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[1] Molybdenum crucibles are commonly used to extract nitrogen from geological samples by induction heating. Because nitrogen is known to be reactive with certain metals (e.g., Ti and Fe), we have tested the reactivity of gaseous nitrogen with a Mo crucible held at 1800°C. The consumption of nitrogen, determined by monitoring the $N_2/^{40}Ar$ ratio of the gas phase, varied between 25 and 100%, depending on the reaction duration. Nitrogen of the reacted gas was found to be systematically enriched in ^{15}N relative to ^{14}N by 10‰ compared to the initial isotopic composition, without any correlation with nitrogen consumption. We propose that a rapid isotopic exchange occurs between nitrogen originally trapped in the crucible and nitrogen from the gas phase, which modifies the isotopic composition of the reacted gas. This process can significantly bias the isotopic determination of nitrogen in rocks and minerals when a Mo furnace is used for gas extraction. Meanwhile, the rate of N-Mo chemical bonding may be controlled by the formation of nitride (rather than solid solution), a process slower than the isotopic exchange. The use of a Mo furnace for the extraction of trace nitrogen from rocks and minerals should therefore be avoided.

1. Introduction

[2] Nitrogen is the major constituent of the atmosphere, as well as an essential element in biological activity. The origin of this element is therefore crucial for understanding the evolution of surface environments and the emergence of life on Earth. As noble gas studies have recognized primordial volatile reservoirs in the mantle [*Clark et al.*, 1969; *Mamyrin et al.*, 1969], primordial nitrogen components may also be expected to exist in the mantle. Moreover, the nitrogen isotopic composition varies among potential cosmochemical precursors (e.g., the Sun and the solar nebula [*Hashizume et al.*, 2000], Carbonaceous chondrites, Enstatite chondrites [*Kung and Clayton*, 1978], etc.), which may provide constraints on the volatile source material of the Earth.

[3] Nitrogen isotopic determinations of mantle-derived silicates, however, have long been hampered by low nitrogen concentrations [*Sakai et al.*, 1984] ($\approx$n mol N_2/g) and possible organic/atmospheric contamination [*Marty*, 1995]. The application of static gas mass spectrometry, originally developed for noble gas analysis, had allowed the analysis of nitrogen isotopic compositions at sub-nanomole levels [*Frick and Pepin*, 1981]. Using his method, it has been suggested recently that mantle-derived silicates might have variable nitrogen isotopic compositions, from $-15.3‰$ [*Mohapatra and Murty*, 2000] to $+30.8‰$ [*Huang*, 1997] ($\delta^{15}N$ relative to atmosphere, $^{15}N/^{14}N_{air} = 272$). Determining whether such variations reflect mantle heterogeneities or organic/atmospheric contamination and/or kinetic isotope effects during thermal gas extraction is important for understanding the origin of this key element in the terrestrial system.

[4] The terrestrial mantle consists of refractory silicates such as olivine and pyroxenes, which have melting temperatures higher than 1500°C. With a melting temperature of 2623°C, Mo is considered to be one of the most suitable furnace materials for noble gas analysis, and this methodology was occasionally applied to the extraction of nitrogen [*Mohapatra and Murty*, 2000; *Mathew and Marti*, 2002; *Marty et al.*, 1995; *Erzinger and Bach*, 1996] under an assumption that nitrogen should behave similarly to noble gases. While noble gases are chemically inert, however, nitrogen is known to be reactive with certain metals [*Kubaschewski and Alcock*, 1979] (e.g., Ti, Fe, Ta, and Mo). In this study, we tested the reactivity of nitrogen with a Mo crucible at the commonly used experimental temperatures and heating durations.

2. Experimental Method

[5] Aliquots (0.3–1.8 nmol N_2) of air purified for CO_2 and H_2O were taken from a glass standard tank prepared online and purified using a CuO furnace and a cryogenic trap held at $-170°C$ in order to remove oxygen and hydrocarbons [*Humbert*, 1997]. The purified gas was subsequently introduced into a Mo induction furnace held at 1800°C (Except for run 15 at 1500°C). This temperature is commonly used for melting refractory minerals [*Mohapatra and Murty*, 2000]. The temperature was calibrated using an optical thermometer. The reaction duration was varied between 30 s and 10 min to evaluate whether or not equilibrium was achieved. In the case of runs 13–15, the total reaction duration was 10 min, but the induction furnace was turned off and cooled during the final 5 min. The reacted gas was released into the main line for 30 s and then introduced to a static gas mass spectrometer.

