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

3  
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16 **ABSTRACT**

17 Nitrogen is the main constituent of Earth’s atmosphere and a key component of the biosphere,  
18 but it is a trace element in the major silicate reservoirs. The relatively low concentrations  
19 (parts per million level) complicate efforts to constrain the nitrogen speciation and abundance  
20 in the mantle and crust. In most silicates, nitrogen occurs as  $\text{NH}_4^+$  (substituting for  $\text{K}^+$ ),  
21 whereas its speciation in hydrous fluids and in silicate melts can vary widely depending in  
22 large part on redox conditions. Current knowledge of nitrogen isotope fractionation among  
23 relevant mineral and fluid/melt phases, and thus more quantitative applications of nitrogen  
24 isotopes to crust-mantle problems, is limited by the lack of experimental data to confirm  
25 theoretical predictions of these fractionations. Understanding of modern and long-term  
26 nitrogen cycling on Earth is limited by uncertainty in the sizes and isotopic compositions of  
27 the major crust and mantle nitrogen reservoirs.  
28  
29

30 **INTRODUCTION**  
31

32 Nitrogen (N) is generally regarded as a volatile element with a behavior similar to that of the  
33 noble gases. However, nitrogen reactivity and its multiple stable redox states make it  
34 compatible in rocks and an important trace element in the silicate Earth. Estimates of the  
35 distribution of nitrogen on modern Earth place the majority of the nitrogen in the mantle,  
36 which has a very low N concentration but constitutes the largest fraction (~50%) of the Earth  
37 by volume (e.g. Kerrich et al. 2006; Palya et al. 2011; Bebout et al. 2013a this issue).  
38 Nitrogen’s large range in stable isotope compositions makes it a useful tracer of mass

39 exchange between the surface and deep-Earth reservoirs and of fluid/melt–rock interactions in  
40 the crust and mantle. The majority of the work on nitrogen isotopes has focused on marine  
41 environments (Sigman et al. 2009) and involves anthropogenic and natural exchanges among  
42 the atmosphere, biosphere, soils, and oceans (see Bebout et al. 2013a). The behavior of  
43 nitrogen isotopes in high-temperature, crust–mantle systems has been investigated by a  
44 relatively small number of laboratories, in part because of the difficulty inherent in analyzing  
45 the very small amounts of nitrogen typically residing in silicate materials (Cartigny and Marty  
46 2013 this issue). In this paper, we provide a brief overview of the present knowledge of the  
47 nitrogen cycle in the silicate Earth, focusing on speciation in mineral–fluid–melt systems in  
48 the crust and mantle and on the utility of nitrogen as a tracer of sedimentary/organic  
49 components in the deep Earth.

50

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

52

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

72 with  $\text{NH}_4^+$  remaining substituted for  $\text{K}^+$  in interlayer sites. For metasedimentary rocks, this  
73 affinity of  $\text{NH}_4^+$  for clays and micas is illustrated by strong correlations between bulk nitrogen  
74 and large-ion lithophile elements (LILEs) such as K, Rb, and Cs (FIG. 1; see also Bebout et al.  
75 2013a).

