Arsenic mobility in a stream affected by acid mine drainage (SW Spain)

A. PARVIAINEN[1]*, A.M. SARMIENTO[2],
D. SÁNCHEZ-RODAS[2] AND J.M. NIETO[2]

[1]Helsinki University of Technology, Geoenvironmental Technology Section, PO Box 6200, 02015-TKK, Finland (*correspondence: annika.parviainen@tkk.fi)
[2]Universidad de Huelva, Dpto. Geología, Campus del Carmen, 21071 Huelva, Spain

The Agua Agria Creek is severely affected by acid mine drainage (AMD) derived from waste rock heaps and tailings of the Tharsis sulfide mining district, SW Spain. 14 surface water samples were collected from two joining creeks during two sampling campaigns in September 2006 and June 2007 to study arsenic speciation by high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry (HPLC-HG-AFS) [1] and to assess the metal concentrations by inductively coupled optical emission spectroscopy (ICP-OES). Corresponding river sediments were drawn for mineralogical studies by scanning electron microscope (SEM) and X-ray diffraction (XRD).

In the first section of the creek, As III/V ratio was close to one with less than 100 μg/L As, whereas in the joining effluent, As(V) dominated and As concentrations varied from 745 μg/L to up to 4971 μg/L. Iron presented similar species distribution: predominantly Fe(II) (16-60 mg/L) in the first section and generally dominating high concentrations of Fe(III) (660-1700 mg/L) in the second section. Elements associated with sulfides, Cd, Co, Cu, Ni and Pb, showed high concentrations, especially in the second section of the creek.

Upon Fe(II) oxidation, Fe(III) may precipitate absorbing and co-precipitating arsenic and heavy metals. Schwertmannite, $Fe(III)_{16}O_{16}(OH)_{12}(SO_4)_2$, and ageing product, more stable goethite, Fe(III)O(OH), were detected in the river sediments. When retained in Fe precipitates arsenic content in surface water is expected to decrease. Yet, in Agua Agria Creek As content increases drastically downstream as a result of continuous sulfide oxidation in the creek. Due to seasonal rains, fine-grained tailings have been washed into the river basin enhancing AMD. Natural attenuation by formation of Fe precipitates does not sufficiently decrease the load of contaminants in the creek, and contamination of the estuary continues.

[1] Sánchez-Rodas *et al.* (2006) *Anal Bioanal Chem* **384**, 1594–1599.

Phosphorus redox chemistry on the early Earth: Clues to biochemistry

MATTHEW A. PASEK[1]*, TERENCE P. KEE[2],
DAVID E. BRYANT[2], DANTE S. LAURETTA[1],
H. JAY MELOSH[1], ALEX A. PAVLOV[1]
AND JONATHAN I. LUNINE[1]

[1]1629 E. University Blvd. Tucson AZ 85721 (*correspondence: mpasek@lpl.arizona.edu)
[2]School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

The redox state of phosphorus (P) on the earth is generally considered to be 5+ as phosphate. We present here evidence that a substantial portion of the total crustal P on the early earth was instead in reduced forms like phosphite (HPO_3^{2-}). We base this claim on the high impact rate on the early earth which delivered abundant schreibersite, on the discovery of phosphite in fulgurites, and on thermodynamic models of large impacts which suggest phosphate in impact melts is reduced. Furthermore, the oxidation of this reduced phosphorus on the early earth by oxidants like H_2O_2 forms abundant condensed phosphates which are critical to the development of life.

Phosphite is one of the major soluble corrosion products of meteoritic phosphides. In addition to phosphite from meteorites, P from six fulgurites from around the globe was extracted and analyzed by ^{31}P NMR. In all six samples, a sizeable portion (10-70%) of P was in phosphite. Additionally, our calculations suggest large impacts produce highly reactive glass droplets with a portion of P as phosphite, and would have been distributed all across the surface of the early Earth.

We also present oxidation studies of reduced P. Phosphite was oxidized on the early earth to form condensed phosphates like pyrophosphate ($P_2O_7^{4-}$), triphosphate ($P_3O_{10}^{5-}$) and trimetaphosphate ($P_3O_9^{3-}$). These phosphates could have phosphorylated organic compounds to form necessary precursors for life.