



The carbonate critical zone: Impacts from recharge, reversing springs, residence times, and redox reactions

Earth's critical zone has been defined as extending from the top of the tree canopy to the base of groundwater and is the focus of much current research in landscapes dominated by silicate minerals. This definition breaks down where landscapes are dominated by carbonate minerals because congruent dissolution creates large subsurface voids that rearrange drainage, alter interactions between surface water and groundwater, and collapse to form sinkholes. The carbonate critical zone is widespread, covering around 15% of Earth's continental ice free surface and provides ecosystem services to ~1.2 billion people. Although extensive, the critical zone in carbonate settings has received little coordinated study within the critical zone science community and instead has mostly been the focus of individual case studies in various carbonate regions with rare broad synthesis or integration of the knowledge derived from these studies. General results from case studies show that subsurface voids and extensive exchange of surface water and groundwater impacts groundwater chemical compositions and the saturation states of groundwater with respect to both carbonate minerals and metal oxides. These interactions and effects are particularly intense where surface water flows into spring vents that during base flow conditions are locations of groundwater discharge to surface water. Spring flow reversals occur when the elevation of the receiving surface water exceeds the hydrologic head at the spring vent, for example, during flooding or at high tides. Spring reversals can lead to residence times ranging from hours to months for water injected during reversals of both terrestrial and submarine coastal

springs. Two sites, one in north-central Florida and the other in the Yucatan Peninsula, provide examples of how reversing spring flow can (1) create undersaturation with respect to carbonate minerals and their dissolution, (2) alternate mobilization and sequestration of metal oxide phases, and (3) alter redox conditions of groundwater causing organic matter remineralization and increasing nutrient availability. These links between flow and changes in water chemistry differ from silicate critical zone processes and suggest that an understanding of hydrologic and geochemical processes of carbonate critical zones will be important for a holistic understanding of all of Earth's critical zone.

Biosketch and Research Interests – Dr. Jonathan B. Martin

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Jon Martin is Professor of Geological Sciences at the University of Florida, where he has worked since 1994. Jon received a BA in Environmental Science from Wesleyan University in Connecticut, an MS in Geology from Duke University, and a PhD in Earth Sciences from Scripps Institution of Oceanography (UCSD). His research interests focus on links between hydrology and water chemistry in various settings including accretionary prisms, coastal aquifers, glacial forelands, and karst aquifers. Jon's karst work does not directly address questions related to sinkholes (except when the media calls), but he is interested in how flow, water chemistry, and surface water and groundwater mixing affect precipitation and dissolution of various mineral phases, particularly carbonates, to create and cement porosity in karst aquifers. Jon's research has been supported by >\$16M in grant funding, mostly from the National Science Foundation, for which he is grateful, and he has co-authored >135 peer-reviewed papers and edited three books. At the University of Florida, he was appointed UF Research Foundation Professor from 2006-2009 and 2012-2015 and Crow Term Professor from 2011-2012 and 2014-2018. He is an emeritus member of the Karst Waters Institute Board of Directors, was associate editor of *Groundwater* from 2005 - 2020, was a visiting professor at the University of Montpellier, France (2007), and University of Bristol, UK (2017) and is a Fellow of the Geological Society of America.