76

77 During metamorphism in the continental crust, above greenschist facies,  $\text{NH}_4^+$  can be released  
78 by continuous metamorphic reactions, thermal decomposition (i.e. complete breakdown of  
79 mineral hosts such as mica), cation exchange, or redox reactions. Over wide ranges in  
80 pressure and temperature, continuous metamorphic devolatilization reactions can result in  
81 changes in mica chemistry in an evolving mineral assemblage, with or without a decrease in  
82 mica modal abundance (Bebout and Fogel 1992; Bebout et al. 2013b). In a sufficiently  
83 oxidizing environment,  $\text{NH}_4^+$  from micas can be stabilized as  $\text{N}_2$  in fluids and lost from the  
84 rock (Duit et al. 1986; Bebout and Fogel 1992; Svensen et al. 2008). During progressive  
85 devolatilization, isotopically “light” nitrogen is preferentially fractionated into the  
86 metamorphic fluids, leading to an increase in the residual mica  $\delta^{15}\text{N}$  value by up to a few per  
87 mil (Bebout et al. 1999; Jia 2006; Svensen et al. 2008). At higher grades of metamorphism,  
88 the breakdown of mica can result in partial melting (i.e. by dehydration melting). Melting can  
89 lead to appreciable loss of nitrogen from the rock, depending on whether or not there are  
90 suitable host mineral phases in the melting residue. Palya et al. (2011) demonstrated the  
91 retention of significant amounts of nitrogen in rock residues during melting, not only as  $\text{NH}_4^+$   
92 in residual K-feldspar, but also as  $\text{N}_2$  in the channels of cordierite (FIG. 2A) produced by mica  
93 dehydration-melting reactions. Nitrogen loss through these different pathways can potentially  
94 be traced by coupling variations in N concentrations and isotope compositions with Cs/K  
95 (FIG. 1D) and Cs/Rb ratios. Cesium is highly mobile in fluids relative to K and Rb; this  
96 mobility is due to the large ionic radius of Cs, such that the size of the Cs ion is much greater  
97 than the size of the crystallographic sites in which K resides (Busigny et al. 2003; Palya et al.  
98 2011; Bebout et al. 2013b; see FIG. 1). Theoretical calculations of fluid speciation and fluid  
99 inclusion studies indicate that, at continental crust metamorphic conditions (lower greenschist  
100 to the granulite facies), nitrogen in fluids in metasedimentary rocks is dominantly present as  
101  $\text{N}_2$  (Duit et al. 1986).  $\text{N}_2$ -bearing fluids liberated by metamorphic reactions can be (1) trapped  
102 as fluid inclusions or in microporous phases, (2) incorporated as  $\text{NH}_4^+$  into newly formed  
103 silicate minerals, or (3) returned to the surface and recycled back to the atmosphere–  
104 hydrosphere system.

105

106 Melts derived from metasedimentary rocks at higher- $P$ - $T$  conditions in the amphibolite and  
107 granulite facies can contain a large amount of nitrogen that is, during crystallization,  
108 incorporated as  $\text{NH}_4^+$  into potassic minerals such as micas and alkali feldspars.  $\text{NH}_4^+$  can be  
109 stabilized within melts under reducing conditions, particularly if the melted metasedimentary  
110 rocks contained graphite (Hall 1999). Ammonium has been shown to be present in all of the  
111 major mineral phases in granites except quartz (Honma and Itihara 1981; Boyd et al. 1993)  
112 and to preferentially enter into biotite (Bi), followed (in order of decreasing concentration) by  
113 muscovite (Mu), K-feldspar (Kf), and plagioclase (Pl), with partition coefficients  $D^{\text{Mu/Bi}}$ ,  
114  $D^{\text{Kf/Bi}}$ ,  $D^{\text{Pl/Bi}}$  of 0.43, 0.38, and 0.11, respectively (Honma and Itihara 1981). Total N  
115 concentrations in granites (average of 35 ppm; Hall 1999) are relatively low compared with  
116 those of sedimentary rocks, and peraluminous granites (S-type granites, resulting from  
117 melting of metasedimentary rocks) are significantly more enriched in N than peralkaline  
118 granites (crystallized from evolved mantle-derived melts). Nitrogen concentrations in granites  
119 can also be increased by hydrothermal alteration (Hall 1999), in some cases involving  
120 hydrothermal fluid produced by dehydration reactions in the wall rocks of contact aureoles  
121 (Bebout et al. 1999). The work to date on nitrogen isotope compositions of granites indicates  
122 a relatively wide range of  $\delta^{15}\text{N}$  values (+1 to +10‰), reflecting heterogeneity of the nitrogen  
123 sources and complex metamorphic–magmatic processes (Boyd et al. 1993; Bebout et al.  
124 1999).

125

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

132

### 133 **NITROGEN IN OCEANIC CRUST: MAGMATIC VERSUS HYDROTHERMAL** 134 **CONTRIBUTIONS**

135 Oceanic crustal sections contain a variety of lithologies, including sediments, basalts,  
136 gabbros, and serpentinitized peridotites. As in sediments and metasedimentary rocks of the  
137 continental crust, nitrogen in oceanic sediments is initially fixed by organic matter and then  
138 released as  $\text{NH}_4^+$ , which can substitute for  $\text{K}^+$  in K-bearing minerals (FIG. 1). During  
139 subduction zone metamorphism of these sediments, the extent of change in the nitrogen

