

Supplementary information

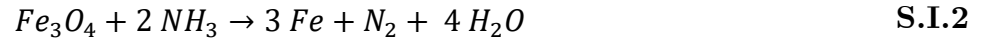
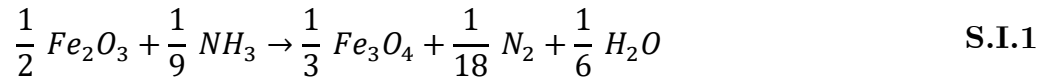
Table S.I.1: Rietveld refinement on XRD analysis of a powdered industrial hematite pellet ($R_{wp} = 9.858\%$).....	4
Table S.I.2: Detail of the degrees of reduction (DoR) and degrees of metallization (DoM) of the samples reduced by hydrogen and ammonia. For the pellets, about 90% of the grinded sample was analysed by XRD. For the disks, two scans per sample were conducted with about 20% of the powder per batch resulting in two DoR and two DoM per sample; the mean value was calculated for each sample.....	13
Figure S.I.1: Schematic of the experimental set-up.....	4
Figure S.I.2: Pictures of the sample holders used for the reductions under concentrated light flux. a) Crucible used for the pellets and b) crucible used for the disks.....	4
Figure S.I.3: Flux received by the top of the crucible. The maximum of $115 W_1/cm^2$ is reached at the center and the average is $75 W_1/cm^2$. On the crucible aperture area, a power of about $150 W_1$ is measured (grey area of the blue curve).	5
Figure S.I.4: XRD analysis at different times of industrial hematite powder heated at $400\text{ }^\circ\text{C}$ under $5\%-\text{NH}_3$ atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.	6
Figure S.I.5: XRD analysis at different times of industrial hematite powder heated at $450\text{ }^\circ\text{C}$ under $5\%-\text{NH}_3$ atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.	7
Figure S.I.6: XRD analysis at different times of industrial hematite powder heated at $500\text{ }^\circ\text{C}$ under $5\%-\text{NH}_3$ atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.	8
Figure S.I.7: XRD analysis at different times of industrial hematite powder heated at $550\text{ }^\circ\text{C}$ under $5\%-\text{NH}_3$ atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.	9
Figure S.I.8: XRD analysis at different times of industrial hematite powder heated at $600\text{ }^\circ\text{C}$ under $5\%-\text{NH}_3$ atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.	10
Figure S.I.9: a) Picture of the perforated crucible used to measure the temperature at the bottom of the samples during reduction using a type K thermocouple. b) Picture of the experimental setup used to measure the temperature at the top of the samples during reduction. A type K thermocouple in contact with the top of the pellet is visible.	11
Figure S.I.10: Temperatures measured at the top (straight lines) and at the bottom (dashed lines) of pellets exposed 28 min to the light flux under hydrogen (green) or ammonia (red) atmosphere.	11
Figure S.I.11: NH_3/H_2 ratio measured by mass spectrometry during the reduction by ammonia of a pellet sample exposed for 28 min to the luminous flux.	12
Figure S.I.12: XRD analysis of the samples reduced for different times under H_2 or NH_3	14
Figure S.I.13: XRD analysis of the disk samples reduced for different times under NH_3 .	15

Figure S.I.14: Rietveld refinements for H2-D2 (a) and NH3-P28 (b) calculated with MAUD. In the first case, the R_{wp} is 7.99% and in the second, it is 6.81%. The black dots are the XRD measurements and the red line is the refinement. The black line below represents the difference between the experiment and the refinement..... 16

A. Ammonia reduction

Ammonia reduction pathways according to the temperature [1,2]:

- 430 °C – 530 °C: Direct reduction by ammonia:



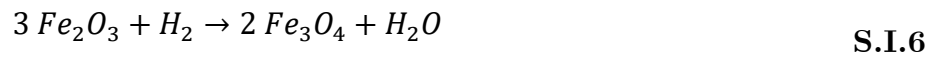
- Over 530 °C: Indirect reduction via decomposition of ammonia [3]:



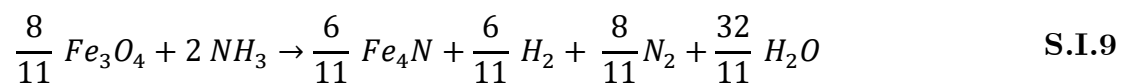
- Below 570 °C:



- Over 570 °C:



- Over 450 °C: Nitriding:



- Nitride decomposition:



B. Experimental setup

Phases	Phase percentage (wt.%)
Hematite - Fe_2O_3	97.80
Magnetite - Fe_3O_4	1.32
Silicon oxide - SiO_2	0.56
Calcite - CaCO_3	0.32

Table S.I.1: Rietveld refinement on XRD analysis of a powdered industrial hematite pellet ($R_{wp} = 9.858\%$).

