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13

Abstract

14 Roaldite (Fe_4N) is one of the few nitride minerals found in meteorites. Their nitrogen (N)
15 isotopic signatures carry important information for understanding the early N cycle in the proto-
16 solar nebula. However, the lack of knowledge on the N isotopic effects from nitride formation to
17 its survival from frictional heating during landing impedes the interpretation and application of N
18 isotope compositions of nitride minerals in meteorites. Here, we carried out laboratory
19 experiments under a recently proposed roaldite forming condition, i.e., NH_3 (as starting N
20 source) reacting with metallic Fe at medium temperatures. We observed Fe_4N formation over a
21 large range of temperatures from 300 °C to 700 °C. The formation of Fe_4N was associated with
22 equilibrium N isotope fractionations with $\alpha_{\text{Fe}_4\text{N-NH}_3}$ values of 0.9907 (± 0.0004) at 300 °C and
23 0.9936 (± 0.0004) at 500 °C, respectively. In the experimental pressure conditions (initial $P_{\text{NH}_3} =$
24 3.9-6.4 bar, $P_{\text{Total}} < 8.3$ bar), the formed Fe_4N remained stable at 300 °C, but was unstable and
25 quickly decomposed to Fe and N_2 at 500 °C and 700 °C. The decomposition of Fe_4N was
26 associated with large kinetic isotope fractionations with $\alpha_{\text{N}_2-\text{Fe}_4\text{N}}$ values of 0.9811 (± 0.0009) at
27 500 °C and 0.9839 (± 0.0011) at 700 °C, respectively. Our experimental results suggest that
28 roaldite formed from NH_3 can carry an isotopic signature very close to that of its source, but
29 partial decomposition (if there is any) can easily shift its N isotope composition for several tens
30 of per mil, and in extreme cases, to $> 300\%$. Thus, great caution is needed when using N isotope
31 composition of roaldite (and probably other nitride minerals as well) to trace source information.

32 **1. Introduction**

33 Nitride minerals, such as carlsbergite (CrN; Buchwald and Scott, 1971), roaldite (Fe₄N;
34 Buchwald and Nielsen, 1981), osbornite (TiN; Bannister, 1941; Keil, 1969), sinoite (Si₂N₂O;
35 Andersen et al., 1964), nierite (Si₃N₄; Leitner et al., 2018), and uakitite (VN; Sharygin et al.,
36 2018), have been discovered in a variety of meteorite samples. These nitride minerals, together
37 with ammonium salts (Poch et al., 2020) and organic compounds (Pizzarello et al., 2011),
38 represent the few major nitrogen (N) carriers in meteorites and other solar material; their N
39 isotope compositions (expressed as either ¹⁴N/¹⁵N ratio or the delta notation $\delta^{15}\text{N} =$
40 $(^{15}\text{N}/^{14}\text{N})_{\text{sample}}/(^{15}\text{N}/^{14}\text{N})_{\text{Air}} - 1$) have been used to infer the isotopic signatures of N reservoirs in
41 the solar system (e.g., Prombo and Clayton, 1993; Pizzarello et al., 1994; Meibom et al., 2007;
42 Ponganis and Marti, 2007; Füri and Marty, 2015; Grewal et al., 2021). In addition, since enstatite
43 chondrites likely contributed to a majority of the building blocks of the Earth (Javoy et al., 2010;
44 Dauphas, 2017; Piani et al., 2020), the nitride in enstatite chondrite (e.g., Rubin and Choi, 2009;
45 Leitner et al., 2018) could have at least partially contributed to Earth's primary N reservoir, and
46 consequently affected the N geochemical and isotope compositions of Earth's reservoirs (Javoy,
47 1998; Marty, 2012).

48 Isotopic studies on nitride minerals in meteorites yielded a huge range of N isotope
49 compositions. For example, a number of studies on iron meteorites and pallasites obtained
50 variable $\delta^{15}\text{N}$ values from -96‰ to 164‰ for these meteorites (Meibom et al., 2007; Grewal et
51 al., 2021 and references therein); Meibom et al. (2007) observed $\delta^{15}\text{N}$ values around -360‰ for
52 osbornite in CAI from the carbonaceous chondrite Isheyevo; whereas Harries et al. (2015)
53 observed $\delta^{15}\text{N}$ values from 44‰ to 64‰ for carlsbergite in the volatile-rich CM2 chondrites
54 Yamato 791198 and Y-793321. To fully interpret these isotopic data, it is crucial to assess the N

55 isotopic effects over the course from the formation of nitride minerals in their source regions to
56 their final landing/emplacement on Earth's surface, which however has not been taken into
57 account in most previous studies due to the lack of N isotope fractionation data.

58 Recently, through laboratory experiments, Li et al. (2016) and Dalou et al. (2019)
59 investigated the N isotope fractionations between silicate melt and metal alloys. These
60 experiments yielded very different isotope fractionation factors, but consistently showed strong
61 ^{15}N -depletion in metal alloys. This mechanism may provide insights into the interpretation of N
62 isotope compositions of nitrides in differentiated planetary bodies, such as iron meteorites, but
63 may not be relevant to nitride minerals in primitive chondrites which have not undergone
64 significant silicate-metal differentiation. Through study of mineral inclusions in primitive
65 chondritic meteorites, Harries et al. (2015) suggested that the nitride mineral (carlsbergite in this
66 case) was likely formed by reaction between (Cr-bearing) metal with ammonia gas at
67 temperatures slightly higher than 300-400 °C.

68 To examine the formation and stability of nitride at medium temperatures and determine
69 the associated N isotope fractionations, we carried out laboratory experiments to study the
70 reaction between metallic Fe powders and NH_3 gas at 300-700 °C. This temperature range spans
71 over the proposed formation temperature of the carlsbergite-bearing sulfide in CM2 chondrite
72 (Harries et al., 2015) and also can be applicable to early Earth's near surface hydrothermal
73 systems. Iron nitride (rather than chromium nitride) was chosen for this study because, as an
74 initial effort to study the metal- NH_3 system, the reaction between NH_3 and Fe can be better
75 constrained and is easier to accomplish in laboratory conditions.