140 concentrations and  $\delta^{15}\text{N}$  values resulting from devolatilization depends on the  $P$ – $T$  path they  
141 follow. Along warm  $P$ – $T$  paths (e.g.  $>13$  °C/km), significant amounts of  $\text{NH}_4^+$  are released  
142 from the rocks into fluids, as  $\text{N}_2$  or  $\text{NH}_3$ , with nitrogen isotope fractionation enriching the  
143 residual rock in  $^{15}\text{N}$  (Haendel et al. 1986; Bebout and Fogel 1992). In contrast, cold  $P$ – $T$  paths  
144 ( $<10$  °C/km) to depths of  $\sim 100$  km are not associated with significant loss of nitrogen into  
145 fluids, reflecting the high stability of  $\text{NH}_4^+$  in phengite (*HP-LT* ferro-magnesian white mica)  
146 and the lower degree of dehydration that occurs (Bebout and Fogel 1992; Busigny et al. 2003;  
147 Bebout et al. 2013b).

148

149 In oceanic mafic and ultramafic rocks formed at ridge axes, N concentrations are low relative  
150 to those in sediments. Nitrogen solubility in basaltic melts is low, similar to that of Ar; thus  
151 nitrogen is strongly partitioned into gas vesicles and escapes from the melt during degassing.  
152 Consequently, fresh basalts erupted onto the seafloor usually have total nitrogen  
153 concentrations lower than 1 ppm, including N in gas vesicles and nitrogen dissolved in glass .  
154 Nitrogen in vesicles in fresh MORB glass extracted by crushing techniques is in the form of  
155  $\text{N}_2$  and displays a large range of  $\delta^{15}\text{N}$  values, converging on the typical mantle value of about  
156  $-5 \pm 2\text{‰}$  (Cartigny and Marty 2013). However, the speciation of nitrogen dissolved in fresh  
157 basalt glasses is poorly constrained. Experimental studies suggest that nitrogen is mostly  
158 dissolved as  $\text{N}_2$  in basaltic melt when the oxygen fugacity ranges between that of the iron-  
159 wüstite buffer and that of air; however, a fraction of the nitrogen may be present as the  
160 nitrosyl group (i.e. the monovalent radical -NO) in highly depolymerized melts (Roskosz et  
161 al. 2006). These experiments were performed under strictly anhydrous conditions, and  
162 nitrogen speciation in the melt could be different if water is added to the system, possibly  
163 producing  $\text{H}_2$  under reduced conditions. At high  $f_{\text{H}_2}$ , amine groups (e.g.  $\text{NH}_3$ ,  $\text{NH}_2$ ) are formed  
164 and stabilized (Mysen and Fogel 2010).

165

166 Interaction of oceanic crust with seawater over a wide range of temperatures produces new  
167 mineral phases able to store nitrogen. Nitrogen concentrations in altered oceanic basalts from  
168 several DSDP/ODP sites range from  $\sim 1.3$  to 18.2 ppm, with  $\delta^{15}\text{N}$  values ranging from  $-11.6$   
169 to  $+8.3\text{‰}$  (Li et al. 2007 and references therein). Relationships among nitrogen enrichments,  
170 mineralogy, and major and trace element concentrations suggest that nitrogen in these rocks  
171 resides dominantly as  $\text{NH}_4^+$  in secondary minerals such as celadonite, feldspar, and smectite.  
172 Nitrogen concentrations and  $\delta^{15}\text{N}$  values of eclogitic metabasalts (2–20 ppm and  $-1$  to  $+8\text{‰}$ ,

173 respectively) fall in the ranges for altered oceanic basalts; these data were interpreted as  
174 reflecting nitrogen enriched on the seafloor and preserved in subduction settings to depths  
175 approaching 100 km. Relationships between the concentrations of nitrogen and other trace  
176 elements suggest that nitrogen in these eclogitic metabasalts occurs mostly as  $\text{NH}_4^+$  in  
177 phengites (Halama et al. 2010), again demonstrating the significance of micas in controlling  
178 deep-Earth N budgets and cycling. Although the nitrogen geochemistry of fresh gabbros from  
179 the oceanic crust has not yet been explored, a recent study of ophiolitic metagabbros from the  
180 Western Alps (Europe) demonstrated nitrogen concentrations and  $\delta^{15}\text{N}$  values of 2.6 to 55  
181 ppm and +0.8 to +8.1‰, respectively (Busigny et al. 2011). The dominant nitrogen species in  
182 these rocks was proposed to be  $\text{NH}_4^+$  substituting for Na–Ca in minerals such as feldspars,  
183 amphiboles, and clinopyroxenes.