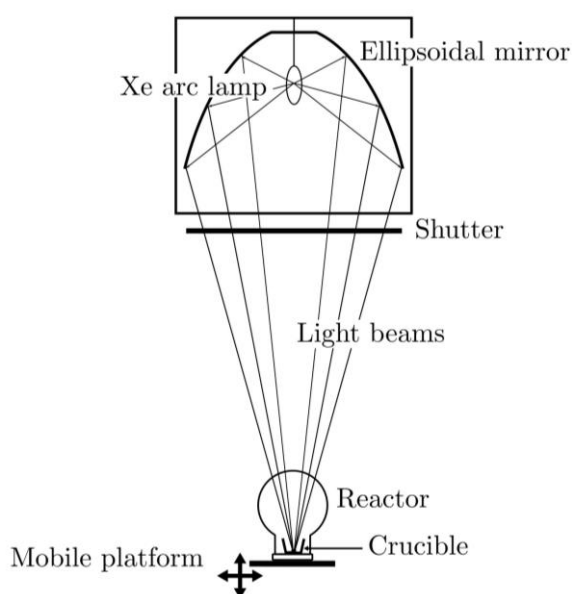


Figure S.I.1: Schematic of the experimental set-up

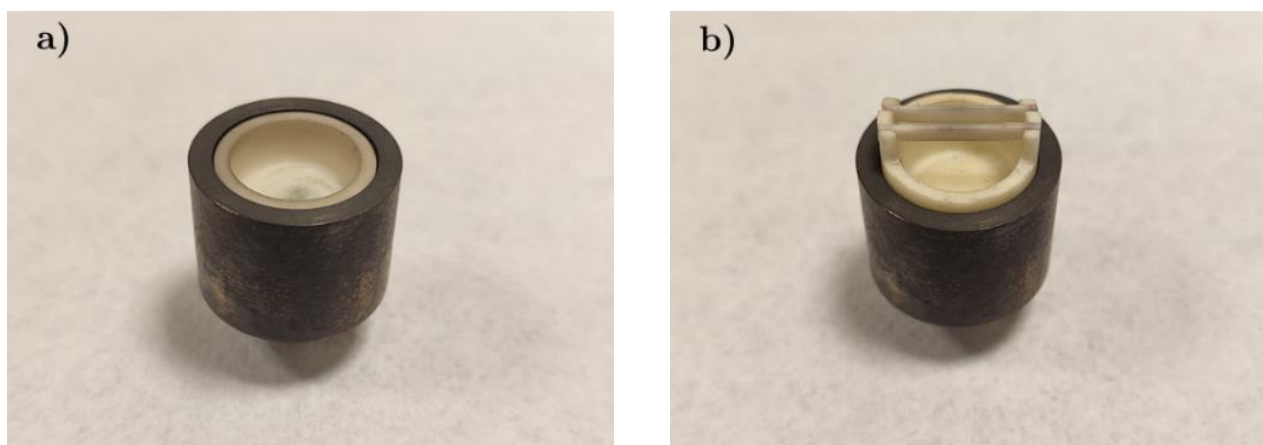


Figure S.I.2: Pictures of the sample holders used for the reductions under concentrated light flux. a) Crucible used for the pellets and b) crucible used for the disks.

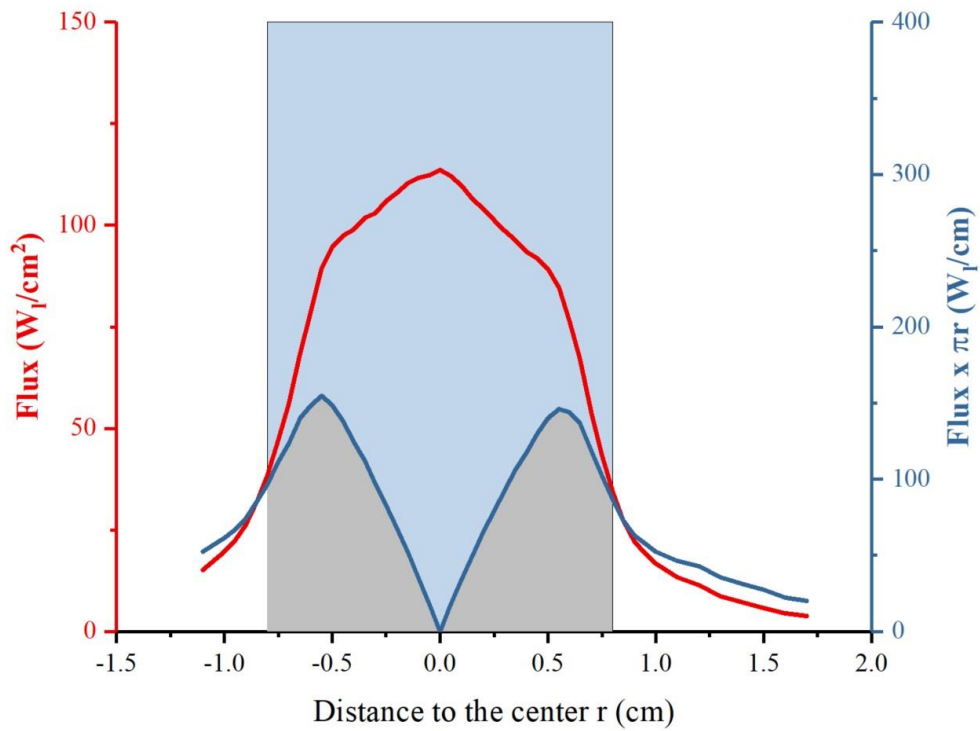


Figure S.I.3: Flux received by the top of the crucible. The maximum of $115 \text{ W}_1/\text{cm}^2$ is reached at the center and the average is $75 \text{ W}_1/\text{cm}^2$. On the crucible aperture area, a power of about 150 W_1 is measured (grey area of the blue curve).

C. Influence of temperature

Diffraction patterns of **Part. III.1.** are presented below.