76

77 **2. Experiment setup and analytical methods**

78 The experimental setup and analytical method employed in this study were similar to
79 those in a previous experimental study on the N isotope fractionations of thermal decomposition
80 of NH₃ without the presence of Fe (Li et al., 2009). But some of the experimental conditions
81 (e.g., temperature, reagents) have been modified for the purpose of this study.

82 In brief, about 20 mg commercial metallic iron (Fe) powders (VWR; purity > 99.5%)
83 were loaded into a one-end sealed, pre-cleaned (by combustion under air at 1200 °C for 2 hours)
84 quartz tube (outer diameter: 6 mm; inner diameter: 4 mm). For comparison, ~ 50 mg and ~ 6 mg
85 Fe powders were also used in the 500 °C experiments. The sample tube was then attached to a
86 glass vacuum line illustrated in Li et al. (2009) to remove air. An aliquot of NH₃ gas (with initial
87 $\delta^{15}\text{N}$ value of -2.2‰; n = 10; $1\sigma = 0.1\%$) was expanded from a large-volume NH₃ gas flask and
88 equilibrated for 2 minutes (to ensure pressure and isotopic homogenization) before it was
89 cryogenically transferred into the sample tube. The method for NH₃ quantification has been
90 described in detail by Li et al. (2009) and not reiterated here. After minor incondensable gases
91 were evacuated, the sample tube was sealed under vacuum, and carefully measured for its inner
92 length to allow the estimation of internal pressure.

93 A number of sample tubes (for parallel experiments) were put into a muffle furnace and
94 carefully positioned to minimize the thermal gradient along and between the tubes. The
95 experiments were proceeded at 300 °C for 28 to 244 hours, 500 °C for 10 minutes to 168 hours,
96 and 700 °C for 2-15 minutes. Temperature monitoring indicates that temperature overshooting
97 only occurred in the 700 °C experiments because a rapid heating ramp was programed to
98 minimize the time to reach peak temperature. But the magnitude of temperature overshooting

99 was small ($< 5\text{ }^{\circ}\text{C}$) and lasted for a short time (a few seconds). The sample tubes were then
100 quenched, loaded into tube crackers attached to the same vacuum line, pumped, and cracked. The
101 released gases, including H_2 , N_2 , and remaining NH_3 , were quantified in sequence using a
102 Toepler pump. N_2 and NH_3 were also measured for N isotope compositions using an isotope ratio
103 mass spectrometer at dual-inlet mode, all described in detail by Li et al. (2009).

104 The solid phases of selected samples from each temperature were investigated by X-ray
105 diffraction (XRD) and scanning electron microscope (SEM) to identify the mineral phases and
106 morphology. The solid phases of ten samples from the $500\text{ }^{\circ}\text{C}$ experiments were also loaded into
107 one end-sealed quartz tubes together with $\sim 1\text{g}$ CuO oxidant, pumped, sealed under vacuum, and
108 combusted at $1000\text{ }^{\circ}\text{C}$ overnight in a muffle furnace to release any N for quantification and
109 isotopic analysis. As control experiments, the remaining solid phases of some of these samples
110 after the measurements were again loaded into quartz tubes with CuO oxidant, evacuated, sealed
111 and combusted at $1000\text{ }^{\circ}\text{C}$ by the same procedure. No N was yielded in these control
112 experiments, indicating that metallic Fe could not re-assimilate N_2 during the cooling of the
113 sample tubes, likely due to the preferential oxidation by O_2 released from CuO.

114 Based on repeated analyses of international standards IAEA-N1 and IAEA-N2 over the
115 course of these experiments, the analytical uncertainty was generally $< 2\%$ (1σ) of the absolute
116 value for N quantity, and $< 0.15\text{‰}$ (1σ) for N isotope composition. The variation of plateau
117 temperature of the muffle furnace during the experiments was $\pm 1\text{ }^{\circ}\text{C}$.

118

119 **3. Results**

120 The quantities and isotope compositions of the reactants and products of all the
121 experiments with their temperature and pressure conditions are listed in Table 1.

122 At each experimental temperature, NH_3 decreased steadily with progressive ^{15}N
123 enrichment in the remaining NH_3 along experimental time (Figs. 1, 2A). N_2 was also detected in
124 the gaseous phases in all experiments (Fig. 1). While the produced N_2 also display progressively
125 larger yields and higher $\delta^{15}\text{N}$ values along experimental time, the $\delta^{15}\text{N}_{\text{N}_2}$ values are all lower
126 than the $\delta^{15}\text{N}$ values of the initial NH_3 (Fig. 2B). This general pattern is similar to the
127 experimental results of thermal decomposition of NH_3 in the absence of Fe (Li et al., 2009),
128 suggesting that NH_3 decomposition and N_2 production occurred in the experiments in this study.

129 The decomposition rates of NH_3 in the experiments in this study were mainly controlled
130 by two factors. One is the amount of Fe. For example, under the same condition of 500 °C and 1
131 hour, the experiments using ~6 mg, ~20 mg, ~50 mg Fe yielded 60% ($1\sigma = 2\%$; $n=2$), 43% (1σ
132 = 1%; $n = 4$), and 40% ($1\sigma = 1\%$; $n = 2$) remaining NH_3 , respectively (Table 1; Fig. 3). The
133 other and the main controlling factor is temperature. For example, in the 300 °C experiments,
134 ~80% of initial NH_3 still remained after 10 days; in the 500°C experiments, ~40% of initial NH_3
135 remained after 1 hour; in the 700°C experiments, only 7% NH_3 was left after 15 minutes (Table
136 1), and no NH_3 was detected after 30 minutes. For comparison, Li et al. (2009) showed that, in
137 similar experimental conditions but with the absence of Fe, NH_3 decomposition at 700 °C
138 occurred at a much slower rate (e.g., ~75% remained after 40 hours and ~40% remained after 10
139 days) and even no decomposition could be detected over months at temperature ≤ 500 °C. This
140 comparison indicates that Fe can accelerate the NH_3 decomposition reaction for orders of
141 magnitude and can expand the reaction to much lower temperatures (≤ 300 °C).

