

Narrative Report 2019

Research Progress

After Year 1, the focus of the project shifted away from the direct application of sulfur isotope chemostratigraphy in dolostones. The project has evolved to focus more heavily on understanding how the early diagenetic history of platform carbonates alters their geochemical records. This change in focus was inspired by new advances in Neogene carbonate geochemistry. In particular, the effects of carbonate mineralogy (aragonite vs. calcite) and early marine diagenesis on carbonate geochemical archives in the Bahamas have been quantified in news ways through the study of calcium isotopes in conjunction with elemental ratios (Sr/Ca) (Higgins et al., 2018; Ahm et al., 2018). These new approaches have reinforced the interpretations in earlier work (Swart and Eberli, 2005; Swart, 2008) demonstrating the susceptibility of shallow water carbonates to alteration of a wide array of geochemical proxies, including sulfur isotopes. In light of these advances, we decided to apply the lessons of the Neogene Bahamas to Paleozoic carbonates before attempting to interpret the sulfur isotope record of Paleozoic dolomites.

In Year 3, we brought the work on early marine diagenesis of Paleozoic carbonates to completion. We finalized a data set of paired calcium isotope and Sr/Ca measurements on dolostone from five stratigraphic sections in the Great Basin (Figure 1). For comparison, we also analyzed coeval limestone from four stratigraphic sections on Anticosti Island. In all we generated data from 328 samples. Our work revealed the following:

- A major carbon isotope excursion on Anticosti is preserved in limestones with low $\delta^{44}\text{Ca}$ and high Sr/Ca, consistent with aragonite as a major component of primary mineralogy.
- Great Basin strata are characterized by lateral gradients in $\delta^{44}\text{Ca}$ and $\delta^{13}\text{C}$ that reflect variations in the extent of early marine diagenesis across the platform.
- In outer-ramp settings, deposition during syn-glacial sea level lowstand and subsequent post-glacial flooding increased the preservation of aragonite with elevated $\delta^{13}\text{C}$ produced in shallow-water environments.
- In contrast, on the inner ramp, extensive early marine diagenesis and dolomitization under seawater-buffered conditions decreased the magnitude of carbon isotope excursions.

