

SPECIATION OF NITROGEN COMPOUNDS IN PLANETARY VOLCANIC GASES. M. Yu. Zolotov^{1,2} and E. Shock¹, ¹Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130-4899. E-mail: zolotov@zonvark.wustl.edu, shock@zonvark.wustl.edu, ²Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin str. 19, Moscow 117975, Russia.

Introduction: Nitrogen compounds are involved in numerous geochemical processes, and the speciation of nitrogen may have influenced early planetary, geological and biological evolution. Ammonia (NH₃) is a strong greenhouse gas that could have affected atmospheric temperature on early Earth and Mars [1,2]. Both ammonia and hydrogen cyanide (HCN) are involved in the Strecker synthesis of amino acids, which could proceed in early and/or present atmospheres, oceanic hydrothermal systems and volcanic gases [3-5]. Production of nitrous and nitric acids from nitric oxide (NO) could have a large effect on the oxidation state of early Earth's atmosphere and ocean [6,7]. Despite the predominance of molecular nitrogen (N₂) in volcanic/magmatic gases on the present Earth, magmatic degassing can contribute to the abundance of other forms of atmospheric nitrogen. Ammonia has been detected in volcanic gases and fumaroles [e.g., 8,9], however it is not clear whether NH₃ is degassed from the magma or is a contaminant, perhaps recycled from biological activity. Here we use thermochemical equilibrium calculations to constrain the speciation of nitrogen compounds in planetary/satellite volcanic gases under plausible ranges of temperature, pressure, oxygen fugacity (*f*O₂) and bulk composition.

Model: Assuming that thermochemical equilibrium exists at plausible temperatures for planetary silicate magmas, we calculated the speciation of the gas phase in the C-O-H-N-S-Cl-F system by the Gibbs free energy minimization method. Thermodynamic data for 123 ideal gases including 27 N-bearing species (N₂, NH₃, HCN, NO, NO₂, SN, HNCO, NH₂, HNC, C₂N₂, ClCN, CN, CN₂, FCN, HNO₃, N, N₂H₂, N₂O, N₂O₃, N₂O₄, N₂O₅, NCO, NH, NO₂Cl, NO₃, NOCl and NOF) were taken from [10]. The calculations were done from 1000-1600 K and 10⁻³ - 100 bars covering much of the plausible range of temperatures and pressures for planetary volcanic gases.

Calculations of this type require bulk composition constraints. In one example, we adopted the average composition of restored 1918-1919 Kilauea summit samples [11] as a nominal model for planetary volcanic gases. The relative elemental bulk composition for that model was taken as follows: C, 2.130; O, 8.898; H, 7.139; S, 1; Cl = F, 9.4 × 10⁻³ at the conditions of the quartz-fayalite-magnetite (QFM) buffer. The nominal elemental balance for N of 1.48 × 10⁻³ was calculated from the CO₂/N₂ molar ratio of ~720 in the present products of terrestrial degassing [12] by assuming that the abundance of CO₂ is 10%. The resulting mole fraction of N₂ in the nominal model is ~1.4 × 10⁻⁴.

To examine the ranges of possible oxidation states in planetary magmas, the *f*O₂ value was varied from iron-wüstite (IW), to one log unit above the Ni-NiO (NNO) buffer. The H/C ratio was varied from 10⁻⁶ to ~10 to model the speciation from water depleted (Venus, Moon, Mercury and Io) to water rich (Earth, Mars) gases.

Results: The calculations indicate the predominance of N₂ in all cases, and that the abundance of N₂ does not change significantly with T, P and *f*O₂. The most abundant microcomponents are: NH₃, NO, SN, HNCO, HCN, HNC, NH₂, NO₂ and NH.

Magma temperature only affects the relative abundances of NO, NO₂, SN, NH₂ and NH (Fig. 1a,b). Reduced conditions favor higher abundances of NH₃, HCN, NHCO, HNC and NH₂ (Fig. 1c). The mole fractions of nitrogen oxides increase with *f*O₂, and NO becomes the major microcomponent above QFM (Fig. 1c).

The abundances of NH₃ and other N- and H-bearing species increase with pressure (Fig. 2). With the exception of SN and NH₂, the abundances of these species are about linearly proportional to pressure.

Fig. 3 shows how the bulk H/C atomic ratio affects the equilibrium speciation. At H/C ratios of 10⁻² to ~10, corresponding to Earth and Mars, the abundance of H-, N-bearing gases remains relatively high. At H/C ratios below ~10⁻², corresponding to water depleted gases on Venus [13] and the Moon [14], NO and NS are the only nitrogen microcomponents with mole fractions > 10⁻¹⁵.