142 In contrast to the experiments by Li et al. (2009), which showed good matches in both
143 nitrogen mass and isotope composition between decomposed NH₃ and produced N₂, the
144 experiments in this study gave obvious mismatches between these two. For example, in the 300
145 °C experiments, NH₃ was the major N-bearing species observed in the remaining gas phases after
146 28 hours and 244 hours, but only accounts for ~80% of initial NH₃ (Fig. 1A); nearly 20% of NH₃
147 was consumed with little production of N₂ but significant production of H₂ (Table 1). This leads
148 to significant amounts of “missing” N. In the 500 °C and 700 °C experiments, more N₂ occurred
149 together with NH₃ in the remaining gas phases (Fig. 1B & C). But again the total amounts of N
150 recovered from NH₃ and N₂ are less than that of the initial NH₃ in the relatively short
151 experiments, leading to various amounts of “missing” N (Table 1).

152 This “missing” N has been recovered by the combustion of the solid phases. For example,
153 in the 500 °C experiments, the mass balance of the quantities and isotope compositions of the
154 recovered NH₃ and N₂ in the gases phases and the recovered N from the solid phases gave a total
155 N yield (relative to the initial NH₃) of 96.7% with a $\delta^{15}\text{N}$ value of -1.9‰ from one of the 10
156 minute experiments, 98.3% ($1\sigma = 0.1\%$; $n = 3$) with a mean $\delta^{15}\text{N}$ value of -2.3‰ ($1\sigma = 0.1\%$; n
157 = 3) from three of the 1 hour experiments, 98.5% ($1\sigma = 1.0\%$; $n = 3$) with a mean $\delta^{15}\text{N}$ value of -
158 2.1‰ ($1\sigma = 0.4\%$; $n = 3$) from three of the 2 hour experiments, 102.6% with a $\delta^{15}\text{N}$ value of -
159 2.8‰ from one of the 3.5 hour experiments, and 99.5% ($1\sigma = 0.4\%$; $n = 2$) with a mean $\delta^{15}\text{N}$
160 value of -3.1‰ ($1\sigma = 0.0\%$; $n = 2$) from two of the 6 hour experiments (Table 1; Fig. 1B & E).
161 These $\delta^{15}\text{N}$ values match well with the $\delta^{15}\text{N}$ value (-2.2‰) of the initial NH₃.

162 H₂ was also examined in some of the experiments. Measurements from a number of
163 experiments ($n = 2, 15$ and 3 for the 300°C, 500°C and 700°C experiments, respectively) indicate
164 that the molar ratio between the H of recovered H₂ and the N of decomposed NH₃ (hereafter

165 referred to as the H:N ratio) is strongly dependent on experimental duration (Fig. 4). The highest
166 H:N ratios (2.8-2.9) observed in the shortest experiments (10 minutes at 500 °C and 700 °C) are
167 close to the H:N stoichiometric ratio of 3 in NH₃, which verifies that the H₂ was produced from
168 the decomposition of NH₃. The H:N ratios progressively decrease along experimental time to as
169 low as ~2.2 in the longest experiment of 244 hours at 300 °C (Table 1; Fig. 4). Because hydrogen
170 solubility in Fe at the experimental temperatures is extremely low ($N_H/N_{Fe} < 10^{-4}$; Kiuchi and
171 McLellan, 1983), it cannot account for any detectable decrease in the H:N ratio. The slightly
172 lowered H:N ratios (by 0.1-0.2) in the short experiments were likely caused by quick oxidation
173 of H₂ by small amounts of Fe oxides on the surface of the Fe reactant or some small oxidizing
174 particles attached on the inner wall of the quartz tubes; whereas the progressively decreasing
175 H:N ratios in long experiments were likely caused by diffusive loss of H₂ out of the quartz tubes
176 (Li et al., 2009). Nevertheless, the reasonably good match between the decomposed NH₃ and
177 recovered H₂ in the short experiments suggests that no H-bearing phase was formed in the solid
178 phases and all H in the decomposed NH₃ was released as H₂ in the gas phases.

179

180 **4. Discussion**

181 **4.1. Formation and stability of Fe₄N**

182 To further understand the form of the fixed N in metallic Fe, we examined the solid phases
183 by XRD and SEM. The XRD spectra (Fig. 4) clearly show that an Fe-nitride phase, Fe₄N, has
184 been formed in the Fe particles at all temperatures. Although thermodynamic models predicted
185 that other nitride phases such as Fe₂₋₃N could also be formed and co-exist with Fe₄N in the high-
186 nitriding potential NH₃ atmosphere (e.g., van Voorthuysen et al., 2002; Pelka et al., 2009), we
187 did not detect these nitride phases in any of our experiments (Fig. 5). This may be attributed

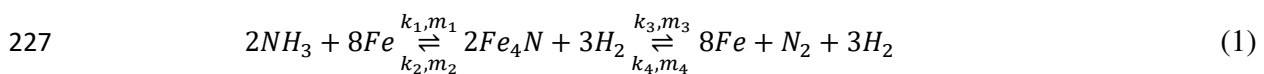
188 either to the relatively short experimental durations which were not long enough to form Fe_{2-3}N
189 or to the decreased nitriding potential as a result of decreased NH_3 partial pressure and increase
190 H_2 partial pressure with the progress of the experiments (van Voorthuysen et al., 2002; Pelka et
191 al., 2014). In all the 300 °C and 500 °C experiments (Fig. 5A & B), Fe_4N is the only detectable
192 nitride phase; whereas in the 700 °C experiments, another Fe nitride phase that can be described
193 as $\text{FeN}_{0.088}$ (a tetragonal phase in $I4/mmm$ space group) was also detected in addition to Fe_4N
194 (Fig. 5C). These results suggest that, Fe_4N is a relatively more stable phase than $\text{FeN}_{0.088}$ and
195 other Fe-nitrides in our experimental conditions.

