Nitrogen in the Silicate Earth: Speciation and Isotopic Behavior
during Mineral–Fluid Interactions

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ABSTRACT
Nitrogen is the main constituent of Earth’s atmosphere and a key component of the biosphere, but it is a trace element in the major silicate reservoirs. The relatively low concentrations (parts per million level) complicate efforts to constrain the nitrogen speciation and abundance in the mantle and crust. In most silicates, nitrogen occurs as NH₄⁺ (substituting for K⁺), whereas its speciation in hydrous fluids and in silicate melts can vary widely depending in large part on redox conditions. Current knowledge of nitrogen isotope fractionation among relevant mineral and fluid/melt phases, and thus more quantitative applications of nitrogen isotopes to crust-mantle problems, is limited by the lack of experimental data to confirm theoretical predictions of these fractionations. Understanding of modern and long-term nitrogen cycling on Earth is limited by uncertainty in the sizes and isotopic compositions of the major crust and mantle nitrogen reservoirs.

INTRODUCTION
Nitrogen (N) is generally regarded as a volatile element with a behavior similar to that of the noble gases. However, nitrogen reactivity and its multiple stable redox states make it compatible in rocks and an important trace element in the silicate Earth. Estimates of the distribution of nitrogen on modern Earth place the majority of the nitrogen in the mantle, which has a very low N concentration but constitutes the largest fraction (~50%) of the Earth by volume (e.g. Kerrich et al. 2006; Palya et al. 2011; Bebout et al. 2013a this issue). Nitrogen’s large range in stable isotope compositions makes it a useful tracer of mass
exchange between the surface and deep-Earth reservoirs and of fluid/melt–rock interactions in the crust and mantle. The majority of the work on nitrogen isotopes has focused on marine environments (Sigman et al. 2009) and involves anthropogenic and natural exchanges among the atmosphere, biosphere, soils, and oceans (see Bebout et al. 2013a). The behavior of nitrogen isotopes in high-temperature, crust–mantle systems has been investigated by a relatively small number of laboratories, in part because of the difficulty inherent in analyzing the very small amounts of nitrogen typically residing in silicate materials (Cartigny and Marty 2013 this issue). In this paper, we provide a brief overview of the present knowledge of the nitrogen cycle in the silicate Earth, focusing on speciation in mineral–fluid–melt systems in the crust and mantle and on the utility of nitrogen as a tracer of sedimentary/organic components in the deep Earth.

**NITROGEN IN CONTINENTAL CRUST: LONG-TERM STORAGE SITE?**

The nitrogen cycle within continental crust can be described in terms of the successive effects of sedimentation, diagenesis, metamorphism, and magmatism. Nitrogen is introduced into the crust mostly via organic matter deposited in sediments. This organic nitrogen typically has a range of $\delta^{15}$N$_{air}$ values between 0 and $+10\%$, with an average value of about $+5\%$ (Sigman et al. 2009; for the definition of $\delta^{15}$N notation, refer to Bebout et al., 2013a). Nitrogen concentrations in sediments are strongly dependent on lithological variations and organic matter input flux, and they show a wide range, from less than 100 to more than 10,000 ppm. During biological and thermal diagenetic degradation of organic matter, a large amount of nitrogen is released into pore fluids as NH$_3$ (ammonia), which is rapidly transformed to NH$_4^+$ (ammonium) by protonation; during these processes, nitrogen largely preserves its organic $\delta^{15}$N signature (Thomazo and Papineau 2013 this issue). Although $>90\%$ of the nitrogen initially present in organic matter is liberated during diagenesis, a small amount of nitrogen is preserved within its structure, seemingly with limited change in $\delta^{15}$N, up to greenschist facies metamorphic grade (Ader et al. 2006). In rocks extremely rich in organic C, such as coals, this residual organic nitrogen constitutes the majority of the “rock” nitrogen. The nitrogen released into porewaters from organic matter in the form of NH$_4^+$ substitutes for K$^+$ in detrital phases such as K-feldspar and authigenic clays such as illite and is thus trapped in the sediment. With an increase in pressure ($P$) and temperature ($T$), both feldspar and clays participate in low-grade metamorphic reactions and illite progressively transforms into micas,
with NH$_4^+$ remaining substituted for K$^+$ in interlayer sites. For metasedimentary rocks, this
affinity of NH$_4^+$ for clays and micas is illustrated by strong correlations between bulk nitrogen
and large-ion lithophile elements (LILEs) such as K, Rb, and Cs (Fig. 1; see also Bebout et al.
2013a).

