Highly siderophile elements in the early Earth: A story told by Barberton komatiites

I.S. PUCHTEL^{1*}, R.J. WALKER¹, C. ROBIN², N.T. ARNDT², E. NISBET³, C. ANHAEUSSER⁴ AND G. BYERLY⁵

¹University of Maryland, College Park, MD 20742, USA (*correspondence: ipuchtel@umd.edu)

²LGCA, Universite de Grenoble, Grenoble 38400, France
³Royal Holloway, University of London, TW20 0EX, UK
⁴University of Witwatersrand, Johannesburg, South Africa
⁵Louisiana State University, Baton Rouge, LA 70803, USA

High-precision highly siderophile element (HSE) data for Archean komatiites afford unique information regarding the early history of the Earth. In this study, we obtained, using state-of-the-art Carius tube digestion technique coupled with isotope dilution thermal ionization mass-spectrometry and inductively coupled plasma mass spectrometry techniques, high-precision HSE abundances and Os isotopic data for representative sets of well-preserved samples from three temporal groups of komatiites from the early Archean Barberton Greenstone Belt (BGB) and, using a previously established protocol, calculated relative and absolute HSE abundances in their respective mantle sources. The absolute HSE abundances progressively increase from the ca. 3.6 Ga Schapenburg through the ca. 3.5 Ga Komati, to the ca. 3.3 Ga Weltevreden sources, which contain, e.g. ~30%, 45%, and 70%, respectively, of Os abundances in the projected sources for the 2.7 Ga Abitibi and Belingwe komatiites. Further, the degree of fractionation of the relative HSE abundances in the projected sources, as compared to Primitive Upper Mantle, progressively decreases with decreasing age. These new data may be reconciled within several scenarios. (1) Involvement of different mechanisms of formation for these komatiites, such as hydrous melting of a mantle wedge in an early Archean subduction zone, re-melting of a majorite-enriched mantle domain formed during solidification of a terrestrial magma ocean, and anhydrous batch melting of ambient mantle in deep, extremely hot mantle plumes. (2) Substantial heterogeneity of the terrestrial mantle with respect to HSE abundances, during the early Archean, caused by incomplete vertical and/or lateral homogenization of large planetesimals accreted to the Earth as late veneer after the last major interaction between the core and the mantle. (3) Failure of our protocol to accurately gauge source concentrations. None of these mechanisms alone can fully explain the available geological, geochemical, and isotopic data for the BGB komatiites.

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pH dependent proton reactivity of rough LPS on live cells

DAN PUDDEPHATT¹ AND SUSAN GLASAUER²

¹School of Environmental Science, The University of Guelph. (dpuddeph@uoguelph.ca)

The surface charges of soil particles including bacteria can affect the mobility and retention of metal ions in solution. The pH dependant charges of the proton reactive groups (PRGs) in rough lipopolysaccharides (LPS) of live bacteria were evaluated using a non-ideal competitive adsorption (NICA) model. This was done by titrating suspensions of the model organism Shewanella putrefaciens CN32 between pH 4 and pH 9. A plot of the titration pH as a function of the change in pH resulted in two peaks, indicating the presence of two PRGs with adsorption coefficients consistent with phosphoryl and carboxyl groups. The parameters of the NICA model provide insight into the relative site occupancy of PRGs [1]. We observe that there exists a continuum of bonding arrangements to the PRGs. Unlike the planar and discrete charge distribution of mineral faces, the carbon-carbon single bonds of membrane molecules extending into the solution are flexible. They contain both positive and negative charges. There is also a strong electrostatic effect on total membrane charge indicating the importance of swarming protons in the Donnan phase.

Charged surfaces can facilitate adsorption of cells to mineral nutrients [2] and can be important for metal sequestration. This research provides a fresh perspective on the reactivity of the whole cell with metal ions.

[1] Koopal, Saito, Pinheiro, and van Riemsdijk (2005), *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **265**, 40 – 54. [2] Glasauer, Langley, and Beveridge (2002), *Science* **295**, 117 – 119.

²School of Environmental Science, The University of Guelph. (glasauer@uoguelph.ca)