184

185 Peridotites serpentized in oceanic and subduction settings contain 1.4 to 15 ppm N and have  
186 positive  $\delta^{15}\text{N}$  values of +4 to +15‰ (Philippot et al. 2007; Halama et al. 2012). Unaltered  
187 lithospheric peridotites have very low N concentrations (<1 ppm; Yokochi et al. 2009). Thus  
188 it appears that serpentization is accompanied by N enrichment. This nitrogen could be  
189 present as  $\text{NH}_4^+$  bound in tremolite (Halama et al. 2012) or as fluid inclusions in sealed voids  
190 or cracks produced during serpentization (Philippot et al. 2007).

191

## 192 **THE ENIGMATIC SPECIATION OF NITROGEN IN THE MANTLE**

193

194 The upper mantle is depleted in  $^{15}\text{N}$  relative to shallower reservoirs, including the oceans, the  
195 atmosphere, and continental and oceanic crust. Numerous studies of mid-ocean ridge basalts  
196 and diamonds point to a mean mantle  $\delta^{15}\text{N}$  value around  $-5 \pm 2\text{‰}$  (Cartigny and Marty 2013).  
197 In contrast with this widely accepted  $\delta^{15}\text{N}$  value, the average nitrogen concentration in the  
198 mantle remains uncertain, with estimates spanning two orders of magnitude, from 0.27 to 36  
199 ppm. This large uncertainty is due to the assumptions employed in various models,  
200 particularly as related to whether nitrogen behaves as a compatible or an incompatible  
201 element during partial melting of mantle peridotite (Cartigny and Marty 2013). Beyond this  
202 crucial question lies the problem of the speciation of nitrogen in the mantle. A detailed study  
203 of peridotite xenoliths from the lithospheric mantle showed bulk nitrogen concentrations  
204 between 0.1 and 0.8 ppm (Yokochi et al. 2009), near the lower estimates derived in the  
205 modeling studies. Comparison of crushing and step-heating extractions of these xenoliths

206 indicated that only a small fraction of the total nitrogen (<10%) is carried in fluid inclusions.  
207 Analyses of mineral separates demonstrate that N is bound in crystal structures, with the  
208 highest affinity for phlogopite, followed by amphibole, clinopyroxene, and olivine. Similar  
209 partitioning of N and Rb among mantle peridotite minerals suggests that the N occurs as  $\text{NH}_4^+$   
210 (Yokochi et al. 2009). However, the authors pointed out that their samples may not be  
211 representative of the average mantle because peridotite xenoliths can be modified by host  
212 magma–mineral interactions (potentially inducing loss or addition of nitrogen) and/or  
213 metasomatic processes at crustal levels. Watenphul et al. (2010), in multianvil experiments at  
214 ultrahigh-pressure conditions (9.5–12.8 GPa), showed that a significant amount of N could be  
215 stored in the deep mantle as  $\text{NH}_4^+$  in clinopyroxene. More-oxidized and lower-pressure  
216 conditions in the shallow mantle would lead to the oxidation of nitrogen into  $\text{N}_2$  and the loss  
217 of nitrogen by magma degassing.

218

219 Diamond also carries important information regarding the global nitrogen concentration, the  
220 isotopic composition of nitrogen and, possibly, the generation of nitrogen-bearing fluid/melt  
221 in the mantle. In diamond, nitrogen substitutes for carbon and concentrations are as high as  
222 3500 ppm, making nitrogen the main impurity. Nitrogen concentrations in diamond were  
223 initially thought to reflect the concentrations of the growth media (i.e. mantle fluid or melt  
224 enriched in carbon) and particularly their C/N ratios. However, further study showed that  
225 nitrogen concentrations in diamond depend primarily on growth rate. The speciation of  
226 nitrogen in mantle fluids and melts, from which diamonds precipitate, is poorly constrained.  
227 This is mostly due to the lack of nitrogen isotope fractionation factors (i.e. the distribution of  
228 N isotopes between two chemical species; see caption in FIG. 3) between diamond and any  
229 other molecular species. Such data would be useful particularly for cases where the N isotope  
230 compositions of a diamond population reflect progressive diamond growth and fluid/melt  
231 chemical evolution (see Thomassot et al. 2007).