During metamorphism in the continental crust, above greenschist facies, NH$_4^+$ can be released
by continuous metamorphic reactions, thermal decomposition (i.e. complete breakdown of
mineral hosts such as mica), cation exchange, or redox reactions. Over wide ranges in
pressure and temperature, continuous metamorphic devolatilization reactions can result in
changes in mica chemistry in an evolving mineral assemblage, with or without a decrease in
mica modal abundance (Bebout and Fogel 1992; Bebout et al. 2013b). In a sufficiently
oxidizing environment, NH$_4^+$ from micas can be stabilized as N$_2$ in fluids and lost from the
rock (Duit et al. 1986; Bebout and Fogel 1992; Svensen et al. 2008). During progressive
devolatilization, isotopically “light” nitrogen is preferentially fractionated into the
metamorphic fluids, leading to an increase in the residual mica $\delta^{15}$N value by up to a few per
mil (Bebout et al. 1999; Jia 2006; Svensen et al. 2008). At higher grades of metamorphism,
the breakdown of mica can result in partial melting (i.e. by dehydration melting). Melting can
lead to appreciable loss of nitrogen from the rock, depending on whether or not there are
suitable host mineral phases in the melting residue. Palya et al. (2011) demonstrated the
retention of significant amounts of nitrogen in rock residues during melting, not only as NH$_4^+$
in residual K-feldspar, but also as N$_2$ in the channels of cordierite (Fig. 2A) produced by mica
dehydration-melting reactions. Nitrogen loss through these different pathways can potentially
be traced by coupling variations in N concentrations and isotope compositions with Cs/K
(Fig. 1D) and Cs/Rb ratios. Cesium is highly mobile in fluids relative to K and Rb; this
mobility is due to the large ionic radius of Cs, such that the size of the Cs ion is much greater
than the size of the crystallographic sites in which K resides (Busigny et al. 2003; Palya et al.
2011; Bebout et al. 2013b; see Fig. 1). Theoretical calculations of fluid speciation and fluid
inclusion studies indicate that, at continental crust metamorphic conditions (lower greenschist
to the granulite facies), nitrogen in fluids in metasedimentary rocks is dominantly present as
N$_2$ (Duit et al. 1986). N$_2$-bearing fluids liberated by metamorphic reactions can be (1) trapped
as fluid inclusions or in microporous phases, (2) incorporated as NH$_4^+$ into newly formed
silicate minerals, or (3) returned to the surface and recycled back to the atmosphere–
hydrosphere system.
Melts derived from metasedimentary rocks at higher-\(P-T\) conditions in the amphibolite and granulite facies can contain a large amount of nitrogen that is, during crystallization, incorporated as \(\text{NH}_4^+\) into potassic minerals such as micas and alkali feldspars. \(\text{NH}_4^+\) can be stabilized within melts under reducing conditions, particularly if the melted metasedimentary rocks contained graphite (Hall 1999). Ammonium has been shown to be present in all of the major mineral phases in granites except quartz (Honma and Itihara 1981; Boyd et al. 1993) and to preferentially enter into biotite (Bi), followed (in order of decreasing concentration) by muscovite (Mu), K-feldspar (Kf), and plagioclase (Pl), with partition coefficients \(D_{\text{Mu/Bi}}\), \(D_{\text{Kf/Bi}}\), \(D_{\text{Pl/Bi}}\) of 0.43, 0.38, and 0.11, respectively (Honma and Itihara 1981). Total N concentrations in granites (average of 35 ppm; Hall 1999) are relatively low compared with those of sedimentary rocks, and peraluminous granites (S-type granites, resulting from melting of metasedimentary rocks) are significantly more enriched in N than peralkaline granites (crystallized from evolved mantle-derived melts). Nitrogen concentrations in granites can also be increased by hydrothermal alteration (Hall 1999), in some cases involving hydrothermal fluid produced by dehydration reactions in the wall rocks of contact aureoles (Bebout et al. 1999). The work to date on nitrogen isotope compositions of granites indicates a relatively wide range of \(\delta^{15}\text{N}\) values (+1 to +10‰), reflecting heterogeneity of the nitrogen sources and complex metamorphic–magmatic processes (Boyd et al. 1993; Bebout et al. 1999).

