

EVIDENCE FOR SORPTIVE FRACTIONATION OF AMINO ACIDS ONTO IRON OXYHYDROXIDES AT MID-ATLANTIC RIDGE HYDROTHERMAL VENTS

Aryani SUMOONDUR¹, Christian OSTERTAG-HENNING² and Andrea KOSCHINSKY³

1. School of Earth & Environment, University of Leeds, Leeds LS2 9JT, UK

2. Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover D-30655, Germany

3. Geosciences and Astrophysics, International University Bremen (IUB), Bremen D-28759, Germany

Large deposits of ferrihydrite, an amorphous Fe-oxyhydroxide, are formed at hydrothermal vent sites as hot Fe rich vent fluids mix with oxic seawater. Due to its fine grain size and large surface area, ferrihydrite is very reactive. Its sorptive capacity for metals and dissolved organic matter (DOM) in a variety of natural environments is well documented. At hydrothermal vents, ferrihydrite acts as a sink for trace metals, metalloids and other elements such as P and Si, which are incorporated into the mineral phase via coprecipitation in the hydrothermal plume or by sorptive scavenging. However, the impact of sorptive processes on the abundance and distribution DOM is largely unknown at hydrothermal vent sites.

Dissolved Free Amino Acids (DFAAs) play a vital role in the biogeochemical processes occurring in hydrothermal vent environments. DFAAs function as an energy source to vent-dwelling organisms and, through their metal-chelating side chains, they can form stable complexes with free metal ions which are found in elevated concentrations in hydrothermal fluids, thereby controlling the speciation and thus bioavailability and toxicity of the metals to the vent fauna. Scavenging of DFAAs by iron oxide phases may however reduce their bioavailability and also modify their metal binding capacity. An experiment was therefore designed in order to investigate the effect of sorption on the abundance and distribution of proteinogenic amino acids (AAs) by reacting synthetic ferrihydrite with a mixture of 19 proteinogenic AAs at seawater pH.

The results indicate that ferrihydrite has a high affinity for AAs as a third of the total AAs in solution were sorbed onto ferrihydrite. The sorption kinetics of the AAs to ferrihydrite was rapid as the adsorption equilibrium was established within the first 5 minutes of the experiment. Ferrihydrite scavenged the AAs differentially; the acidic AAs, aspartic and glutamic acids were the most influenced by sorption, with a net loss of 88 % and 69 % respectively (Fig. 1). On average, the order of removal of AAs from solution by ferrihydrite was as follows: acidic > neutral > basic. The selective sorption can thus be correlated to the side groups of the AAs, where negatively charged carboxylate groups adhere preferentially to the positively charged mineral surface, resulting in a sorptive fractionation effect.

This effect might explain the distinct distribution of AAs observed at Mid-Atlantic Ridge (MAR) vent sites. Seawater samples with variable amounts of hydrothermal fluid were collected during the cruises M64/1 and M64/2 of RV Meteor which targeted the Logatchev hydrothermal field, lying at 14°45'N and newly discovered vent fields at 4-11°S along the MAR. The DFAA distribution pattern was marked by a depletion of acidic AAs while neutral AAs glycine and serine were dominant at all study sites. A similar compositional profile was observed for the total dissolved hydrolyzable AAs measured in hydrothermal vent fluids at the Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean (Horiuchi *et al.*, 2004).

The combination of field and experimental data indicate that the sorptive scavenging of DOM and resulting fractionation may be a universal phenomenon at hydrothermal vent sites and imply that sorptive scavenging of DOM by iron oxyhydroxides acts as a major control on the composition and abundance of DOM at marine environments. Furthermore, the removal of AAs by mineral phases implies the loss of a potentially important source of energy for vent organisms as mineral associated OM is less bioavailable. On the other hand, the sorption of AAs and other organic compounds might enhance the uptake of trace metals by the mineral phases by the formation of ternary complexes, hence detoxifying the milieu.

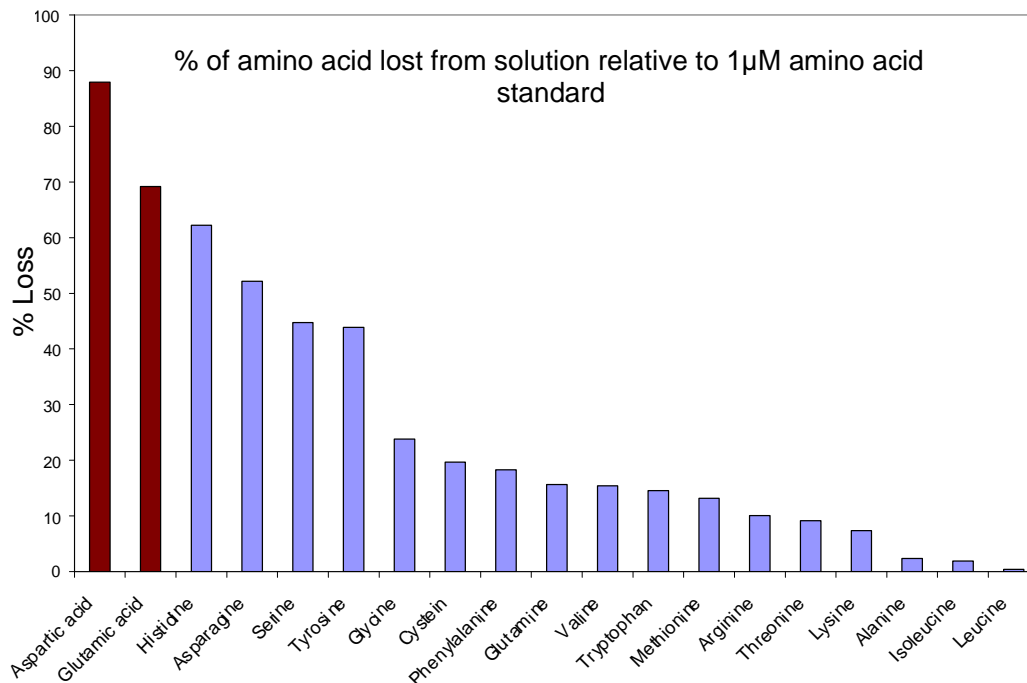


Figure 1. Sorptive fractionation of amino acids onto synthetic ferrihydrite

REFERENCES

- Horiuchi, T., Takano, Y., Ishibashi, J., Marumo, K., Urabe, T., Kobayashi, K., 2004. Amino acids in water samples from deep sea hydrothermal vents at Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean. *Organic Geochemistry* 35, 1121-1128.