196 Thermodynamically, Fe_4N is unstable at relatively low (e.g., atmospheric) N_2 pressures
197 (Ertl et al., 1979; Wriedt et al., 1987). However, the proceeding of Fe_4N decomposition is
198 believed to be strongly controlled by N desorption from “surface nitride” and followed migration
199 of N from the depth to the surface in the solid phases, which are only significant above 400-450
200 °C because of the high kinetic energy required for N desorption from Fe and for recombination
201 of N atoms to N_2 (Ertl et al., 1979; van Voorthuysen et al., 2002). These high kinetic barriers
202 maintain Fe_4N as a metastable phase in the 300 °C experiments (with no sign of decomposition
203 after more than 10 days). At 500 °C and 700 °C, the energy is high enough to facilitate the
204 decomposition of Fe_4N (van Voorthuysen et al., 2002). As a result, Fe_4N can only occur for a
205 short time period at these temperatures and be inevitably decomposed with the consumption of
206 the limited NH_3 reservoir. Fe_4N could occur persistently in these high temperature conditions if
207 an unlimited NH_3 reservoir exists to maintain the $\text{NH}_3 - \text{Fe}_4\text{N}$ reaction.

208 The entire process from uptake of N by Fe (to form Fe_4N) to subsequent decomposition of
209 Fe_4N is clearly illustrated by the SEM images (Fig. 6). Compared with the relatively rough and
210 random surface features of initial Fe particles (Fig. 6A), the solid phases from the experiment at

211 300 °C for 244 hours display clear growth of nanocrystals on Fe surface (Fig. 6B), which has
 212 been verified to be Fe₄N by XRD (Fig. 5A) and EDX-SEM analyses. The growth of Fe₄N on Fe
 213 surface was not well ordered but in an indistinct morphology at the early stage (e.g., Fig. 6C, F),
 214 suggesting that the formation of Fe₄N on Fe surface occurred very fast. With the further
 215 processing of the reaction along time, Fe₄N was reorganized into nanocrystals in an octahedral
 216 geometry (Fig. 6B, E & G), which is consistent with the structure of Fe₄N, but different to the
 217 hexagonal structure of Fe₃N (Inokuti et al., 1975; Jacobs et al., 1995) or the tetragonal structure
 218 of FeN_{0.088}. Another interesting feature on Fe surface is the annular stepped surface morphology
 219 (Fig. 6E, G), which may be related to the reorganization of Fe after Fe₄N decomposition. EDX-
 220 SEM analysis also detected a small oxygen peak from the initial Fe particles, implying the Fe
 221 reagent in our experiments contained small amount of oxygen, which could explain the slightly
 222 lowered H:N ratios in the short experiments (Fig. 4).

223 Based on above observations, our experiments demonstrates that NH₃ decomposition
 224 occurred through denitridation, which was ultimately destabilized to produce N₂ gas. It can be
 225 described by at least two sets of reactions between (1) NH₃ and Fe₄N and (2) Fe₄N and N₂. The
 226 total reaction in the system can be described using a general reaction formula:



228 in which k₁ and k₃ denote the reaction rate constants of the forward reactions and k₂ and k₄
 229 denote the reaction rate constants of the inverse reactions; m₁ to m₄ denote the order of
 230 corresponding reaction.

231 Our 500°C experiments gave the largest number of time-series data from 10 minutes to 168

232 hours (Table 1), which provide a best opportunity to quantitatively model the reactions. Based on
 233 the comparison of the NH₃ decomposition extents among various Fe quantity (Fig. 3), it appears
 234 that that 20 mg Fe, which was used in most of the experiments, was in (or at least close to)
 235 excess for the reactions and thus not rate-limiting. Therefore, in the modeling, the reaction rates
 236 were assumed to be independent of the Fe amounts.

237 Based on Equation (1), the decomposition rate of NH₃ and the production rates of Fe₄N and
 238 N₂ can be written as:

$$239 \quad \frac{dn_{NH_3}}{dt} = -k_1 \cdot n_{NH_3}^{m_1} + k_2 \cdot n_{Fe_4N}^{m_2} \quad (2)$$

$$240 \quad \frac{dn_{Fe_4N}}{dt} = k_1 \cdot n_{NH_3}^{m_1} - k_2 \cdot n_{Fe_4N}^{m_2} - k_3 \cdot n_{Fe_4N}^{m_3} + k_4 \cdot n_{N_2}^{m_4} \quad (3)$$

$$241 \quad \frac{dn_{N_2}}{dt} = k_3 \cdot n_{Fe_4N}^{m_3} - k_4 \cdot n_{N_2}^{m_4} \quad (4)$$

242 Using Equations (2)-(4), we modeled the quantity evolution of NH₃, Fe₄N and N₂ along
 243 experimental time for the 500 °C experiments. The modeling employed a simplified forward
 244 numeric calculation approach using a time increment of 1 minute and artificially assigned values
 245 for k₁ to k₄ and m₁ to m₄. The best fitting curves shown in Fig. 7A capture most of the
 246 experimental data and more importantly the overall evolution trend, although a perfect match of
 247 data was not achieved. Possible uncertainties that may account for the discrepancy between the
 248 experimental and modeling results include (1) reactions in the temperature ramping stage (< 2
 249 minutes); (2) potential effect of H₂ (and its diffusive loss over time); (3) the partially oxidized
 250 surface (although very minor) of the initial Fe powders which could have affected NH₃
 251 decomposition rate, at least at the beginning before its surface was completely reduced; (4) the

252 grain size/shape of Fe particles, which could affect the interaction between N and Fe (e.g. Pelka
253 et al., 2009); (5) some other kinetic effects, such as kinetic crystallization, migration of N
254 between the depth and the reaction surface of Fe. All these factors could play a role but are
255 difficult to be quantitatively assessed in the modeling.

