

**Experimental constraints on N cycle on Titan: From NH<sub>3</sub>-rich hydrothermal fluids to atmospheric N<sub>2</sub> and possible deep rock storage.** C. Fauguerolles<sup>1</sup>, Y. Morizet<sup>1</sup>, E. Le Menn<sup>1</sup>, A.-C. Gaillot<sup>2</sup> and G. Tobie<sup>1</sup>, <sup>1</sup>Laboratoire de Planétologie et de Géodynamique, CNRS/Université de Nantes, France. (colin.fauguerolles@univ-nantes.fr), <sup>2</sup>Institut des Matériaux Jean Rouxel, Nantes, France.

**Introduction:** Atmospheric composition measurements performed by the mass spectrometer (GCMS) onboard the Huygens probe [1] show a very low <sup>36</sup>Ar/N<sub>2</sub> ratio suggesting an *in situ* production of N<sub>2</sub> on Titan from more condensable phases such as NH<sub>3</sub> or N-bearing organics [2, 3, 4]. Several mechanisms involving exogenous causes to this *in situ* production of N<sub>2</sub> have been proposed but fails to explain the large amounts of N<sub>2</sub> observed today in Titan's atmosphere [5, 6]. Another possibility would be endogenous production of N<sub>2</sub> in the rock-rich deep interior, associated with hydrothermal processes involving NH<sub>3</sub>-rich fluids and/or thermal decomposition of N-bearing organics [3, 4, 7]. An internal origin, implying similar processes, could also be invoked to explain the N<sub>2</sub>-rich atmospheres of Triton and Pluto.

The experimental study presented here aims to provide constraints on the possible production of N<sub>2</sub> associated with hydrothermal interactions between NH<sub>3</sub>-rich fluids and olivine plus orthopyroxene crystals, the main silicate constituents of ordinary chondrites. For this purpose, a series of syntheses involving the previously mentioned reagents were carried out under conditions of pressure and temperature expected beneath the thick hydrosphere of large ice moons. Multiple analyses were performed on the products in order to determine the fate of the nitrogen during the aqueous alteration of silicate minerals.

**Experimental methods:** The experiments have been carried out in piston-cylinder apparatus at 400, 600 and 800°C and 1GPa, representative of conditions beneath the rock-ice interface on Titan, for about 96 hours. The solid reagent used in all experiments consisted in a finely crushed powder (< 50 μm) made up of equal parts by mass of olivine (Fo<sub>91</sub>, from San Carlos xenolith, US-AZ) and orthopyroxene (En<sub>90</sub>, from Maar de Borée xenolith, France). The powders were loaded into Pt capsules with demineralized water (resistivity 15 Ω.cm) enriched in NH<sub>3</sub> (aq) so as to obtain a fluid/rock mass ratios equal to 5. For each temperature, three initial NH<sub>3</sub> (aq) concentrations (*w*<sub>NH<sub>3</sub></sub>) have been considered: 0, 5 and 10 wt.%. In addition to this systematic batch of experiments, three specific experiments, all carried out with *w*<sub>NH<sub>3</sub></sub> = 5wt.%, have been conducted out in order to evaluate the influence of specific parameters: an experiment at intermediate temperature of 500°C, an experiment with a NaCl assembly allowing more reducing conditions at 600°C, and a shorter duration experiment (17.4 h) at 800°C.

At the end of each experiment, the recovered Pt capsule was perforated and the released gas was collected to quantify the produced N<sub>2</sub> by gas chromatography (GC). The recovered solutions were analyzed by Raman spectroscopy in order to evaluate the amounts of residual NH<sub>3</sub>. The solid phases were systematically characterized by XRD and Raman microspectrometry. In addition, TEM analyses were carried out on a specific sample.