232

233 Nitrides have also been proposed as possible host phases for nitrogen in the deep mantle.  
234 They form under highly reducing conditions, can be stable at very high pressures in the  
235 mantle, and could also be a significant nitrogen host in the Earth's core. In the deep mantle,  
236 nitrogen may be present in solid phases such as osbornite, a titanium nitride (TiN), and/or  
237 dissolved in melts, where it could occur in  $\text{N}^{3-}$  groups (Roskosz et al. 2006).

238

239 **TRACKING MINERAL–FLUID INTERACTION IN THE SILICATE EARTH**



240

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

256

257 Nitrogen isotope compositions have been shown to be powerful tools for delineating mineral–  
258 fluid interaction in crust–mantle systems. However, experimentally determined nitrogen  
259 isotope fractionation factors are conspicuously lacking. The currently available fractionation  
260 factors for these systems have mostly been derived by theoretical calculations using  
261 spectroscopic data (Scalan 1958; Richet et al. 1977; Hanschmann 1981; see FIG. 3). Needed  
262 are (1) a critical evaluation of the quality of the spectroscopic data on which these  
263 calculations are based, and (2) experimental studies of nitrogen isotope fractionation in  
264 relevant mineral–fluid systems. FIGURE 3A reports the temperature dependence of available  
265 fractionation factors for pairs of molecular species relevant to study of the silicate Earth  
266 ( $\text{NH}_4^+ - \text{NH}_3$ ,  $\text{NH}_4^+ - \text{N}_2$ , and  $\text{NH}_3 - \text{N}_2$ ). This figure clearly shows the discrepancies among the  
267 various calculations (for instance, for  $\text{NH}_3 - \text{N}_2$ ), with a range of uncertainty significantly  
268 higher than natural  $\delta^{15}\text{N}$  variation. The origin of these discrepancies is difficult to determine  
269 but may derive from error-inducing approximations made in the calculations and/or imprecise  
270 spectroscopic data. Nevertheless, a number of authors have suggested that the directions and  
271 magnitudes of isotopic evolution in natural crustal settings match the fractionation factors for  
272  $\text{NH}_4^+ - \text{N}_2$  and  $\text{NH}_4^+ - \text{NH}_3$  calculated by Hanschmann (1981) (see Haendel et al. 1986; Bebout  
273 and Fogel 1992; Jia 2006). As an example, FIG. 2B shows that, in pegmatite samples

274 containing both beryl and muscovite, the  $\Delta^{15}\text{N}_{\text{beryl-muscovite}}$  (mean = +2.9‰;  $1\sigma = 1.1\%$ ,  
275  $\delta^{15}\text{N}_{\text{beryl}} - \delta^{15}\text{N}_{\text{muscovite}}$ ) closely matches that predicted theoretically by Hanschmann (1981) for  
276 the fractionation between  $\text{N}_2$  and  $\text{NH}_4^+$  for geologically plausible crystallization temperatures  
277 of  $\sim 550 \pm 50$  °C (data from Lazzeri et al. 2011; see the plot of fractionation factors in Fig. 3A)  
278 In these nearly bi-mineralic pegmatite samples, the beryl is assumed to contain nitrogen as  $\text{N}_2$   
279 and the coexisting muscovite is assumed to contain nitrogen as  $\text{NH}_4^+$ . Another possibility to  
280 consider, in interpreting nitrogen data for silicate systems, is that crustal minerals and fluids  
281 are not necessarily fully equilibrated with respect to nitrogen concentrations and isotope  
282 compositions, pointing to the need for experiments aimed at determining kinetic fractionation  
283 factors (Li et al. 2009). Given the various magnitudes and directions of nitrogen isotope  
284 fractionations among the different fluid species of nitrogen, it is evident that changes in redox  
285 conditions can exert a strong influence on the nitrogen isotope signature in any given system  
286 (see FIG. 3). At high metamorphic grades and in magmatic systems, where mineralogy and  
287 melt/fluid chemistry evolve during changes in temperature and/or redox conditions, nitrogen  
288 isotope fractionation could occur among hydrous fluids, melts, and minerals (Roskosz et al.  
289 2006; Mysen and Fogel 2010). Finally, it is not yet known whether nitrogen isotopes are  
290 fractionated during partial melting reactions or provide a true record of the  $\delta^{15}\text{N}$  of their  
291 sources.

