vacuum (emitting) surface. Electrons entering the film from the back contact can be heated (that is, enter energy states far from the conduction band edge) during transport to the vacuum (emitting) surface due to the high field within the film. The probability of electron emission will be high at the surface if such electron heating occurs, because the electrons are energetically closer to the vacuum level. This may explain the apparently low barrier obtained for the Fowler–Nordheim region in Fig. 1. For field emission from polymers, it appears that there is a small positive barrier—according to the Fowler–Nordheim relationship—before 'conditioning'. But after conditioning, the J–F data, when plotted in the Fowler–Nordheim axes, has no region indicating a negative slope. This indicates that field emission is no longer limited by a positive barrier at the polymer–vacuum interface. Possible limiting mechanisms are the flow of SCLC in the bulk of the film, or in the vacuum immediately above the emission spot.

The gradient of 1.8 obtained from the log I–log V plot of Fig. 2 does not make it clear whether one type of space-charge-limiting mechanism dominates over the other. A slope of 1.5 is predicted by the Langmuir–Child[8] law for SCLC in a vacuum, and a slope of at least 2.0 is predicted for SCLC in the film bulk from the Lampert–Rose model[9]. We note that a very similar gradient value of ~1.75 has been measured for nitrogenated diamond[3], which showed the lowest emission threshold field of any carbon-based material before the present results from conjugated polymers. It is known that C–H bonding in polymeric carbon materials can lead to negative electron affinity, as in the case of H-terminated diamond {111} and {100} surfaces[10]. The relative energies of the conduction band edge and the vacuum level are largely determined by C–H bonding at the surface. We speculate that the conditioning in Fig. 1 reflects a change in polymer structure at the high-field sites from which electron emission originates. The concentration of carriers and electric field at these local emission sites could in principle lead to a significant rise in the local temperature. If the transformation of the polymer gives it a negative or very low electron affinity at the emission sites, then post-conditioning current characteristics similar to those of diamond would be expected[11].

The extremely low threshold field for electron emission in conjugated polymers offers the prospect of an all-polymer flat-panel display, in which polymer thin-film transistors are used for switching the pixels, and polymer field-emission cathodes stimulate light emission from phosphor screens.

Note added in proof: Since submission of this Letter, an electron emission process based on a triple junction effect at a diamond/metal/vacuum interface has been proposed[11]. Such a process may also be relevant for emission from the surface of the polymer void. □

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Abiotic nitrogen reduction on the early Earth

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The production of organic precursors to life depends critically on the form of the reactants. In particular, an environment dominated by N_2 is far less efficient in synthesizing nitrogen-bearing organics than a reducing environment rich in ammonia (refs 1, 2). Relatively reducing lithospheric conditions on the early Earth have been presumed to favour the generation of an ammonia-rich atmosphere, but this hypothesis has not been studied experimentally. Here we demonstrate mineral-catalysed reduction of N_2, NO_2^- and NO_3^- to ammonia at temperatures between 300 and 800 °C and pressures of 0.1–0.4 GPa—conditions typical of crustal and oceanic hydrothermal systems. We also show that only N_2 is stable above 800 °C, thus precluding significant atmospheric ammonia formation during hot accretion. We conclude that mineral-catalysed N_2 reduction might have provided a significant source of ammonia to the Hadean ocean. These results also suggest that, whereas nitrogen in the Earth's early atmosphere was present predominantly as N_2, exchange with oceanic, hydrothermally derived ammonia could have provided a significant amount of the atmospheric ammonia necessary to resolve the early-faint-Sun paradox[3].

To assess the extent to which N_2 might have been reduced to NH_3 via mineral-catalysed reduction, we have conducted a series of high-temperature, high-pressure experiments. If the early Earth's lithosphere was more reduced than it is today with a higher percentage of iron in the FeO state[4], then reaction of this reduced iron with H_2O might have provided the necessary H_2 gas for N_2 reduction[5]. Furthermore, the reduction of N_2 to NH_3 might have been catalysed by iron oxides as these are used as the starting material for catalysts in industrial nitrogen reduction[6]. The first reaction considered was that of metallic iron with N_2 and H_2O to form NH_3 and iron oxides:

$$3(1 - x)Fe + N_2 + 3H_2O \rightarrow 3Fe_{(1 - x)}O + 2NH_3 \qquad (1)$$
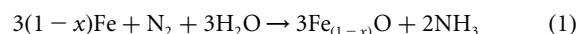
This reaction has been postulated to occur on the early Earth between metallic iron or reduced iron oxides within the lithosphere and degassing N_2 from the Earth's interior[7]. In the present experiments the ratio of H_2O to Fe in the sample capsules was varied to generate a range of conditions from highly reducing (H_2O:Fe = 1) to mildly reducing (H_2O:Fe~1 to 1.5) and oxidizing with excess H_2O (H_2O:Fe > 1.5). Under the most reducing conditions, at 700 °C and 0.1 GPa, up to 17 mol% of N_2 was reduced to NH_3, whereas under mildly reducing conditions 1–3% of N_2 was reduced (Fig. 1). Under the most oxidizing conditions with excess H_2O present, only trace amounts of N_2 were reduced to NH_3. Interestingly, no NH_3 was produced at 900 °C, even under the most reducing conditions, indicating the inherent thermodynamic instability of NH_3 at this high temperature.

To examine the system with more oxidized catalysts, experiments were conducted in N_2 atmosphere in which magnetite (Fe_3O_4) with formic acid was used as a reducing agent. It has long been established that, in the presence of a strong reductant (H_2 or hydride donor), pure synthetic magnetite acts as a catalyst for N_2 reduction[6]. Notably, magnetite is a major form of iron oxide in the present-day crust[8]. The potential for this reaction was explored with natural magnetite under geochemically relevant conditions spanning a range of temperatures and pressures. Yields of NH_3 for the Fe_3O_4/N_2/HCO_2H system were comparable to those obtained under

equivalent reducing conditions from the $Fe/N_2/H_2O$ system (Fig. 2). Although the temperature of maximum yield dropped to 500 °C, the upper thermal limit of reduction remained at ~900 °C. Increasing the pressure at 500 °C had only a small effect (from 0.53% at 0.1 GPa to 0.58% at 0.4 GPa) on NH_3 yields. Low pressures (0.01 GPa) resulted in a marked decrease in NH_3 yields to less than 10% of comparable high-pressure values in both systems (Figs 1 and 2). In a similar manner to the Fe/H_2O system, N_2 reduction was strongly inhibited by excess water (Fig. 2). Most gas compositions in metamorphic systems have ratios of H_2O to total gas of 0.5 or greater[9], although gases trapped in some mid-ocean ridge basalts have been shown to have very low ratios of H_2O to total gas[10]. Thus, N_2 reduction would be restricted to localized regions from which H_2O had been removed by reaction with reduced minerals to form H_2 and oxides[5,7]. A plausible scenario for the production of NH_3 in the crust involves the initial production of H_2 from the reaction of H_2O with reduced minerals, followed by the reduction of N_2 on the mineral surfaces. The high temperatures and pressures required in these experiments (0.1 GPa, 300–800 °C) are consistent with this hypothesis.

The fate of the more oxidized forms of nitrogen, NO_2^- and NO_3^-, presumed to be in the Hadean ocean[11] (generated by atmospheric reactions driven by electrical discharge or cometary shock[12]) was also investigated. These compounds are of interest because they represent an additional source of reactive nitrogen to the Hadean ocean, whereas hydrothermal systems have been suggested as a possible sink for oxidized nitrogen[11]. Experiments were conducted in which NO_2^- and NO_3^- solutions were reacted with mineral catalysts at high temperatures and pressures. We find that NO_2^- and NO_3^- in contact with iron sulphides are quickly and efficiently reduced to NH_3 at higher temperatures (Table 1). Reactions at 500 °C reached 80% conversion efficiency within the 15 minutes required to bring the pressure vessel up to constant temperature (Table 1). Pyrite was as efficient as pyrrhotite in catalysing the conversion of NO_3^- to NH_3 and no added reductant (H_2S or H_2) was required. Magnetite and basalt, however, did not catalyse the reaction to NH_3 as efficiently or as rapidly as iron sulphides. Both magnetite and basalt quickly (<15 min at 500 °C) converted NO_3^- and NO_2^- to species that could not be detected as solutes in aqueous solution. After 24 hours, significant amounts of NH_3 were produced, although yields were not as great as those found with iron sulphides. We hypothesize that the pathway for this reaction[13] proceeds through NO or NO_2, not N_2, on the basis of the difficulty of N_2 reduction in the presence of excess water. Reduction of NO_3^- does not appear to pass through NO_2^- (as it does in the biological pathway[14]), as yields of NH_3 from NO_3^- are higher than those from NO_2^-. Lower temperatures decreased the amount of conversion of nitrogen oxides to NH_3. The addition of reducing agents within hydrothermal systems, however, might improve the conversion efficiency at low temperatures[15]. Because iron sulphides are ubiquitous in hydrothermal systems, it is likely that both NO_2^- and NO_3^- carried into such systems are eventually converted into NH_3. After conversion, the NH_3 is quite stable, even at very high temperatures (700 °C). Only at $T > 800$ °C are both nitrogen oxides and NH_3 destroyed. Studies of hydrothermal systems indicate that high temperatures do not exceed 700 °C (ref. 16). Thus, hydrothermal systems represent regions of the highest NH_3 conversion rates and stability on the Earth.

