Abiotic ammonium formation in the presence of Ni-Fe metals and alloys and its implications for the Hadean nitrogen cycle

Alexander Smirnov*¹, Douglas Hausner², Richard Laffers¹, Daniel R Strongin² and Martin AA Schoonen¹

Address: ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11794, USA and ²Department of Chemistry, Temple University, Philadelphia, PA 19122, USA

Email: Alexander Smirnov* - asmirnov@ms.cc.sunysb.edu; Douglas Hausner - dugh@temple.edu; Richard Laffers - rlaffers@ic.sunysb.edu; Daniel R Strongin - dstrongin@temple.edu; Martin AA Schoonen - mschoonen@notes.cc.sunysb.edu

* Corresponding author

Abstract

Experiments with dinitrogen-, nitrite-, nitrate-containing solutions were conducted without headspace in Ti reactors (200°C), borosilicate septum bottles (70°C) and HDPE tubes (22°C) in the presence of Fe and Ni metal, awaruite (Ni₈₀Fe₂₀) and tetrataenite (Ni₅₀Fe₅₀). In general, metals used in this investigation were more reactive than alloys toward all investigated nitrogen species. Nitrite and nitrate were converted to ammonium more rapidly than dinitrogen, and the reduction process had a strong temperature dependence. We concluded from our experimental observations that Hadean submarine hydrothermal systems could have supplied significant quantities of ammonium for reactions that are generally associated with prebiotic synthesis, especially in localized environments. Several natural meteorites (octahedrites) were found to contain up to 22 ppm Ntot. While the oxidation state of N in the octahedrites was not determined, XPS analysis of metals and alloys used in the study shows that N is likely present as nitride (N³⁻). This observation may have implications toward the Hadean environment, since, terrestrial (e.g., oceanic) ammonium production may have been supplemented by reduced nitrogen delivered by metal-rich meteorites. This notion is based on the fact that nitrogen dissolves into metallic melts.

Introduction

Ammonia (NH₃) or ammonium (NH₄⁺), henceforth NH₃/NH₄⁺, are necessary precursors for reactions associated with prebiotic syntheses, such as the Strecker synthesis. It has been experimentally shown that NH₃/NH₄⁺ environments are more efficient in organic synthesis than those dominated by dinitrogen (henceforth N₂) in both aqueous and gaseous environments [e.g., [1]] [2,3]. This notion is not unexpected, considering that the strong triple bond (948 kJ/mol) of the N₂ would presumably result in large reaction activation barriers (i.e., low conversion rates), even if the overall reaction is thermodynamically favored.

Several possible pathways to abiotic NH₃/NH₄⁺ on early Earth have been proposed: reduction of NO₂⁻/NO₃⁻ by Fe³⁺/FeS in the ocean [e.g., [4]] [5,6]; atmospheric production from N₂ and HCN [e.g., [7]] [8]; release from rocks and minerals [e.g., [9]]; photoreduction on mineral surfaces [e.g., [10]] [11,12]; and hydrothermal aqueous reduction from N₂ in the presence of minerals under conditions typical of submarine hydrothermal systems [e.g.,...
Each of the mechanisms relies on a different set of assumptions and none of the proposed mechanisms has, in our opinion, gained universal acceptance in the scientific community as the predominant source of abiotic NH₃/NH₄⁺.

In this scientific contribution we focus on the catalytic properties of Ni and Fe metals and their alloys which can form in submarine hydrothermal systems (SHS), especially those driven by exothermic hydration reactions (e.g., serpentinization) in an off-axis tectonic setting. Upon dissolution of Ni-containing rock-forming minerals (e.g., olivine, pyroxene, amphibole), released Ni and Fe can react to form metals and alloys under extreme reducing conditions imposed on the system by the serpentinization processes [16-18]. The conditions are commonly reducing enough to stabilize Ni-Fe alloys (e.g., awaruite – Ni₃Fe), metallic nickel (Ni⁰) and even iron (Fe⁰). These minerals occur regularly, albeit in small quantities in both ancient and modern serpentinites [19-26]. A compilation of representative chemical analyses of metals and alloys found in serpentinites is presented in Fig. 1. The observations from natural systems have been corroborated by laboratory experiments [27,28].

An active global tectonic cycle is not required for the formation and operation of serpentinization-driven SHS and hence we assume that these environments were commonly present on the Hadean Earth. Moreover, the lack of oxygen and the possible presence of significant amounts of hydrogen gas in the Hadean atmosphere (and consequently in the ocean water) may have further enhanced the stability of base metals and their alloys [29,30].

The most abundant reactant for abiotic NH₃/NH₄⁺ formation in the Hadean was N₂ dissolved in the seawater from the N₂-rich atmosphere. NO₂⁻ and NO₃⁻ are also thought to have been available, although likely in low concentrations. These oxidized N species could have formed in high energy events such as lightning, corona discharge and/or impacts and subsequently rain out into the ocean [31-34].

In this contribution we report the results of an experimental study undertaken to evaluate the hypothesis that abiotic NH₄⁺ formation from dissolved N₂, NO₂⁻ and NO₃⁻ in the presence of Ni₃Fe, NiFe, Ni⁰ and Fe⁰ was an operative synthetic route at anaerobic conditions potentially present in the Hadean Ocean. Furthermore, we attempt to quantify global NH₄⁺ yields in the Hadean Ocean produced by investigated mechanisms.

Figure 1
A ternary diagram of naturally occurring Ni-Fe-M (M = Cr, Sb, Pb, Cu, Co, As, Ag, PGE) alloys and their comparison to synthetic alloys used in this study. Analyses of natural samples were adapted from: [19] [22] [109-115]. Each data point represents an electron microprobe analysis expressed in weight percent.
Methods and materials

Reduction experiments

Three sets of experiments were conducted at three different temperatures: 200°C (runs 1–36), 70°C (runs 37–59) and 22°C (runs 60–83). The choice of reactors was based on experimental temperature: 15 mL passivated HIP Titanium 64 tube reactors (200°C); 20 mL I-Chem borosilicate vials with PTFE/Si septum caps (70°C) and 15 mL BD HDPE Falcon tubes (22°C). Reactors were kept at constant temperature in a heated water bath (20, 70°C) or an Isotemp oven (200°C). All experiments lasted 24 hours and were conducted in the absence of headspace (e.g., no gas phase). No additional pressure other than that of expanding liquid was imposed on the vessels (~400 psi/27 bars with Ni0 to ~800 psi/55 bars with Fe0 at 200°C).

All reacting solutions were prepared from freshly drawn UV/LIF deionized water (henceforth DI) either by purging with a UHP gas of interest (e.g., Ar, N2, H2/N2) and/or by dissolving appropriate amounts of reagents. NH4+ content of all unreacted reagent solutions (e.g., blanks) was below the detection limit of ion chromatography (<0.1 μmol kg⁻¹) reported by the manufacturer). DI purged with N2 gas under ambient conditions results in equilibrium N2(aq) concentration of 0.59 mmol kg⁻¹. The effect of O2 was, however, also determined (runs 39, 41, 45, 47, 50, 52, 56, 58, 62, 64, 68, 70, 74, 76, 80, 82) in experiments with DI equilibrated with present-day atmosphere (e.g., no N2 purging).

To ensure clean and fresh mineral surfaces (e.g., free of oxidation products and/or atmospheric sorbed gases), all metal/alloys were ultrasonically cleaned for 1 hour in 0.06 M HCl immediately preceding the experiments. Subsequently they were washed three times with the designated reacting solution and loaded into reactors in the form of slurry. This "wet loading" procedure eliminated sorption of gases from the atmosphere onto freshly cleaned metal surfaces which was especially important in blank experiments.

Background NH4+ production (e.g., release from reactants, reaction vessels, etc.) was assessed in blank experiments. The pH was not buffered and was allowed to change as a result of solution-metal/alloy interactions and was recorded before and after the experiment. After pH measurements, all samples were acidified with 0.2 M HCl to ensure the conversion of NH3 to NH4⁺ and to prevent the formation of Fe precipitates. The samples were stored at 1°C and analyzed within 24–48 hours. The summary of all experimental conditions is presented in Tab. 1.

Analysis of solids, their surfaces, and reaction products

Metals and alloys representing an fcc solid solution of Ni in Fe were purchased from Alfa Aesar® and Goodfellow. All starting and selected reacted solids were characterized by X-Ray Diffractometry, X-Ray Photoelectron Spectroscopy, Scanning Electron Microscopy, B.E.T. surface analysis, and Electron Microprobe. The results of metal/alloy characterization are summarized in Tab. 1 and Fig. 2, 3.

X-Ray Diffractometry (XRD) data were collected using a Scintag PAD X diffractometer under the following conditions: CuKα1, 40 kV, 25 mA, 5°–90° 2Θ, step 0.02° 2Θ and variable scan rates.

Scanning Electron Analysis (SEM) was performed on the LEO 1550 SFEG scanning electron microscope equipped with an EDAX energy dispersive X-ray spectrometer (EDS) using an accelerating voltage of 15 kV and a 30 μm aperture.

