.D. Holland and K.K. Turekian, Eds., *Treatise on Geochemistry*, 4, pp. 1–51. Elsevier, Amsterdam.
- Ruiz Cruz, M.D., and Sanz de Galdeano, C. (2008) High-temperature ammonium white mica from the Betic Cordillera (Spain). *American Mineralogist*, 93, 977–987.
- Sadofsky, S.J., and Bébout, G.E. (2000) Ammonium partitioning and nitrogen-isotope fractionation among coexisting micas during high-temperature fluid-rock interactions: examples from the New England Appalachians. *Geochimica et Cosmochimica Acta*, 64, 2835–2849.
- (2003) Record of forearc devolatilization in low-*T*, high-*P/T* metasedimentary suites: significance for models of convergent margin chemical cycling. *Geochemistry, Geophysics, Geosystems*, 4, 9003, <http://dx.doi.org/10.1029/2002GC000412>, 4.
- Sadofsky, S.J., and Bébout, G.E. (2004) Nitrogen geochemistry of subducting sediments: new results from the Izu-Bonin-Mariana margin and insights regarding global N subduction. *Geochemistry, Geophysics, Geosystems*, 5, Q03115, <http://dx.doi.org/10.1029/2003GC000543>.
- Sano, Y., Takahata, N., Nishio, Y., Fischer, T.P., and Williams, S.N. (2001) Volcanic flux of nitrogen from the Earth. *Chemical Geology*, 171, 263–271.
- Scalan, R.S. (1958) The isotopic composition, concentration, and chemical state of the nitrogen in igneous rocks. Ph.D. dissertation, University of Arkansas.
- Schmidt, M.W., and Poli, S. (2014) Devolatilization during subduction. In R.L. Rudnick, Ed., *Treatise on Geochemistry: The Crust*, 2nd ed., 3, p. 669–701. Elsevier, Amsterdam.
- Schreyer, W. (1965) Synthetische und natürliche Cordierit II. Die chemischen Zusammensetzung natürlicher Cordierite und ihre Abhängigkeit von den PTX-Bedingungen bei der Gesteinsbildung. *Neues Jahrbuch für Mineralogie-Abhandlung*, 103, 35–79.
- Schroeder, P.A., and McLain, A.A. (1998) Illite-smectites and the influence of burial diagenesis on the geochemical cycling of nitrogen. *Clay Minerals*, 33, 539–546.
- Staudigel, H., Furnes, H., McLoughlin, N., Banerjee, N.R., Connell, L.B., and Templeton, A. (2008) 3.5 billions years of glass bioalteration: Volcanic rocks as a basis for microbial life? *Earth-Science Reviews*, 89, 156–176.
- Svensen, H., Bébout, G.E., Kronz, A., Li, L., Planke, S., Chevallier, L., and Jamtveit, B. (2008) Nitrogen geochemistry as a tracer of fluid flow in a hydrothermal vent complex in the Karoo Basin, South Africa. *Geochimica et Cosmochimica Acta*, 72, 4929–4947.
- Sverjensky, D.A., Stagno, V., and Huang, F. (2014) Important role for organic carbon in subduction-zone fluids in the deep carbon cycle. *Nature Geoscience*, 7, 909–913.
- Thomazo, C., and Papineau, D. (2013) Biogeochemical cycling of nitrogen on the early Earth. *Elements*, 9, 345–352.
- Thomazo, C., Ader, M., and Philippot, P. (2011) Extreme ¹⁵N-enrichments in 2.72-Gyr-old sediments: Evidence for a turning point in the nitrogen cycle. *Geobiology*, 9, 107–120.
- Tolstikhin, I.N., and Marty, B. (1998) The evolution of terrestrial volatiles: a view from helium, neon, argon and nitrogen isotope modeling. *Chemical Geology*, 147, 27–52.
- Touret, J.L.R. (2001) Fluids in metamorphic rocks. *Lithos*, 55, 1–25.
- van Hinsberg, V.J., Henry, D.J., and Dutrow, B.L. (2011) Tourmaline as a petrologic forensic mineral: A unique recorder of its geologic past. *Elements*, 7, 327–332.
- Vernon, R.H., Clarke, G.L., and Collins, W.J. (1990) Local, mid-crustal granulite facies metamorphism and melting: an example in the Mt. Stafford area, central Australia. In J.R. Ashworth and M. Brown, Eds., *High Temperature Metamorphism and Crustal Anatexis*, p. 272–319. Unwin Hyman, London.
- Visser, D. (1992) On ammonium in upper-amphibolite facies cordierite-orthoamphibole-bearing rocks from Rod, Bamble Sector, south Norway. *Norsk Geologisk Tidsskrift*, 72, 385–388.
- Vry, K.J., Brown, P.E., and Valley, J.W. (1990) Cordierite volatile content and the role of CO₂ in high grade metamorphism. *American Mineralogist*, 75, 71–88.
- Watenphul, A., Wunder, B., Wirth, R., and Heinrich, W. (2010) Ammonium-bearing clinopyroxene: A potential nitrogen reservoir in the Earth's mantle. *Chemical Geology*, 270, 240–248.
- Watson, E.B., and Cherniak, D.J. (2014) Diffusion and solubility of nitrogen in olivine. *Goldschmidt Conference Abstract 2664*.
- Wedepohl, H. (1995) The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59, 1217–1239.
- White, R.W., Powell, R., and Clarke, G.I. (2003) Prograde metamorphic assemblage evolution during partial melting of metasedimentary rocks at low pressures: migmatites from Mt. Stafford, Central Australia. *Journal of Petrology*, 44, 1937–1960.
- Williams, L.B., Ferrell, R.E. Jr., Chinn, E.W., and Sassen, R. (1989) Fixed-ammonium in clays associated with crude oils. *Applied Geochemistry*, 4, 605–616.
- Williams, L.B., Ferrell, R.E. Jr., Hutcheon, I., Bakel, A.J., Walsh, M.M., and Krouse, H.R. (1995) Nitrogen isotope geochemistry of organic matter and minerals during diagenesis and hydrocarbon migration. *Geochimica et Cosmochimica Acta*, 59, 765–779.
- Wlotzka, F. (1972) *Handbook of Geochemistry*, vol. II. Springer-Verlag, Berlin.
- Wunder, B., Berryman, E., Plessen, B., Rhede, D., Koch-Müller, M., and Heinrich, W. (2015) Synthetic and natural ammonium-bearing tourmaline. *American Mineralogist*, 100, 250–256.
- Yokochi, R., Marty, B., Chazot, G., and Burnard, P. (2009) Nitrogen in peridotite xenoliths: Lithophile behavior and magmatic isotope fractionation. *Geochimica et Cosmochimica Acta*, 73, 4843–4861.
- Zhang, Y., and Zindler, A. (1993) Distribution and evolution of carbon and nitrogen in Earth. *Earth and Planetary Science Letters*, 117, 331–345.

MANUSCRIPT RECEIVED MARCH 23, 2015

MANUSCRIPT ACCEPTED JUNE 16, 2015

MANUSCRIPT HANDLED BY PAUL TOMASCAK