Three important conclusions follow from this study. First, the instability of NH_3 at $T > 800$ °C strongly indicates that planetary bodies that undergo a 'hot accretionary' mechanism (including the Earth[17]) have their earliest atmospheres dominated by nitrogen in the N_2 form. Regardless of the degree to which the interior of the planet is reducing in nature, during the initial period of accretion where temperatures are above 800 °C no NH_3 will form and any NH_3 derived from the thermal decomposition of organic matter in chondrites[18] will be converted to N_2. Indeed, most of the Archaean atmosphere is assumed to have formed under these conditions[19]. These results also indicate that surficial N_2 reduction would have been precluded by the high H_2O content and low pressures of the Hadean atmosphere. Thus it is likely that the very reducing conditions required for N_2 reduction would have been found only in high-pressure environments well beneath the Earth's surface.

Second, NH_3 produced by crustal N_2 reduction might have been an important source of reduced nitrogen to the Hadean ocean. After atmospheric formation a significant percentage of total Earth N is thought to have remained within the crust and mantle. Conversion of even a small percentage of this nitrogen to NH_3 after crustal temperatures dropped below 800 °C would have provided a vast reservoir of reduced nitrogen for the early Earth. The total nitrogen budget of the Earth's crust and atmosphere is estimated to be 2×10^{20} mol (ref. 19). Conservatively assuming that only 25% of the total nitrogen remained within the crust and mantle after initial atmosphere formation, and that of this only 1% was converted to NH_3, then it is calculated that a reservoir of 5×10^{17} mol N in reduced form would have resulted. In the absence of any losses or other inputs, this NH_3 was presumably transferred to the ocean from the crust by hydrothermal systems over timescales of 10^7 to 10^9 years. Such a source of ammonia would have been comparable in magnitude (10^9–10^{11} mol N yr^{-1}) to the proposed oceanic reduction of NO_3^- by Fe^{2+} (ref. 11) and terrestrial TiO_2 photochemical catalysis of N_2 (ref. 20). Transfer of crustal ammonia to the ocean might
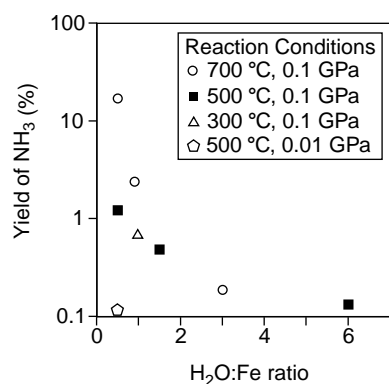

Figure 1 N_2 reduction to NH_3 plotted against initial Fe:H_2O ratio at 300, 500 and 700 °C. All reactions were conducted over a 24-h period. No detectable NH_3 was obtained in experiments conducted at 900 °C or in experiments conducted at 0.01 GPa and H_2O:Fe ratios larger than 0.5.
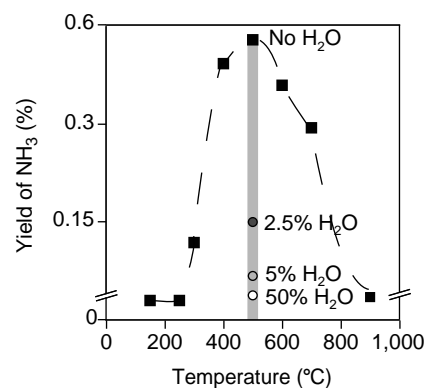

Figure 2 N_2 reduction to NH_3 plotted against temperature at 0.1 GPa in the $HCO_2H/N_2/Fe_3O_4$ system (squares). Also shown are yields at 500 °C with different amounts of H_2O (given in mol%) added to the initial HCO_2H solution (circles). The 0.03% yield at 150 °C represents the blank concentration of NH_3. No detectable NH_3 above blank was obtained in experiments conducted at 0.01 GPa and 500 °C.