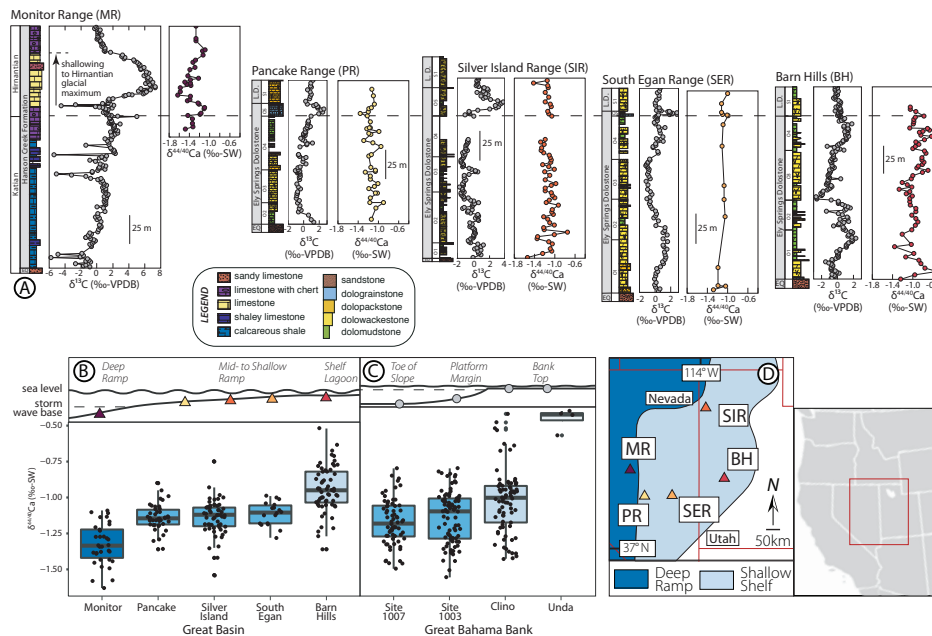


Figure 1. Data from Great Basin. A) Stratigraphic plots of geochemical data from Great Basin – $\delta^{13}\text{C}$ and $\delta^{44}\text{Ca}$. Datum (horizontal dashed line) is top of Katian-aged strata at each section. O1-O5 and S1 refer to stratigraphic sequences identified by Harris and Sheehan (1997), with O1-O4 in the Katian and O5 representing the Hirnantian. B) Ordovician and C) Neogene calcium isotope gradients across carbonate platforms (not to scale). Both settings demonstrate a pattern of increasing $\delta^{44}\text{Ca}$ toward the basin margin, interpreted to represent increasing magnitude of seawater fluid-buffered diagenesis. Bahamas data from Higgins et al. (2018). D) Simplified paleogeographic map of Great Basin carbonate ramp after Harris and Sheehan (1997).

The processes documented in our work provide an alternative explanation for variability in a range of geochemical proxies preserved in shallow-water carbonates at other times in Earth history and challenge the notion that these proxies necessarily record changes in the global ocean (Figure 2). This work has been undergone peer review at *Geology* and is currently in revision. We anticipate publication in early 2020.

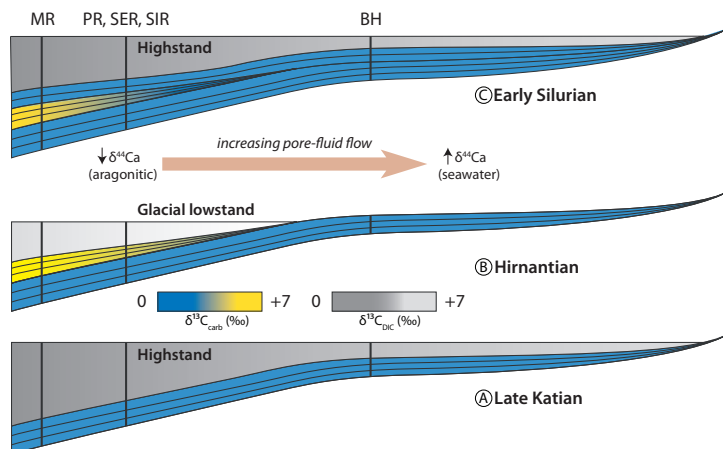


Figure 2. Conceptual model of geochemical development during Hirnantian sea level fall and rise. Aragonite is the primary carbonate mineral precipitate throughout. Secular increase in platform (not necessarily open ocean) $\delta^{13}\text{C}$ during Hirnantian sea level low results in deposition of sediment with elevated $\delta^{13}\text{C}$ in offshore settings. Pore fluid is extensively flushed by seawater in nearshore settings, leading to seawater-buffered geochemistry. Low magnitude fluid flow rates in offshore settings allows sediment-buffered diagenesis, which largely retains the geochemistry of the primary sediment.

With a more robust understand of the processes controlling the geochemistry of these Paleozoic dolomites, we are now in a position to apply this new framework to the sulfur isotope record. That will be a focus in 2019-2020 during our no-cost grant extension. We will also work on Cambrian carbonates collected during field work in Summer 2019 in collaboration with Sara Pruss (Smith College). Finally, we plan to undertake field and lab studies of the dolomitized Ordovician Fremont Formation with Paul Myrow (Colorado College)

Impact on PI

The grant facilitated collaboration between the PI and several collaborators: David Fike (Washington University in Saint Louis); Paul Myrow (Colorado College); André Desrochers (University of Ottawa); Sara Pruss (Smith College); and John Higgins and Anne-Sofie Crüger Ahm (both Princeton University). It also provided critical funds for analysis of sulfur isotope ratios of carbonate associated sulfate in Fike's lab at WUSTL.

Impact on Undergraduate Students

The grant supported the work of several undergraduate students in the PI's geochemistry laboratory. Students continued to completion their work on the extraction of carbonate associated sulfate from the expanded Hirnantian section from western Anticosti Island. Other students participated in field work in Summer 2019. All students funded through the grant are continuing with geology coursework at Amherst.

References

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