256 The best fitting of the experimental data (Fig. 7A) yielded 2, 1, and 0.5 for m_1 to m_3 ,
257 respectively. The value of m_4 does not significantly affect the results. The best fitting also gave
258 $k_1/k_2 \approx 2.5$, $k_2/k_3 \approx 100$, and $k_3/k_4 \approx 100$. This indicates that k_1 and k_2 are close, and about two
259 orders of magnitude larger than k_3 ; the latter is another two orders of magnitude larger than k_4 .
260 The fact that k_1 and k_2 are close strongly suggests that the reaction between NH_3 and Fe_4N is
261 relatively fast and reversible, which are consistent with the quick development of a metastable
262 state of the $\text{NH}_3 - \text{Fe}_4\text{N}$ system in the 300 °C experiments (Fig. 1A) and the experiments in the
263 first 2 hours at 500 °C (Figs. 1B & 7).

264 Compared with the $\text{NH}_3 - \text{Fe}_4\text{N}$ reaction, Fe_4N decomposition proceeded much more
265 slowly in the experiments. Because the back-reaction (i.e., N_2 conversion to Fe_4N) is two orders
266 of magnitude slower and thus can be neglected, the Fe_4N decomposition reaction can be
267 considered as unidirectional and the rate-limiting step in the entire system.

268 **4.2. Nitrogen isotope fractionations during formation and decomposition of Fe_4N**

269 **4.2.1. Modeling of nitrogen isotope fractionation factors**

270 In our experiments, the remaining NH_3 and the produced Fe_4N and N_2 show large $\delta^{15}\text{N}$
271 variations (Figs. 1-2). With the proceeding of NH_3 decomposition and N_2 production, both the
272 remaining NH_3 and produced N_2 are progressively more enriched in ^{15}N . However, compared

273 with the initial NH₃, all the remaining NH₃ is more ¹⁵N-enriched, whereas all the produced N₂ is
 274 more ¹⁵N-depleted and only reaches the δ¹⁵N value of the initial NH₃ when all the initial NH₃ is
 275 converted into N₂ (Figs. 1 & 3). In contrast, Fe₄N shows more variable δ¹⁵N values, which can
 276 be either lower or higher than that of the initial NH₃ (Table 1; Fig. 1E). This indicates strong
 277 isotopic effects associated with the NH₃ – Fe₄N and Fe₄N – N₂ reactions.

278 To model the isotope fractionation factor, Equations (5) and (6) can be used for
 279 equilibrium isotope fractionations:

$$280 \quad \alpha_{P-R} = \frac{(\delta_{R0}+1) - (\delta_R+1) \cdot f_R}{(\delta_R+1) \cdot (1-f_R)} \quad (5)$$

$$281 \quad \alpha_{P-R} = \frac{(\delta_P+1) \cdot (1-f_P)}{(\delta_{R0}+1) - (\delta_P+1) \cdot f_P} \quad (6)$$

282 in which α is the fractionation factor, P denotes product, R denotes reactant, f denotes fraction,
 283 and δ_{R0} is the initial isotope composition of the reactant, i.e., NH₃ in this case.

284 Equations (7) and (8) can be used for the modeling of kinetic isotope fractionation:

$$285 \quad \alpha_{P-R} = \frac{\ln\left(f_R \cdot \frac{1+R_{R0}}{1+R_R} \cdot \frac{R_R}{R_{R0}}\right)}{\ln\left(f_R \cdot \frac{1+R_{R0}}{1+R_R}\right)} \quad (7)$$

286 in which R_{R0} and R_{R0} denote the initial and final isotopic ratio of the reactant, respectively.

287 Replacement of isotopic ratio by δ (= R_R/R_{STD} - 1) value yields:

$$288 \quad \alpha_{P-R} = \frac{\ln\left[f_R \cdot \frac{1+(1+\delta_{R0}) \cdot R_{STD}}{1+(1+\delta_R) \cdot R_{STD}} \cdot \frac{1+\delta_R}{1+\delta_{R0}}\right]}{\ln\left[f_R \cdot \frac{1+(1+\delta_{R0}) \cdot R_{STD}}{1+(1+\delta_R) \cdot R_{STD}}\right]} \quad (8)$$

289 in which R_{STD} is the isotopic ratio of standard, i.e., 0.0036765 for the N isotope standard of

290 atmospheric N₂ (Coplen et al., 1992).

291 It is noted that Equations (5)-(8) are derived with no or minimum (and valid)
292 approximation (Hayes, 2004), and thus are more complicated than the commonly used Rayleigh
293 or batch fractionation equations derived with approximations. Hayes (2004) and Scott et al.
294 (2004) have demonstrated that the simplified equations with approximations can introduce large
295 errors in the calculation of isotope fractionation factors when involve data with f_R values close to
296 0 (i.e., the reaction proceeds close to completion), which is the case of some of our experiments.

