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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 NH_4^+ (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

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 NH_3 (ammonia), which is rapidly transformed to 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 NH_4^+ substitutes for 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 NH_4^+ remaining substituted for K^+ in interlayer sites. For metasedimentary rocks, this
73 affinity of 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, 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, NH_4^+ from micas can be stabilized as 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 NH_4^+
92 in residual K-feldspar, but also as 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 N_2 (Duit et al. 1986). N_2 -bearing fluids liberated by metamorphic reactions can be (1) trapped
102 as fluid inclusions or in microporous phases, (2) incorporated as 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 NH_4^+ into potassic minerals such as micas and alkali feldspars. 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 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 (NH_4Cl) or ammoniojarosite [$(\text{NH}_4)\text{Fe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$] can be identified. Significant NH_4^+
129 enrichment also occurs in buddingtonite (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 NH_4^+ , which can substitute for 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 NH_4^+ are released
142 from the rocks into fluids, as N_2 or NH_3 , with nitrogen isotope fractionation enriching the
143 residual rock in ^{15}N (Haendel et al. 1986; Bebout and Fogel 1992). In contrast, cold P – T paths
144 (<10 °C/km) to depths of ~ 100 km are not associated with significant loss of nitrogen into
145 fluids, reflecting the high stability of 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 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 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 H_2 under reduced conditions. At high f_{H_2} , amine groups (e.g. NH_3 , 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 ~ 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 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 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 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 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}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 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 NH_4^+ in clinopyroxene. More-oxidized and lower-pressure
216 conditions in the shallow mantle would lead to the oxidation of nitrogen into 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 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 NH_4^+ , which substitutes for
243 K^+ , Na^+ , and/or 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 N_2 and NH_3 (e.g. Duit et al. 1986). The
249 stability of nitrogen oxides (NO_2 , N_2O , NO , 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 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 N_2 and 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 N_2
279 and the coexisting muscovite is assumed to contain nitrogen as 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.