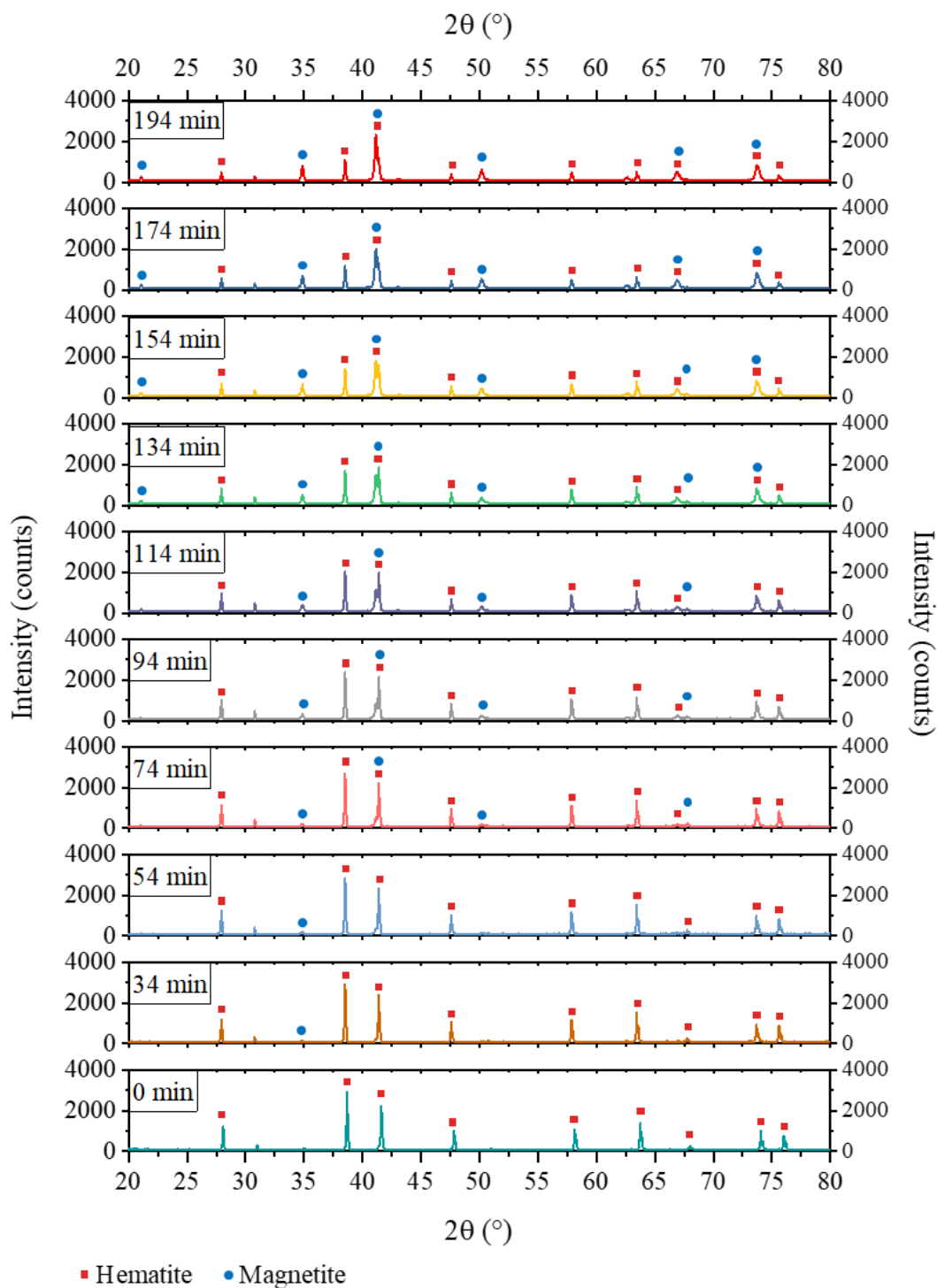


Figure S.I.4: XRD analysis at different times of industrial hematite powder heated at 400 °C under 5% NH_3 atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.

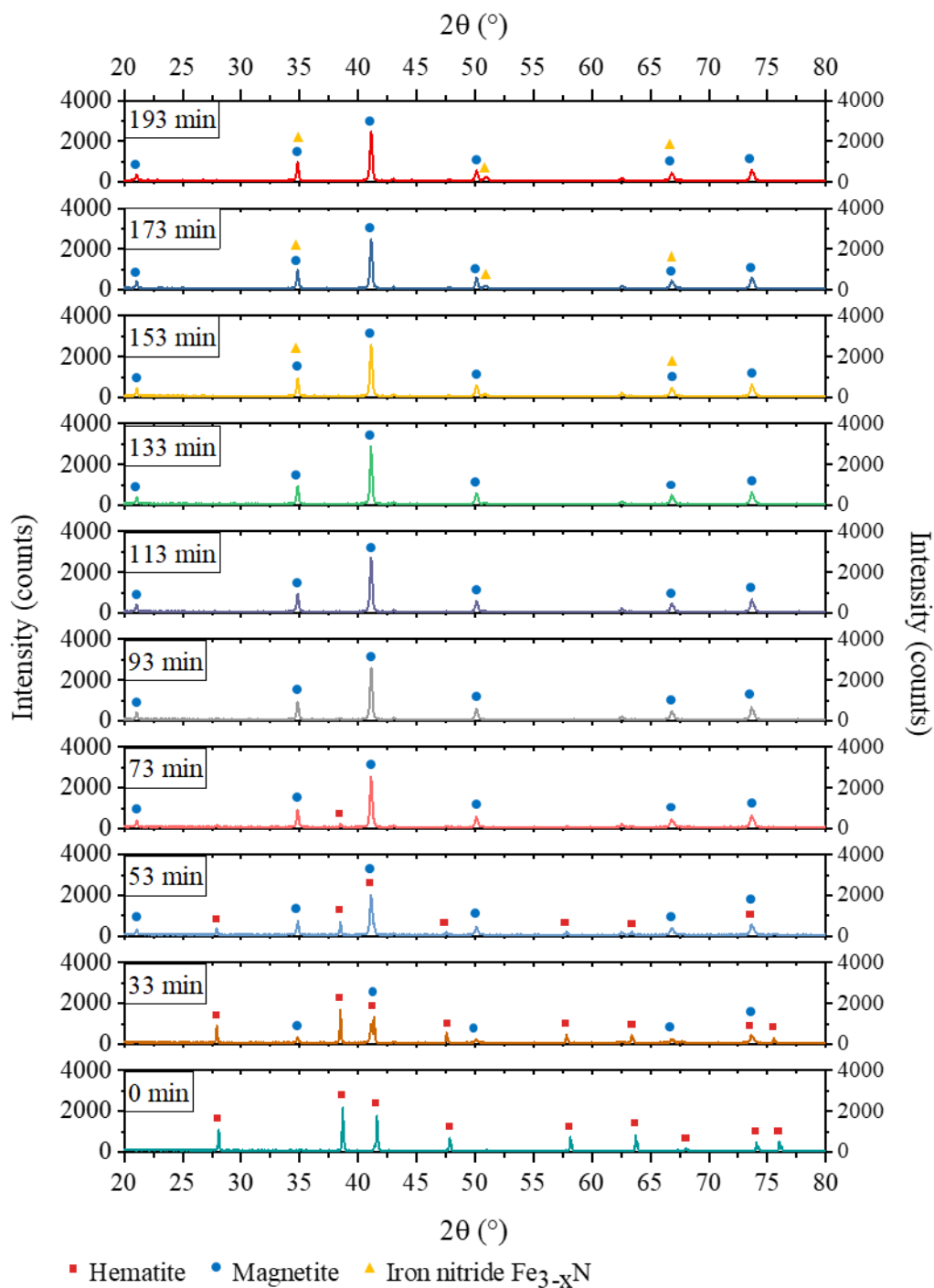


Figure S.I.5: XRD analysis at different times of industrial hematite powder heated at 450 °C under 5% NH_3 atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.