One of the strongest \(\text{NH}_4^+\) enrichments in continental crustal rocks occurs in hydrothermal deposits in the vicinity of volcanic systems, where ammonium salts such as sal ammoniac (\(\text{NH}_4\text{Cl}\)) or ammoniojarosite [\(\text{NH}_4\text{Fe}^{3+}_3\text{(SO}_4\text{)}_2\text{(OH)}_6\)] can be identified. Significant \(\text{NH}_4^+\) enrichment also occurs in buddingtonite (\(\text{NH}_4^+\) feldspar, \(\text{NH}_4\text{AlSi}_3\text{O}_8\)), which is commonly associated with mercury- and gold-bearing hot spring deposits and occurs as an authigenic diagenetic phase (Svensen et al. 2008).

**NITROGEN IN OCEANIC CRUST: MAGMATIC VERSUS HYROTHERMAL CONTRIBUTIONS**

Oceanic crustal sections contain a variety of lithologies, including sediments, basalts, gabbros, and serpentinized peridotites. As in sediments and metasedimentary rocks of the continental crust, nitrogen in oceanic sediments is initially fixed by organic matter and then released as \(\text{NH}_4^+\), which can substitute for K\(^+\) in K-bearing minerals (FIG. 1). During subduction zone metamorphism of these sediments, the extent of change in the nitrogen
Nitrogen concentrations and $\delta^{15}$N values resulting from devolatilization depends on the $P$–$T$ path they follow. Along warm $P$–$T$ paths (e.g. >13 °C/km), significant amounts of NH$_4^+$ are released from the rocks into fluids, as N$_2$ or NH$_3$, with nitrogen isotope fractionation enriching the residual rock in $^{15}$N (Haendel et al. 1986; Bebout and Fogel 1992). In contrast, cold $P$–$T$ paths (<10 °C/km) to depths of ~100 km are not associated with significant loss of nitrogen into fluids, reflecting the high stability of NH$_4^+$ in phengite ($HP$-$LT$ ferro-magnesian white mica) and the lower degree of dehydration that occurs (Bebout and Fogel 1992; Busigny et al. 2003; Bebout et al. 2013b).

In oceanic mafic and ultramafic rocks formed at ridge axes, N concentrations are low relative to those in sediments. Nitrogen solubility in basaltic melts is low, similar to that of Ar; thus nitrogen is strongly partitioned into gas vesicles and escapes from the melt during degassing. Consequently, fresh basalts erupted onto the seafloor usually have total nitrogen concentrations lower than 1 ppm, including N in gas vesicles and nitrogen dissolved in glass. Nitrogen in vesicles in fresh MORB glass extracted by crushing techniques is in the form of N$_2$ and displays a large range of $\delta^{15}$N values, converging on the typical mantle value of about $-5 \pm 2\%$ (Cartigny and Marty 2013). However, the speciation of nitrogen dissolved in fresh basalt glasses is poorly constrained. Experimental studies suggest that nitrogen is mostly dissolved as N in basaltic melt when the oxygen fugacity ranges between that of the iron-wüstite buffer and that of air; however, a fraction of the nitrogen may be present as the nitrosyl group (i.e. the monovalent radical -NO) in highly depolymerized melts (Roskosz et al. 2006). These experiments were performed under strictly anhydrous conditions, and nitrogen speciation in the melt could be different if water is added to the system, possibly producing H under reduced conditions. At high $f_{H_2}$, amine groups (e.g. NH$_3$, NH$_4^+$) are formed and stabilized (Mysen and Fogel 2010).