292

## 293 **OUTLOOK**

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

300 **Continental Crust** Continental crust is extremely heterogeneous. Current estimates of deep-  
301 continental-crust concentrations and  $\delta^{15}\text{N}$  (see Bebout et al. 2013a) are based on a very small  
302 number of analyses of exhumed suites and xenoliths. Badly needed are additional studies of  
303 nitrogen in exposed continental-crust sections to evaluate, among other issues, the possible  
304 role of continental crust formation in the uptake of nitrogen from the atmosphere during the  
305 early evolution of the biosphere (Goldblatt et al. 2009).

306 **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  
320 mantle.

321 **Need for Fluid/Melt–Mineral Studies of Fractionation Factors** There is a critical need for  
322 experiments to determine nitrogen isotope fractionation associated with fluid–mineral or  
323 melt–mineral exchange. Particularly useful would be studies of fractionation between fluids  
324 of various types—and with varying nitrogen speciation (particularly as  $N_2$  and  $NH_3$ )—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.

331 **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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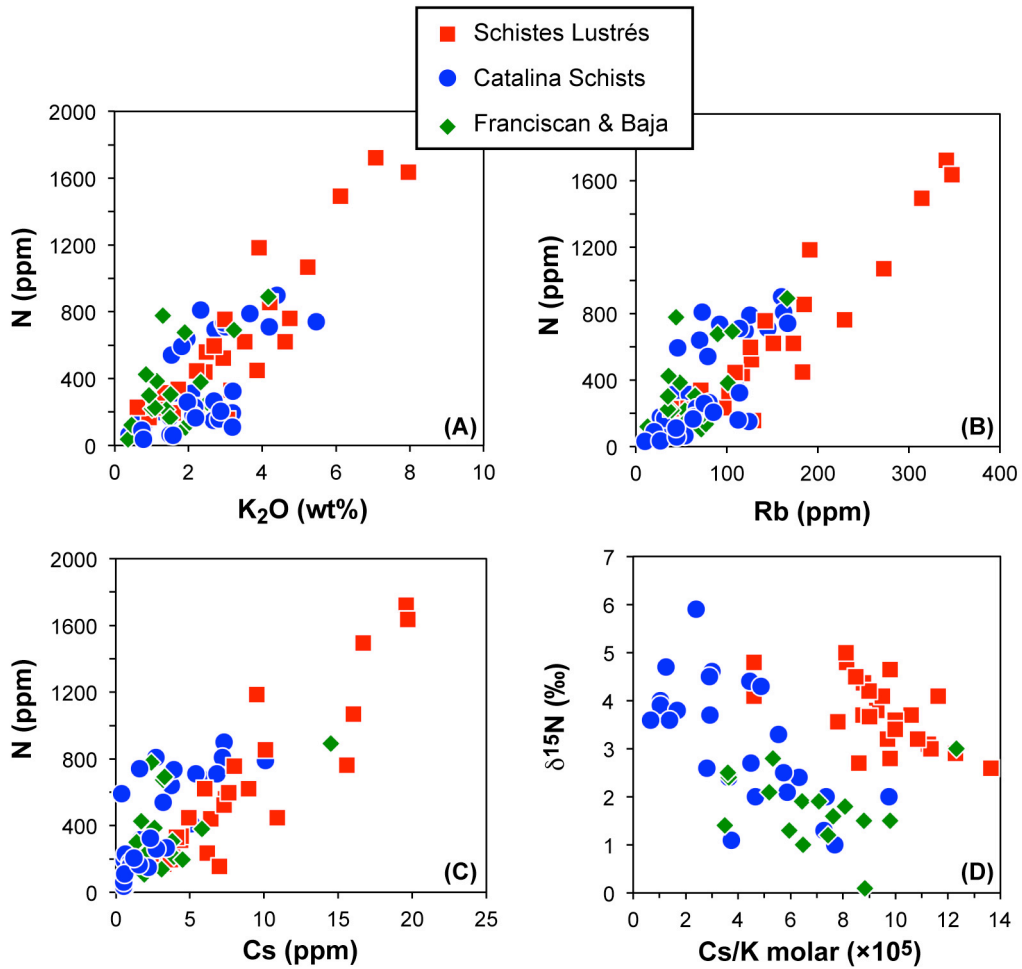