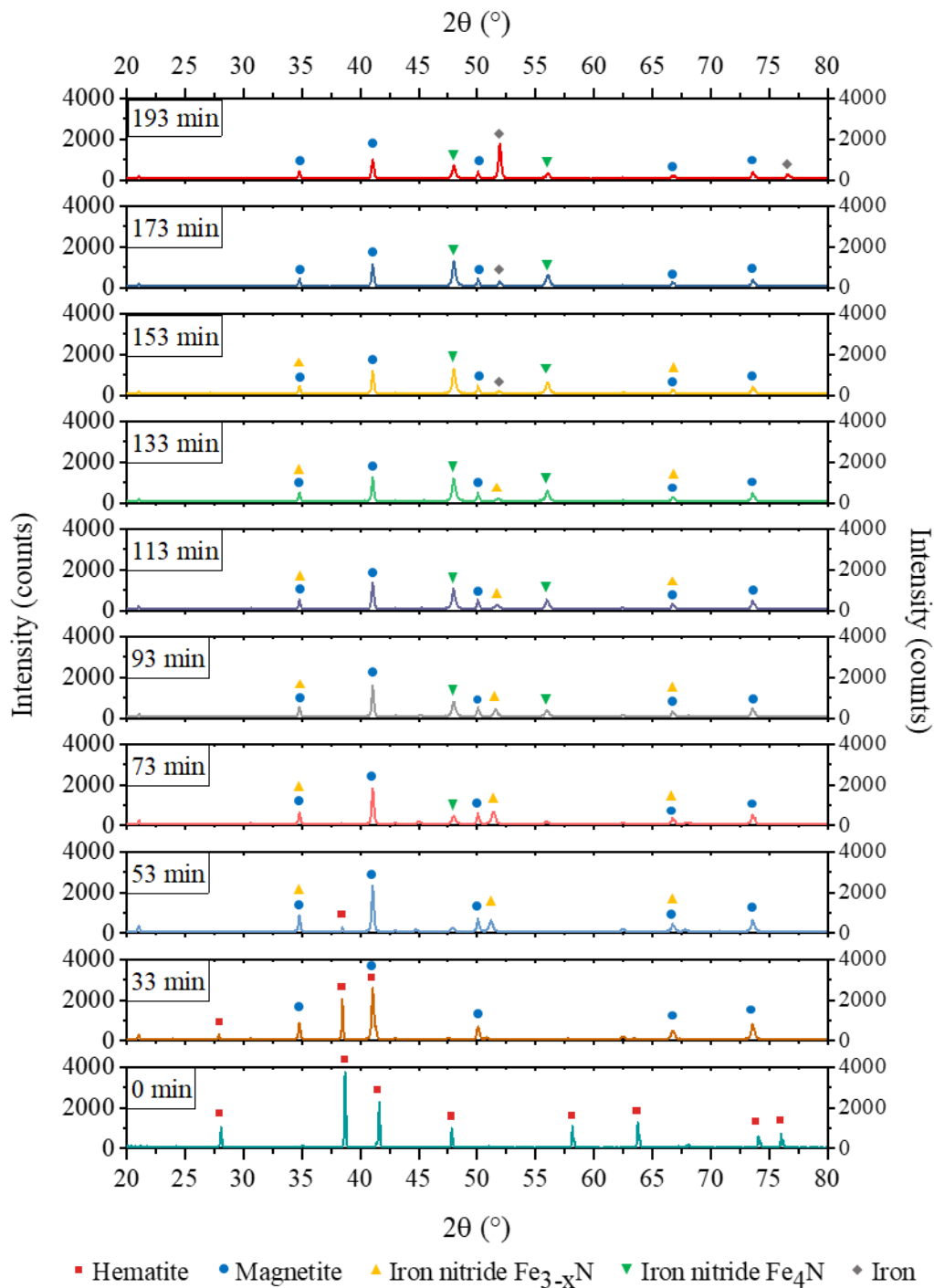


Figure S.I.6: XRD analysis at different times of industrial hematite powder heated at 500 °C under 5% NH_3 atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.

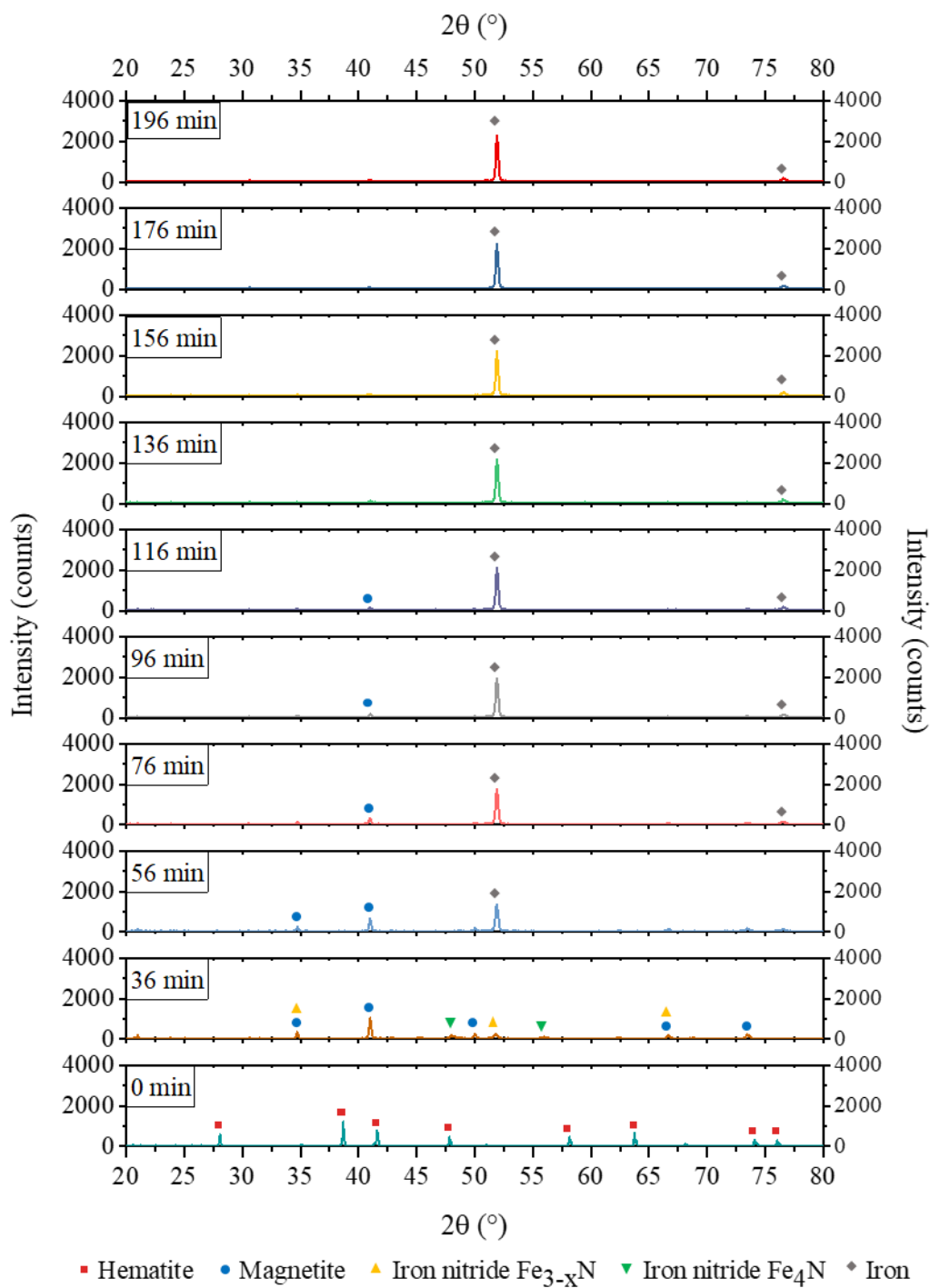


Figure S.I.7: XRD analysis at different times of industrial hematite powder heated at 550 °C under 5% NH_3 atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.

