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Experimental investigation of formation and decomposition of roaldite in ammonia atmosphere at 300-700 °C and associated nitrogen isotope fractionations

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Abstract

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

1. Introduction

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

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

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

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

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

2. Experiment setup and analytical methods

The experimental setup and analytical method employed in this study were similar to those in a previous experimental study on the N isotope fractionations of thermal decomposition of NH_3 without the presence of Fe (Li et al., 2009). But some of the experimental conditions (e.g., temperature, reagents) have been modified for the purpose of this study.

In brief, about 20 mg commercial metallic iron (Fe) powders (VWR; purity > 99.5%) were loaded into a one-end sealed, pre-cleaned (by combustion under air at 1200 °C for 2 hours) quartz tube (outer diameter: 6 mm; inner diameter: 4 mm). For comparison, ~ 50 mg and ~ 6 mg Fe powders were also used in the 500 °C experiments. The sample tube was then attached to a glass vacuum line illustrated in Li et al. (2009) to remove air. An aliquot of NH_3 gas (with initial $\delta^{15}\text{N}$ value of -2.2‰; $n = 10$; $1\sigma = 0.1\text{‰}$) was expanded from a large-volume NH_3 gas flask and equilibrated for 2 minutes (to ensure pressure and isotopic homogenization) before it was cryogenically transferred into the sample tube. The method for NH_3 quantification has been described in detail by Li et al. (2009) and not reiterated here. After minor incondensable gases were evacuated, the sample tube was sealed under vacuum, and carefully measured for its inner length to allow the estimation of internal pressure.

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

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

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

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

3. Results

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

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

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

In contrast to the experiments by Li et al. (2009), which showed good matches in both nitrogen mass and isotope composition between decomposed NH_3 and produced N_2 , the experiments in this study gave obvious mismatches between these two. For example, in the 300 °C experiments, NH_3 was the major N-bearing species observed in the remaining gas phases after 28 hours and 244 hours, but only accounts for ~80% of initial NH_3 (Fig. 1A); nearly 20% of NH_3 was consumed with little production of N_2 but significant production of H_2 (Table 1). This leads to significant amounts of “missing” N. In the 500 °C and 700 °C experiments, more N_2 occurred together with NH_3 in the remaining gas phases (Fig. 1B & C). But again the total amounts of N recovered from NH_3 and N_2 are less than that of the initial NH_3 in the relatively short experiments, leading to various amounts of “missing” N (Table 1).

This “missing” N has been recovered by the combustion of the solid phases. For example, in the 500 °C experiments, the mass balance of the quantities and isotope compositions of the recovered NH_3 and N_2 in the gases phases and the recovered N from the solid phases gave a total N yield (relative to the initial NH_3) of 96.7% with a $\delta^{15}\text{N}$ value of -1.9‰ from one of the 10 minute experiments, 98.3% ($1\sigma = 0.1\%$; $n = 3$) with a mean $\delta^{15}\text{N}$ value of -2.3‰ ($1\sigma = 0.1\%$; $n = 3$) from three of the 1 hour experiments, 98.5% ($1\sigma = 1.0\%$; $n = 3$) with a mean $\delta^{15}\text{N}$ value of -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 -2.8‰ from one of the 3.5 hour experiments, and 99.5% ($1\sigma = 0.4\%$; $n = 2$) with a mean $\delta^{15}\text{N}$ value of -3.1‰ ($1\sigma = 0.0\%$; $n = 2$) from two of the 6 hour experiments (Table 1; Fig. 1B & E). These $\delta^{15}\text{N}$ values match well with the $\delta^{15}\text{N}$ value (-2.2‰) of the initial NH_3 .

H_2 was also examined in some of the experiments. Measurements from a number of experiments ($n = 2, 15$ and 3 for the 300°C, 500°C and 700°C experiments, respectively) indicate that the molar ratio between the H of recovered H_2 and the N of decomposed NH_3 (hereafter

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

4. Discussion

4.1. Formation and stability of Fe₄N

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

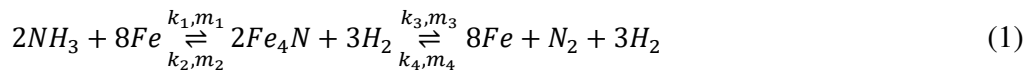
either to the relatively short experimental durations which were not long enough to form Fe_{2-3}N or to the decreased nitriding potential as a result of decreased NH_3 partial pressure and increase H_2 partial pressure with the progress of the experiments (van Voorthuysen et al., 2002; Pelka et al.,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

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

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

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

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



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

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

hours (Table 1), which provide a best opportunity to quantitatively model the reactions. Based on the comparison of the NH_3 decomposition extents among various Fe quantity (Fig. 3), it appears that that 20 mg Fe, which was used in most of the experiments, was in (or at least close to) excess for the reactions and thus not rate-limiting. Therefore, in the modeling, the reaction rates were assumed to be independent of the Fe amounts.

