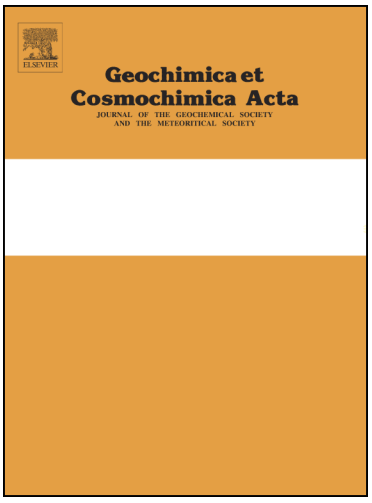

Geochemistry of Al and Fe in freshwater and coastal water colloids from the west coast of Southern Africa

Bjorn P. von der Heyden, Matthew G. Frith, Steven Bernasek, Tolek Tylizszak, Alakendra N. Roychoudhury, Satish C. B. Myneni

PII: S0016-7037(18)30496-4
DOI: https://doi.org/10.1016/j.gca.2018.08.043
Reference: GCA 10916

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 28 September 2017
Accepted Date: 29 August 2018

Please cite this article as: von der Heyden, B.P., Frith, M.G., Bernasek, S., Tylizszak, T., Roychoudhury, A.N., C. B. Myneni, S., Geochemistry of Al and Fe in freshwater and coastal water colloids from the west coast of Southern Africa, *Geochimica et Cosmochimica Acta* (2018), doi: https://doi.org/10.1016/j.gca.2018.08.043

Geochemistry of Al and Fe in freshwater and coastal water colloids from the west coast of Southern Africa

Bjorn P. von der Heyden[a,*], Matthew G. Frith[b, c], Steven Bernasek[c], Tolek Tylizszak[d], Alakendra N. Roychoudhury[a], Satish C. B. Myneni[b]

a. Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa

b. Department of Geosciences, Princeton University, Princeton, NJ 08544, USA.

c. Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

d. Advanced Light Source, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, USA.

* Corresponding author. Email: bvon@sun.ac.za

Phone: +27 21 808 3122

Abstract

Suspended iron-rich colloids play an important role in nutrient and contaminant transport in fluvial systems, and may ultimately provide an important source of Fe which is required for marine biological productivity. Despite being fundamental to Fe colloid behaviour in biogeochemical systems, the physical and chemical characteristics of these colloids are poorly constrained, especially at the molecular level. Here we combine traditional chemical extraction techniques with X-ray Absorption Near-edge Structure (XANES) spectroscopy to investigate and compare the bulk and molecular-level speciation of Fe and Al in suspended colloids from fluvial (Berg, Olifants and Orange Rivers) and marine sampling sites on the western margin of Southern Africa. The bulk extraction methodology shows a variable distribution of Fe among five different operationally-defined Fe pools, yet our spectroscopy results reveal that the majority of particles in the 10 nm – 4 µm size fraction do not match crystalline or residual Fe spectral signatures and are thus likely to be poorly-crystalline. Aluminium K-edge XANES reveals that the Al coordination environment in aquatic colloids is diverse (e.g., relative to oxo ligands, the number of coordinated OH^- ligands ranges between 0 – 6), and that the smallest sized colloids are always highly hydroxylated (i.e., their coordination environment is similar to Al in $Al(OH)_3$ or 1:1 clays). The Al XANES further reveals a common association between Al and Fe-rich colloids, where the average measured Al/Fe ratio is 0.10 (± 0.09) among all the particles measured in this study. The Al that co-occurs with Fe preferentially has a coordination environment similar to Al in 1:1 clays (i.e., two oxo ligands and four hydroxyl ligands), either further implying the