

Supplementary Information for “Meteorite Impacts on Ancient Ocean Opened Up Multiple NH₃ Production Pathways”

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Rough Estimate of Production Amount of NH₃ Using the MSST-AIMD Simulation

Results

From previous simulation studies,¹⁻³ time scale of shock compression is assumed to be ~10 ps. In our 6 km/s shock-wave simulation based on the MSST-AIMD, five NH₃ molecules were produced on the surface of Fe₃₆ slab during 4 ps, *i.e.*, about 0.35 NH₃ molecules are produced per Fe atom during 10 ps. The estimated amount of meteorite accretion 4×10^{24} g during 4.4 to 3.8 billion years ago⁴ is also used. Assuming that the whole accretion occurred by ordinary chondrites contained 10 wt.% iron,⁵ Fe atoms of about 1.2×10^{13} mol were annually supplied to the early Earth during 4.4 to 3.8 billion years ago. We therefore estimate that NH₃ of about 7.2×10^7 tons yr⁻¹ (or 4.2×10^{12} mol yr⁻¹) were produced. It should be noted that the amount is larger than 1.1×10^7 tons yr⁻¹ estimated from the experimental result by Nakazawa *et al.*⁶ (whose impact velocity corresponds to that of our 4 km/s shock-wave simulation⁶) and the estimated amount from our 5 km/s shock-wave simulation (4.3×10^7 tons yr⁻¹).⁶ This implies that shocks with greater impact velocities would provide further increase in the yield if all of them can survive after quenching.

Another Desorption Process of an NH₃ Fragment in the Dissociative Mechanism

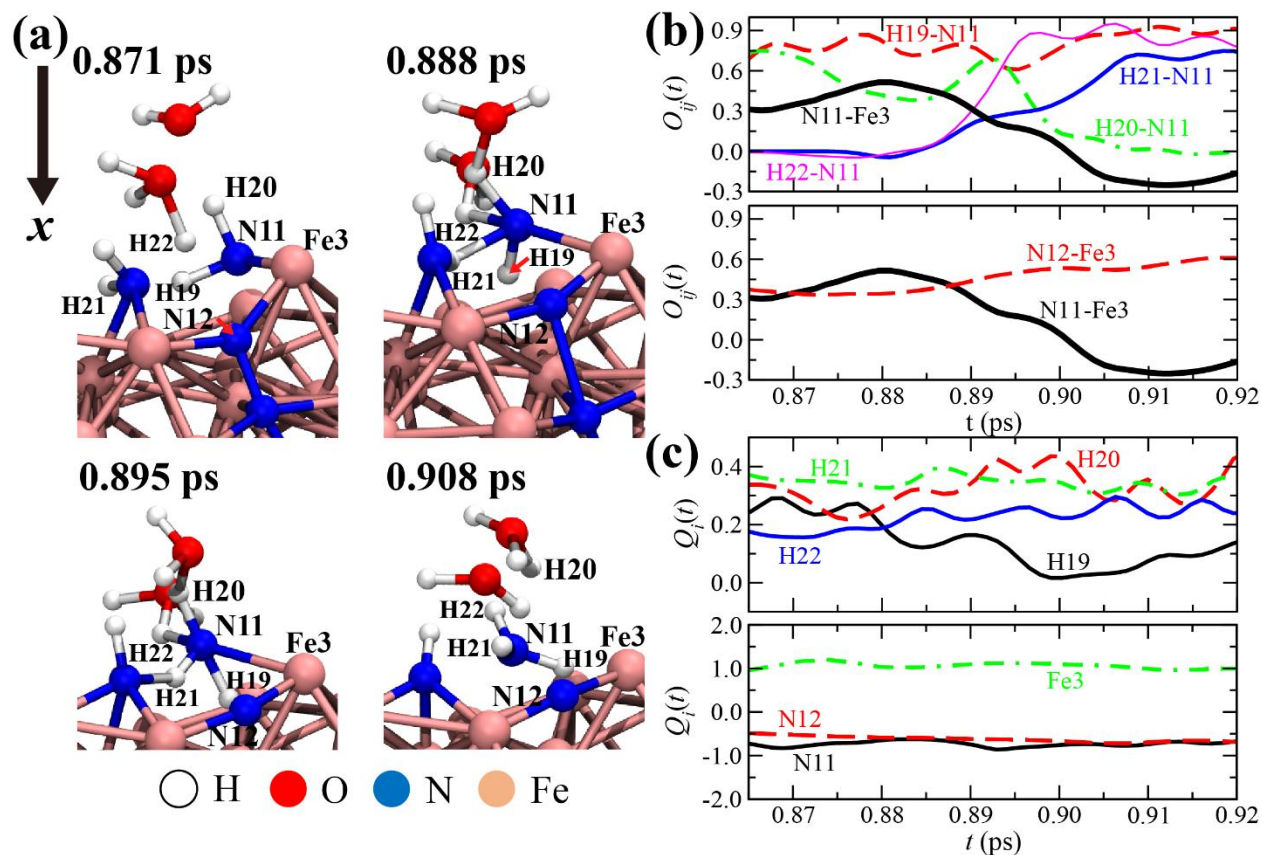


Figure S1. (a) Atomistic configurations at 0.871, 0.888, 0.895, and 0.908 ps during the desorption of an NH₃ fragment from the Fe slab surface, where white, red, blue, and pink spheres represent H, O, N, and Fe atoms, respectively. Time evolution of (b) the bond-overlap populations $O_{ij}(t)$ and (c) the Mulliken charges $Q_i(t)$ associated with the atoms labeled in (a).

Figure S1 shows another example of the desorption process of an NH₃ fragment in the dissociative mechanism observed in the 6 km/s shock-wave simulation. (It occurred at [a] of Fig. 2(e) in main text.) The time evolution of the atomic configuration is shown in Figure S1(a), where the NH₃ fragment consisting of H19, H21, H22, and N11 was desorbed from Fe3. Figures S1(b) and S1(c) show the time evolution of the bond-overlap populations

$O_{ij}(t)$ and the Mulliken charges $Q_i(t)$ for specified atoms using the Mulliken bond-overlap population analysis.

At 0.871 ps, two NH_2 fragments and one N_2 molecule existed on the Fe slab surface. In addition, one H_3O^+ and one H_2O molecule were present near the NH_2 fragment consisting of H19, H20, and N11, but these would be not important for the desorption of the NH_3 fragment because they were only involved in exchanging their H atoms via N11. At 0.888 ps, the H_2O molecule and H_3O^+ began to interact with the former NH_2 fragment via H20 and H22, respectively. Subsequently, by proton transfers, N11 obtained H22 instead of releasing H20.

The key atom for the desorption is N12 contained in the N_2 molecule. At 0.888 ps, the N_2 molecule was dissociated and then the single N atom N12 was formed. N12 gradually strengthened the bond with Fe3 (see $O_{\text{N12-Fe3}}(t)$) from about 0.88 ps. In contrast to this, the bond strength of N11-Fe3 began to decrease (see $O_{\text{N11-Fe3}}(t)$). This is because electrons from Fe3, which formed bonds with N11, were subsequently involved in the strengthening of bond with N12. Along with increasing $O_{\text{N12-Fe3}}(t)$, the bond strength of N22-H11 rapidly increased, and then the NH_3 fragment consisting of H19, H21, H22, and N11 was desorbed from Fe3 at 0.908 ps ($O_{\text{N11-Fe3}}(t)$ reached zero). Therefore, it is considered that the N atoms bidentate-coordinated to Fe atoms such as N12 play a role to catalytically support the desorption of NH_3 fragments from the Fe slab surface.

References for Supplementary Information

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