[6] Nitrogen (Z = 7) has two stable isotopes, 14 and 15, with natural (atmospheric) abundances of 99.634 and 0.366%, respectively (defined as $\delta^{15}N \equiv 0‰$ [*Mariotti*, 1983]). The nitrogen isotopic composition was analyzed by static mass spectrometry using a Faraday collector at m/z = 28 and 29. Contributions of isobar (CO) were evaluated using the ratio of m/z = 30/29, and corrected when necessary [*Hashizume and Marty*, 2004]. The reproducibility of $\delta^{15}N$ for 8 standards during the experiments was 1.2‰ (1σ). Subsequent to the nitrogen isotope analyses, argon peak heights were measured for the same aliquot. Nitrogen blank constituted <2% of the signal for all runs and no blanks correction was applied for N. Ar Blank constituted< 10% of the signals, and the argon data is corrected for blank.

[7] The consumption of nitrogen by molybdenum was estimated from deviations of the $N_2/^{40}Ar$ ratio relative to the initial value (that is, the $N_2/^{40}Ar$ ratio of unreacted gas) assuming that argon is not reactive with Mo. First, the dilution procedure was evaluated to investigate whether it affects $N_2/^{40}Ar$ ratio or nitrogen isotopic composition, at the shortest reaction time of 30 s. The Mo crucible was set at room temperature (runs 5 and 6). There was no significant change in either the elemental ratio or $\delta^{15}N$. It confirms that the

Table 1. Experimental Conditions and Results of the Mo-N Reaction Experiments[a]

Run	Pipette	Temperature, °C	Duration, s	$N_2/^{40}Ar$	$N_2/^{40}Ar$ Error	$\delta^{15}N$, ‰	$\delta^{15}N$ Error	N_2 Loss, %	N_2 Loss Error	Nitrogen Loss, pmol/sec
					Standards					
1				78.7	4.3	−1.1	1.2	5.3	5.2	
2				82.0	4.5	0.3	1.2	1.3	5.4	
3				82.2	4.5	0.5	1.2	1.0	5.4	
4				89.5	4.9	0.3	1.2	−7.7	5.9	
					Reacted with Mo					
5	3	23	30	81.2	4.5	0.2	1.2	2.3	5.4	
6	3	23	30	82.7	4.5	−0.3	1.2	0.5	5.5	
7	3	1800	30	62.1	3.4	9.8	1.2	25.3	4.1	7.6
8	3	1800	60	54.1	3.0			34.9	3.6	5.2
9	3	1800	60	50.2	2.8	10.3	1.3	39.6	3.3	5.9
10	1	1800	60	36.1	2.0	10.1	2.8	56.5	2.4	2.8
11	3	1800	180	30.7	1.7	11.3	1.4	63.0	2.0	3.2
12	6	1800	300	37.9	2.1	9.5	1.3	54.4	2.5	3.3
13	2	1800	600	16.1	0.9			80.6	1.1	0.8
14	3	1800	600	18.5	1.0			77.8	1.2	1.2
15	2	1500	600	0.13	0.03			99.8	0.03	1.0

[a] Pipette represents the quantity of gas introduced to the Mo induction furnace. One pipette corresponds to 0.3 nmol N_2. For runs 13–15 the quantities of the residual gases were too small for the nitrogen isotopic determination. Errors on $\delta^{15}N$ are 1σ.

analytical procedure is not the cause of the variation we report.

3. Results

[8] The elemental ratios and isotopic compositions of the reacted gases are listed in Table 1. The $N_2/^{40}Ar$ ratios decreased significantly due to contact with the hot Mo crucible (25.3–99.8% nitrogen loss). The degree of nitrogen loss increased with the reaction duration (Figure 1), suggesting that it takes more than 200 s to be in chemical equilibrium. The higher partial pressure of nitrogen appears to result in a higher rate of loss: when runs 8–10 are compared, the rate of loss (pmol/s) is highest for run 10. However, the degree of loss (%/s) is smallest for this run. The dependence of this loss with reaction duration (Figure 1) indicates that an irreversible rate process is taking place. Indeed the trend of nitrogen loss is consistent with creation of a N-Mo chemical bond. Runs 13–15 were characterized by the largest degrees of loss, due either to longer reaction times or to cooling of the crucible.

