Application of CSIA for evaluating the fate of chlorinated compounds in low permeability sediments

 $\begin{array}{c} R. \ ARAVENA^{1*}, B. L. \ PARKER^2, G. \ LIMA^3, S. \ CHAPMAN^4 \\ AND \ D. \ ADAMSON^5 \end{array}$

 ¹University of Waterloo, Waterloo, Ontario, Canada (*correspondence : roaraven@uwaterloo.ca)
 ^{2,4}University of Guelph, Guelph, Ontario, Canada
 ³University of Toronto, Toronto, Ontario, Canada
 ⁵GSI Environmental, Houston, Texas, USA

Clayey and silty aquitards are natural barriers that can protect aquifers at sites impacted by DNAPL contamination, with the degree of protection depending on geologic, hydrogeologic and geochemical characteristics. The most effective aquitards are those in which contaminant transport is diffusion controlled, provided the aquitard is sufficiently thick (>20 ft or so) to prevent diffusive breakthrough. If the aquitard is thin but unfractured, upward hydraulic gradients and/or chemical or biological degradation may be required to prevent diffusive breakthrough. The purpose of this presentation is to discuss the state of the art of the science relevant for evaluating processes of contaminant distribution and fate in clay aquitards with emphasis on the application of CSIA.

Two sites contaminated with chlorinated compounds were used in the investigation. A high resolution monitoring network, aquitard cores, microbiological tools and CSIA were used to evaluate the distribution and fate of the contaminants in the aquifer and the aquitards.

VOC's concentration profiles showed the highest concentration of parents and daughter products are observed near the aquitard and difussion was controlling contaminant transport in the aquitards. Much lower concentration or no VOC's were observed in the underlying aquifer at both sites. The isotope data showed that biodegradation was also controlling the VOC's concentration in the aquitard. The microbial data is also in agreement with the isotope data. Results of the detailed investigation confirmed the aquitard at both sites has apparently good integrity, therefore no or minor impact in the underlying aquifer is expected at the study sites.

Tracing perturbations in the oxygenation of the Cenozoic ocean using Molybdenum isotopes

COREY ARCHER¹, SUNE NIELSEN², KEVIN BURTON³ AND JAMES R. HEIN⁴

¹Institue of Geochemistry and Petrology, Dept. of Earth Sciences, ETH Zurich, Switzerland (corey.archer@erdw.ethz.ch)

- ²Dept. of Geology and Geophysics, Woods Hole Oceanographic Institution, MA, USA
- ³Department of Earth Sciences, Durham University, Science Labs, Durham, UK
- ⁴US Geological Survey, 400 Natural Bridges Dr., Santa Cruz, CA, USA

In recent years studies of Mo and its isotopes have come to the fore as indicators of palaeoredox conditions of the Earths atmosphere and oceans. Particular interest has focussed on tracing the evolution of the oxygenation of the atmosphere and oceans during key periods of Earths history such as the Great Oxidation event¹, or the resultant changes in ocean chemistry during the Proterozoic Eon². By contrast few studies have focussed on changes in oceanic redox conditions through the Cenozoic, with existing data suggesting that essentially constant, and modern like redox conditions have prevailed for the last 60-70 Myr³. This observation is perhaps surprising considering evidence for substantial changes to the oceanatmosphere system at the start of the Cenozoic^{e.g.4}.

Here we present new Mo isotope data from a well dated Pacific Ocean ferromanganese crust, potentially unique tracres of ocean chemistry, spanning the entire Cenozoic. Our data shows a small but significant 0.3% ($\delta^{98/95}$ Mo) positive Mo isotope anomaly from modern ferromanganese crust values starting at the beginning of the Cenozoic, and lasting for much of the Cenozoinc before returning to modern values. These data therefore imply a Cenozoic ocean with a heavier Mo isotope composition than the present day. The Mo isotope anomaly is consistent with the processes inferred to have caused major changes in seawater sulphur and thallium isotopes during the Early Cenozoic^{4,5}, and indicates that marine ferromanganese precipitation and organic carbon burial rates were significantly higher and lower, respectively, in the Early Cenozoic than present day.

[1] A.D. Anbar et al, Science, 2007, 317, 1903. [2] G.L.
Arnold et al, Science, 2004, 304, 87. [3] C. Siebert et al, 2003, Earth Planet. Sci. Lett. 211, 159. [4] U.G Wortmann & A.
Paytan, 2012, Science 337, 334. [5] S.G. Nielsen et al, 2009, Earth Planet. Sci. Lett. 278, 297