Interaction of oceanic crust with seawater over a wide range of temperatures produces new mineral phases able to store nitrogen. Nitrogen concentrations in altered oceanic basalts from several DSDP/ODP sites range from $-1.3$ to 18.2 ppm, with $\delta^{15}$N values ranging from $-11.6$ to $+8.3\%$ (Li et al. 2007 and references therein). Relationships among nitrogen enrichments, mineralogy, and major and trace element concentrations suggest that nitrogen in these rocks resides dominantly as NH$_4^+$ in secondary minerals such as celadonite, feldspar, and smectite. Nitrogen concentrations and $\delta^{15}$N values of eclogitic metabasalts (2–20 ppm and $-1$ to $+8\%$),
respectively) fall in the ranges for altered oceanic basalts; these data were interpreted as reflecting nitrogen enriched on the seafloor and preserved in subduction settings to depths approaching 100 km. Relationships between the concentrations of nitrogen and other trace elements suggest that nitrogen in these eclogitic metabasalts occurs mostly as NH$_4^+$ in phengites (Halama et al. 2010), again demonstrating the significance of micas in controlling deep-Earth N budgets and cycling. Although the nitrogen geochemistry of fresh gabbros from the oceanic crust has not yet been explored, a recent study of ophiolitic metabasalts from the Western Alps (Europe) demonstrated nitrogen concentrations and $\delta^{15}$N values of 2.6 to 55 ppm and +0.8 to +8.1‰, respectively (Busigny et al. 2011). The dominant nitrogen species in these rocks was proposed to be NH$_4^+$ substituting for Na–Ca in minerals such as feldspars, amphiboles, and clinopyroxenes. Peridotites serpentinized in oceanic and subduction settings contain 1.4 to 15 ppm N and have positive $\delta^{15}$N values of +4 to +15‰ (Philippot et al. 2007; Halama et al. 2012). Unaltered lithospheric peridotites have very low N concentrations (<1 ppm; Yokochi et al. 2009). Thus it appears that serpentinization is accompanied by N enrichment. This nitrogen could be present as NH$_4^+$ bound in tremolite (Halama et al. 2012) or as fluid inclusions in sealed voids or cracks produced during serpentinization (Philippot et al. 2007).

THE ENIGMATIC SPECIATION OF NITROGEN IN THE MANTLE

The upper mantle is depleted in $^{15}$N relative to shallower reservoirs, including the oceans, the atmosphere, and continental and oceanic crust. Numerous studies of mid-ocean ridge basalts and diamonds point to a mean mantle $\delta^{15}$N value around $-5 \pm 2$‰ (Cartigny and Marty 2013). In contrast with this widely accepted $\delta^{15}$N value, the average nitrogen concentration in the mantle remains uncertain, with estimates spanning two orders of magnitude, from 0.27 to 36 ppm. This large uncertainty is due to the assumptions employed in various models, particularly as related to whether nitrogen behaves as a compatible or an incompatible element during partial melting of mantle peridotite (Cartigny and Marty 2013). Beyond this crucial question lies the problem of the speciation of nitrogen in the mantle. A detailed study of peridotite xenoliths from the lithospheric mantle showed bulk nitrogen concentrations between 0.1 and 0.8 ppm (Yokochi et al. 2009), near the lower estimates derived in the modeling studies. Comparison of crushing and step-heating extractions of these xenoliths
indicated that only a small fraction of the total nitrogen (<10%) is carried in fluid inclusions. Analyses of mineral separates demonstrate that N is bound in crystal structures, with the highest affinity for phlogopite, followed by amphibole, clinopyroxene, and olivine. Similar partitioning of N and Rb among mantle peridotite minerals suggests that the N occurs as NH$_4^+$ (Yokochi et al. 2009). However, the authors pointed out that their samples may not be representative of the average mantle because peridotite xenoliths can be modified by host magma–mineral interactions (potentially inducing loss or addition of nitrogen) and/or metasomatic processes at crustal levels. Watenphul et al. (2010), in multianvil experiments at ultrahigh-pressure conditions (9.5–12.8 GPa), showed that a significant amount of N could be stored in the deep mantle as NH$_4^+$ in clinopyroxene. More-oxidized and lower-pressure conditions in the shallow mantle would lead to the oxidation of nitrogen into N$_2$ and the loss of nitrogen by magma degassing.