Table 1 Conversion efficiencies to NH$_3$ from NO$_2^-$ and NO$_3^-$ solutions in contact with catalysts

Mineral	Compound	T (°C)	Time (h)	Solution type	Product yield (%)
Fe$_{(1-x)}$S	NO$_3^-$	300	24	H$_2$O	53
Fe$_{(1-x)}$S	NO$_2^-$	300	24	H$_2$O	21
Fe$_{(1-x)}$S	NO$_3^-$	500	24	H$_2$O	73
Fe$_{(1-x)}$S	NO$_2^-$	500	24	H$_2$O	37
Fe$_{(1-x)}$S	NO$_3^-$	700	24	H$_2$O	89
Fe$_{(1-x)}$S	NO$_2^-$	700	24	H$_2$O	74
Fe$_{(1-x)}$S	NO$_2^-$	900	24	H$_2$O	0
Fe$_{(1-x)}$S	NO$_3^-$	500	0.033	H$_2$O	74
FeS$_2$	NO$_3^-$	500	24	H$_2$O	70
95%Fe,5%Ni	NO$_3^-$	500	24	H$_2$O	41
95%Fe,5%Ni	NO$_2^-$	500	24	H$_2$O	45
Fe$_3$O$_4$	NO$_3^-$	900	24	H$_2$O	0
Fe$_3$O$_4$	NO$_3^-$	500	24	H$_2$O	46
Fe$_3$O$_4$	NO$_2^-$	500	24	H$_2$O	9.4
Fe$_3$O$_4$	NO$_3^-$	500	0.033	H$_2$O	4.1
Fe$_3$O$_4$	NO$_2^-$	500	0.033	H$_2$O	1.0
Basalt	NO$_3^-$	500	24	H$_2$O	20
Basalt	NO$_2^-$	500	24	H$_2$O	14
Fe$_{(1-x)}$S	NO$_3^-$	500	24	Sea water	84
Fe$_3$O$_4$	NO$_3^-$	500	24	Sea water	1.2
Basalt	NO$_3^-$	500	24	Sea water	1.0

therefore have provided an early boost to oceanic NH$_3$ concentrations, and thus improved the prospects for synthesis and stability of N-containing organic compounds[21]. The results discussed here point to a probably oceanic or hydrothermal source for a large fraction of reduced nitrogen. Steady-state oceanic NH$_3$ concentrations would have depended on atmospheric loss rates[3,11]; locally, however, hydrothermal environments and adjacent waters would clearly have exhibited the highest NH$_3$ concentrations in the prebiotic world. After the genesis of life, hydrothermal environments would have continued to be oases, providing NH$_3$ to early life forms until the advent of enzymatic systems capable of reducing NO$_3^-$ and N$_2$ (ref. 22).

Last, these results on potential sources of ocean NH$_3$ must be factored into estimates of the NH$_3$ content of the Archaean atmosphere. Even low concentrations of atmospheric NH$_3$ could be of great importance to photolytically driven organic synthesis[1]. Furthermore, Sagan and Chyba[3] have demonstrated that an atmospheric mixing ratio of 10^{-5} for ammonia would have been sufficient, through greenhouse warming, to resolve the early-faint-Sun paradox. Maintenance of this mixing ratio over the first 10^9 years of the Earth would have required a supply of 1.4×10^{18} g NH$_3$ (ref. 3). These results indicate that mineral-catalysed synthesis of NH$_3$ could have met at least one-third of this requirement, with the possibility that all of the necessary supply could have been produced in this manner if one assumes a highly reducing lithosphere during the Hadean. □

Methods

All experiments were run in sealed, N$_2$-purged, acid-washed, pure gold tubes. Iron sulphide and iron-metal catalysts were prepared from semiconductor-grade metals and pure elemental sulphur, with elemental compositions verified by ion-probe analysis. Magnetite catalyst was a very pure natural sample of fumarolic origin[23], whereas the basalt used was a natural alkali basalt (65992, ref. 28). Solution phases added to N$_2$ reduction capsules were either distilled deionized water or mixtures of formic acid and water. Solutions phases for NO$_3^-$ and NO$_2^-$ were 5 mM in either distilled deionized water or low-nutrient sea water. Tubes were loaded, purged with N$_2$ gas, welded shut and incubated in an internally heated pressure vessel under argon-medium[24,25]. Tubes were opened, extracted with distilled water and analysed for NO$_3^-$, NO$_2^-$ and NH$_3$ by spectrophotometric methods[26,27].

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Quantification of dust-forced heating of the lower troposphere

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Aerosols may affect climate through the absorption and scattering of solar radiation and, in the case of large dust particles, by interacting with thermal radiation[1-3]. But whether atmospheric temperature responds significantly to such forcing has not been determined; feedback mechanisms could increase or decrease the effects of the aerosol forcing. Here we present an indirect measure of the tropospheric temperature response by explaining the 'errors' in the NASA/Goddard model/data-assimilation system. These errors, which provide information about physical processes