Oxidation state of Ni, Fe and the presence of N in alloys were determined by X-Ray Photoelectron Spectroscopy (XPS). The data were acquired with unmonochromatized MgKα and AlKα radiation at 1253.6 eV and 1486.7 eV using a Physical Electronics source controller in a vacuum chamber with a base pressure of 1 × 10⁻⁹ Torr. A VG Microtech hemispherical analyzer was used to obtain the energy distribution of the photoemitted electrons at pass energies of 50 and 75 eV. The binding energies were calibrated by fixing the Au 4p3/2 and 4f7/2 peaks (546.3 eV, 87.5 eV) from a gold standard, and the metallic Fe 2p3/2 and Ni 2p3/2 cores (707.0 eV, 852.3 eV). Selected particles were sputtered with Ar⁺ accelerated to 2 kV to expose their inte-

Table 1: Physical and chemical characteristics of alloys/metals used in study. Formula and the “a” parameter determined from EPMA analyses and from LeBail refinement of XRD data, respectively. The chemical composition of Ni-Fe alloys was confirmed by EPMA as: Ni₉₄.₇₇Fe₂₉.₆₄(± 0.₄₉)Fe₁₀.ₒ₂(± 0.₄₉) and Ni₇₉.₁₄Fe₁₉.₇₁(± 0.₄₃)Fe₁₀.₉₆(± 0.₄₃).

| Metal/Alloy | Formula | Manufacturer | Surface Area [m²] | Space Group | Unit cell [Å] | Natural analog |
|-------------|---------|--------------|------------------|-------------|-------------|----------------|
| Iron        | Fe      | Alfa Aesar   | 0.6536 ± 0.0776   | Im-3m       | 2.866(1)    | Iron           |
| Nickel      | Ni      | Alfa Aesar   | 0.5044 ± 0.0309   | Fm-3m       | 3.523(1)    | Nickel         |
| Ni₂₅Fe₇₅   | NiFe    | Goodfellow   | 0.3685 ± 0.0094   | Fm-3m       | 3.586(3)    | Tetrataenite   |
| Ni₇₅Fe₂₅   | Ni₃.₇Fe | Goodfellow   | 0.1877 ± 0.0131   | Fm-3m       | 3.547(6)    | Awaruite       |
Table 2: Conditions and results of reduction experiments conducted in this study. All concentrations are in \(\mu\text{mol.kg}^{-1}\). Values and their errors bigger than 10 are rounded to the nearest whole number, those smaller than 10 are rounded to the nearest tenth.

| Metal/Alloy | Run | Solution | T°C | pH pre | pH post | \(\text{NH}_4^+\) \% | \(\text{NH}_4^+\) norm * | \(\text{NO}_2^-\)** | \(\text{NO}_3^-\)** |
|------------|-----|----------|-----|--------|---------|-------------------|-------------------|-------------------|-------------------|
| Fe         | 1   | Ar       | 200 | 5.7    | 9.9     | 171 ± 1           | 340 ± 21         | n.a.              | n.a.              |
| Ni         | 9   | Ar       | 200 | 5.8    | 8.7     | 18 -              | 27 ± 3           | n.a.              | n.a.              |
| Ni         | 15  | Ar       | 200 | 6.0    | 9.3     | 544 ± 7           | 833 ± 99         | 0                 | 0                 |
| Ni50Fe50   | 17  | Ar       | 200 | 5.8    | 8.6     | 18 -              | 98 ± 7           | n.a.              | n.a.              |
| Ni50Fe50   | 32  | Ar       | 200 | 5.8    | 8.6     | 18 -              | 98 ± 7           | n.a.              | n.a.              |
| Ni81Fe19   | 25  | Ar       | 200 | 5.7    | 7.9     | 19 ± 1            | 99 ± 7           | n.a.              | n.a.              |
| Ni81Fe19   | 26  | Ar       | 200 | 5.7    | 7.9     | 19 ± 1            | 99 ± 7           | n.a.              | n.a.              |
| Ni81Fe19   | 33  | Ar       | 200 | 5.7    | 7.9     | 19 ± 1            | 99 ± 7           | n.a.              | n.a.              |
| Ni81Fe19   | 43  | Ar       | 200 | 5.7    | 7.9     | 19 ± 1            | 99 ± 7           | n.a.              | n.a.              |
| Ni50Fe50   | 49  | Ar       | 200 | 5.7    | 8.2     | 12 ± 1            | 129 ± 2          | 129 ± 2          | 129 ± 2          |

*Note: n.a. = not available.
prior and check for the presence of nitrogen using a Physical Electronics ion gun controller.

B.E.T. surface analysis (BET) was performed using a Micromeritics ASAP 2010 analyzer with a 10-mm Hg transducer using UHP N2 gas. The surface area was calculated from measurements at 5 different N2(g) pressures (42.58196, 85.30770, 132.82384, 180.25029 and 227.66101 Torr).

Chemical composition of alloys/metals was determined by a Cameca Camebax Micro electron microprobe (EPMA) equipped with four wavelength dispersive spectrometers and a Kevex Analyst 8000 energy dispersive detector. During all analyses, the accelerating voltage and beam current used were 15 kV and 10 nA (nominal), respectively.

Molecular hydrogen was analyzed on a SRI 8610C single column gas chromatograph (GC) with a TCD detector, 6' Hayesep D column and N2 carrier gas. The sample (~0.2 mL) was withdrawn from the reaction vessel into a gas-tight Hamilton™ syringe with a Mininert™ valve and immediately analyzed using a 4-point calibration curve. Gas mixtures (Matheson™) of known composition were used as calibration standards.

Total nitrogen content of metals/alloys was analyzed by IMR Test Labs (Lansing, NY) by inert gas fusion [35]. During the analysis, N is released from the metal at 1900°C into the stream of He gas and analyzed in a thermal conductivity cell.

Experimental solutions were analyzed for NH4+ using a Dionex DX-500 ion chromatograph (IC) with a 100 μL sample loop. NH4+ and NO3-/NO2- were analyzed using a 4 mm Dionex IonPac® CS-16 (40°C, 34 mN H2SO4 eluent) and IonPac® AS4A-SC (22°C, 5 mmol.kg-1 Na2B4O7 eluent), respectively. Concentrations were calculated from a 4-point calibration curve with R² values above 0.99.

No other compounds were analyzed. It is expected, however, that other reaction products and/or intermediates (e.g., NO) may have formed during a complex sequence of electron transfer reactions.

Geochemical equilibrium modeling was performed with the Geochemist’s Workbench 5 [36] software package with the thermo.com.V8.R6.full thermodynamic database complemented with data for Ni3Fe and NiFe [37].

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**Table 2: Conditions and results of reduction experiments conducted in this study. All concentrations are in μmol.kg⁻¹. Values and their errors bigger than 10 are rounded to the nearest whole number, those smaller than 10 are rounded to the nearest tenth. (Continued)**

| Ni81Fe19 | 58 | 511 KNO3 in O2 | 70 | 6.7 | 8.6 | 35 | 6.8 | 186 ± 13 | 13 ± 1 | 425 ± 2 |
|----------|----|----------------|----|-----|-----|----|-----|----------|--------|--------|
| Fe       | 60 | Ar             | 22 | 5.7 | 6.4 | 0.7 | -   | 1.4      | n.a.   | n.a.   |
| Fe       | 61 | 650 N2         | 22 | 5.8 | 6.6 | 0.7 | 0   | 1.4      | n.a.   | n.a.   |
| Fe       | 62 | 541KNO3 in O2  | 22 | 6.2 | 10.8 | 544 ± 6 | 100 | 1078 ± 66 | 0     | 0      |
| Fe       | 63 | 549KNO3 in N2  | 22 | 6.0 | 10.6 | 542 ± 5 | 99  | 1075 ± 66 | 0     | 0      |
| Fe       | 64 | 529KNO3 in O2  | 22 | 6.4 | 10.5 | 527 ± 4 | 100 | 1044 ± 64 | 0     | 0      |
| Fe       | 65 | 521KNO3 in N2  | 22 | 5.9 | 10.8 | 486 ± 5 | 93  | 963 ± 59  | 0     | 0      |
| Ni       | 66 | Ar             | 22 | 5.7 | 6.9 | 0.4 | -   | 0.6      | n.a.   | n.a.   |
| Ni       | 67 | 650 N2         | 22 | 5.8 | 6.6 | 0.4 | 0   | 0.6      | n.a.   | n.a.   |
| Ni       | 68 | 541KNO3 in O2  | 22 | 6.2 | 10.6 | 422 ± 3 | 78  | 646 ± 77  | 0     | 0      |
| Ni       | 69 | 549KNO3 in N2  | 22 | 6.0 | 10.7 | 451 ± 5 | 82  | 690 ± 82  | 0     | 0      |
| Ni       | 70 | 529KNO3 in O2  | 22 | 6.4 | 10.2 | 139 ± 26 | 213 ± 25 | 43    | 36     |
| Ni       | 71 | 521KNO3 in N2  | 22 | 5.9 | 10.1 | 364 ± 1 | 70  | 557 ± 66  | 1.2    | 22     |
| Ni50Fe50 | 72 | Ar             | 22 | 5.7 | 6.3 | 0   | -   | 0        | n.a.   | n.a.   |
| Ni50Fe50 | 73 | 650 N2         | 22 | 5.8 | 6.3 | 0   | 0   | 0.6      | n.a.   | n.a.   |
| Ni50Fe50 | 74 | 541KNO3 in O2  | 22 | 6.2 | 6.8 | 1.4 | 0.3 | 3.9 ± 0.1 | 553 ± 2 | 0      |
| Ni50Fe50 | 75 | 549KNO3 in N2  | 22 | 6.0 | 7.7 | 1.1 ± 0.1 | 0.2 | 3.1 ± 0.1 | 556    | 0      |
| Ni50Fe50 | 76 | 529KNO3 in O2  | 22 | 6.4 | 7.2 | 0.8 | 0.2 | 2.1 ± 0.1 | 0      | 526 ± 1 |
| Ni50Fe50 | 77 | 521KNO3 in N2  | 22 | 5.9 | 7.3 | 1   | 0.2 | 2.7 ± 0.1 | 0      | 523 ± 2 |
| Ni81Fe19 | 78 | Ar             | 22 | 5.7 | 6.9 | 0   | -   | 0        | n.a.   | n.a.   |
| Ni81Fe19 | 79 | 650 N2         | 22 | 5.8 | 6.6 | 0   | 0   | 0.6      | n.a.   | n.a.   |
| Ni81Fe19 | 80 | 541KNO3 in O2  | 22 | 6.2 | 9.4 | 3 ± 0.1 | 0.6 | 16 ± 1    | 515 ± 2 | 0      |
| Ni81Fe19 | 81 | 549KNO3 in N2  | 22 | 6.0 | 9.3 | 1.9 ± 0.1 | 0.4 | 10 ± 1    | 539 ± 3 | 0      |
| Ni81Fe19 | 82 | 529KNO3 in O2  | 22 | 6.4 | 8.9 | 0   | 0   | 0.4      | 0      | 493 ± 1 |
| Ni81Fe19 | 83 | 521KNO3 in N2  | 22 | 5.9 | 9.0 | 1.9 ± 0.1 | 0.4 | 10 ± 1    | 0      | 482    |