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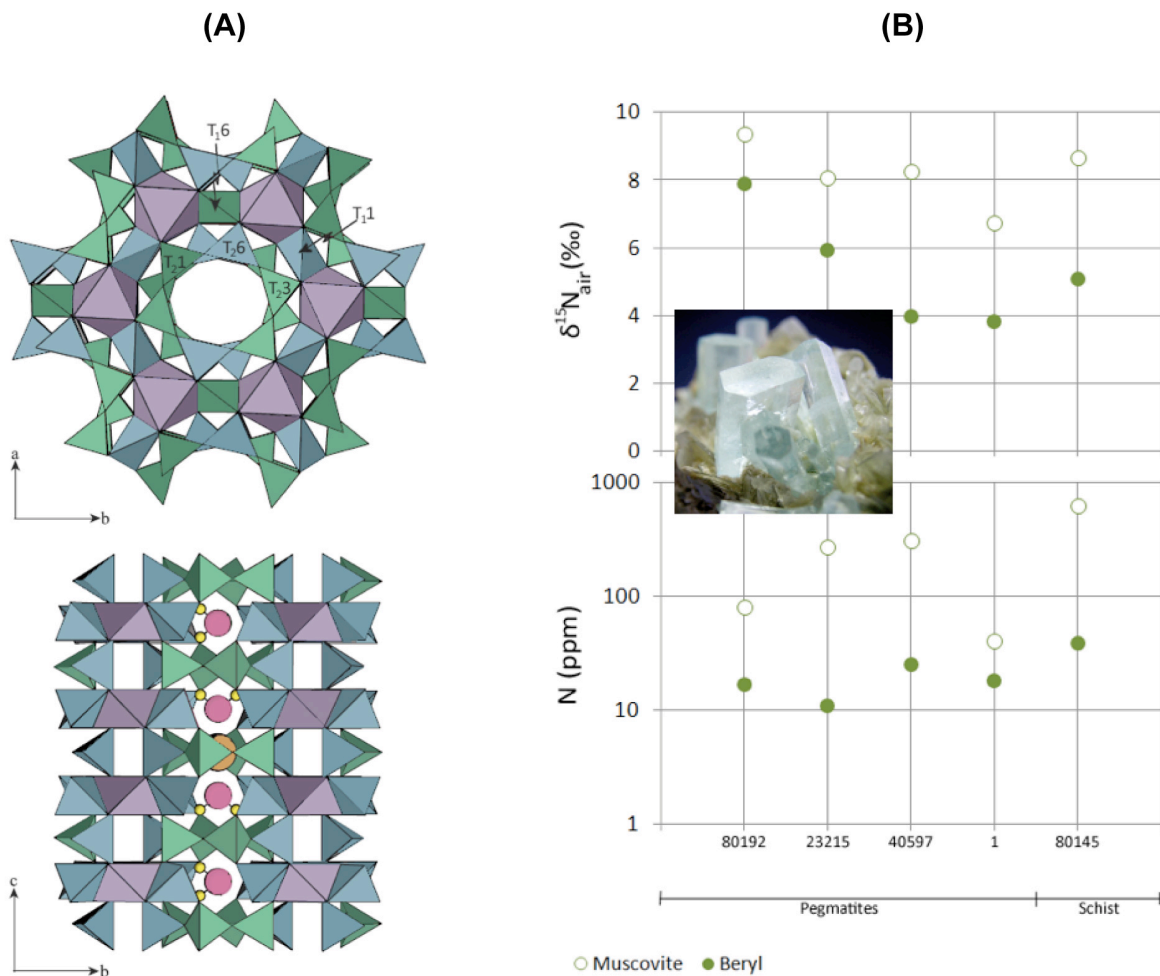
455 FIGURES  
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459 **FIGURE 1.** Illustration of the similar geochemical behaviors of nitrogen (as NH<sub>4</sub><sup>+</sup>) and some  
460 of the large-ion lithophile elements (LILEs). Plotted in (A), (B) and (C) are concentrations  
461 of N, K, Rb, and Cs in metasedimentary rocks from the Schistes Lustrés, Italian Alps  
462 (data from Busigny et al. 2003; Bebout et al. 2013b); Catalina Schists, California  
463 (data from Bebout and Fogel 1992); and Franciscan Complex and Western Baja Terrain,  
464 California. (D) Nitrogen isotope composition versus Cs/K ratio in the same  
465 metasedimentary sequences. Data on the Schistes Lustrés and Catalina Schists illustrate  
466 that subtle N release from the rocks to fluids during metamorphism can be traced from  
467 their N isotope composition (i.e. progressively increasing δ<sup>15</sup>N in the residual rock) and  
468 Cs/K ratio (decreasing due to preferential Cs loss)—see discussion in text. In contrast,  
469 metasedimentary rocks from the Franciscan Complex and Western Baja Terrain show  
470 more limited variation in Cs/K and δ<sup>15</sup>N, suggesting preservation of these elements (Cs, K  
471 and N) during metamorphism.

