Controls on Sedimentation and Diagenesis in Groundwater-fed Alkaline Lake Critical Zones.

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SUBSURFACE APPLICATION: Analogs for pre-salt Brazil and offshore Angola
STATUS: Ongoing with results to report
TIMING: major phase of project completed by May 2016
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Purpose
Saline groundwater-fed interface environments in arid and semi-arid regions are critical zones of lacustrine and palustrine carbonate precipitation. These areas include chotts, sabkha, salars, salt pans, and alkaline or salt lakes. Although climatic conditions clearly play a first order role in the chemical evolution of these environments, the early diagenetic processes are highly variable and have strong linkages to microbial processes. Reclassification of some lacustrine oil “shales” as carbonates from alkaline lakes, accentuates the importance of gaining insights from modern analogues on the development of these facies (Alonso-Zarza and Wright 2010, Wright 2012). This recent attention has highlighted the variation of microbial build-ups, and the large differences between marine and lacustrine carbonates precluding a “simple comparison” between the two depositional environments (Wright 2012). Mg-silicates, a common precipitate in alkaline lakes, could affect carbonate formation and subsequent preservation, possibly limiting microbial carbonate production (Wright and Barnett, 2014). As a result, it is critical for research to be conducted on facies models related to silicate-carbonate interactions and microbial build-ups (Wright 2012). The goal of this study is to use a group of groundwater fed lakes of varying salinity to study the physiochemical controls on abiotic and microbially mediated carbonate and silicate formation. Studying these processes will lend insight into the formation of microbialites in saline environments, their morphogenesis and potential tool in biostratigraphic correlation, diagenesis and reservoir development, with relevance towards a number of carbonate reservoirs.

Project Description
The study site is located in the Western Lakes region of the Nebraska Sand Hills. This region contains hundreds of compositionally diverse lakes, with dissolved solids ranging from 0.2 g/L to 384 g/L (e.g. Gosselin et al. 1994, Gosselin 1997). Salinity within and between lakes can vary both spatially and temporally. Lakes are found in interdunal areas; in this high sand environment, the lakes receive little to no surface runoff. Thus, groundwater provides the main source of water solutes to the lakes (Gosselin et al. 1994). Groundwater flow paths can be complex, ranging from local (i.e., hundreds of meters) to intermediate (i.e., kilometers) lengths; however, the primary source of water is local precipitation (Gosselin et al. 1994). The saltiest lakes serve only as groundwater discharge zones, while some of the fresher lakes are flow-through. Although the dunes were active as recently as 1500 years ago, evidence indicates at least a few of the lakes have existed continuously for at least 13,000 years, originating as freshwater lakes (Swinehart 1989, Zlotnik et al. 2012). Previous investigations in the area which have been primarily hydrogeological in nature, have used XRD to identify the most abundant evaporite species as carbonate and sulfate.
mineral precipitates: trona (Na₃H(CO₃)₂⋅2H₂O), thermonatrite (Na₂HCO₃⋅H₂O), aphytite (K₂Na(SO₄)₂), mirabilite (Na₂SO₄⋅10H₂O), and calcite (Gosselin et al. 1994). High organic carbon concentrations (130-600 mg/L), up to 1% organic carbon in lake sediments, extensive microbial mats and sulfide generation were attributed to sulfate reduction, potentially driving oxidation of carbon, and in turn generation of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ as a product of the reaction (Gosselin et al. 1994, Stotler 2012, data not shown).

We propose that this is an ideal location to discriminate the differential influences of physiochemical and microbial processes on carbonate formation. Specifically this environment is ideal because: (1) solute delivery by groundwater has been well characterized and is relatively constant; (2) the lakes represent a large geochemical and salinity variation in a small geographical area enabling sampling and experimentation in a range of evaporative stages (3) the microbial ecology of the lakes will be geochemically rather than biogeographically controlled (e.g. all lakes have access to the same species of microbes)

We will investigate carbonate formation in the lakes through a combination of biogeochemical mineralogical and isotopic analysis and in situ experimentation. Briefly, we will characterize the carbonate formation environment in several lakes with varying salinity by measuring lake chemistry (transects) and pore waters (push cores up to 1m) for major and trace elements including nutrients, organic carbon and stable isotopes (O, C) (e.g. Crowe et al. 2008). In the corresponding filtrate and sediment (or mat) samples we will digest the samples for the same parameters and additionally characterize the mineralogy, morphology, and relationships therein (e.g. Lander et al., 2013) using XRD, thin sections, TEM, and SEM. Finally we will seed lake water with reactors similar those we have used previously (Lander et al., 2013) with and without microspheres with carboxylated functionalities to investigate microbial carbonate formation in a more controlled fashion in these environments.

**Deliverables**
Specific deliverables include: 1) Development of a new conceptual model of the role of salinity gradients in groundwater – large aquatic ecosystem interfaces with a focus on microbial controls and silicate-carbonate interactions; 2) Preliminary mechanistic, morphological and kinetic data on in situ of carbonate formation with and without reactive surfaces in the same environment; 3) a comprehensive bibliography of references pertaining to climatic, tectonic, chemical, microbial, and digenetic controls in alkaline lakes; and 4) At least one manuscript and development of a larger NSF or industry supported proposal.

**References**