"n.a." denotes "not analyzed," "-" not applicable. * denotes NH4+ concentration formed in the experiment normalized to 1 m² of surface area of the metal/alloy. ** denote residual concentration after the experiment was completed.
Results

Dinitrogen reduction

The results of NH$_4^+$ formation from N$_2$ and the effect of added H$_2$ and KCl at 200°C (normalized to 1 m$^2$ surface area) are shown in Fig. 4 and summarized in Tab. 1 (runs 1–32). All results are compared with respect to blank experiments conducted with Ar and no N$_2$ added. The blank experiments thus represent the background NH$_4^+$ production from the metal/alloy involved and reactor catalysis. Error bars were calculated by propagating errors from solution dilutions and B.E.T. and IC analyses. Due to relatively large error bars, only results differing from the blank (or each other) by more than the calculated error will be discussed.

In the presence of N$_2$, only Ni$_{81}$Fe$_{19}$ did not show appreciable activity toward NH$_4^+$ formation (Fig. 4d). Within our experimental certainty, Fe$^0$ was the material associated with the most NH$_4^+$ production (31 µmol.kg$^{-1}$.m$^2$, Fig.
4a), followed by Ni\textsuperscript{0} (16 μmol.kg\textsuperscript{-1}.m\textsuperscript{2}, Fig. 4b) and Ni\textsubscript{50}Fe\textsubscript{50} (7 μmol.kg\textsuperscript{-1}.m\textsuperscript{2}, Fig. 4c). H\textsubscript{2}(aq) was observed to form in the presence of all studied metals and alloys. Representative concentrations of H\textsubscript{2}(aq) at 200°C (measured in one experiment with N\textsubscript{2}-saturated, O\textsubscript{2}-free DI per metal/alloy only) were 0.38 mmol.kg\textsuperscript{-1} with Ni\textsuperscript{0}, 0.28 mmol.kg\textsuperscript{-1} with Ni\textsubscript{81}Fe\textsubscript{19}, 0.7 mmol.kg\textsuperscript{-1} with Ni\textsubscript{50}Fe\textsubscript{50} and 21 mmol.kg\textsuperscript{-1} with Fe\textsuperscript{0}. We point out that this H\textsubscript{2} production is relatively large compared to the background H\textsubscript{2} production of the Ti reaction vessels that was determined to be 12 μmol.kg\textsuperscript{-1} in an experiment with DI saturated with Ar at 200°C. An interesting observation during our experiments was that the reactivity of Fe\textsuperscript{0} towards O\textsubscript{2}-free DI was so rapid that gas bubbles were forming on its surface after just a few hours of exposure at 22°C (by analogy with 200°C experiments we assume it is H\textsubscript{2}).

Our results showed that the addition of H\textsubscript{2} (5%/95% H\textsubscript{2}/N\textsubscript{2}) into the reaction mixture only resulted in change in the Fe\textsuperscript{0} circumstance where 158 μmol.kg\textsuperscript{-1}.m\textsuperscript{2} NH\textsubscript{4}\textsuperscript{+} was produced (Fig. 4a). Fe\textsuperscript{0} was also the material most affected by the addition of K\textsuperscript{+} (KCl). In this case, 189 μmol.kg\textsuperscript{-1}.m\textsuperscript{2} of NH\textsubscript{4}\textsuperscript{+} was produced, 158 μmol.kg\textsuperscript{-1}.m\textsuperscript{2} more than with N\textsubscript{2} alone (Fig. 4a). In general, our experiments showed that Ni\textsubscript{81}Fe\textsubscript{19} was the least, and Fe\textsuperscript{0}, the most, affected by the addition of H\textsubscript{2} or KCl into the reacting solution (Fig. 4d, a).

Aqueous Fe and Ni cations (NiCl\textsubscript{2}, FeCl\textsubscript{2}) only had a small effect on N\textsubscript{2} reduction chemistry, converting about 1% of the total available N into NH\textsubscript{4}\textsuperscript{+} at 200°C (Tab. 1). A post-reaction visual inspection of the FeCl\textsubscript{2} solution showed a fine-grained colloid of reddish color that, in the presence of atmospheric O\textsubscript{2} changed color to light brown. The amount of recovered solids was insufficient for analysis by XRD.

At temperatures of 70 and 22°C no NH\textsubscript{4}\textsuperscript{+} formation from N\textsubscript{2} was observed (Tab 1, runs 38, 44, 50, 55, 61, 67, 73, 79). Use of these lower temperatures also resulted in
lower background NH$_4^+$ production in solutions containing the metals/alloys. The yield of NH$_4^+$ ranged from 7.4 (Fe$^0$) to 1.2 μmol.kg$^{-1}$.m$^{-2}$ (Ni$^{50}$Fe$^{50}$) at 70°C (Tab. 1, runs 37, 43, 49, 54) and 1.4 (Fe$^0$) to 0 μmol.kg$^{-1}$.m$^{-2}$ (Ni$^{50}$Fe$^{50}$, Ni$_{81}$Fe$_{19}$) at 22°C (Tab. 1, runs 60, 66, 72, 78).

**Nitrite and nitrate reduction**

The results of our NO$_2^-$ and NO$_3^-$ reduction experiments are shown in Fig. 5. At 200°C all tested metals/alloys were found to be very effective in converting NO$_2^-$/NO$_3^-$ into NH$_4^+$. To assess if the presence of NO$_2^-$ or NO$_3^-$ in the solution had any effect on N$_2$ reduction, each experiment was conducted in duplicate with Ar (Tab. 1, runs 7, 8, 15, 16, 23, 24, 31, 32) and N$_2$ (Tab. 1, runs 5, 6, 13, 14, 21, 22, 29, 30) saturated solutions (e.g., Fe$^0$ with NO$_2^-$/N$_2$ and NO$_2^-$/Ar). These experiments taken in sum showed that there was no difference between the N$_2$ and Ar runs (Fig. 5a).

The results collected at 70°C reveal prominent differences between alloys and metals (Fig. 5b). While Ni and Fe achieved almost 100% conversions of NO$_2^-$/NO$_3^-$ to NH$_4^+$ (Tab. 1, runs 40, 42, 46, 48), interestingly, no- or insignificantly reduced (less than 20%) was observed in solutions reacted with alloys (Tab. 1, runs 51, 53, 57, 59). The presence of O$_2$ in the solution appears to have an inhibitive effect on the reduction process, especially in the presence of Ni$_{81}$Fe$_{19}$ alloy (Tab. 1, runs 56, 58; Fig. 5b).

Low temperature experiments (22°C) further confirmed the temperature dependence of NO$_2^-$/NO$_3^-$ reduction in the presence of alloys (Fig. 5c). Compared to 200°C and even at 70°C, NH$_4^+$ formation was negligible (less than 1% conversion) (runs 63, 65, 69, 71, 75, 77, 81, 83). The effect of O$_2$ in the reacted solution was most pronounced with NO$_3^-$ in the presence of Ni$^0$ (run 70). In general, at 22°C Fe$^0$ was the most efficient material in converting NO$_2^-$/NO$_3^-$ to NH$_4^+$, regardless of the O$_2$ content (Tab. 1, runs 62–65; Fig. 5c).