**Results:** The N<sub>2</sub> concentration (*b*<sub>N<sub>2</sub></sub>) measured at the end of the experiments are compiled in Fig. 1. *b*<sub>N<sub>2</sub></sub> is below the detection limit for T < 600°C which is consistent with the large amounts of NH<sub>3</sub> (aq) in recovered solutions. At 600°C *b*<sub>N<sub>2</sub></sub> decreases when *w*<sub>NH<sub>3</sub></sub> increases by 5 to 10 wt.% while *b*<sub>N<sub>2</sub></sub> increases with *w*<sub>NH<sub>3</sub></sub> at 800°C. Measurements of residual NH<sub>3</sub> (aq) in the recovered solutions show that at 800°C there is no more NH<sub>3</sub> (aq), while at 600°C the amounts of NH<sub>3</sub> (aq) are similar regardless of *w*<sub>NH<sub>3</sub></sub>. At 600 °C, the decrease of *b*<sub>N<sub>2</sub></sub> with *w*<sub>NH<sub>3</sub></sub> increasing while the residual NH<sub>3</sub> (aq) are equivalent implies a N deficit in the fluid recovered from the experiment carried out with *w*<sub>NH<sub>3</sub></sub> = 10 wt.%. Additional specific experiments show a very fast (< 17.37 h) N<sub>2</sub> production at 800°C, while at 600°C, the use of an assembly inducing more reducing conditions significantly decreases the amount of produced N<sub>2</sub>.

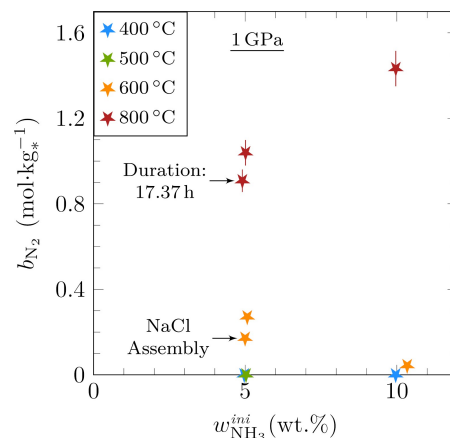


Fig. 1: N<sub>2</sub> molalities recorded at the end of the experiments vs. starting NH<sub>3</sub> (aq) concentrations.

The recovered solid charges produced in the 400°C experiments show an almost complete transformation of the solid reagents into serpentine. Only very small fractions of olivine persist. The produced serpentine

corresponds mainly to lizardite while a few occurrences of chrysotile are observed. In experiments conducted at higher temperatures, olivine is systematically present in large quantities in the recovered charges, suggesting that the stability domain of olivine is reached between 400 and 500°C. The same is true for orthopyroxene in samples recovered from 800 °C experiments in which no newly formed minerals are observed. This suggests that the stability domain of orthopyroxene is reached is between 600 and 800°C.

For experiments conducted at 500 and 600°C, the amounts of residual orthopyroxene and the nature of newly formed minerals are more diverse and vary according to temperature, redox and  $w_{\text{NH}_3}$ . At 500°C, although in smaller amounts than initially, orthopyroxene is still present while substantial amounts of serpentine are produced. Some occurrences of talc are also observed locally.

At 600°C and without  $\text{NH}_3$  (aq), orthopyroxene is entirely replaced by a mixture of talc and serpentine. When  $\text{NH}_3$  (aq) is added, phlogopite is observed while serpentine is not. However significant variations in the proportions of the different phases are to be noted. For  $w_{\text{NH}_3} = 10$  wt.%, only a fraction of the orthopyroxene reacts to give mainly phlogopite and some talc. When  $w_{\text{NH}_3} = 5$  wt.%, the orthopyroxene reacts very little and only small amounts of phlogopite and talc are observed, however, for the same  $w_{\text{NH}_3}$  but under more reducing conditions (specific experiment), the orthopyroxene is totally replaced by a mixture in comparable proportions of phlogopite and talc.