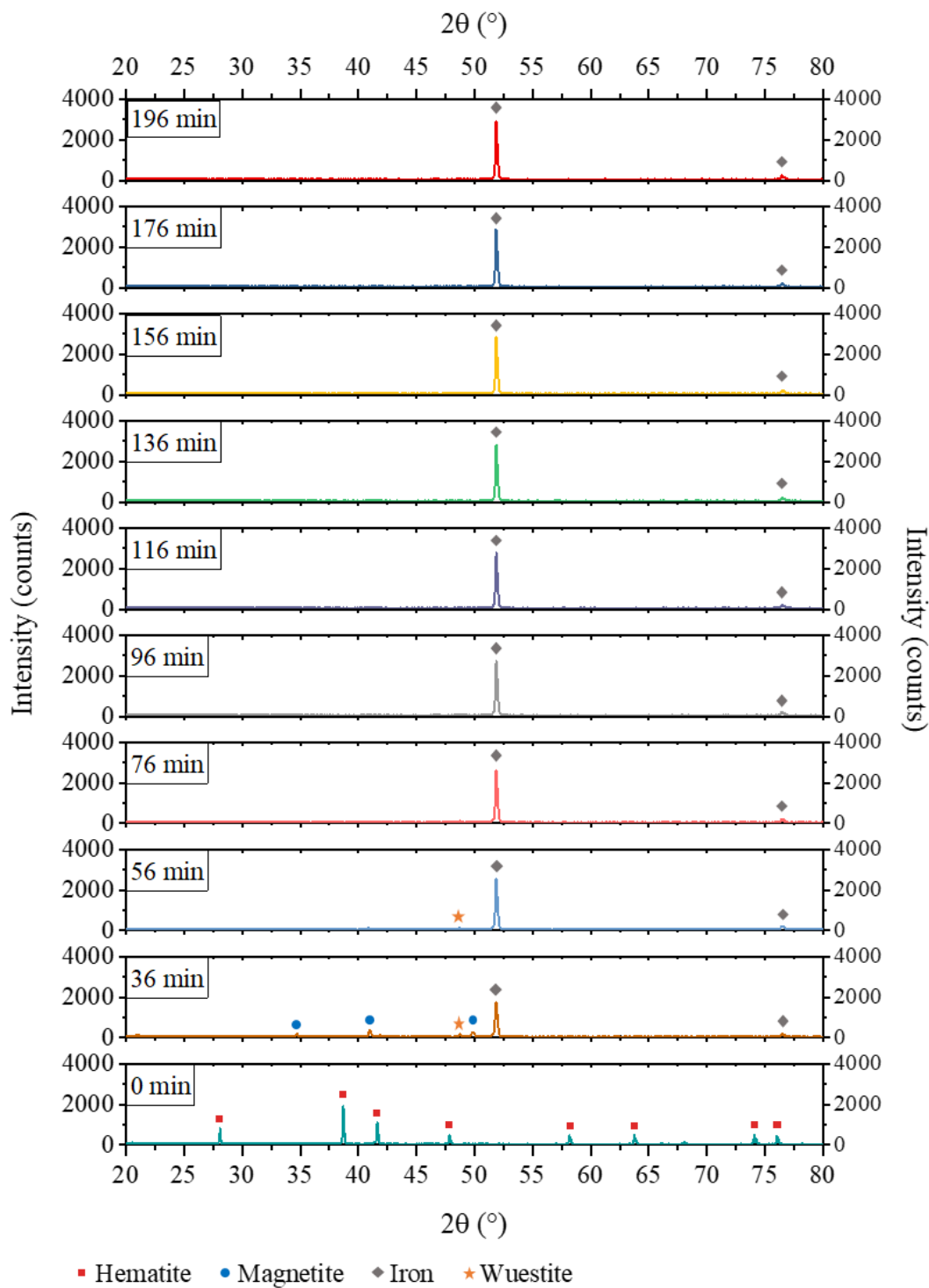


Figure S.I.8: XRD analysis at different times of industrial hematite powder heated at 600 °C under 5%- NH_3 atmosphere. The first scan is taken before heating and the second starts when the setpoint temperature is reached.

D. Temperature and gas composition measurements

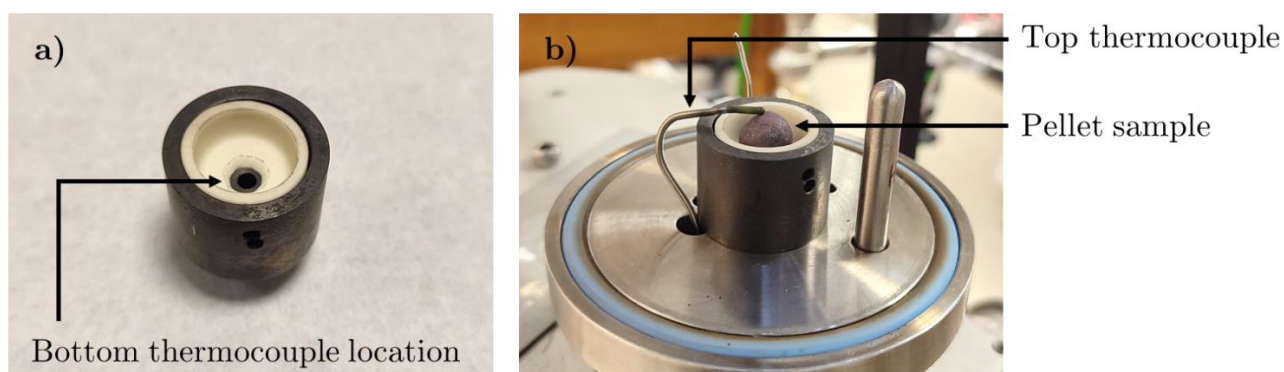


Figure S.I.9: a) Picture of the perforated crucible used to measure the temperature at the bottom of the samples during reduction using a type K thermocouple. b) Picture of the experimental setup used to measure the temperature at the top of the samples during reduction. A type K thermocouple in contact with the top of the pellet is visible.