297 Equations (5)-(8) are effective for the modeling of isotope fractionations in relatively
298 simple reactions but difficult for complicated system involving multiple simultaneous reactions
299 with both equilibrium and kinetic isotopic effects. By integrating equilibrium and kinetic isotope
300 fractionation factors into a group of functions, Li et al. (2021) introduced a more sophisticated
301 model to account for the nitrogen isotopic pattern in the process of NH₄⁺ dissociation into
302 aqueous ammonia (NH₃·nH₂O) followed by ammonia degassing. The NH₄⁺ – NH₃·nH₂O – NH₃
303 system is similar to the NH₃ – Fe₄N – N₂ system studied here in that the first reaction is
304 reversible with possible achievement of isotope equilibration, whereas the second reaction is
305 unidirectional and dominated by kinetic isotopic effect. Following Li et al. (2021), the isotopic
306 evolution of NH₃, Fe₄N and N₂ in the system can be modeled by rewriting Equations (2)-(4) for
307 ¹⁴N and ¹⁵N, respectively:

$$308 \quad \frac{dn_{(^{14}\text{NH}_3)}}{dt} = -^{14}k_1 \cdot n_{(^{14}\text{NH}_3)}^{m_1} + ^{14}k_2 \cdot n_{(^{14}\text{Fe}_4\text{N})}^{m_2} \quad (9)$$

$$309 \quad \frac{dn_{(^{15}\text{NH}_3)}}{dt} = -^{15}k_1 \cdot n_{(^{15}\text{NH}_3)}^{m_1} + ^{15}k_2 \cdot n_{(^{15}\text{Fe}_4\text{N})}^{m_2} \quad (10)$$

$$310 \quad \frac{dn_{(^{14}\text{Fe}_4\text{N})}}{dt} = {}^{14}k_1 \cdot n_{(^{14}\text{NH}_3)}^{m_1} - {}^{14}k_2 \cdot n_{(^{14}\text{Fe}_4\text{N})}^{m_2} - {}^{14}k_3 \cdot n_{(^{14}\text{Fe}_4\text{N})}^{m_3} + {}^{14}k_4 \cdot n_{(^{14}\text{N}_2)}^{m_4}$$

$$311 \quad (11)$$

$$312 \quad \frac{dn_{(^{15}\text{Fe}_4\text{N})}}{dt} = {}^{15}k_1 \cdot n_{(^{15}\text{NH}_3)}^{m_1} - {}^{15}k_2 \cdot n_{(^{15}\text{Fe}_4\text{N})}^{m_2} - {}^{15}k_3 \cdot n_{(^{15}\text{Fe}_4\text{N})}^{m_3} + {}^{15}k_4 \cdot n_{(^{15}\text{N}_2)}^{m_4}$$

$$313 \quad (12)$$

$$314 \quad \frac{dn_{(^{14}\text{N}_2)}}{dt} = {}^{14}k_3 \cdot n_{(^{14}\text{Fe}_4\text{N})}^{m_3} - {}^{14}k_4 \cdot n_{(^{14}\text{N}_2)}^{m_4}$$

$$(13)$$

$$315 \quad \frac{dn_{(^{15}\text{N}_2)}}{dt} = {}^{15}k_3 \cdot n_{(^{15}\text{Fe}_4\text{N})}^{m_3} - {}^{15}k_4 \cdot n_{(^{15}\text{N}_2)}^{m_4}$$

$$(14)$$

316 in which ${}^{14}K_1$ to ${}^{14}K_4$ and ${}^{15}K_1$ to ${}^{15}K_4$ denote the reaction rates of ${}^{14}\text{N}$ and ${}^{15}\text{N}$ in corresponding
 317 reactions, respectively. Consequently, the N isotope fractionations for the $\text{NH}_3 - \text{Fe}_4\text{N}$ reaction
 318 and the $\text{Fe}_4\text{N} - \text{N}_2$ reaction can be described as:

$$319 \quad \alpha_{\text{Fe}_4\text{N}-\text{NH}_3} = \frac{{}^{15}k_2 \cdot {}^{14}k_1}{{}^{14}k_2 \cdot {}^{15}k_1}$$

$$(15)$$

$$320 \quad \alpha_{\text{N}_2-\text{Fe}_4\text{N}} = \frac{{}^{15}k_4 \cdot {}^{14}k_3}{{}^{14}k_4 \cdot {}^{15}k_3}$$

$$(16)$$

321 This model involves several parameters, such as the equilibrium and kinetic isotope fractionation
 322 factors and the order of each reaction. If more than 1 of these parameters are unknown, the
 323 modeling results may give relatively large errors and require a large dataset for the modeling in
 324 order to minimize the errors.

325 4.2.2. Equilibrium isotope fractionation factors between Fe_4N and NH_3

326 The modeling for the 300 °C experiments is relatively simple because only the first step
327 reaction of NH₃–Fe₄N occurred in the system. The modeling yielded a good linear relationship
328 ($R^2 = 0.999$) using Equation 5 (for equilibrium isotope fractionations; Fig. 8A) but a bad linear
329 relationship ($R^2 = 0.24$; not shown here) using Equation 8 (for kinetic isotope fractionations).
330 This is consistent with an equilibrium isotope fractionation dominating the reaction. The slope on
331 Fig. 8A gave the equilibrium isotope fractionation factor $\alpha_{\text{Fe}_4\text{N-NH}_3} = 0.9907 \pm 0.0004$, or
332 $1000\ln\alpha_{\text{Fe}_4\text{N-NH}_3} = -9.3 \pm 0.4\text{‰}$ at 300 °C.

