

Probing siderophore-mineral interaction using force measurements

T.A. KENDALL¹ AND M.F. HOCELLA, JR¹

¹Dept. of Geological Sciences, Virginia Tech,
Blacksburg, VA, 24061 (tkendall@vt.edu)

Introduction

The involvement of siderophores in the dissolution of Fe containing minerals is well documented [1-4]. Recent studies explore the effect of siderophores on the sorption of actinide and heavy metals [5], further emphasizing their role in mediating the availability of Fe, other nutrients, and contaminants in soils. Our work employs a novel chemical force microscopy (CFM) technique that measures the forces of interaction between a siderophore and a mineral at the nano-to picoNewton level. Using these force signatures, we hope to obtain further insight into the mechanism by which siderophores release iron (and potentially other metals) from mineral surfaces.

Methods and Results

Azotobactin, a 1.3 kDa pyoverdine-type siderophore, was covalently attached to a hydrazide-activated AFM tips using a standard protein linkage reaction. Force measurements were then made between these tips and two minerals: goethite and its isostructural Al equivalent diaspore. Adhesion forces between azotobactin and the goethite surface (4.46±/−0.09 nN) were consistently 2-3 times the forces measured on the Al-oxide surface (1.52±/−0.12 nN) under the same solution conditions. Force magnitudes varied under different pH and ionic strengths, however, the relative force relationship associated with goethite and diaspore remained intact. Further, the large adhesion forces observed between the azotobactin and goethite surface could be suppressed upon the addition of soluble ferric iron, and partially regenerated with subsequent addition of high concentrations of EDTA.

Conclusions

We conclude that force signatures collected with this CFM technique reflect a specific interaction between azotobactin and goethite that correlates with azotobactin's large affinity for aqueous Fe(III). Future investigation will attempt to identify the primary azotobactin functional groups involved during this surface interaction, and explore force signatures associated with other siderophores.

References

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Alkanes with a quaternary carbon centre: a 2,200 Myr. record of sulfide oxidizing bacteria

F. KENIG¹, D.-J.H. SIMONS¹, D. CRICH², J.P. COWEN³,
G.T. VENTURA¹, T.C. BROWN¹ AND T. REHBEIN¹

¹University of Illinois at Chicago, Earth and environmental
Sciences, m/c 186, Chicago, Illinois 60607, USA
(fkenig@uic.edu)

²University of Illinois at Chicago, Dept. of Chemistry, m/c
111, Chicago, Illinois 60607, USA (dcrich@uic.edu)

³University of Hawai'i, SOEST, Department of
Oceanography, 1000 Pope Road, Honolulu, HI 96822,
USA (jcowen@soest.hawaii.edu)

Novel branched alkanes with quaternary substituted carbon atoms (BAQCAs) identified in hydrothermal waters escaping the ODP site 1026B on the flanks of the Juan de Fuca ridge (Northeast Pacific) are biosynthetic and occur in non hydrothermal modern and ancient sediments as old as 2,200 Myr. These hydrothermal lipids are dominated by families of 2,2-dimethylalkanes (2,2-DMAAs) and 5,5-diethylalkanes (5,5-DEAs) with exclusively even and odd number of carbon atoms, respectively. These compounds (C₁₅ to C₂₆) were identified on the basis of their mass spectra. The structure of 5,5-diethylpentadecane (**I**), was verified by chemical synthesis of an authentic standard.

To determine if the paleobiogeographic range of the source organisms of BAQCAs extends beyond hydrothermal systems, the distribution of 5,5-DEAs was monitored in samples spanning the last ~800 Myr. of the sedimentary record. This record was extended to ~2,200 Myr. using the geochemical literature for gas chromatography-mass spectrometry data that indicate the presence of 5,5-DEAs. These compounds are present in the branched and cyclic hydrocarbon fraction of the lipid extracts of thermally immature Cenomanian and Turonian black-shales (Cretaceous, Canada) and other Mesozoic and Paleozoic shales where they were previously misidentified as 3,7-dimethylalkanes. 5,5-DEAs were also observed in extracts of Proterozoic shales, microbial mats, and were released by hydrogenolysis of ~1.5 and ~2,200 Myr. pyrite (Mycke et al., 1988). 2,2-DMAAs and 5,5-DEAs were also identified in modern and Holocene shelf sediments from the Russian Arctic and Abu Dhabi (UAE). The paleobiogeographic range of BAQCAs appears consistent with a bacterial microaerophilic sulfide oxidizing source.

References

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Appendix