It is important to note that at 200°C both NO$_2^-$ and NO$_3^-$ decomposed in the absence of metal/alloys as well (Tab. 1, runs 34, 34). 42% of the initial 497 μmol.kg$^{-1}$ KNO$_2$ solution was converted into NO$_3^-$ (~15%), NH$_4^+$ (~9%) and other N compounds (~18%) that were not analyzed. Of the initial 444 μmol.kg$^{-1}$ KNO$_3$ solution, 71% was converted into NO$_2^-$ (~61%), NH$_4^+$ (~1%) and about 9% corresponds to other unanalyzed N compounds. It is not clear if this is a result of thermally induced decomposition, catalysis or reaction by/with the titanium reaction vessel, or a combination of all; nevertheless, NH$_4^+$ was not the dominant reaction product. At 70 and 22°C, both NO$_2^-$ and NO$_3^-$ solutions were found to be stable in experiments without metals or alloys for the 24-hour reaction period.

**Figure 5**

NH$_4^+$ formation from nitrite and nitrate, expressed in terms of % conversion. Panels A, B and C correspond to sets of experiments at 200, 70 and 22°C, respectively.

**Metal/alloy alteration**

Generally, the extent of alteration of Fe-containing metal/ alloy increased with temperature, as demonstrated by the presence of secondary minerals (Fig. 6). Magnetite (Fe$_3$O$_4$) was the most abundant alteration product, predominantly forming euhedral to subhedral crystals up to several μm in size (Fig. 6a, b, d, e). Pseudomorphs of magnetite after reacted spherical Fe$^0$ particles were common (Fig. 6d). The second most common alteration phase were Fe-(oxy)hydroxides (e.g., lepidocrocite) usually of amorphous appearance or forming needle-like (Fig. 6c) and platy crystals several tens of nm thin and several μm long. Both magnetite and Fe-(oxy)hydroxides commonly occur simultaneously in all reacted samples (SEM) (Fig.
6a,b); however, only magnetite is identified by the XRD method (Fig. 7). This suggests that the Fe-(oxy)hydroxides either lack long range order (e.g., “X-ray amorphous”) and/or their abundance is less than 5%, the approximate detection limit of XRD. In general, the lower the Fe content, the lower the extent of alteration (Fig. 6e). In contrast, reacted Ni0 exhibited no microscale (SEM) evidence of reaction (Fig. 6f, compare with Fig. 3a), as corroborated by the XPS spectra documenting the presence of residual zero-valent Ni species on the surface (Fig. 8). As a result of solution interactions with metals/alloys, the resulting pH in most experiments was higher than the starting value (see discussion) (Tab. 1).

**Discussion**

**Nitrogen in alloys and metals**

All the metals and alloys investigated in this work were found to contain N, which resulted in a background production of NH₄⁺. The presence of atomic N was based on two lines of evidence: 1) The presence of the N1s peak in the XPS spectra of starting metals and alloys even after “cleaning” the surface by sputtering with Ar⁺ ions (Fig. 9) and; 2) quantitative analysis of N_{tot} content of the starting materials by inert gas fusion with a thermal conductivity detection (Tab. 3).

Commercially available Ni, Fe metals/alloys may contain N due to the manufacturing process which employs either inert (N₂, Ar) or reducing (NH₃, H₂) atmospheres to prevent oxidation [38,39] [Alfa Aesar, Goodfellow – pers.comm]. For example, during the synthesis, N₂ chemisorbs on the surface of molten/hot metal and dissociates (Equation 1).

\[
N_2 \text{(gas)} \rightarrow 2N \text{(in metal)} \quad (1)
\]
In the subsequent step N enters the structure via diffusion or convection to form primarily monoatomic interstitial and to lesser extent substitutional solid solutions. This process is governed by the Sievert’s law (Equation 2), which predicts that diatomic gases such as N$_2$ dissolve in metals ($c_N$) proportionally to the square root of the partial pressure ($p_{N2}$) in the coexisting gas phase [40,41].

\[
K = \frac{c_N}{p_{N2}^{1/2}}
\]  

Assuming homolytic N$_2$ bond cleavage, each N atom would have three unpaired electrons available for bonding with the surrounding metal atoms. XPS spectra collected from unreacted metals/alloys in our experiments point to nitride (N$_3^-$, 398.6 eV) as the likely N species (Fig. 9) [42]. Consequently, upon release into the solution, N$_3^-$ is expected to react with available protons to form NH$_3$/NH$_4^+$ (Reaction 3, 4) and contribute to their high background productivity.

\[
N_3^- + 3H^+ \rightarrow NH_3 \]  

(3)

\[
N_3^- + 4H^+ \rightarrow NH_4^+ \]  

(4)

However, undissociated N$_2$ gas may get trapped in the molten metal (e.g., in inclusions) as well.

**Dinitrogen reduction**

Although batch-type experiments, such as the ones described above, provide little insight into the kinetics of a reaction and much less the reaction mechanism, the results do allow one to compare the amount of NH$_3$/NH$_4^+$ formed under different conditions. In addition the results can be placed in the context of previously published research related to the reduction of N-species to NH$_3$/NH$_4^+$. Due to the immense importance of NH$_3$/NH$_4^+$ in industry and agriculture, several decades of research exist on its synthesis and production from N$_2$ gas [e.g., 43]. The industrial Haber-Bosch process utilizes Fe$^0$ catalyst at high temperatures and pressures (~500°C, ~100 bars) to synthesize NH$_3$ from H$_2$ and N$_2$ gas (Reaction 5).

\[
N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \]  

(5)

In brief, the reaction proceeds as follows: sorption of H$_2$ and N$_2$ gases on the surface is followed by the formation of atomic H$_{ads}$ and N$_{ads}$ (dissociative sorption). Fe$^0$ then facilitates electron transfer from H$_{ads}$ to N$_{ads}$ (e.g., N reduction), followed by the formation of NH$_3$ gas on the surface and subsequent desorption. The dissociative chemisorption of N$_2$ is generally taken to be the rate-limiting step [44]. For comparison, modern life overcomes the reaction’s activation barrier using the enzyme nitrogenase composed of dinitrogenase (MoFe center) and dinitrogenase reductase (Fe center) proteins. In Reaction 6, Fd stands for ferredoxin, the electron-transfer protein [45,46].

\[
N_2(g) + 8Fd^0_{red} + 10H^+ \rightarrow 2NH_4^+ + 8Fd^{+ox} + H_2(g) \]  

(6)

Analogous overall reactions of abiotic N$_2$ reduction can be written for aqueous solutions (Reaction 7, 8), although it is important to note that since this reaction requires a transfer of multiple electrons, several reaction intermediates must be involved. Once in solution, NH$_3$ and NH$_4^+$ exist in a pH dependent equilibrium (Equation 9; valid for 25°C).

\[
N_2(aq) + 2H^+ + 3H_2(aq) \rightarrow 2NH_4^+ \]  

(7)

\[
N_2(aq) + 3H_2(aq) \rightarrow 2NH_3(aq) \]  

(8)

\[
pH = 9.25 + \log \left( \frac{[NH_3]}{[NH_4^+]} \right) \]  

(9)

We hypothesize that reactions between H$_2$, N$_2$ and the metal/alloy surface are taking place in our experiments;
The thermodynamic equilibrium models predict NH$_4^+$ to be the dominant N species (Tab. 4). We speculate that in the presence of Fe$^0$ most of the NH$_4^+$ is provided by a number of processes, especially by Fe$^{2+}$ oxidation during alteration of rock-forming silicates [17,47].