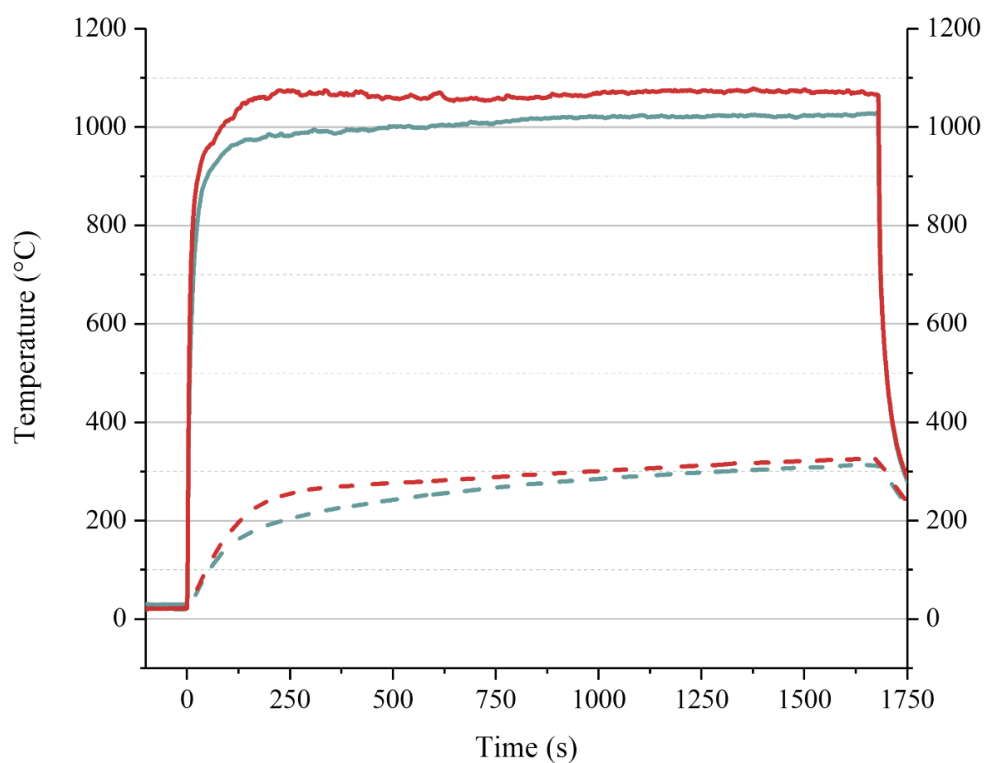


Figure S.I.10: Temperatures measured at the top (straight lines) and at the bottom (dashed lines) of pellets exposed 28 min to the light flux under hydrogen (green) or ammonia (red) atmosphere.

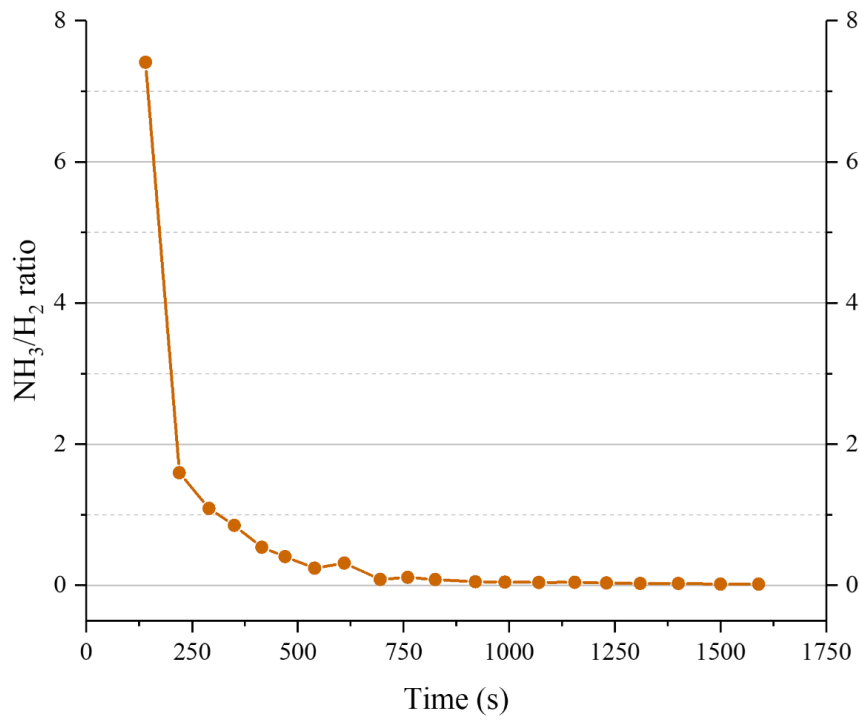


Figure S.I.11: NH_3/H_2 ratio measured by mass spectrometry during the reduction by ammonia of a pellet sample exposed for 28 min to the luminous flux.

E. Comparison with hydrogen-based reduction for different samples

Table S.I.2: Detail of the degrees of reduction (DoR) and degrees of metallization (DoM) of the samples reduced by hydrogen and ammonia. For the pellets, about 90% of the grinded sample was analysed by XRD. For the disks, two scans per sample were conducted with about 20% of the powder per batch resulting in two DoR and two DoM per sample; the mean value was calculated for each sample.

Samples	DoR (%) for each measurement	Mean DoR (%)	DoM (%) for each measurement	Mean DoM (%)
H2-P28	71.14	71.14	71.14	71.14
	/		/	
H2-P16	95.86	95.86	95.86	95.86
	/		/	
H2-P12	96.19	96.19	96.19	96.19
	/		/	
H2-D2	95.78	95.64	95.78	95.64
	95.51		95.51	
NH3-P28	57.52	57.52	57.52	57.52
	/		/	
NH3-P16	98.06	98.06	97.00	97.00
	/		/	
NH3-P12	77.09	77.09	45.75	45.75
	/		/	
NH3-D2	57.00	57.75	39.18	39.73
	58.49		40.29	
NH3-D3	78.71	79.27	66.80	67.47
	79.83		68.13	
NH3-D4	88.63	87.19	86.68	84.94
	85.76		83.20	
NH3-D5	92.15	92.36	91.72	91.99
	92.58		92.26	
NH3-D6	97.76	97.54	97.76	97.54
	97.32		97.32	
NH3-D7	96.18	95.82	96.18	95.82
	95.45		95.45	
NH3-D8	97.23	97.52	97.23	97.52
	97.81		97.81	

Diffractograms of samples studied in **Part III.2.** are presented below.

