Isotopic and sequence stratigraphic constraints on the duration of Neoproterozoic cap carbonate deposition

KENNEDY, M.J. CHRISTIE-BLICK, N.

Department of Earth Science, University of California,
Riverside, Riverside, CA 92527 USA
martink@mail.ucr.edu
Lamont Doherty Earth Observatory of Columbia University,
Palisades NY 10964 USA ncb@ldeo.columbia.edu

The timing and duration of strongly negative excursions in the δ^{13}C record have featured prominently in the current debate about Neoproterozoic glacial and associated carbonate rocks, and we think they represent the key. Positive carbon isotopic values were obtained from *in situ* peloids, ooids, and stromatolitic carbonate within Neoproterozoic glacial successions in northern Namibia, central Australia, and the North American Cordillera suggesting that the glacial oceans had normal marine carbon isotopic composition. Positive values are present at the base of postglacial cap carbonates, but become increasingly negative upward before returning to positive values in the overlying highstand sediments. These data constrain the negative excursion to the postglacial interval. Timing of the negative excursion and the anomalous alkalinity flux the cap carbonate records is possible in outcrop exposures in the Amadeus Basin of central Australia where the deposition of the cap carbonate can be compared to the rate of isostatic rebound recorded in the stratigraphic architecture that developed as a Neoproterozoic ice sheet withdrew. By analogy with modern rates of isostatic rebound, deposition of the cap carbonate occurred on the order of 10,000 y. This short duration argues for mechanisms that call on reorganization of pre-existing alkalinity within the oceans (the turnover models), or rapid release of alkalinity (clathrate model). These data argues against a silicate weathering origin for the cap carbonate as called on in the snowball Earth hypothesis because that hypothesis requires unrealistic weathering rates of 1000 times preglacial rates.

Modeling the influence of variable pH on zinc contamination in a quartz-sand aquifer

D. B. KENT[1], J. A. WILKIE[2], G. P. CURTIS[1], J. A. DAVIS[1]

[1]USGS, Menlo Park, CA, 94025, USA, (dbkent@usgs.gov,
gpcurtis@usgs.gov, jadavis@usgs.gov)
[2]ENVIRON International Corp, Deerfield, IL, 60015 USA,
(jwilkie@Environcorp.com)

A field-scale transport experiment was conducted to examine critical issues in modeling the influence of variable pH on the transport of strongly adsorbing metal ions. The experiment was conducted in a shallow aquifer that had been contaminated by 60 years of discharge of effluent from a sewage treatment facility serving a military base (USGS research site on Cape Cod, Massachusetts, USA). Groundwater velocities were approximately 0.4 meters per day. Uncontaminated groundwater with 2 mM chemically inert bromide (Br), added as potassium Br (KBr), and acidified to pH 4.5 by equilibrating with carbon dioxide was injected into a region where the pH was 6.0 and the aquifer was contaminated with dissolved and adsorbed sewage-derived Zn and phosphate (P). The tracer cloud induced fluctuations in pH, Zn, and other solute concentrations. For example, 2.4 meters downgradient from the injection, a decrease in pH from 5.9 to 4.9 coincided with breakthrough of Br and alkalinity. Increases in Zn concentrations from approximately 2 to 45 μM coincided with the decrease in pH. Following Br breakthrough, alkalinity and Zn concentrations returned to near-ambient values but pH increased more slowly, during which time P concentrations increased then decreased to ambient values (approximately 40 μM), and fluctuations in K, Na, and Ca concentrations were observed. The magnitudes of these fluctuations decreased with increasing transport distance except for alkalinity, which first increased then decreased with transport distance. Principal objectives of reactive transport modeling are to predict the influence of temporal variations in pH on Zn concentrations and transport using laboratory batch and column experiments for model calibration and to examine the trade-off between model parsimony (i.e., using the simplest reaction networks) and the ability to predict propagation of the pH pulse through the aquifer and its influence on Zn transport. A 2-site semi-empirical surface complexation model predicts the influence of the pH fluctuation on Zn concentrations during peak breakthrough but additional reactions are required to account for attenuation of the pH pulse, increase in alkalinity with transport distance, and the slow return of pH to ambient values following breakthrough of Br. Addition of surface protonation reactions improves prediction of the pH-pulse-attenuation and increase in alkalinity with transport distance but cannot predict the tail in the pH pulse. Work in progress involves assessing the relative contribution of ion exchange reactions and P adsorption to the evolution of pH during the transport experiment.