Diamond also carries important information regarding the global nitrogen concentration, the isotopic composition of nitrogen and, possibly, the generation of nitrogen-bearing fluid/melt in the mantle. In diamond, nitrogen substitutes for carbon and concentrations are as high as 3500 ppm, making nitrogen the main impurity. Nitrogen concentrations in diamond were initially thought to reflect the concentrations of the growth media (i.e. mantle fluid or melt enriched in carbon) and particularly their C/N ratios. However, further study showed that nitrogen concentrations in diamond depend primarily on growth rate. The speciation of nitrogen in mantle fluids and melts, from which diamonds precipitate, is poorly constrained. This is mostly due to the lack of nitrogen isotope fractionation factors (i.e. the distribution of N isotopes between two chemical species; see caption in Fig. 3) between diamond and any other molecular species. Such data would be useful particularly for cases where the N isotope compositions of a diamond population reflect progressive diamond growth and fluid/melt chemical evolution (see Thomassot et al. 2007).

Nitrides have also been proposed as possible host phases for nitrogen in the deep mantle. They form under highly reducing conditions, can be stable at very high pressures in the mantle, and could also be a significant nitrogen host in the Earth’s core. In the deep mantle, nitrogen may be present in solid phases such as osbornite, a titanium nitride (TiN), and/or dissolved in melts, where it could occur in N$_3$ groups (Roskosz et al. 2006).

**TRACKING MINERAL–FLUID INTERACTION IN THE SILICATE EARTH**
In considering the distribution of nitrogen in the silicate Earth, one emerging theme is that the predominant nitrogen species in minerals (at least in the crust) is NH$_4^+$, which substitutes for K$, Na^+$, and/or Ca$^{2+}$ in phases such as illites, micas, feldspars, clinopyroxenes, and amphiboles. A part of the nitrogen from sediments and metasedimentary rocks is likely preserved in organic matter affected to varying degrees by metamorphism (Ader et al. 2006). In the mantle, diamonds and nitrides are possible nitrogen hosts, but their abundance, and thus their importance for the mantle nitrogen inventory, remains uncertain. Metamorphic fluids under crustal conditions are likely dominated by N$_2$ and NH$_3$ (e.g. Duit et al. 1986). The stability of nitrogen oxides (NO$_2$, N$_2$O, NO, NO$_3^-$) requires highly oxygenated conditions, and thus these species are mostly limited to surface/near-surface environments. The exchange of nitrogen among minerals and fluid species can be tracked by coupling nitrogen concentrations and isotope compositions with other geochemical tracers considered less mobile during fluid circulation (such as Al and Ti) or by normalizing to C for assessments of the chemical evolution of the organic components. Tracers tightly associated with NH$_4^+$ in minerals (e.g. the LILEs) can also be used (Fig. 1).

Nitrogen isotope compositions have been shown to be powerful tools for delineating mineral–fluid interaction in crust–mantle systems. However, experimentally determined nitrogen isotope fractionation factors are conspicuously lacking. The currently available fractionation factors for these systems have mostly been derived by theoretical calculations using spectroscopic data (Scalan 1958; Richet et al. 1977; Hanschmann 1981; see Fig. 3). Needed are (1) a critical evaluation of the quality of the spectroscopic data on which these calculations are based, and (2) experimental studies of nitrogen isotope fractionation in relevant mineral–fluid systems. Figure 3A reports the temperature dependence of available fractionation factors for pairs of molecular species relevant to study of the silicate Earth (NH$_4^+$–NH$_3$, NH$_4^+$–N$_2$, and NH$_3$–N$_2$). This figure clearly shows the discrepancies among the various calculations (for instance, for NH$_3$–N$_2$), with a range of uncertainty significantly higher than natural $\delta^{15}$N variation. The origin of these discrepancies is difficult to determine but may derive from error-inducing approximations made in the calculations and/or imprecise spectroscopic data. Nevertheless, a number of authors have suggested that the directions and magnitudes of isotopic evolution in natural crustal settings match the fractionation factors for NH$_4^+$–N$_2$ and NH$_4^+$–NH$_3$ calculated by Hanschmann (1981) (see Haendel et al. 1986; Bebout and Fogel 1992; Jia 2006). As an example, Fig. 2B shows that, in pegmatite samples
containing both beryl and muscovite, the $\Delta^{15}$N$_{\text{beryl-muscovite}}$ (mean = +2.9‰; 1$\sigma$ = 1.1‰, 
$\delta^{15}$N$_{\text{beryl}} - \delta^{15}$N$_{\text{muscovite}}$) closely matches that predicted theoretically by Hanschmann (1981) for the fractionation between N$_2$ and NH$_4^+$ for geologically plausible crystallization temperatures of ~550±50 °C (data from Lazzeri et al. 2011; see the plot of fractionation factors in Fig. 3A).