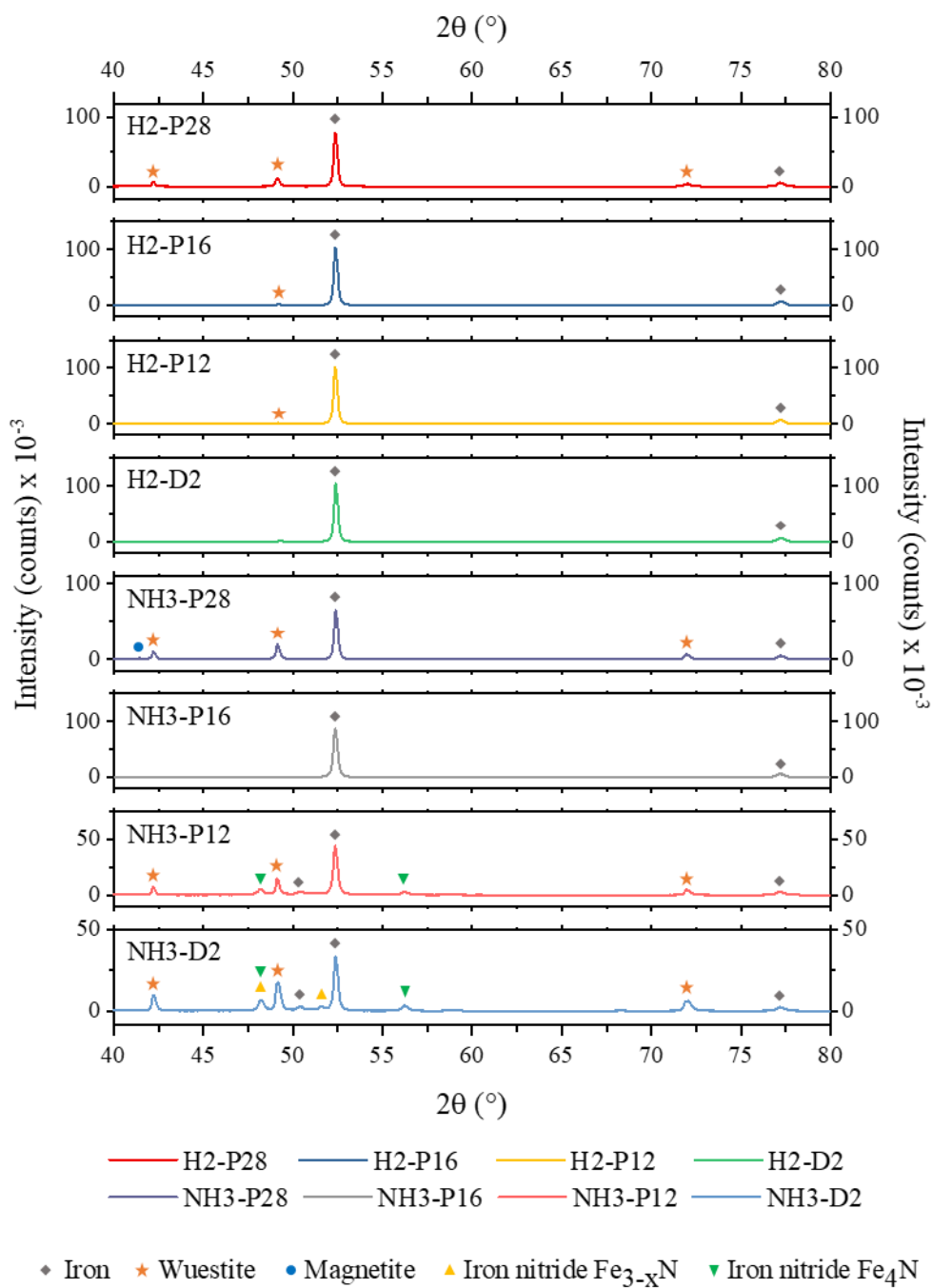


Figure S.I.12: XRD analysis of the samples reduced for different times under H_2 or NH_3 .

F. Reduction by ammonia of disk samples

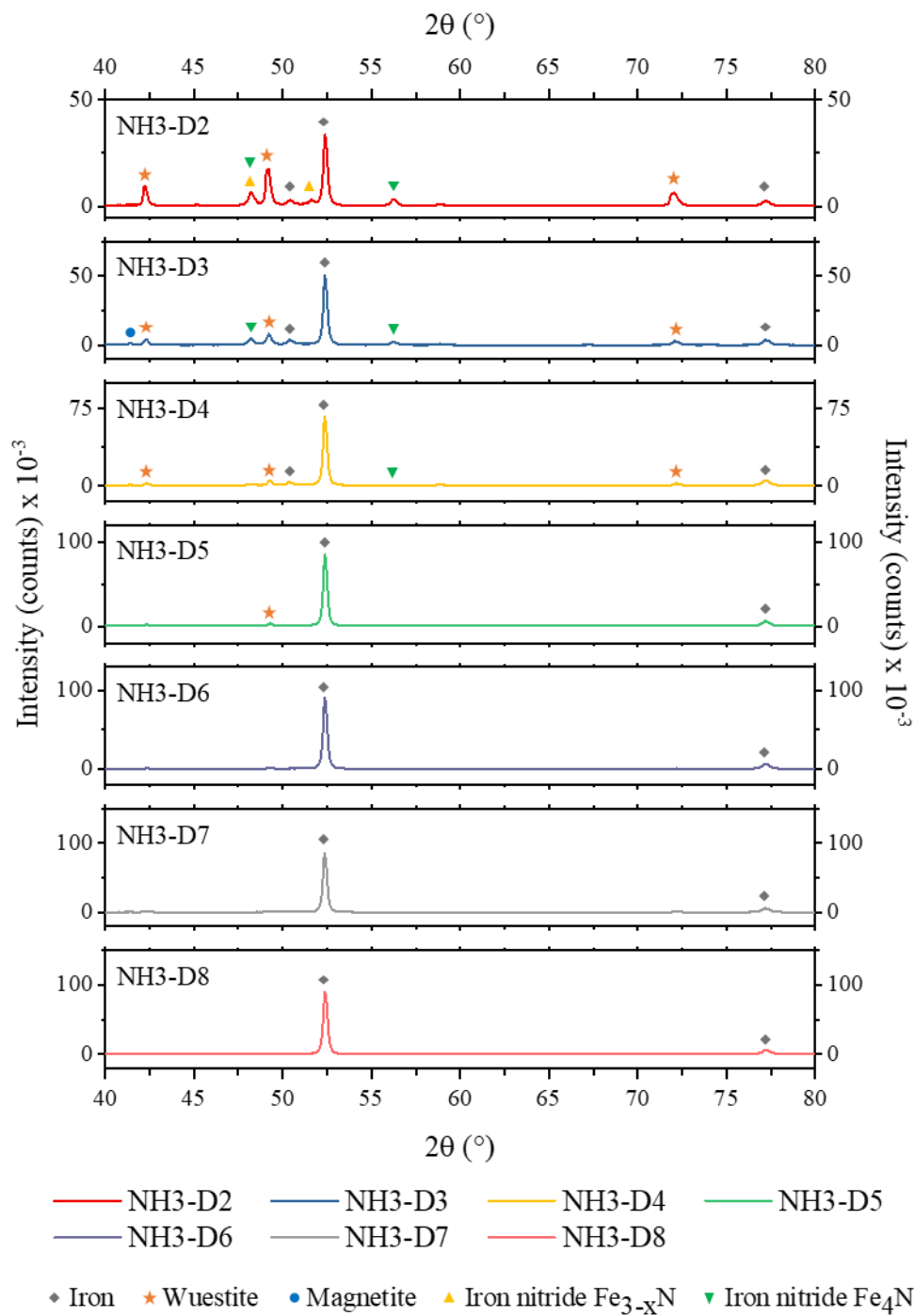


Figure S.I.13: XRD analysis of the disk samples reduced for different times under NH_3 .