336

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342

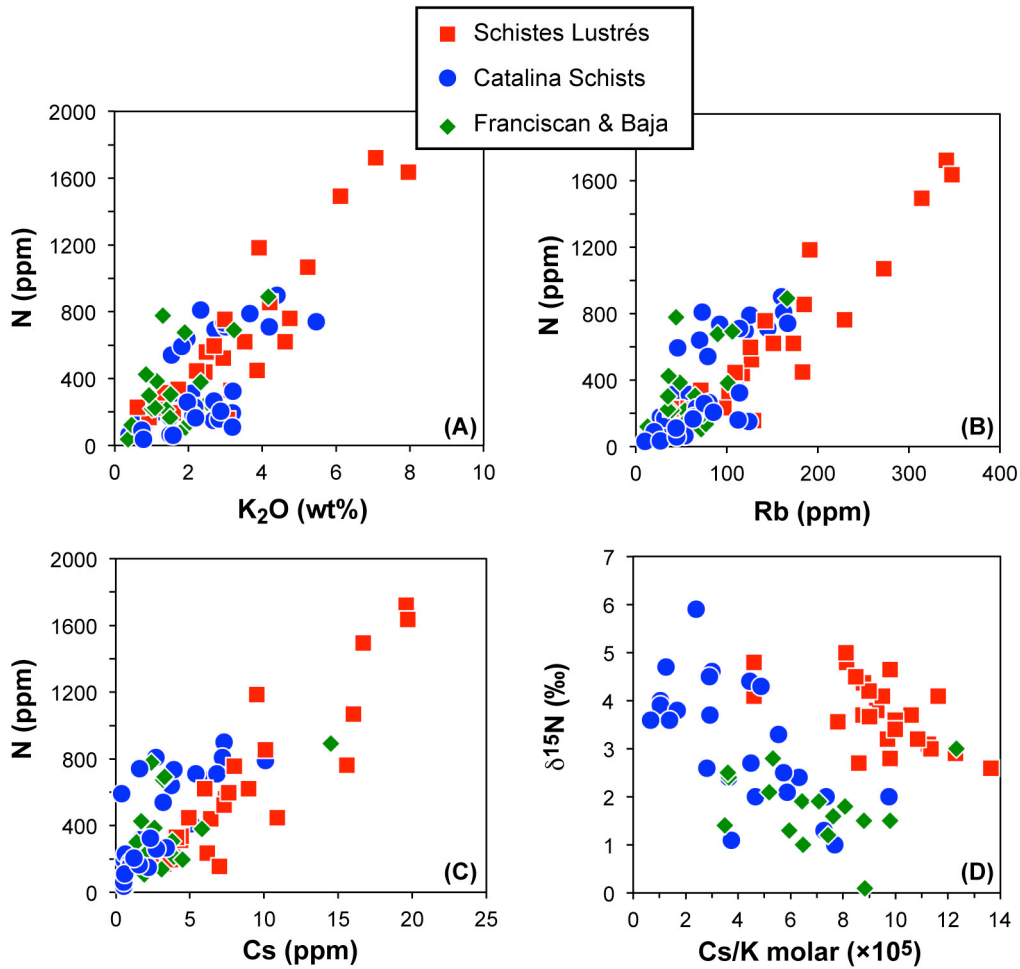
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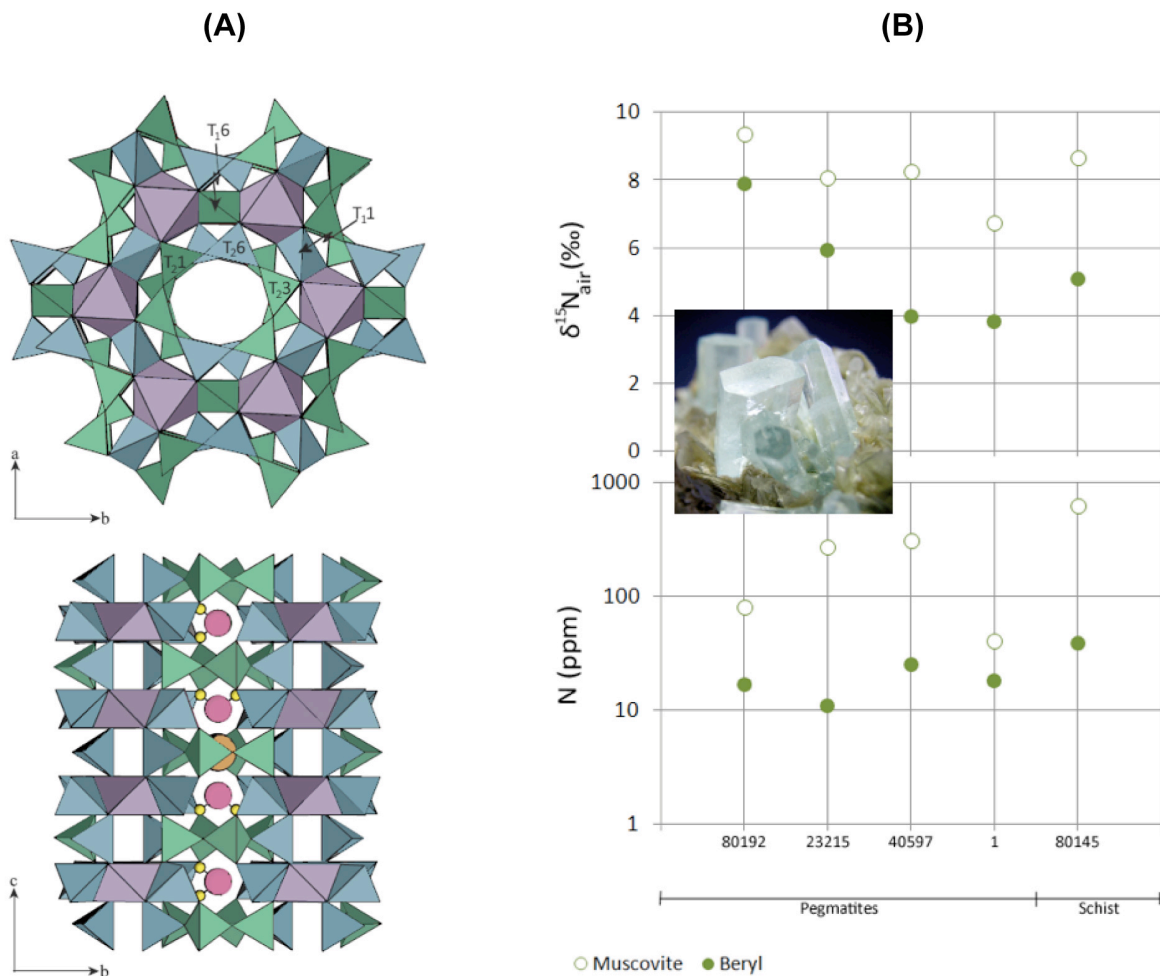
455 FIGURES
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459 **FIGURE 1.** Illustration of the similar geochemical behaviors of nitrogen (as NH₄⁺) and some
460 of the large-ion lithophile elements (LILEs). Plotted in (A), (B) and (C) are concentrations
461 of N, K, Rb, and Cs in metasedimentary rocks from the Schistes Lustrés, Italian Alps
462 (data from Busigny et al. 2003; Bebout et al. 2013b); Catalina Schists, California (data
463 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 δ¹⁵N 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 δ¹⁵N, suggesting preservation of these elements (Cs, K
471 and N) during metamorphism.