[9] Nitrogen in the reacted gases is enriched in ^{15}N by 10‰ compared to the initial isotopic composition. The ^{15}N enrichment appears to be independent of the degree of nitrogen loss (Figure 2) or duration of the reaction, which might indicate that the nitrogen compounds in both the molybdenum crucible and the gas phase were in isotopic equilibrium even after the shortest experimental dura-

tion of 30 s. As mentioned above, however, the chemical equilibrium is not achieved until at least 200 s of run time. This contrast may suggest that the isotopic effect has a cause different from that of the chemical fractionation. Alternatively, the isotopic composition of gas phases might not have been exactly identical, but simply indistinguishable due to large uncertainties. In such case, the observed isotopic range is difficult to be explained by simple
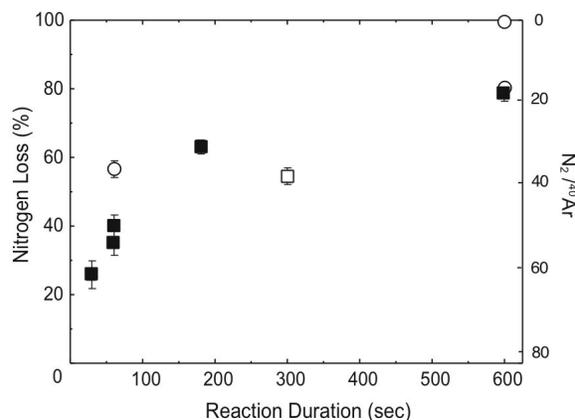

Figure 1. Time dependence of nitrogen loss from the gas phase was observed, which implied an irreversible rate process for N-Mo reaction. Data for the experiments using nitrogen quantity of 3 pipettes (0.9 nmol) are shown as solid squares. Open square represents the experiment using 6 pipettes, and open circles represents the experiments with 1 or 2 pipettes.
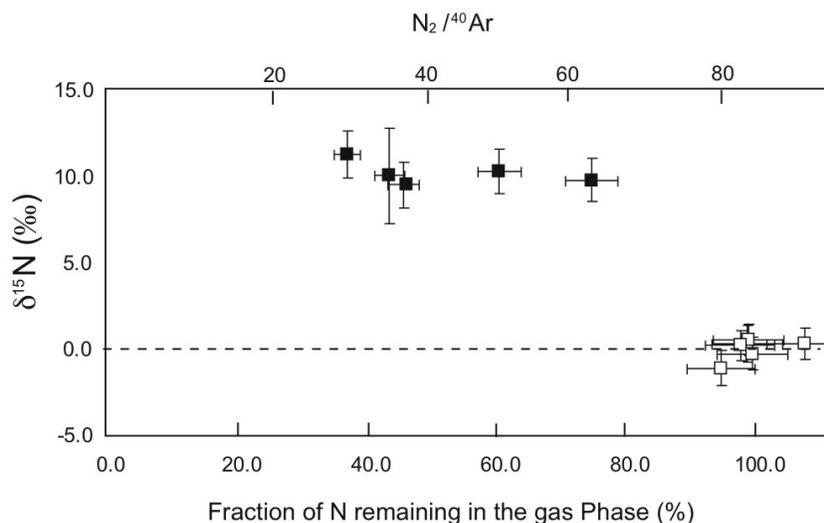
Figure 2. The fraction of nitrogen remained in the gas phase is plotted against $\delta^{15}N$. Solid squares are reacted gases, and open squares are nonreacted gases or gases that were in contact with Mo at room temperature. No correlation between the degree of nitrogen loss and that of isotopic modification was observed.

distillation process, thus we discuss the first possibility in section 4.

4. Discussion: Possible Processes and Effects on the Analytical Data

[10] In the experimental system, nitrogen may occur as (1) N_2 in the gas phase, (2) nitrogen atoms chemisorbed on the molybdenum surface, (3) nitrogen atoms dissolved in molybdenum and forming a Mo-N solid solution, and/or (4) molybdenum nitride. Assuming that the bulk nitrogen isotopic composition of the system is determined by the small quantity of air introduced into the volume ($\delta^{15}N = 0‰$), the ^{15}N enrichment in the gas phase needs to be explained by a fractionation process. Significant (>2‰) equilibrium isotopic fractionation between the solid phases (phases 2, 3, and 4) may be excluded as the temperature of the system far exceeded the range in which observable nitrogen isotopic fractionation is expected (<700°C) [*Richet et al.*, 1977; *Urey*, 1947]. Estimates for the diffusivity of nitrogen (solid solution) in Mo are high enough (8.9×10^{-5} to 9.8×10^{-2} cm²/s [*Zamalin and Bodnar*, 2001, and reference therein]) at 1800°C to allow effective diffusive exchange for the experimental timescale.

