

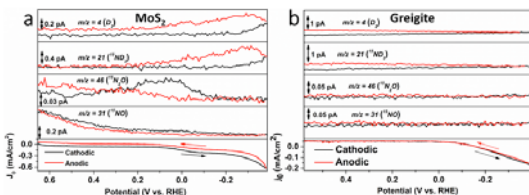
# Molybdenum bearing sulfide: A Prebiotic Catalyst for Dissimilatory Ammonia Synthesis with Geo-electrical Current

Y. LI<sup>1</sup>, A. YAMAGUCHI<sup>1</sup> AND R. NAKAMURA<sup>1\*</sup>

<sup>1</sup>Biofunctional Catalyst Research Team, CSRS, Riken, 2-1 HiroSawa, Wako, Saitama 351-0198, Japan (\*correspondence: [ryuhei.nakamura@riken.jp](mailto:ryuhei.nakamura@riken.jp), [yamei.li@riken.jp](mailto:yamei.li@riken.jp))

## Prebiotic denitrification

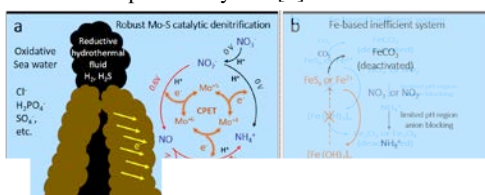
Probing the mechanism how nitrate and nitrite were reduced to ammonia by natural minerals is essential for the understanding of geochemical nitrogen cycles and early evolution of nitrogen metabolisms on the ancient Earth [1,2]. Recent model on geoelectrical current driven prebiotic synthesis makes possible that less abundant transition metals could play a significant role. Here we report [3] that the reduction of nitrate/nitrite can be effectively catalyzed by molybdenum disulfide within wide pH region, with nitrogen oxides and ammonia as the main products, as analyzed using on-line electrochemical mass spectroscopy.



**Figure 1:** on-line electrochemical mass method for detection of products during nitrite reduction by using  $\text{MoS}_2$  and  $\text{Fe}_3\text{S}_4$  as catalysts. Isotope labeled  $\text{D}_2\text{O}$  and  $^{15}\text{NO}_2^-$  were utilized.

## Mechanisms

A concerted proton electron transfer feature in edge  $[-\text{Mo}(\text{S}_2)_2^-]$  cluster was clarified, which resembles the Mo-S<sub>2</sub> pterin cofactors in nitrate reductase enzymes, indicating a probable evolutionary link between inorganic  $\text{MoS}_2$  and denitrification proto-enzymes [3].



**Figure 2.** Denitrification by  $\text{MoS}_2$  in primitive ocean.

[1] Summers (2005) *Orig. Life Evol. Biosph.* **35**, 299–312. [2] Orge et al. (1974) *Acc. Chem. Res.* **7**, 368–377. [3] Yamei Li, Akira Yamaguchi, Ryuhei Nakamura, et al., in preparation.