

Carbonate concretions as a window to the evolving chemistry of the early ocean and atmosphere

T. LYONS¹, R. RAISWELL², A. ROBINSON¹, C. SCOTT¹, X. CHU³, C. LI¹, G. LOVE¹, A. SESSIONS⁴ AND B. GILL¹

¹Department of Earth Sciences, University of California, Riverside, CA, USA (timothy.lyons@ucr.edu)

²School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK (raiswell@earth.leeds.ac.uk)

³Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China (xlchu@mail.igcas.ac.cn)

⁴Division of Geological & Planet. Sciences, California Inst. of Tech., Pasadena, CA, USA (als@gps.caltech.edu)

Ellipsoidal calcium carbonate concretions with diameters ranging up to meter-scale are common in organic-rich shales throughout the Phanerozoic. These features arise through early (pre-compactional), highly localized cementation. This precipitation is catalyzed by enhanced alkalinity production and corresponding carbonate supersaturation linked to bacterial sulfate reduction (BSR) with concomitant anaerobic oxidation of organic matter (OM) and/or methane. Identical features are well expressed in the upper portions of the late Neoproterozoic Doushantuo Formation in south China, which shows trace metal enrichments consistent with increasing oxygenation of the ocean and atmosphere.

Several factors are important in the formation of large, distinct, shale-hosted concretions, including (1) availability of sulfate as an electron acceptor for BSR, (2) pore-water saturation states that are strongly elevated relative to ambient bottom water, and (3) sites of decaying OM that act to initiate localized cementation. Each of these conditions was likely well established by the late Neoproterozoic, when sulfate delivery to the ocean increased through greater oxidative continental weathering while pyrite burial decreased, and carbonate saturation decreased in the global ocean well below the hypersaturated conditions of the earlier Proterozoic. With decreasing ambient saturation, localized cementation became more likely and easier to sustain in response to sharp concentration gradients. Also, the Neoproterozoic advent of fecal pellet production enhanced the delivery of labile OM to the seafloor. This study seeks to explore the relationship of these late Neoproterozoic examples to carbonate concretions described from earlier Precambrian units. The paleoceanographic implications of older "concretions" can be obscured by the frequently generic use of the term to describe masses that differ in mineralogy, morphology, and likely mode of formation compared to those of the late Neoproterozoic/Phanerozoic. The suggestion is that the upper Doushantuo and equivalent strata may mark the beginning of Phanerozoic-style ocean chemistry as expressed in concretion formation, implied carbonate saturation, metal enrichments, and perhaps other tracers of the evolving biosphere.

Hydrochemistry of four tropical watersheds in central Panama

W. B. LYONS¹, R. S. HARMON², H. MITASOVA³, I. FÓRIZS⁴ AND A. DEMÉNY⁴

¹Ohio State University, Columbus, OH, USA

²Army Research Office, Research Triangle Park, NC, USA

³North Carolina State University, Raleigh, NC, USA

⁴Hungarian Academy of Sciences, Budapest, Hungary

Surface waters from 4 watersheds in central Panama that have similar pristine source regions in steep mountainous tropical rain forest, but are affected by different downstream land-use practices were sampled for major element chemistry during the dry season in 2005 and 2006. The bedrock geology of the region consists of Upper Cretaceous to Tertiary age basalts, basaltic andesites, gabbros, and diorites plus less-abundant granodiorites, tonalities, and plagiogranites. The Rio Pacora (374 km²) watershed is developed on gabbro-dioritic lithologies, whereas the Upper RioChagres (580 km²), Rio Pequini (281 km²), and Rio Cuango (175 km²) are formed on mixed terrains consisting of hydrothermally altered andesite, mafic-intermediate volcanic rocks, and minor felsic intrusive lithologies.

Overall, δD and $\delta^{18}O$ values for the Chagres region waters fall on the Global Meteoric Water Line without systematic d-excess change, suggesting that the H and O isotope variations are governed by air mass trajectories rather than altitude or topographic effects. There is a geospatial trend in Cl that mirrors the NE-SW precipitation gradient across the region. Low-order streams in the Pacora watershed have distinctly higher TDS values plus H₄SiO₄ and Ca²⁺ concentrations than those forming in the mixed lithology terrain. The gabbro terrane streams and rivers are also slightly more enriched in cations (TZ⁺) and HCO₃⁻, relative to H₄SiO₄, than streams and rivers in the mixed lithology terrane, whereas K⁺ concentrations are uniformly low and, like Mg²⁺ and Na⁺, are similar in both terranes. Major rivers in both areas are similar in chemical character to their respective headwater streams, indicating that the most intense chemical weathering within the watersheds occurs in the headwater regions, and dilution of these solute-rich waters occurs at lower elevations downstream. Ca/Mg ratios for all watersheds are lower than the world river average, indicating the importance of the weathering of Mg-rich minerals. The Ca/Na, HCO₃/Na and Mg/Na ratios for the Rio Pacora streams and rivers fall within the mid-range of what has been observed globally for other streams/rivers draining mafic rocks. Estimated TZ⁺ yields are very large, suggesting significant weathering rates in headwater watersheds of the Chagres region in central Panama.