In these nearly bi-mineralic pegmatite samples, the beryl is assumed to contain nitrogen as N$_2$ and the coexisting muscovite is assumed to contain nitrogen as NH$_4^+$. Another possibility to consider, in interpreting nitrogen data for silicate systems, is that crustal minerals and fluids are not necessarily fully equilibrated with respect to nitrogen concentrations and isotope compositions, pointing to the need for experiments aimed at determining kinetic fractionation factors (Li et al. 2009). Given the various magnitudes and directions of nitrogen isotope fractionations among the different fluid species of nitrogen, it is evident that changes in redox conditions can exert a strong influence on the nitrogen isotope signature in any given system (see Fig. 3). At high metamorphic grades and in magmatic systems, where mineralogy and melt/fluid chemistry evolve during changes in temperature and/or redox conditions, nitrogen isotope fractionation could occur among hydrous fluids, melts, and minerals (Roskosz et al. 2006; Mysen and Fogel 2010). Finally, it is not yet known whether nitrogen isotopes are fractionated during partial melting reactions or provide a true record of the $\delta^{15}$N of their sources.

OUTLOOK

Nitrogen as a Biogeochemical Tracer in the Deep Earth For the most part, nitrogen in the deep Earth owes its existence to initial incorporation by biological processes at the Earth’s surface, followed by mobilization at depth via sediment burial, devolatilization, and melting. Nitrogen should see expanded use, in tandem with C and the LILEs, in studies seeking to evaluate the transfer of sedimentary/organic components among and within the major reservoirs of the silicate Earth.

Continental Crust Continental crust is extremely heterogeneous. Current estimates of deep-continental-crust concentrations and $\delta^{15}$N (see Bebout et al. 2013a) are based on a very small number of analyses of exhumed suites and xenoliths. Badly needed are additional studies of nitrogen in exposed continental-crust sections to evaluate, among other issues, the possible role of continental crust formation in the uptake of nitrogen from the atmosphere during the early evolution of the biosphere (Goldblatt et al. 2009).
Oceanic Crust Sections  The evaluation of the nitrogen reservoir in variably altered oceanic
307 crust is hampered by low N concentrations. The analysis of nitrogen at these levels requires
308 specialized extraction methods and high-sensitivity mass spectrometry (see the Analytical
309 Box). Studies of nitrogen in modern and ancient oceanic crustal sections are crucial for
310 determining the fluxes of nitrogen from external reservoirs (atmosphere, hydrosphere,
311 biosphere) into the deep mantle through subduction zones.
312 The Mantle  Our knowledge of the nitrogen concentration and isotopic composition of the
313 mantle is based on the fragmentary record of exhumed rocks, xenoliths/xenocrysts, and
314 mantle-derived igneous rocks. Future work on mantle nitrogen (and carbon) should seek to
315 better constrain the magnitude of isotope fractionation among minerals and “fluids” within the
316 mantle and to determine whether subduction inputs can locally result in deviations from more
317 “normal” mantle isotopic compositions. Better knowledge of the nitrogen isotope composition
318 of the mantle would elucidate (among other issues) processes of early-Earth formation, core–
319 mantle segregation, atmospheric evolution, and the recycling of surface material to the
mantle.