333 The modeling of equilibrium isotope fractionation factor for 500°C is more challenging
334 because the Fe₄N in most of the experiments has decomposed to various extents (Fig. 1B). An
335 additional isotopic effect associated with Fe₄N decomposition could have influenced the isotope
336 composition of the remaining Fe₄N, which was further passed on to impact the isotope
337 composition of the remaining NH₃ due to the fast isotopic exchange between NH₃ and Fe₄N. As
338 a result, the $\delta^{15}\text{N}$ values of the remaining NH₃ in the time-series experiments (Fig. 1E) show a
339 more complicated pattern. Ideally, these experimental data can be modeled by Equations (9)-
340 (16). However, because the parameters of m_1 to m_4 are not well constrained and the isotope
341 fractionation factor for Fe₄N – N₂ at 500 °C is unknown, the modeling is more empirical.
342 Nevertheless, the best fitting of the large isotopic dataset from the 500 °C experiments (Fig. 7B)
343 yielded an equilibrium isotopic fractionation factor of $\alpha_{\text{Fe}_4\text{N-NH}_3} = 0.9936$, and a kinetic isotope
344 fractionation factor of $\alpha_{\text{N}_2\text{-Fe}_4\text{N}} = 0.9811$.

345 To verify the equilibrium isotope fractionation factor between Fe₄N and NH₃ at 500 °C, we
346 examined the experiments with minor amounts of N₂ production, i.e., the experiments with
347 durations up to 3.5 hours, in which the effect of N₂ production is not significant and the f_R and

348 δ_{RO} values can be corrected from the produced N_2 . Such a modeling (using Equation 5 with the
349 corrected f_R and δ_{RO} values) yielded an $\alpha_{Fe_4N-NH_3}$ value of 0.9936 ± 0.0004 (Fig. 8B) at 500 °C.
350 Incorporation of longer-duration experimental data in this modeling would result in significant
351 decrease in the R^2 value of the linear fitting and consequently large shift of the α value. For this
352 reason, the estimate of equilibrium isotope fractionation factor at 700 °C is not feasible because
353 N_2 recovered from any of the experiments is more than half of the total N (Table 1; Fig. 1C). The
354 experimental data at 700 °C are also too few to allow for an empirical modeling for the
355 equilibrium and kinetic isotope fractionation factors using Equations (9)-(16).

356 With the $1000\ln\alpha_{Fe_4N-NH_3}$ values determined here, and the $1000\ln\alpha_{NH_4+-NH_3}$ and $1000\ln\alpha_{N_2-}$
357 NH_3 values from Li et al. (2021), we can further obtain $1000\ln\alpha_{Fe_4N-N_2} = -15.7\text{‰}$ and $1000\ln\alpha_{Fe_4N-}$
358 $NH_4+ = -22.5\text{‰}$ at 300 °C and $1000\ln\alpha_{Fe_4N-N_2} = -10.2\text{‰}$ and $1000\ln\alpha_{Fe_4N-NH_4+} = -14.9\text{‰}$ at 500 °C.

359 These yielded N isotope fractionation factors are self-consistent with the characteristic
360 temperature dependence of equilibrium isotope fractionation with greater magnitude at lower
361 temperature and lesser magnitude at higher temperature. In contrast, kinetic N isotopic effect
362 diminishes quickly with the increase in temperature (Deng et al., 2018) and shows no obvious
363 temperature dependence in the high-temperature reactions of $NH_3 \rightarrow N_2$ (Li et al., 2009). Our
364 estimates are also consistent with theoretical predictions (Schauble et al., 2004) and experimental
365 observations (Li et al., 2016; Dalou et al., 2019), which indicate that, at isotope equilibration, Fe-
366 nitride is more ^{15}N -depleted than other N species (e.g., NH_4^+ , NH_3 , N_2) in the lithosphere.

367 **4.2.3. Kinetic isotope fractionation during decomposition of Fe_4N**

368 As discussed above, Fe_4N decomposition to N_2 is considered to be unidirectional and the
369 rate-limiting step of the entire process in our experiments. This is likely attributed to the strong N

370 $\equiv\text{N}$ bond of N_2 that makes isotopic exchange between N_2 and other N species difficult (Li et al.,
371 2009). Li et al. (2014) suggested that a kinetic isotope effect would be expected for most of the
372 reactions involving N_2 in either reactant or product at relatively low pressures, which has already
373 been observed in thermal decomposition of NH_3 without catalyst (Li et al., 2009) and abiotic
374 synthesis of N-bearing compounds from N_2 (Kuga et al., 2014; Li et al., 2014). Accordingly, a
375 kinetic isotope fractionation is also expected to be expressed in the produced N_2 in our
376 experiments. Consistently, all the produced N_2 are more depleted in ^{15}N than the initial NH_3 ,
377 which is in the opposite direction of the ^{15}N enrichment order between NH_3 and N_2 at
378 thermodynamic equilibrium (Li et al., 2021). The $\delta^{15}\text{N}$ values of the produced N_2 show an
379 exponential increase pattern with the proceeding of Fe_4N decomposition (Fig. 2B), a typical
380 feature of kinetic isotope fractionation that contrasts to the linear increase pattern of equilibrium
381 isotope fractionation.

382 Through the sophisticated modeling of the 500 °C experimental data above (Fig. 7B), a
383 kinetic N isotope fractionation factor of 0.9811 has been obtained for the Fe_4N decomposition
384 reaction. To further verify this modeling result, a more straightforward Rayleigh fractionation
385 model using Equation 7 was carried out. In this modeling, the “initial Fe_4N ” reservoir in each
386 experiment did not have identical quantity and initial isotope composition but had variable
387 values depending on the extent of NH_3 decomposition. The quantity and $\delta^{15}\text{N}$ value of the
388 “initial Fe_4N ” from each experiment can be obtained by mass balance calculations from the
389 quantities and isotope compositions of the recovered Fe_4N and N_2 products. Using such a
390 method, the modeling using Equation 7 with f value as low as 0.01 (Fig. 9) gave an $\alpha_{\text{N}_2\text{-Fe}_4\text{N}}$
391 value of 0.9811 ± 0.0009 at 500 °C and 0.9839 ± 0.0011 at 700 °C, which can also be expressed
392 as isotopic enrichment factor $\epsilon_{\text{N}_2\text{-Fe}_4\text{N}}$ of $-18.9 \pm 0.9\text{‰}$ at 500°C and $-16.1 \pm 1.1\text{‰}$ at 700 °C,

393 respectively. These values interestingly fall into the range (i.e., $\epsilon_{\text{N}_2\text{-NH}_3} = -19.2\text{‰}$ to -15.3‰ at
394 $600 - 800\text{ °C}$; Li et al., 2009) of the kinetic N isotope fractionations associated with the
395 decomposition of NH_3 to N_2 without occurrence of Fe.