| Mineral | T [°C] | pH | mNH$_3$ | mNH$_4^+$ | mN$_2$ | mH$_2$ | fNH$_3$ | fN$_2$ | fH$_2$ | Assemblage |
|---------|--------|----|---------|-----------|--------|--------|--------|--------|--------|------------|
| Nickel  | 200    | 6.95 | 6.4·10$^{-4}$ | 4.63·10$^{-5}$ | 2.47·10$^{-4}$ | 3.73·10$^{-5}$ | 1.24·10$^{-3}$ | 0.2769 | 0.24 | BN, NI |
| Nickel  | 70     | 8.92 | 1.00·10$^{-1}$ | 1.34·10$^{-4}$ | 2.2·10$^{-5}$ | 2.68·10$^{-7}$ | 9.98·10$^{-5}$ | 0.0477 | 3.68·10$^{-4}$ | BN, NI |
| Nickel  | 22     | 10.2 | 1.03·10$^{-1}$ | 1.34·10$^{-4}$ | 8.12·10$^{-4}$ | 2.18·10$^{-4}$ | 1.41·10$^{-5}$ | 0.0119 | 2.71·10$^{-5}$ | BN, NI |
| Awaruite | 200    | 7.07 | 1.12·10$^{-1}$ | 6.1·10$^{-4}$ | <1·10$^{-4}$ | 0.0597 | 2.16·10$^{-3}$ | <1·10$^{-8}$ | 38.54 | AW, MT, NI |
| Awaruite | 70     | 8.93 | 1.04·10$^{-3}$ | 1.37·10$^{-4}$ | <1·10$^{-4}$ | 0.0152 | 1.04·10$^{-4}$ | <1·10$^{-8}$ | 20.85 | AW, MT, NI |
| Awaruite | 22     | 10.2 | 1.05·10$^{-3}$ | 1.35·10$^{-4}$ | <1·10$^{-4}$ | 0.0103 | 1.44·10$^{-5}$ | <1·10$^{-8}$ | 12.82 | AW, MT, NI |
| Tetrataenite | 200 | 8.7 | 5.92·10$^{-4}$ | 7.96·10$^{-7}$ | <1·10$^{-8}$ | 0.0865 | 1.14·10$^{-3}$ | <1·10$^{-8}$ | 55.85 | AW, MT, TT |
| Tetrataenite | 70 | 8.93 | 1.04·10$^{-3}$ | 1.37·10$^{-4}$ | <1·10$^{-4}$ | 0.0222 | 1.04·10$^{-4}$ | <1·10$^{-8}$ | 30.51 | AW, MT, TT |
| Tetrataenite | 22 | 10.2 | 1.05·10$^{-3}$ | 1.35·10$^{-4}$ | <1·10$^{-4}$ | 0.0159 | 1.44·10$^{-5}$ | <1·10$^{-8}$ | 19.73 | AW, MT, TT |
| Iron | 200 | 7.07 | 1.15·10$^{-3}$ | 6.22·10$^{-5}$ | <1·10$^{-4}$ | 1.532 | 2.2·10$^{-3}$ | <1·10$^{-8}$ | 989.1 | MT, FE |
| Iron | 70 | 8.93 | 1.06·10$^{-3}$ | 1.38·10$^{-4}$ | <1·10$^{-4}$ | 0.785 | 2.05·10$^{-4}$ | <1·10$^{-8}$ | 1077 | MT, FE |
| Iron | 22 | 10.2 | 1.06·10$^{-3}$ | 1.36·10$^{-4}$ | <1·10$^{-4}$ | 0.623 | 1.45·10$^{-5}$ | <1·10$^{-8}$ | 771.5 | MT, FE |
| Goethite | 200 | 5.59 | <1·10$^{-8}$ | <1·10$^{-8}$ | 5.86·10$^{-4}$ | <1·10$^{-8}$ | <1·10$^{-8}$ | 0.6574 | <1·10$^{-9}$ | HM |
| Goethite | 70 | 6.1 | <1·10$^{-8}$ | <1·10$^{-8}$ | 5.86·10$^{-4}$ | <1·10$^{-8}$ | <1·10$^{-8}$ | 1.273 | <1·10$^{-9}$ | HM |
| Goethite | 22 | 6.22 | <1·10$^{-8}$ | <1·10$^{-8}$ | 5.86·10$^{-4}$ | <1·10$^{-8}$ | <1·10$^{-8}$ | 0.8475 | <1·10$^{-9}$ | HM |
| Magnetite | 200 | 6.08 | 1.04·10$^{-5}$ | 5.42·10$^{-4}$ | 5.82·10$^{-4}$ | 1.79·10$^{-6}$ | 2.0·10$^{-5}$ | 0.653 | 1.16·10$^{-3}$ | HM, MT |
| Magnetite | 70 | 8.47 | 1.26·10$^{-4}$ | 4.73·10$^{-3}$ | 5.04·10$^{-4}$ | 2.36·10$^{-6}$ | 1.25·10$^{-5}$ | 1.094 | 3.24·10$^{-5}$ | HM, MT |
| Magnetite | 22 | 9.97 | 3.1·10$^{-4}$ | 7.35·10$^{-3}$ | 3.98·10$^{-4}$ | <1·10$^{-4}$ | 4.26·10$^{-6}$ | 0.5759 | 3.32·10$^{-6}$ | HM, MT |
| Ferrhydrite | 200 | 5.59 | <1·10$^{-8}$ | <1·10$^{-8}$ | 5.81·10$^{-4}$ | <1·10$^{-8}$ | <1·10$^{-8}$ | 0.6512 | <1·10$^{-9}$ | HM |
| Ferrhydrite | 70 | 6.1 | <1·10$^{-8}$ | <1·10$^{-8}$ | 5.81·10$^{-4}$ | <1·10$^{-8}$ | <1·10$^{-8}$ | 1.261 | <1·10$^{-9}$ | HM |
| Ferrhydrite | 22 | 6.22 | <1·10$^{-8}$ | <1·10$^{-8}$ | 5.81·10$^{-4}$ | <1·10$^{-8}$ | <1·10$^{-8}$ | 0.8396 | <1·10$^{-9}$ | HM |

Abbreviations: BN = bunsenite, NI = Ni metal, AW = awaruite, MT = magnetite, TT = tetrataenite, FE = Fe metal, HM = hematite.

however, they are orders of magnitude slower than those described above in the gas phase. Undoubtedly, this is due to the fact that aqueous reactions occurring in our experiments are not only more complex but also take place at much lower T, P conditions and H$_2$/N$_2$ concentrations than those typical for Haber-Bosch synthesis. Such kinetic constraints could explain low NH$_4^+$ yields, even though the surface, reduces the availability of suitable H$_2$/N$_2$ sorption sites and the overall yield of the N$_2$-reduction reaction.

Fe + 2H$_2$O → H$_2$ + Fe$^{2+}$ + 2OH $\quad (10)$

This notion is corroborated by experiments carried out with conditions in which H$_2$ was present in the system from the start of the reaction (e.g., run 3), as a result of purging the solution with a H$_2$/N$_2$ mixture prior to loading (e.g., mH$_2$ > 0 at t$_0$). Abundant H$_2$ in this run correlates with greater NH$_4^+$ production as the overall N$_2$ conversion rate increases from 2.5 to 10% (Tab. 2). Assuming that in both cases Fe$^0$ surface passivates at the same rate, then the H$_2$ purged system produces more NH$_4^+$ per unit of time because it does not depend on the Fe$^0$ alteration process (Reaction 10) to provide H$_2$. This circumstance may be more typical of natural serpentinitization-driven SHS where H$_2$ can be provided by a number of processes, especially by Fe$^{2+}$ oxidation during alteration of rock-forming silicates [17,47].

Similar assumptions can be made about Ni$_81$Fe$_{19}$ and Ni$_{88}$Fe$_{12}$ assuming that Fe atoms exposed on the surface played a role in the reduction process. Due to good corrosion resistance, Ni$^0$ reacted to a much lesser extent and consistent with this lower activity is our experimental observation that the Ni$^0$ surface was not significantly altered (e.g., by precipitation of neoformed phases) throughout the experiment. Different modes of metal/alloy participation in studied reactions are discussed below.

The addition of KCl into the Fe$^0$-H$_2$O-N$_2$ system in our experiments resulted in higher NH$_4^+$ yield (Fig. 4a). While it may be intriguing to draw parallels with the Haber-Bosh process, where K is added to improve sticking coefficients and to help stabilize sorbed species [44], the apparent promoting effect of KCl may be partially or entirely caused
by the presence of chloride ion (Cl\textsuperscript{−}) in the solution. Cl\textsuperscript{−} can react with dissolved iron in the solution (Reaction 11) and remove products from the Fe\textsuperscript{0} dissolution reaction (Reaction 10).

\[
\text{Fe}^{2+} + 2\text{Cl}^{-} \rightarrow \text{FeCl}_2
\] (11)

Such a complexation reaction would result in an equilibrium shift towards the product side and further drive the dissolution process and release of structurally bound reduced N species into the solution (Reactions 3, 4). This is in agreement with the results of Reardon [48] who observed an increase in Fe\textsuperscript{0} corrosion rates in low ionic strength (~0.02 m) anaerobic NaCl, NaHCO\textsubscript{3} and Na\textsubscript{2}SO\textsubscript{4} solutions compared to DI water. The NH\textsubscript{4}\textsuperscript{+} content of the KCl reagent solution at concentrations used in our experiments was found to be below the detection limit of ion chromatography.

**Nitrite and Nitrate Reduction**

Due to their status as environmental contaminants, NO\textsubscript{2}\textsuperscript{−}/NO\textsubscript{3}\textsuperscript{−} reduction has been extensively studied, especially focused on the reduction of NO\textsubscript{3}\textsuperscript{−} by Fe\textsuperscript{0}. Most of the published results concur that the reduction reaction (Reaction 12) at anaerobic ambient conditions exhibits the following set of features: 1) reaction rates decrease with increasing pH; 2) pH in unbuffered solutions becomes more alkaline as the reaction progresses; 3) NH\textsubscript{4}\textsuperscript{+} and Fe\textsubscript{3}O\textsubscript{4} are the dominant reaction products; 4) NO\textsubscript{3}\textsuperscript{−} reduction slows down once Fe\textsuperscript{0} is coated with Fe\textsubscript{3}O\textsubscript{4} unless Fe\textsuperscript{2+}, Cu\textsuperscript{2+}, Al\textsuperscript{3+} or Fe\textsuperscript{3+} are present; 5) SO\textsubscript{4}\textsuperscript{2−} inhibits the reaction; and 6) the molar N\textsubscript{2}/NH\textsubscript{4}\textsuperscript{+} ratio in reaction products increases with pH [49-57].

\[
4\text{Fe}^0 + 10\text{H}^+ + \text{NO}_3^- \rightarrow \text{NH}_4^+ + 4\text{Fe}^{2+} + 3\text{H}_2\text{O}
\] (12)

\[
3\text{Ni}_2\text{Fe} + 4\text{NO}_2^- + 24\text{H}_2\text{O} \rightarrow 32\text{OH}^- + 4\text{NH}_4^+ + 3\text{Fe}^{2+} + 9\text{Ni}^{2+}
\] (13)

Analogous reactions can be written for other metals/alloys as well as NO\textsubscript{2} (Reaction 13), although they have been by comparison less studied. The absence of resonance structures in the NO\textsubscript{2} molecule makes it easier to reduce than NO\textsubscript{3} [58], which is reflected in reduction reaction rates. For example, NO\textsubscript{3} reduction to NH\textsubscript{4}\textsuperscript{+} in the presence of Fe\textsuperscript{2+} was found to be a factor of 8 slower than that of NO\textsubscript{3} [5]. Because the reduction from NO\textsubscript{3} to NH\textsubscript{4}\textsuperscript{+} requires transfer of at least 8 electrons, several intermediates must be formed in the process. Moreover, the formation of any N-N bonds must be avoided because it is effectively inert under all but the highest temperatures investigated here.