Based on Equation (1), the decomposition rate of NH_3 and the production rates of Fe_4N and N_2 can be written as:

$$\frac{dn_{\text{NH}_3}}{dt} = -k_1 \cdot n_{\text{NH}_3}^{m_1} + k_2 \cdot n_{\text{Fe}_4\text{N}}^{m_2} \quad (2)$$

$$\frac{dn_{\text{Fe}_4\text{N}}}{dt} = k_1 \cdot n_{\text{NH}_3}^{m_1} - k_2 \cdot n_{\text{Fe}_4\text{N}}^{m_2} - k_3 \cdot n_{\text{Fe}_4\text{N}}^{m_3} + k_4 \cdot n_{\text{N}_2}^{m_4} \quad (3)$$

$$\frac{dn_{\text{N}_2}}{dt} = k_3 \cdot n_{\text{Fe}_4\text{N}}^{m_3} - k_4 \cdot n_{\text{N}_2}^{m_4} \quad (4)$$

Using Equations (2)-(4), we modeled the quantity evolution of NH_3 , Fe_4N and N_2 along experimental time for the 500 °C experiments. The modeling employed a simplified forward numeric calculation approach using a time increment of 1 minute and artificially assigned values for k_1 to k_4 and m_1 to m_4 . The best fitting curves shown in Fig. 7A capture most of the experimental data and more importantly the overall evolution trend, although a perfect match of data was not achieved. Possible uncertainties that may account for the discrepancy between the experimental and modeling results include (1) reactions in the temperature ramping stage (< 2 minutes); (2) potential effect of H_2 (and its diffusive loss over time); (3) the partially oxidized surface (although very minor) of the initial Fe powders which could have affected NH_3 decomposition rate, at least at the beginning before its surface was completely reduced; (4) the

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

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

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

4.2. Nitrogen isotope fractionations during formation and decomposition of Fe_4N

4.2.1. Modeling of nitrogen isotope fractionation factors

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

with the initial NH_3 , all the remaining NH_3 is more ^{15}N -enriched, whereas all the produced N_2 is more ^{15}N -depleted and only reaches the $\delta^{15}\text{N}$ value of the initial NH_3 when all the initial NH_3 is converted into N_2 (Figs. 1 & 3). In contrast, Fe_4N shows more variable $\delta^{15}\text{N}$ values, which can be either lower or higher than that of the initial NH_3 (Table 1; Fig. 1E). This indicates strong isotopic effects associated with the $\text{NH}_3 - \text{Fe}_4\text{N}$ and $\text{Fe}_4\text{N} - \text{N}_2$ reactions.

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

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

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

in which α is the fractionation factor, P denotes product, R denotes reactant, f denotes fraction, and δ_{R0} is the initial isotope composition of the reactant, i.e., NH_3 in this case.

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

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

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

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

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

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
$$\frac{dn_{(^{14}NH_3)}}{dt} = -^{14}k_1 \cdot n_{(^{14}NH_3)}^{m_1} + ^{14}k_2 \cdot n_{(^{14}Fe_4N)}^{m_2} \quad (9)$$

309
$$\frac{dn_{(^{15}NH_3)}}{dt} = -^{15}k_1 \cdot n_{(^{15}NH_3)}^{m_1} + ^{15}k_2 \cdot n_{(^{15}Fe_4N)}^{m_2} \quad (10)$$

$$\frac{dn_{(^{14}\text{Fe}_4\text{N})}}{dt} = {}^{14}k_1 \cdot n_{(^{14}\text{NH}_3)}^{m_1} - {}^{14}k_2 \cdot n_{(^{14}\text{Fe}_4\text{N})}^{m_2} - {}^{14}k_3 \cdot n_{(^{14}\text{Fe}_4\text{N})}^{m_3} + {}^{14}k_4 \cdot n_{(^{14}\text{N}_2)}^{m_4} \quad (11)$$

$$\frac{dn_{(^{15}\text{Fe}_4\text{N})}}{dt} = {}^{15}k_1 \cdot n_{(^{15}\text{NH}_3)}^{m_1} - {}^{15}k_2 \cdot n_{(^{15}\text{Fe}_4\text{N})}^{m_2} - {}^{15}k_3 \cdot n_{(^{15}\text{Fe}_4\text{N})}^{m_3} + {}^{15}k_4 \cdot n_{(^{15}\text{N}_2)}^{m_4} \quad (12)$$

$$\frac{dn_{(^{14}\text{N}_2)}}{dt} = {}^{14}k_3 \cdot n_{(^{14}\text{Fe}_4\text{N})}^{m_3} - {}^{14}k_4 \cdot n_{(^{14}\text{N}_2)}^{m_4} \quad (13)$$

$$\frac{dn_{(^{15}\text{N}_2)}}{dt} = {}^{15}k_3 \cdot n_{(^{15}\text{Fe}_4\text{N})}^{m_3} - {}^{15}k_4 \cdot n_{(^{15}\text{N}_2)}^{m_4} \quad (14)$$

in which ${}^{14}\text{K}_1$ to ${}^{14}\text{K}_4$ and ${}^{15}\text{K}_1$ to ${}^{15}\text{K}_4$ denote the reaction rates of ${}^{14}\text{N}$ and ${}^{15}\text{N}$ in corresponding reactions, respectively. Consequently, the N isotope fractionations for the $\text{NH}_3 - \text{Fe}_4\text{N}$ reaction and the $\text{Fe}_4\text{N} - \text{N}_2$ reaction can be described as:

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

$$\alpha_{\text{N}_2-\text{Fe}_4\text{N}} = \frac{{}^{15}k_4 \cdot {}^{14}k_3}{{}^{14}k_4 \cdot {}^{15}k_3} \quad (16)$$

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

4.2.2. Equilibrium isotope fractionation factors between Fe_4N and NH_3

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

The modeling of equilibrium isotope fractionation factor for 500°C is more challenging because the Fe_4N in most of the experiments has decomposed to various extents (Fig. 1B). An additional isotopic effect associated with Fe_4N decomposition could have influenced the isotope composition of the remaining Fe_4N , which was further passed on to impact the isotope composition of the remaining NH_3 due to the fast isotopic exchange between NH_3 and Fe_4N . As a result, the $\delta^{15}\text{N}$ values of the remaining NH_3 in the time-series experiments (Fig. 1E) show a more complicated pattern. Ideally, these experimental data can be modeled by Equations (9)-(16). However, because the parameters of m_1 to m_4 are not well constrained and the isotope fractionation factor for $\text{Fe}_4\text{N} - \text{N}_2$ at 500 °C is unknown, the modeling is more empirical. Nevertheless, the best fitting of the large isotopic dataset from the 500 °C experiments (Fig. 7B) yielded an equilibrium isotopic fractionation factor of $\alpha_{\text{Fe}_4\text{N-NH}_3} = 0.9936$, and a kinetic isotope fractionation factor of $\alpha_{\text{N}_2\text{-Fe}_4\text{N}} = 0.9811$.

To verify the equilibrium isotope fractionation factor between Fe_4N and NH_3 at 500 °C, we examined the experiments with minor amounts of N_2 production, i.e., the experiments with durations up to 3.5 hours, in which the effect of N_2 production is not significant and the f_R and

δ_{R0} values can be corrected from the produced N_2 . Such a modeling (using Equation 5 with the corrected f_R and δ_{R0} values) yielded an $\alpha_{Fe_4N-NH_3}$ value of 0.9936 ± 0.0004 (Fig. 8B) at 500 °C. Incorporation of longer-duration experimental data in this modeling would result in significant decrease in the R^2 value of the linear fitting and consequently large shift of the α value. For this reason, the estimate of equilibrium isotope fractionation factor at 700 °C is not feasible because N_2 recovered from any of the experiments is more than half of the total N (Table 1; Fig. 1C). The experimental data at 700 °C are also too few to allow for an empirical modeling for the equilibrium and kinetic isotope fractionation factors using Equations (9)-(16).

With the $1000\ln\alpha_{Fe_4N-NH_3}$ values determined here, and the $1000\ln\alpha_{NH_4+-NH_3}$ and $1000\ln\alpha_{N_2-NH_3}$ values from Li et al. (2021), we can further obtain $1000\ln\alpha_{Fe_4N-N_2} = -15.7\text{‰}$ and $1000\ln\alpha_{Fe_4N-NH_4+} = -22.5\text{‰}$ 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.

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

4.2.3. Kinetic isotope fractionation during decomposition of Fe_4N

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

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

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

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

4.3. Applications to roaldite tracer in meteorite

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

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

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

5. Conclusions

To help understand the nitrogen isotope compositions of iron meteorites and nitride minerals in other meteorites, laboratory experiments were carried out to examine the nitridation and denitridation of metallic iron in an NH_3 atmosphere and associated nitrogen isotopic effects. The results show that Fe-nitrides, in particular, Fe_4N , a chemical formula equivalent to roaldite mineral, can be formed in NH_3 atmosphere at a large temperature range from below 300 °C to 700 °C. An equilibrium isotope fractionation between Fe_4N and NH_3 is observed during the formation of Fe_4N , with $\alpha_{\text{Fe}_4\text{N}-\text{NH}_3} = 0.9907 (\pm 0.0004)$ at 300 °C and $0.9936 (\pm 0.0004)$ at 500 °C, implying strong back reactions during Fe_4N formation which have not been documented in relevant literature. At low-pressure conditions, Fe_4N is stable at 300 °C but decomposes quickly into Fe and N_2 at temperatures ≥ 500 °C. Kinetic isotope fractionations with $\alpha_{\text{N}_2-\text{Fe}_4\text{N}}$ values of $0.9811 (\pm 0.0009)$ and $0.9839 (\pm 0.0011)$ were obtained for 500 °C and 700 °C, respectively. These observations suggest that roaldite (if not suffer denitridation by heat wave) can record the isotopic signature of its source nitrogen, but great caution is needed when using nitrogen isotope composition of roaldite mineral to trace source information because large isotopic shift up to $>300\text{‰}$ can be induced by partial decomposition of roaldite.

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