[11] One possible process to produce the observed isotopic change in the reacted gas is a tunneling effect [*Haase et al.*, 1989] taking place when nitrogen molecules dissociate at the metal-gas interface. This effect results in a significant ^{14}N

enrichment in the adsorbed phase [*Nakamura*, 1987; *Romm et al.*, 2000]. Because the quantity of the gas phase is not infinite, however, the isotopic fractionation should covary with the degree of nitrogen loss from the gas phase, which was not observed. It is therefore difficult to explain the observed isotopic variation by assuming that the nitrogen isotopic composition of the system is equal to that of the introduced gas.

[12] Alternatively, the nitrogen isotopic composition of the system may be dominated by a component different from the small quantity of atmosphere introduced to the volume. In other words, the N isotopic composition of the gas phase would be rapidly buffered by that of the nitrogen originally trapped in the crucible. The quantity of nitrogen introduced into the system was at 1.8 nmol (run 12) or lower while the Mo crucible of 7.5 g contains 0.078 mol of molybdenum. If the nitrogen concentration in the Mo crucible is higher than e.g., 10 ppm, then the introduced nitrogen constitutes less than 1% of total N in the system. Thus the nitrogen isotopic composition of the gas phase could be dominated by that of nitrogen originally trapped in Mo, provided that the mixing (i.e., isotopic exchange) occurs rapidly. In this case, the diffusion and redistribution of nitrogen between the gas and the solid phases need to be fast enough to achieve the isotope exchange within the shortest experimental duration of 30 s, and the $N_2/^{40}Ar$ fractionation requires another slower process, presumably a formation of molybdenum

nitride from the N-Mo solid solution. Nitrogen in the gas phase was consumed with time, indicating that the N-Mo bond (either solid solution or nitride) is a stable phase at experimental temperature and pressure. The extremely low blanks recorded during the blank experiments may indeed be due to the stability of nitrogen-bearing solid phase(s), and does not necessarily mean that the quantity of nitrogen in the crucible is small.

[13] If this interpretation is correct, the effect of the phenomenon on analytical data is difficult to be corrected, because the isotopic composition of the crucible may be variable depending on a number of factors, such as the initial isotopic composition of nitrogen impurity when molybdenum was processed, gas-metal exchange during manufacturing of the crucible that might have isotopically fractionated nitrogen, and previous samples (containing variable N isotopic compositions and absolute quantities of nitrogen) analyzed in the crucible. A precise determination of the nitrogen isotopic composition in the crucible before and after the analyses of the samples may help understanding the observed signature, but the quantity of chemisorbed nitrogen cannot be determined. Molybdenum is therefore not a favorable crucible material for the analysis of nitrogen isotopes.

[14] In standard procedures gases evolved from the heated sample are continuously trapped in a finger containing activated charcoal and held at the boiling temperature of liquid nitrogen (77 K). This procedure may limit the effect mentioned above. However, the possibility that an isotopic exchange affects the isotopic composition of nitrogen in the extracted gas cannot be excluded. Because such effects are likely to depend on the geometry of each vacuum system (thus depend on laboratories), this point cannot be tested here. The published data on nitrogen isotopic compositions and concentrations for which molybdenum crucibles (or Mo wrapping foils at high temperature) were used needs to be reconsidered with caution. The use of platinum is recommended for thermal extraction crucible of nitrogen analyses [e.g., *Wright et al.*, 1988; *Boyd and Pillinger*, 1990]. Finally, it is highly desirable to develop a standardization procedure for stepwise heating N extraction from silicates using geostandard samples (known $\delta^{15}N$ and N contents).

5. Conclusion

[15] Nitrogen chemisorption onto a heated (1800°C) molybdenum crucible occurs at a time-scale of tens of seconds. Furthermore, a significant change in the N isotope composition of the gas phase was observed, which did not correlate with the amount of reacted N. These behaviors may suggest a buffering of gaseous N isotope composition by nitrogen originally present in the crucible. Molybdenum is therefore not a favorable crucible material for the analysis of nitrogen at low level in geological samples.

Acknowledgments

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