396 **4.3. Applications to roaldite tracer in meteorite**

397 In previous studies, nitride minerals have been considered to be able to record the isotopic
398 signature of the material from which they were formed (e.g. Meibom et al., 2007; Harries et al.,
399 2015; Grewal et al., 2021). Given the large range in $^{15}\text{N}/^{14}\text{N}$ ratios ($2-7 \times 10^{-3}$, corresponding to a
400 range of 1500‰ ; e.g. Meibom et al., 2007; Marty et al., 2011; Cartigny and Marty, 2013 for
401 review), isotopic effects associated with formation and destabilization of nitrides have not been
402 seriously considered in previous studies.

403 Our experimental results demonstrate that the formation of roaldite is fast and the produced
404 roaldite is metastable at medium temperatures. The roaldite formation reaction can probably be
405 extended to much lower temperatures. For example, Han et al. (2008) successfully observed
406 Fe_4N at temperatures $< 300\text{ °C}$ by reacting NH_3 using amorphous Fe. Although ammonia is not a
407 significant component in the solar nebula, it can be in the atmosphere of ice bodies such as
408 comets and more importantly in the atmosphere of giant planets. It is worth noting that, the NH_3
409 pressure required for Fe_4N formation is not high, e.g., Ertl et al. (1979) suggested that an NH_3
410 pressure as low as 4×10^{-7} bar could support the formation of Fe_4N at room temperature, despite
411 that the reaction rate may be very slow in low- NH_3 pressure, low-temperature conditions. Even
412 lower NH_3 pressure is required with increase in temperature. Such a low NH_3 pressure can be
413 easily satisfied (Harries et al., 2015). The isotopic effects associated with Fe_4N formation is
414 relatively small. As a result, the isotopic signature of the source N can be recorded in Fe_4N .

415 Our experimental results at 500 °C and 700 °C also verify previous suggestions that, under
416 low pressures, Fe₄N is unstable above 400 °C (van Voorthuysen et al., 2002). Interestingly, after
417 most of the Fe₄N being decomposed, a small amount of Fe₄N survived and evolved into well
418 crystalized shape in the long experiments (Figs. 5-6). The kinetic isotopic effect resulted in
419 significant ¹⁵N enrichment in the survived roaldite (Fig. 10). In extreme cases, the δ¹⁵N value of
420 the remaining roaldite can be shifted from its original value for > 300‰, a magnitude that cannot
421 be neglected even for meteorite studies. For example, the δ¹⁵N values (~50‰; Harries et al.,
422 2015) of carlsbergite crystals (CrN) are very different from solar values (δ¹⁵N ~ -200‰, Marty et
423 al., 2011; Meibom et al., 2007) but close to Earth's air (δ¹⁵N ~ 0‰) than most other N reservoirs
424 in the early Solar System. Consequently, the carlsbergite crystals were considered to be derived
425 from ices within regions of the protoplanetary disk that were affected by the distal wakes of
426 shock waves (Harries et al., 2015). In another recent study, Grewal et al. (2021) found that the
427 iron meteorites from non-carbonaceous reservoirs had a δ¹⁵N range from -96‰ to -1‰, whereas
428 the iron meteorite from carbonaceous reservoirs had a δ¹⁵N range from 3‰ to 164‰. This
429 difference was interpreted to reflect distinct nitrogen isotopic signature between their sources
430 (Grewal et al., 2021). While we have no intention to argue against these interpretations, we point
431 out that nitride denitridation could possibly lead to such large δ¹⁵N variations as well. Therefore,
432 great caution should be taken to assess whether a nitride mineral has been partially decomposed
433 before it can be used to infer source N signature.

434

435 **5. Conclusions**

436 To help understand the nitrogen isotope compositions of iron meteorites and nitride
437 minerals in other meteorites, laboratory experiments were carried out to examine the nitridation
438 and denitridation of metallic iron in an NH₃ atmosphere and associated nitrogen isotopic effects.
439 The results show that Fe-nitrides, in particular, Fe₄N, a chemical formula equivalent to roaldite
440 mineral, can be formed in NH₃ atmosphere at a large temperature range from below 300 °C to
441 700 °C. An equilibrium isotope fractionation between Fe₄N and NH₃ is observed during the
442 formation of Fe₄N, with $\alpha_{\text{Fe}_4\text{N-NH}_3} = 0.9907 (\pm 0.0004)$ at 300 °C and $0.9936 (\pm 0.0004)$ at 500 °C,
443 implying strong back reactions during Fe₄N formation which have not been documented in
444 relevant literature. At low-pressure conditions, Fe₄N is stable at 300 °C but decomposes quickly
445 into Fe and N₂ at temperatures ≥ 500 °C. Kinetic isotope fractionations with $\alpha_{\text{N}_2\text{-Fe}_4\text{N}}$ values of
446 $0.9811 (\pm 0.0009)$ and $0.9839 (\pm 0.0011)$ were obtained for 500 °C and 700 °C, respectively.
447 These observations suggest that roaldite (if not suffer denitridation by heat wave) can record the
448 isotopic signature of its source nitrogen, but great caution is needed when using nitrogen isotope
449 composition of roaldite mineral to trace source information because large isotopic shift up to
450 $>300\text{‰}$ can be induced by partial decomposition of roaldite.

451

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457

458

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