It is widely recognized, however, that NO\textsubscript{3} is a reaction intermediate in NO\textsubscript{3} reduction [e.g., [51]] [57,59]. For example, Wärna et al [59] proposed a reaction sequence from NO\textsubscript{3} and NO\textsubscript{2} through nitric oxide (NO), imidogen (HN) and aminyl radical (H\textsubscript{2}N\textsuperscript{¨}) to NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} on the surface of Fe\textsuperscript{0}. Several studies with NO\textsubscript{2}/NO\textsubscript{3} as well as some organic compounds suggest that Fe\textsuperscript{2+}, Fe\textsuperscript{0}, and Fe\textsuperscript{2+} sorbed on neoformed Fe minerals (e.g., magnetite) are likely electron donors for the reduction reactions [e.g., [60]] [61,62]. The intriguing consequence of such a reaction mechanism in natural systems is that precipitation of secondary (neoformed) Fe minerals further along the flow path followed by surface sorption of Fe\textsuperscript{2+} would provide additional reaction sites for the reduction of NO\textsubscript{2}/NO\textsubscript{3} [e.g., [63]].

**The role of alloys/metals**

Based on the XPS (oxidation state of Ni) and SEM (abundance of Fe- and the absence of Ni alteration phases) results it is possible to construct an order of apparent stability of studied alloys and metals

\[
\text{Ni}^0 > \text{Ni}_{81}\text{Fe}_{19} > \text{Ni}_{50}\text{Fe}_{50} > \text{Fe}^0
\]

where Ni\textsuperscript{0} is most- and Fe\textsuperscript{0} is least stable under the studied experimental conditions. This enables us to generalize that the higher the Fe content, the higher the reactivity towards potential oxidizing agents (e.g., H\textsubscript{2}O, NO\textsubscript{2}−, NO\textsubscript{3}−) and thus the higher extent of alteration. Metals and alloys typically undergo reductive dissolution (e.g., Reaction 10); however alloys frequently dissolve the less noble metal preferentially, leaving the surface enriched in the more noble metal [e.g., [64]]. For example, the reductive dissolution of Ni\textsubscript{50}Fe\textsubscript{50} alloys is expected to result in preferential release of Fe and a concomitant increase in the Ni:Fe ratio of the residual alloy.

Our findings are in agreement with metallurgical studies in which it has been demonstrated that Ni\textsuperscript{0} is more corrosion resistant than Fe\textsuperscript{0}, a notion that serves as a basis for their frequent alloying [38,65]. Unlike Fe\textsuperscript{0}, Ni\textsuperscript{0} reacts to a lesser degree in aqueous environments (reaction produces H\textsubscript{2} and Ni\textsuperscript{2+}), especially under reducing conditions. The presence of an oxidizing agent is usually required for significant corrosion; however, a protective oxide film may develop and impede further reactions [38,66]. Ni\textsuperscript{0} with a combination of catalytic properties and corrosion resistance (e.g., slow dissolution kinetics) may serve as a basis for a unique mechanism of N\textsubscript{2} reduction, where Ni acts both as a reactant and a catalyst. We hypothesize that Ni\textsuperscript{0} reacts with H\textsubscript{2}O to produce H\textsubscript{2}, a portion of which may stay adsorbed on the surface in its atomic form (H\textsubscript{ads}) (Reaction 14). If N\textsubscript{2} is also dissociatively chemisorbed (Reaction 15), surface-mediated reduction reactions may proceed (Reaction 16).

\[
\text{Ni} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_\text{ads} + \text{Ni}^{2+} + 2\text{OH}^-
\] (14)

\[
\text{Ni}^0 > \text{Ni}_{81}\text{Fe}_{19} > \text{Ni}_{50}\text{Fe}_{50} > \text{Fe}^0
\]
\[ \text{N}_2(aq) \rightarrow 2\text{N}_{\text{ads}} \quad \text{(15)} \]
\[ 2\text{N}_{\text{ads}} + 2\text{H}^+ + 6\text{H}_{\text{ads}} \rightarrow 2\text{NH}_4^+ \quad \text{(16)} \]

This set of reactions may operate until all plausible sorption sites are exhausted and/or deactivated. By analogy, we argue that if the experimental conditions were approaching the stability field of Fe metal (e.g., at sufficiently high \( f_{\text{H}_2} \)) it could behave in a similar manner.

There exist, however, "true" catalytic systems for \( \text{NO}_2^-/\text{NO}_3^- \) reduction, such as bimetallic Cu-Pt and Cu-Pd, Ag-Pd, Ag-Pt, which couple a noble metal and an oxidizable promoter. The reactions take place on the surface of Cu\(^0\) which acts as an electron donor for the reduction of N species and as an acceptor of electrons from dissociative sorption of \( \text{H}_2 \) on the surface of Pt [67,68]. Even though natural alloys of platinum group elements (Pt, Pd, Ir, Os, Rh, Ru) are scarce on modern Earth and are almost exclusively limited to magmatic segregation deposits, placers, and meteorites [e.g., [69]] [70,71], their significance for prebiotic synthesis should not be overlooked [72].

The predominantly alkaline pH in reacted samples (Tab. 2) is likely a result of several pH controlling reactions such as reductive dissolution of metals (e.g., Reaction 10), mineral formation (e.g., magnetite), and the buffering reactions involving charged species including, but not limited to \( \text{NO}_3^- \), \( \text{NO}_2^- \), \( \text{NH}_3 \), or \( \text{NH}_4^+ \). The fate of Fe\(^{2+}\) in the experiments reported here is difficult to constrain. Assuming completely anoxic conditions, temperatures below 85°C and a negligible \( p_{\text{CO}_2} \) in our experiments, \( \text{Fe(OH)}_2 \) (white rust) could precipitate (Reaction 17) and due to its instability serve as a precursor to other Fe oxides and hydroxides, most notably \( \text{Fe}_3\text{O}_4 \) (Reaction 18).

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \quad \text{(17)} \]
\[ 3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \quad \text{(18)} \]

At higher temperatures and/or in the presence of trace levels of \( \text{O}_2 \) or other oxidizing agents (e.g., \( \text{NO}_3^- \)), mineral intermediates such as green rust (mixed-valence hydroxide) may have been involved [e.g., [73]] [74,75].

The conversion of the original metal/ alloy into a new mineral phase (e.g., coatings) may not necessarily negatively affect the \( \text{NH}_3/\text{NH}_4^+ \) production. For example, wüstite (FeO) and green rust – both possible reaction intermediates such as green rust (mixed-valence hydroxide) may have been involved [e.g., [73]] [74,75].

Implications for the Hadean Earth

Different modes of metal/alloy participation have different implications for natural systems, especially in terms of the amount of metal/alloy required to achieve the same \( \text{NH}_3/\text{NH}_4^+ \) production. A catalyst remains stable during the reaction and therefore a small amount can, in theory, catalyze the formation of large amounts of \( \text{NH}_3/\text{NH}_4^+ \). Conversely, a reactant would have to be present in sufficient amounts and/or would have to be continually formed in order to achieve comparable \( \text{NH}_3/\text{NH}_4^+ \) production. While both mechanisms are plausible on the Hadean Earth, it is hard to assess which of the two would be prevalent. Based of equilibrium geochemical modeling, Smirnov [28] concluded that at 200°C Ni metal is stable at \( f_{\text{H}_2} \) orders of magnitude lower than Fe metal and even Ni\(_{50}\)Fe\(_{50}\) (tetrataenite) and Ni\(_{81}\)Fe\(_{19}\) (awaruite). Combined with results acquired from this study, it would appear that Ni metal is the most suitable candidate for a sustained long-term \( \text{NH}_3/\text{NH}_4^+ \) formation. Moreover, if we consider that the Hadean atmosphere may have had up to 30% \( \text{H}_2 \) [29], the primordial ocean would contain significantly higher concentrations of dissolved \( \text{H}_2 \) than today. In SHS, \( \text{H}_2 \) from advected seawater combined with \( \text{H}_2 \) formed by serpentinization could create conditions sufficiently reducing for stabilization of Fe containing alloys (e.g., awaruite, tetrataenite) and possibly even Fe\(^0\). Furthermore, as shown by Schoonen et al [72], seawater trapped in closed SHS (i.e., not open to seawater circulation) evolves to become extremely reduced as the partial pressure of hydrogen builds up.

