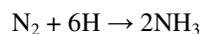


**The Role of Mo, V, (Fe, S) Substrates in Abiotic Nitrogen Fixation.** Alexander Smirnov, Matthew DeCesare and Martin Schoonen, Department of Geosciences, Stony Brook University, Stony Brook, NY 11794 and Astrobiology Biogeochemistry Research Center, Montana State University, Bozeman, MT 59717

Catalysis of nitrogen reduction reactions by mineral surfaces on the prebiologic Hadean Earth offers a plausible pathway to ammonia or ammonium ( $\text{NH}_3/\text{NH}_4^+$ ) required for synthesis of organic molecules, and ultimately the origin of life. The necessity of catalysis arises from high activation energy ( $E_A = 420 \text{ kJ mol}^{-1}$ ) of the otherwise thermodynamically favorable and exothermic dinitrogen ( $\text{N}_2$ ) reduction reaction to ammonia:



due to the presence of a N-N triple bond [1]. A variety of naturally occurring mineral surfaces have been experimentally tested to date, most recently Fe, Ni metals and their alloys [2]. The reported  $\text{N}_2$  to  $\text{NH}_3/\text{NH}_4^+$  yield in aqueous solution at  $200^\circ\text{C}$  is typically less than 2% (Industrial Haber process at higher T, P operates at about 15% efficiency per reaction cycle). To overcome this reaction barrier, some organisms (diazotrophs) evolved with the enzyme *nitrogenase* which facilitates the synthesis of biologically usable  $\text{NH}_3$  directly from  $\text{N}_2$ . This reaction is catalyzed with the assistance of one or more transition metal centers (Fe, Mo, or V) in the structure of the enzyme [3, 4].

In this contribution, we are focusing on the hypothesis that inorganic Mo, V, (Fe, S)-containing materials and their surfaces (Tab 1, Fig. 1) were able to facilitate abiotic nitrogen reduction reactions at conditions typical of the Hadean Ocean and thus preceded modern enzymatic systems.

Tab 1. Some of the Mo, V materials available for this study.

Substrate	Occurrence	Wt.%
Molybdenum metal	synthetic	100% Mo
Molybdenite ( $\text{MoS}_2$ )	natural, synthetic, common	~60% Mo
Vanadium metal	synthetic	100% V
Patronite ( $\text{VS}_4$ )	natural, synthetic, very rare	~28% V
V-Magnetite	natural, synthetic, common	~<1% V

Our preliminary results (Fig. 2) of hydrothermal experiments ( $200^\circ\text{C}$ ) suggest that both Mo and V metal successfully reduced some aqueous  $\text{N}_2$  into ammonium ( $48 \mu\text{mol/kg/m}^2 \text{NH}_4^+$  with V metal;  $12$

$\mu\text{mol/kg/m}^2 \text{NH}_4^+$  with Mo metal). Post-experimental analysis revealed the presence of secondary solid phases suggesting both metal participated as reactants, rather than catalysts. Both metals, especially Vanadium, exhibit very high background  $\text{NH}_4^+$  concentration caused by the commercial manufacturing process (e.g., thermal spray in  $\text{N}_2$  or  $\text{NH}_3$  atmospheres)[2]. We are currently experimenting with N-free in-house synthesis of these metals to minimize the  $\text{NH}_4^+$  background and expanding our experimental matrix.

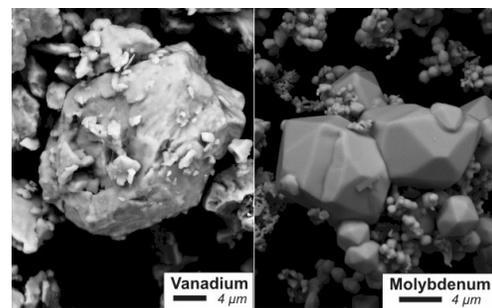


Fig. 1. SEM images of unreacted V and Mo metals

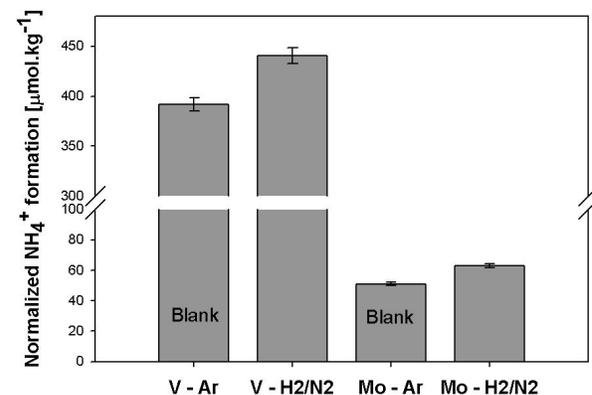


Fig. 2.  $\text{NH}_4^+$  formation in the presence of V and Mo metal in N-free, Ar-purged DI water (Blank) and  $5\% \text{H}_2/95\% \text{N}_2$ -purged DI water at  $200^\circ\text{C}$ . Note the net  $\text{NH}_4^+$  formation illustrated by the difference between the Ar- and  $\text{H}_2/\text{N}_2$  runs.

#### References:

- [1]Modak, J., *Resonance*, 2002. 7(9): p. 69-77.  
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