Need for Fluid/Melt–Mineral Studies of Fractionation Factors  There is a critical need for
321 experiments to determine nitrogen isotope fractionation associated with fluid–mineral or
322 melt–mineral exchange. Particularly useful would be studies of fractionation between fluids
324 of various types—and with varying nitrogen speciation (particularly as N\textsubscript{2} and NH\textsubscript{3})—and
325 micas (muscovite and biotite), K-feldspars, cyclosilicates (beryl and cordierite) and diamonds.
326 For example, knowledge of nitrogen speciation in diamond-forming fluids could place
327 constraints on the oxygen fugacity of the mantle. The availability of experimentally
328 confirmed nitrogen isotope fractionations factors for mica–fluid pairs would improve
329 estimates of the proportions of initially subducted nitrogen either released into fluids during
330 subduction of oceanic crustal sections or returned to the deep mantle.

Diffusion Rates for Nitrogen in Silicate Materials  Still unknown is the rate at which, and
332 the mechanisms by which, nitrogen diffuses in minerals such as the micas, alkali feldspars,
333 clinopyroxenes, and cyclosilicates, potentially affecting closure temperatures. This
334 information is important for evaluating the extent to which these minerals can preserve
335 information regarding nitrogen behavior during high-temperature processes.

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**FIGURES**

**FIGURE 1.** Illustration of the similar geochemical behaviors of nitrogen (as NH$_4^+$) and some of the large-ion lithophile elements (LILEs). Plotted in (A), (B) and (C) are concentrations of N, K, Rb, and Cs in metasedimentary rocks from the Schistes Lustrés, Italian Alps (data from Busigny et al. 2003; Bebout et al. 2013b); Catalina Schists, California (data from Bebout and Fogel 1992); and Franciscan Complex and Western Baja Terrain, California. (D) Nitrogen isotope composition versus Cs/K ratio in the same metasedimentary sequences. Data on the Schistes Lustrés and Catalina Schists illustrate that subtle N release from the rocks to fluids during metamorphism can be traced from their N isotope composition (i.e. progressively increasing $\delta^{15}$N in the residual rock) and Cs/K ratio (decreasing due to preferential Cs loss)—see discussion in text. In contrast, metasedimentary rocks from the Franciscan Complex and Western Baja Terrain show more limited variation in Cs/K and $\delta^{15}$N, suggesting preservation of these elements (Cs, K and N) during metamorphism.
FIGURE 2. (A) Polyhedral structural model of low cordierite (from Bertoldi et al. 2004), known to house N$_2$ in its channels. Si occupies the tetrahedra shown in shades of green (T$_{16}$, T$_{21}$, and T$_{23}$) and Al the tetrahedral in shades of blue (T$_{11}$ and T$_{26}$). The large orange sphere represents Na$^+$ within large spaces in the channels (Ch0 site). The small yellow spheres connected to a pink sphere represent water molecules within the channels. Not pictured are other molecules or neutral tetrahedral atoms that may be present within the channels (CO$_2$, N$_2$, CO, O$_2$, H$_2$S, Ar, He). (B) Nitrogen concentrations and isotopic compositions of coexisting muscovite and beryl from various pegmatite samples (inset photo shows a similar beryl- and muscovite-bearing pegmatite sample not analyzed; data from Lazzeri et al. 2011; Photo courtesy of Desert Winds Gems and Minerals, www.desertwindsgemsandminerals.com). Note the relatively uniform N isotope fractionation ($\Delta^{15}$N; upper plot) of the coexisting minerals (near that predicted for appropriate temperatures by the calculations for the pair of molecules NH$_4^+$ and N$_2$ by Hanschmann 1981; see Fig. 3) and the higher N concentrations in mica relative to beryl in these samples (lower plot).
FIGURE 3. Theoretical N isotope fractionation factors for various pairs of molecules.

Triangles: data from Scalan (1958); diamonds: data from Richet et al. (1977); squares: data from Hanschmann (1981). The fractionation factor represents the N isotope distribution between two molecules A and B, and can be written as $\alpha_{A:B} = \frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}/^{14}\text{N}}_A$. Using approximation, it can be shown that $1000\ln \alpha_{A:B} \sim \Delta^{15}\text{N} = \delta^{15}\text{N}_A - \delta^{15}\text{N}_B$, thus corresponding to the N isotope fractionation between the two species A and B. The N isotope fractionation between any pair of molecules is an inverse function of temperature, with high fractionation at low temperature and decreasing fractionation at higher temperature.