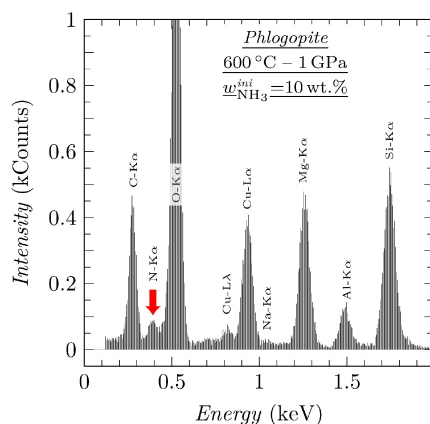


Fig. 2: EDS spectrum acquired with MET on phlogopite crystal showing significant amounts of N in its structure.

Since phlogopite can incorporate a significant amount of  $\text{NH}_4^+$  in its structure [8, 9], TEM analyses were carried out on the load with the highest content (i.e., 600°C -  $w_{\text{NH}_3} = 10$  wt.%) and have, indeed, shown the notorious presence of N in this phase (Fig. 2). This

observation may satisfactorily explain the origin of the nitrogen deficit in the fluid phase resulting from this experiment.

**Discussion - Conclusion:** Under our experimental conditions, we show that the production of  $\text{N}_2$  from  $\text{NH}_3$  (aq) becomes possible at temperatures above 500–600°C at 1 GPa, confirming previous theoretical predictions [4]. Such temperatures that could have been reached in Titan’s interior during the ice/water/rock segregation that led to the formation of a differentiated structure comprising a rock core and a thick hydrosphere [3]. During the subsequent evolution, radioactive heating combined with tidal heating may also promote circulation of warm liquid water (> 500–600°C) beneath the rock/ice interface [10]. Assuming a conversion rate of 50 %, obtained for our experiment carried out at 600°C with  $w_{\text{NH}_3} = 5$  wt.%, an aqueous fluid volume equivalent to about 5 % of the total hydrosphere (ice + water) volume needs to circulate through the production zone in order to produce a mass of  $\text{N}_2$  comparable to the present-day Titan’s atmosphere. Transient  $\text{NH}_3$ -rich aqueous fluid circulation in the 200–300 km outermost part of the core may produce the present-day  $\text{N}_2$  atmospheric inventory.

Moreover, our experimental results indicate that this  $\text{N}_2$  production from silicate mineral alteration by  $\text{NH}_3$ -rich aqueous fluid would be accompanied with the formation of hydrated minerals such as talc and/or phlogopite rather than serpentine which appears to be stable at lower temperatures or in the absence of  $\text{NH}_3$ . Our results show that increasing the  $\text{NH}_3$  content lead in a reduction of  $\text{N}_2$  production and formation of  $\text{NH}_4^+$ -bearing phlogopite. Beyond Titan, these new experimental results may have implications for the N cycle on Triton and Pluton [11], and the formation of  $\text{NH}_4^+$ -bearing minerals on Ceres [12].

**Acknowledgments:** This work received financial support from the ANR OASIS project (grant N° ANR-16-CE31-0023-01).

**References:** [1] Niemann H. B. et al. (2010) *JGR*, 115, E12006. [2] Atreya S. K. et al. (2009) In: *Titan from Cassini-Huygens*, 177–199. [3] Tobie G. et al. (2012) *Astrophys. J.*, 752:125. [4] Miller K. E. et al. (2019) *Astrophys. J.*, 871:59. [5] Marounina N. et al. (2015) *Icarus*, 257, 324–335. [6] Marounina N. et al. (2018) *Icarus*, 310, 127–139. [7] Glein C. R. (2015) *Icarus*, 250, 570–586. [8] Vedder W. (1965) *Geochim. Cosmochim. Acta*, 29, 221–228. [9] Eugster H. P. and Munoz J. (1966) *Science*, 151, 683–686. [10] Castillo-Rogez J. C. and Lunine J. I. (2010). *Geophys. Res. Lett.*, 37, L20205. [11]. Shock E. L. and McKinnon W. B. (1993) *Icarus*, 106, 464–477. [12] De Sanctis M. C. et al. (2015) *Nature*, 528, 241–244.