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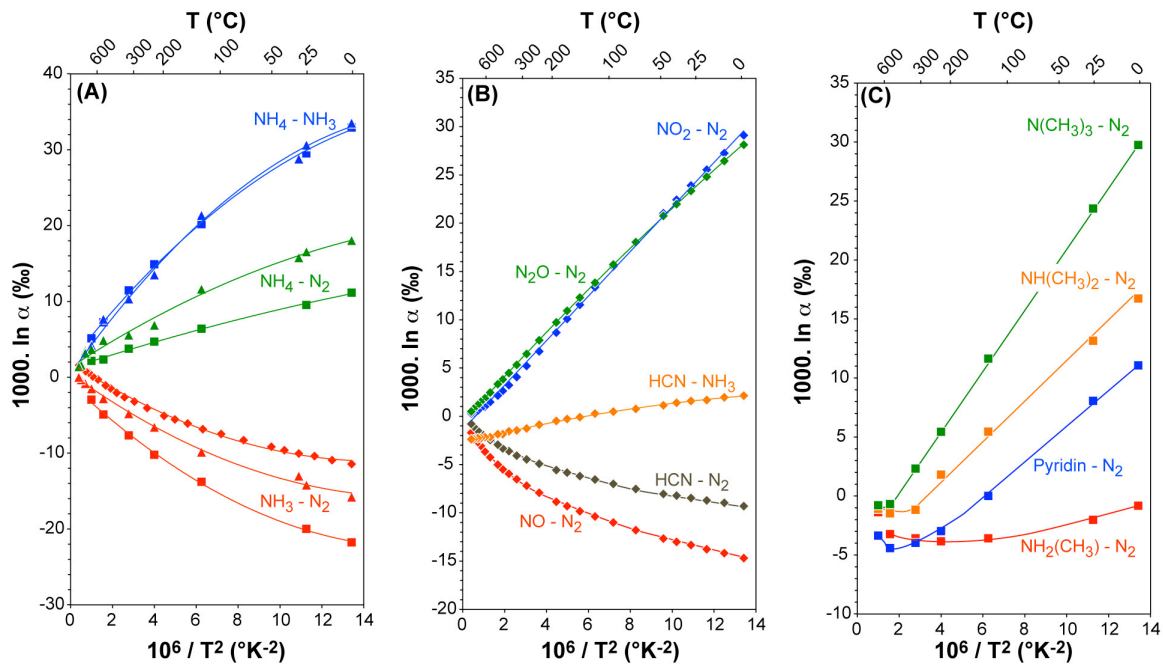


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**FIGURE 2.** (A) Polyhedral structural model of low cordierite (from Bertoldi et al. 2004), known to house N<sub>2</sub> in its channels. Si occupies the tetrahedra shown in shades of green (T<sub>1,6</sub>, T<sub>2,1</sub>, and T<sub>2,3</sub>) and Al the tetrahedra in shades of blue (T<sub>1,1</sub> and T<sub>2,6</sub>). The large orange sphere represents Na<sup>+</sup> 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<sub>2</sub>, N<sub>2</sub>, CO, O<sub>2</sub>, H<sub>2</sub>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](http://www.desertwindsgemsandminerals.com)). Note the relatively uniform N isotope fractionation (Δ<sup>15</sup>N; upper plot) of the coexisting minerals (near that predicted for appropriate temperatures by the calculations for the pair of molecules NH<sub>4</sub><sup>+</sup> and N<sub>2</sub> by Hanschmann 1981; see Fig. 3) and the higher N concentrations in mica relative to beryl in these samples (lower plot).



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**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  $\alpha_{A-B} =$

$(^{15}\text{N}/^{14}\text{N})_A / (^{15}\text{N}/^{14}\text{N})_B$ . 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.