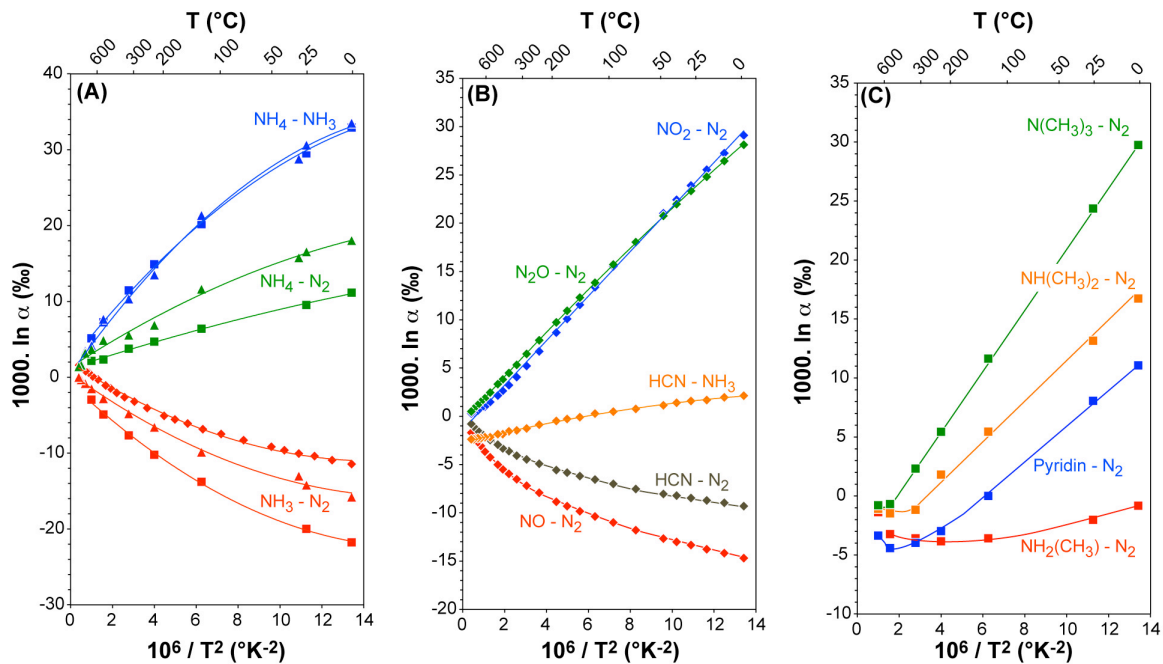
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482 **FIGURE 2.** (A) Polyhedral structural model of low cordierite (from Bertoldi et al. 2004),
483 known to house N₂ in its channels. Si occupies the tetrahedra shown in shades of green
484 (T₁₆, T₂₁, and T₂₃) and Al the tetrahedra in shades of blue (T₁₁ and T₂₆). The large
485 orange sphere represents Na⁺ within large spaces in the channels (Ch0 site). The small
486 yellow spheres connected to a pink sphere represent water molecules within the channels.
487 Not pictured are other molecules or neutral tetrahedral atoms that may be present within
488 the channels (CO₂, N₂, CO, O₂, H₂S, Ar, He). (B) Nitrogen concentrations and isotopic
489 compositions of coexisting muscovite and beryl from various pegmatite samples (inset
490 photo shows a similar beryl- and muscovite-bearing pegmatite sample not analyzed; data
491 from Lazzeri et al. 2011; Photo courtesy of Desert Winds Gems and
492 Minerals, www.desertwindsgemsandminerals.com). Note the relatively uniform N isotope
493 fractionation (Δ¹⁵N; upper plot) of the coexisting minerals (near that predicted for
494 appropriate temperatures by the calculations for the pair of molecules NH₄⁺ and N₂ by
495 Hanschmann 1981; see Fig. 3) and the higher N concentrations in mica relative to beryl in
496 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 $\alpha_{A-B} = \frac{(^{15}\text{N}/^{14}\text{N})_A}{(^{15}\text{N}/^{14}\text{N})_B}$. 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.