The possibility of hydrothermal reduction of \( \text{N}_2 \) to \( \text{NH}_4^+ \) permits us to attempt to constrain the total \( \text{NH}_4^+ \) flux from Hadean off-axis SHS. The following set of assumptions and variables were taken into account:

1) The total heat production of the Hadean Earth was several times higher than today [81,82]. Because the exact value is unknown, we calculated scenarios for 2- to 8-times the present day heat flow (PDHF = 4.3 × 10\(^{13}\) W) [83] (Fig. 10); however, only values between 4 and 8 times PDHF are reported.

2) Because it is unclear if a global tectonic cycle was operational during the Hadean, we are unable to comment on the dissipation of Earth’s internal heat, especially on the percentage of heat released through SHS. Therefore, two endmember scenarios are considered: a) heat is dissipated predominantly via volcanism (possibly through several supervolcanoes) and only 5% is released through hydro-
thermal activity; and b) 80% of heat is dissipated predominantly through hydrothermal activity (Fig. 10). For comparison, presently about 20% of PDHF is released through hydrothermal activity [83].

3) Due to the increased heat flow and possibly due to the blanketing effect of the atmosphere [e.g., [84]], we assume the mean ocean water temperature to be 70°C. Although modern serpentinization-driven SHS commonly vent fluids below 100°C [85-87], we assume that the higher overall heat flow in the Hadean would also increase the fluid temperature of hydrothermal vents [e.g., [88]]. The temperature of the discharging fluid is thus assumed to be 200°C for the purpose of this calculation. Although the temperature of ambient seawater and of discharging fluid directly influences the total hydrothermal fluid mass flux (equation 19), their variations (± 20°C) only produced small changes in the final NH₄⁺ fluxes (usually within the same order of magnitude; data not shown). The heat capacity (cₚ) of hydrothermal seawater at 200°C and P ≈ 100–600 bar is 4.1 J⋅g⁻¹⋅K⁻¹[89].

4) Ocean water is assumed to be in equilibrium with 1 bar of N₂, resulting in a dissolved N₂(aq) concentration of 0.481 mmol⋅kg⁻¹ at 70°C [90]. For simplicity, no other gases and/or aqueous ions were taken into consideration.

5) Even though experimental results reported in this study suggest a conversion of N₂-to-NH₄⁺ 0.2 to 2.5% we calculate a variety of scenarios ranging from 0.1% to 10%. Although the 10% conversion may appear overly optimistic, our experiments suggest that the presence of advected H₂ and or K⁺ may significantly improve the NH₄⁺ production (Tab. 2; Fig. 4a). Metals/alloys may act as either catalysts or reactants, however, if metals/alloys do react, it must be assumed that the rate of their destruction (e.g., passivation, poisoning) is equal to their rate of formation (e.g., via serpentinization). It is important to point out that for simplicity, we do not distinguish between respective metals/alloys and we are only concerned with their capability to facilitate the conversion of N₂ to NH₄⁺ (in %).

The mass flux of seawater through hydrothermal systems (F) can be estimated from heat flux (H) in Watts, heat capacity of seawater (cₚ at 200°C) in J⋅g⁻¹⋅K⁻¹ and temperature anomaly ΔT in Kelvin [83]:

\[
F = \frac{H}{c_p \Delta T}. \quad (19)
\]

Using hydrothermal heat fluxes from Fig. 10 we can calculate annual seawater mass fluxes from SHS. Subsequently, using various N₂-to-NH₄⁺ conversion percentages (0.1 to 10%), annual NH₄⁺ production of Hadean SHS is calculated (Fig. 11). Assuming the most conservative scenario with 0.1% conversion of N₂ to NH₄⁺, the annual NH₄⁺ production would be between 5.9 × 10⁸ mol (4 × PDTH).

---

**Table 5: Total N content of four octahedrites analyzed by inert gas fusion (IMR Test Labs).**

| Sample                  | N TOTAL [wt.%] |
|-------------------------|----------------|
| Bogou Meteorite         | 0.0032 ± 0.0005|
| N’Goureyma Meteorite    | 0.0022 ± 0.0005|
| Sikhote Alin Meteorite  | 0.0032 ± 0.0005|
| Canyon Diablo Meteorite | 0.0022 ± 0.0005|

---

**Figure 10**

Hadean hydrothermal flow as a function of total Earth’s heat flow (expressed as multiplicities of present day heat flow – PDHF). Each data line thus represents percentage of the total heat flow released through hydrothermal systems at a given value of Hadean heat flow. The shaded area represents assumed realistic scenarios for the Hadean.

---

**Figure 11**

NH₄⁺ formation from N₂ in Hadean hydrothermal systems. Fluxes are calculated as a function of N₂ conversion between 1 and 10%. NH₄⁺ formation from NO₂⁻/NO₃⁻ is not included in these calculations.
and $1.2 \times 10^9$ mol (8 × PDTH) if 5% of Earth’s heat is removed via SHS and between $9.4 \times 10^9$ mol (4 × PDTH) and $1.9 \times 10^{10}$ mol (8 × PDTH) if 80% of heat is removed via SHS. Conversely, with a 10% N$_2$ conversion efficiency, the annual NH$_4^+$ production would be between $5.9 \times 10^9$ mol (4 × PDTH) and $1.2 \times 10^{10}$ mol (8 × PDTH) if 5% of heat is removed via SHS and between $9.4 \times 10^{10}$ mol (4 × PDTH) and $1.9 \times 10^{11}$ mol (8 × PDTH) if 80% of heat is removed by SHS (Table 5). To place these modeled fluxes in context we can compare their magnitude to those of other proposed NH$_3$ formation mechanisms (Fig. 11). An annual NH$_4^+$ flux at 1% conversion efficiency, for example, would be comparable to that based on a homogeneous reaction (Reaction 20) of Summers and Chang [4] or to the flux calculated by Brandes et al [13], which was based on NH$_3$ formation in the presence of various minerals between 300 and 800°C.

$$6\text{Fe}^{2+} + 7\text{H}^+ + \text{NO}_2^- \rightarrow 6\text{Fe}^{3+} + 2\text{H}_2\text{O} + \text{NH}_3$$ \hspace{1cm} (20)

Although we cannot comment on the total NH$_4^+$ content of the Hadean Ocean, we can estimate the contribution of hydrothermal N$_2$ reduction per unit of time. For timescales longer than 1 year, the following equation may be used (21):

$$\text{NH}_4^+ \text{addition to the ocean} = \frac{\text{annual NH}_4^+ \text{production}}{V_{\text{Hadean Ocean}}} \cdot t.$$ \hspace{1cm} (21)

NH$_4^+$ production in mol yr$^{-1}$ can be taken from Fig. 11 or Tab. 6 (or supplied from reader’s own sources), t denotes the time period in years and $V_{\text{Ocean}}$ is the total volume of Hadean Ocean in liters. We have calculated a scenario for one million years using the present-day global ocean vol-

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**Table 6: NH$_4^+$ formation from N$_2$ in Hadean hydrothermal systems. Fluxes (mol kg$^{-1}$ yr$^{-1}$) are calculated as a function of N$_2$ conversion between 1 and 10%. Note that NH$_4^+$ formation from NO$_2$/NO$_3$ is not included in these calculations.**

| N$_2$ conversion | Hadean heat flow (× PDHF) |
|-----------------|--------------------------|
| %               | 4                        | 5                        | 6                        | 7                        | 8                        |
| 0.1             | $5.9 \times 10^8$        | $7.3 \times 10^8$        | $8.8 \times 10^8$        | $1.0 \times 10^9$        | $1.2 \times 10^9$        |
| 0.5             | $2.9 \times 10^9$        | $3.7 \times 10^9$        | $4.4 \times 10^9$        | $5.1 \times 10^9$        | $5.9 \times 10^9$        |
| 1               | $5.9 \times 10^9$        | $7.3 \times 10^9$        | $8.8 \times 10^9$        | $1.0 \times 10^{10}$     | $1.2 \times 10^{10}$     |
| 2               | $1.2 \times 10^{10}$     | $1.5 \times 10^{10}$     | $1.8 \times 10^{10}$     | $2.1 \times 10^{10}$     | $2.4 \times 10^{10}$     |
| 5               | $2.9 \times 10^{10}$     | $3.7 \times 10^{10}$     | $4.4 \times 10^{10}$     | $5.1 \times 10^{10}$     | $5.9 \times 10^{10}$     |
| 10              | $5.9 \times 10^{10}$     | $7.3 \times 10^{10}$     | $8.8 \times 10^{10}$     | $1.0 \times 10^{11}$     | $1.2 \times 10^{11}$     |

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volume \((1.37 \times 10^{21} \text{ L})\) but alternative calculations can be quickly performed for different volumes (e.g., if the Hadean ocean had twice the volume of the present-day ocean, the \(\text{NH}_4^+\) concentrations in Fig. 12 and Tab 7 would be 50% smaller). For example, the conversion of 0.5% of \(\text{N}_2\) entrained in the advecting seawater would raise the \(\text{NH}_4^+\) content of the (completely homogenized) Hadean ocean by \(\sim 8 \text{ to } 17 \mu\text{mol.kg}^{-1} \times \text{PDHF}\) every 1 Ma (Tab 7). These results (Fig. 12, Tab 7) represent an upper contribution limit of this reaction, because no sinks (ion exchange, photooxidation, loss to the gas phase, formation of organic molecules, etc) were taken into account. In the absence of a comprehensive Hadean Nitrogen Cycle model, it is difficult to quantitatively assess the annual loss of \(\text{NH}_3/\text{NH}_4^+\) from the ocean; however, the numbers in Fig. 12, Tab 7 can be simply amended by assumption of loss expressed in %.