An increase in the elemental abundance of nitrogen and/or mole fraction of N₂ in a volcanic gas leads to increasing abundances of all N-bearing microcomponents. However, that increase is not linearly proportional to the abundance of nitrogen. In particular, the mole fractions of NH₃ and HCN are linearly proportional to the square root the mole fraction of N₂ (Fig. 4).

Discussion and Summary: (1) Our results reinforce the conclusion of Holland [15] that N₂ was almost certainly the dominant nitrogen species in the degassing products and atmosphere throughout terrestrial history. (2) At reduced conditions and high pressures, NH₃ and HCN can be produced in volcanic gases at relatively high abundances (up to ~10⁻⁵ for NH₃ and ~10⁻⁸ for HCN). At least some of these conditions could have existed during the early evolutionary stages of planets and satellites. In addition, volcanic gases may contribute NO at mole fractions of 10⁻⁹ to 10⁻⁷ to planetary atmospheres. At high bulk nitrogen content suggested for degassing products during early planetary evolution [12], the abundance of these and other N-bearing gases should have been higher. Our results place quantitative constraints on the abundances of these and other nitrogen species involved in abiotic synthesis of organic compounds. (3) Ammonia is detected in terrestrial volcanic/fumarolic gases at abundances higher than the calculated values, and may represent recycled biological material, consistent with conclusion from [9].

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Fig. 1. Equilibrium abundances of N-bearing volcanic gases as functions of temperature and oxidation state. Other gases considered have mole fractions $<10^{-14}$.

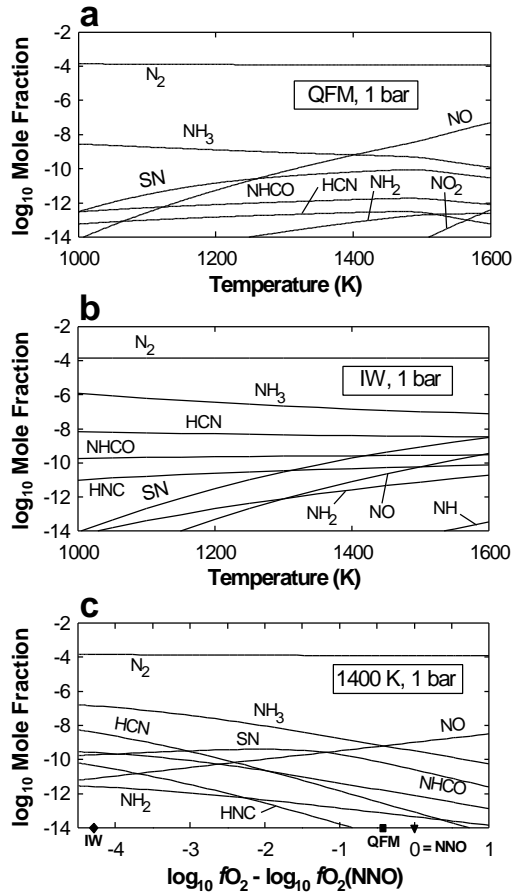


Fig. 2. The speciation of N-bearing gases as a function of total pressure.

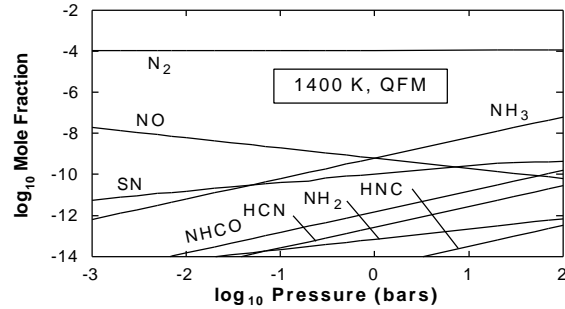


Fig. 3. The abundance of N-bearing gases as a function of the bulk H/C ratio. The condition of Venus's atmosphere is shown as a proxy for the H/C ratio in degassing products.

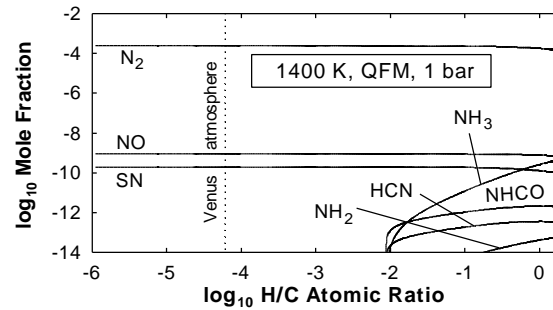


Fig. 4. The influence of the mole fraction of N_2 in volcanic gases on equilibrium abundance of NH_3 and HCN .