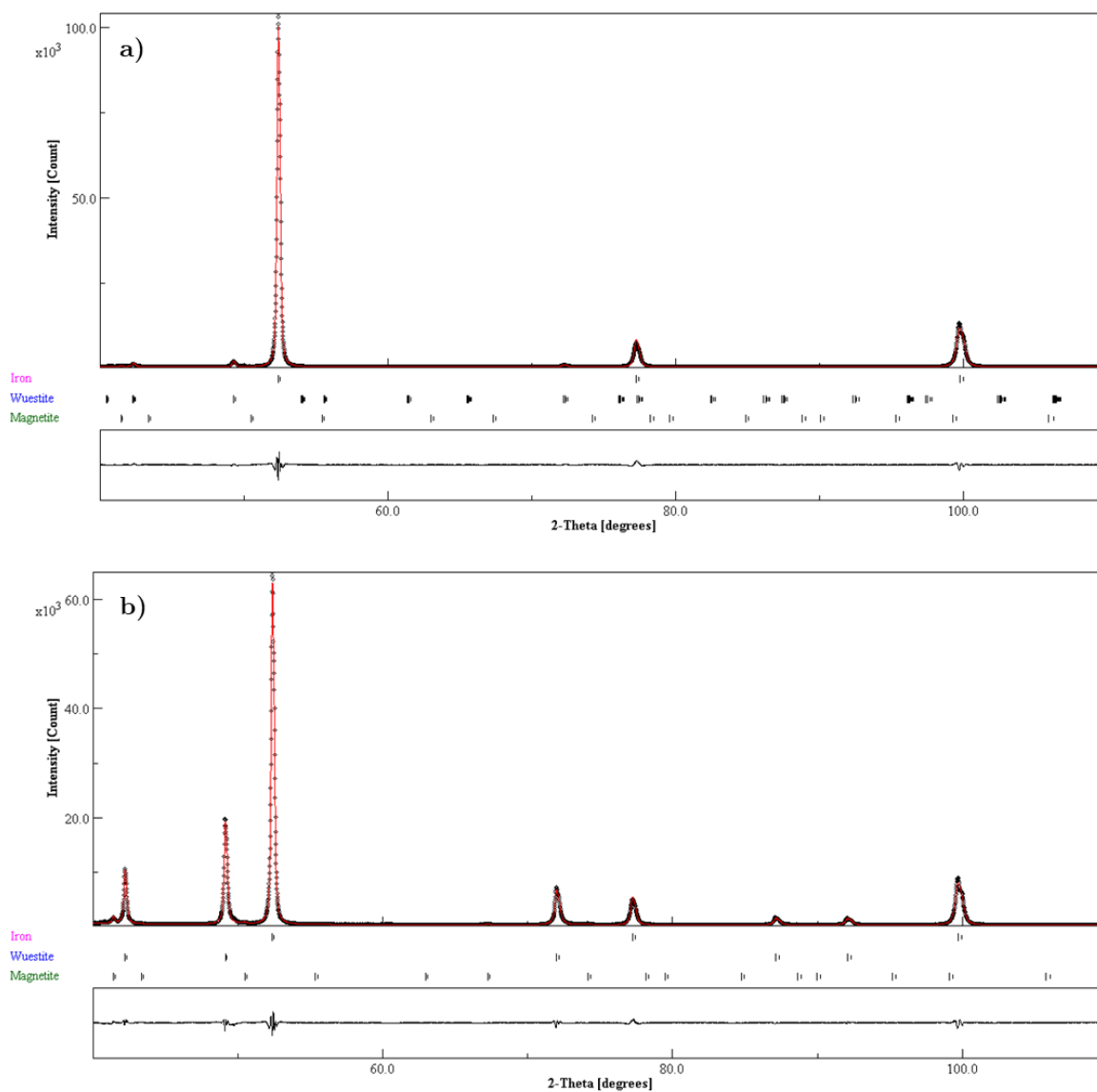


Figure S.I.14: Rietveld refinements for H₂-D₂ (a) and NH₃-P28 (b) calculated with MAUD. In the first case, the R_{wp} is 7.99% and in the second, it is 6.81%. The black dots are the XRD measurements and the red line is the refinement. The black line below represents the difference between the experiment and the refinement.

G. Energy necessary to produce the reducers

Hydrogen

- Via electrolysis, around 52 kWh are needed to produce 1 kg of H₂ [4]
- According to the reduction equation: $\text{Fe}_2\text{O}_3 + 3 \text{H}_2 \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O}$, $\frac{3}{2}$ mol of H₂ are needed to produce 1 mol of Fe.
- Using the molar masses of H₂ (2 g/mol) and of Fe (55.8 g/mol), one deduces that: 1 t of Fe (17920 mol of Fe) requires 26882 mol of H₂ (54 kg of H₂) to be produced, corresponding to 2808 kWh/t of iron.
- In 2021, 1951 Mt of steel were produced [5], so 5478 TWh of electricity would be needed to produce the necessary hydrogen to decarbonize the process.
- The global electricity production of 2021 is 28000 TWh, so 19.5% of the global electricity production should be dedicated to the production of the hydrogen required to produce iron.

Ammonia

- Via electrolysis and Haber-Bosh, 0.177 kg of H₂ are needed to produce 1 kg of NH₃ [6] *i.e.* 9.2 kWh.
- The production of hydrogen represents around 80% of the energy needed to produce ammonia [4], which means that 11.5 kWh are needed in total to produce 1 kg of NH₃.
- $\frac{2}{3}$ mol of NH₃ are needed to produce 1 mol of H₂.
- With the molar masses of NH₃ (17 g/mol), H₂ (2 g/mol) and of Fe (55.8 g/mol), one deduces that: 1 t of Fe requires 17920 mol of NH₃ (305 kg of NH₃) to be produced, corresponding to around 3510 kWh/t of iron.
- 6848 TWh of electricity would be needed to produce the ammonia necessary to decarbonize 2021 steel production, corresponding to 24.5% of the global electricity production.

One should note that these calculations depend on the exact numbers chosen for the electricity needed to produce 1 kg of hydrogen or ammonia and that values slightly vary depending on sources. We took the most coherent values and/or averages. These calculations aim at providing orders of magnitude, which are in principle correct.

References

- [1] S. Hosokai, Y. Kasiwaya, K. Matsui, N. Okinaka, and T. Akiyama, Ironmaking with Ammonia at Low Temperature, *Environ. Sci. Technol.* 45, 821 (2011).
- [2] N. Yasuda, Y. Mochizuki, N. Tsubouchi, and T. Akiyama, Reduction and Nitriding Behavior of Hematite with Ammonia, *ISIJ Int.* 55, 736 (2015).
- [3] A. Ranzani Da Costa, *La Réduction Du Minerai de Fer Par l'hydrogène : Étude Cinétique, Phénomène de Collage et Modélisation*, Institut National Polytechnique de Lorraine, 2011.
- [4] *The Future of Hydrogen*, International Energy Agency (2019)
- [5] *World Steel in Figures 2022*, <https://worldsteel.org/steel-topics/statistics/world-steel-in-figures-2022/>.
- [6] Y. Bicer and I. Dincer, Life cycle assessment of nuclear-based hydrogen and ammonia production options: A comparative evaluation, *Int. J. Hydrog. Energy* 42, 21559 (2017).