It is imperative to note that due to a large number of unknown and/or poorly constrained variables, these calculations should only be regarded as a first order approximation. However, it is clear that \(\text{N}_2\) reduction, albeit very inefficient, could have been a significant source of \(\text{NH}_4^+\), especially in localized environments.

Because \(\text{NO}_2^-/\text{NO}_3^-\) are inherently easier to reduce than \(\text{N}_2\), its presence in advected seawater could have significantly increased the annual \(\text{NH}_4^+\) hydrothermal flux. It is unclear; however, how much \(\text{NO}_2^-/\text{NO}_3^-\) would be advected into the crust, especially in the presence of such significant sinks as the reduction by \(\text{Fe(II)}\) [5]. While this process is a viable pathway to abiotic \(\text{NH}_3/\text{NH}_4^+\), its operation is dependent on atmospherically-driven processes of \(\text{NO}_2^-/\text{NO}_3^-\) formation as well as chemical composition of the Hadean Ocean, especially \(\text{pH}\) and \(\text{fH}_2\). A change in one of the parameters (e.g., a shift in oceanic \(\text{pH}\)) may have negatively affected or completely halted this pathway. We assume that serpentinization-driven SHS would have been less affected by changes in ocean water chemistry because their physico-chemical conditions (e.g., \(\text{pH}\), \(\text{fH}_2\)) are determined by fluid-rock interactions (e.g., availability of fresh rock) and possibly magmatic input rather than ocean composition. Moreover, the high temperature and pressure conditions combined with accumulations of suitable minerals would make these environments well suited for a long term, sustained \(\text{NH}_3/\text{NH}_4^+\) production on the Hadean Earth.

Besides facilitating the production of \(\text{NH}_3/\text{NH}_4^+\), metals and alloys in SHS may have been involved in other reac-

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**Table 7: Estimated increase in \(\text{NH}_4^+\) concentration of the Hadean Ocean (in \(\mu\text{mol.L}^{-1}\)) from the hydrothermal \(\text{N}_2\) reduction reaction per 1 Ma as a function of \(\text{N}_2\)-to-\(\text{NH}_4^+\) conversion percentages, heat flow and percentage of heat released via hydrothermal systems.**

| \(\text{N}_2\) conversion (%) | Hadean heat flow (× PDHF) | 4 | 5 | 6 | 7 | 8 |
|-----------------------------|---------------------------|---|---|---|---|---|
| 0.1                         | 0.4                       | 0.5 | 0.6 | 0.8 | 0.9 |
| 0.5                         | 2.1                       | 2.7 | 3.2 | 3.8 | 4.3 |
| 1                           | 4.3                       | 5.4 | 6.4 | 7.5 | 8.6 |
| 2                           | 8.6                       | 10.7 | 12.9 | 15.0 | 17.2 |
| 5                           | 21.4                      | 26.8 | 32.2 | 37.5 | 42.9 |
| 10                          | 42.9                      | 53.6 | 64.3 | 75.0 | 85.8 |

| \(\text{N}_2\) conversion (%) | Hadean heat flow (× PDHF) | 4 | 5 | 6 | 7 | 8 |
|-----------------------------|---------------------------|---|---|---|---|---|
| 0.1                         | 1.7                       | 2.1 | 2.6 | 3.0 | 3.4 |
| 0.5                         | 8.6                       | 10.7 | 12.9 | 15.0 | 17.2 |
| 1                           | 17.2                      | 21.4 | 25.7 | 30.0 | 34.3 |
| 2                           | 34.3                      | 42.9 | 51.5 | 60.0 | 68.6 |
| 5                           | 85.8                      | 107 | 129 | 150 | 172 |
| 10                          | 172                       | 214 | 257 | 300 | 343 |

| \(\text{N}_2\) conversion (%) | Hadean heat flow (× PDHF) | 4 | 5 | 6 | 7 | 8 |
|-----------------------------|---------------------------|---|---|---|---|---|
| 0.1                         | 6.9                       | 8.6 | 10.3 | 12.0 | 13.7 |
| 0.5                         | 34.3                      | 42.9 | 51.5 | 60.0 | 68.6 |
| 1                           | 68.6                      | 85.8 | 103 | 120 | 137 |
| 2                           | 137                       | 172 | 206 | 240 | 274 |
| 5                           | 343                       | 429 | 515 | 600 | 686 |
| 10                          | 686                       | 858 | 1030 | 1200 | 1370 |
tions potentially important for prebiotic synthesis. In the context of environmental science, for example, Fe⁰ was found to reduce nitrobenzene [91] or to facilitate reductive dehalogenation of carbon tetrachloride and chloroform [92-94]; Fe²⁺ sorbed on Fe(III) minerals decomposes nitrobenzene [60]. Our future research will also assess SHS as potential sinks of prebiotic molecules during the late Hadean/early Archaean.

The notion that N is commonly present in Fe⁰ in its reduced form presents a possibility of meteoritic delivery of reduced N species to Earth, especially during the periods of heavy bombardment. Fe⁰ and its alloys (e.g., tetrataenite, awaruite, kamacite) are among the dominant mineral phases in iron meteorites and to a lesser extent in stony-iron meteorites [e.g., [95]] [96-99].

To assess the possible importance of meteoric delivery of reduced N to Earth, we submitted four octahedrites for inert gas fusion analyses (IMR Test Labs, Lansing, NY). The meteorites – Bogou (IAB), Sikhote Alin (IIAB), Canyon Diablo (IAB), N’Goureyma (Ungrouped) [100-103] (Stony Brook University’s meteorite collection) contained 22 to 32 ppm of N_TOT (Tab. 5). Although these analyses provided no insight into the oxidation state or speciation of nitrogen in these meteorites, it is likely to be present predominantly in the form of nitride (N³⁻) as is the case in similar commercially available metals, alloys and known meteorite minerals (e.g., roaldite, carlsbergite). Hence in the following calculation we assume that all meteorite-associated nitrogen is present as nitride. Nitride would be readily released from meteorites after falling into the Hadean Ocean as a result of the rapid and complete dissolution due to inherent instability of Fe⁰ in aqueous solutions (even in O₂-free solutions). Aqueous nitride is expected to react quickly with protons to form NH₃/NH₄⁺. Similar scenario for meteoritic delivery of phosphorus has already been proposed by Pasek and collaborators [104,105].

To constrain the influx of meteoritic N to the Hadean Ocean we have adapted the meteorite flux values used by Pasek et al [104,105]: 2 × 10⁵ kg.year⁻¹ (current flux of iron meteorites to Earth; 50% of total meteoritic flux by weight) and meteoritic flux 10⁵-10⁶ times the present-day value during the Late Heavy Bombardment Period. Using these values we have created models for varying total reduced N content of iron meteorites: 5, 10, 15, 20, and 30 ppm. For comparison, average and median values for N_TOT from 91 published analyses [106,107] and four analyses acquired in this study were 20.1 and 12.3 ppm respectively.

The results presented in Fig. 13 show that during the Late Heavy Bombardment Period, iron meteorites could have delivered ~10³ to 10⁴ mol.yr⁻¹ of N_TOT to Earth which is approximately six to nine orders of magnitude less than our estimates for hydrothermal production (Fig. 11). Although the N influx was likely negligible on the global scale it is possible that crater lakes associated with iron meteorite impacts [108] may have contained significant concentrations of NH₃/NH₄⁺. Environments containing NH₃/NH₄⁺ and organic phosphorous compounds (e.g., phosphonates, organophosphates) from corroding iron meteorites ((Fe,Ni₃)P) [104,105] thus could have created very favorable, spatially-restricted conditions for prebiotic synthesis, perhaps unparalleled on the prebiotic Earth.

**Conclusion**

1) N₂ reduction to NH₄⁺ was found to be limited (up to 2.5% at 200°C) compared to NO₂⁻/NO₃⁻ (100% at 200°C)

2) Metals are more effective at reducing NO₂⁻/NO₃⁻ than alloys; NH₄⁺ is the dominant reaction product.

3) The reduction process exhibits a strong temperature dependence.

4) Fe⁰ and Ni⁰ were found to be least- and most resistant to alteration, respectively.

5) Ni⁰, Fe⁰, Ni₅₀Fe₅₀, Ni₈₁Fe₁₉ were found to contain up to 124 ppm of nitrogen in their structures, some of which is released upon dissolution and reacts to form NH₄⁺.
6) Serpentinization-driven SHS were likely important sources of abiotic NH$_3$/NH$_4^+$ in the Hadean Ocean.

Competing interests
The authors declare that they have no competing interests.

Acknowledgements
This research was funded by NASA Exobiology Program (grant NAG 513438) to Martin Schoonen. Francis Mc Cubbin is thanked for help with electron probe microanalysis. Matthew Wander’s (SBU) comments and 513438) to Martin Schoonen. Francis McCubbin is thanked for help with their valuable comments on an earlier version of this article. Dr. Ken B. Anderson is thanked for editorial handling of the manuscript.

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