A revised paradigm for the interpretation of δ^{238} U during periods of calcite seas

STEPHEN J ROMANIELLO¹, KIMBERLY V LAU², MONIA SABBATINO³ AND MARIANO PARENTE³

¹University of Tennessee ²The Pennsylvania State University ³Università di Napoli Federico II

Presenting Author: sromanie@utk.edu

Uranium isotope variations (δ^{238} U) recorded in marine carbonates are emerging as a potentially powerful tracer of redox conditions in ancient oceans. In order for these proxies to be interpreted as a record of ocean oxygenation, the data must first be corrected for syndepositional and early diagenetic processes which result in an offset between seawater and syngenetic carbonate. The existing paradigm for interpreting these variations is based mainly on observations from modern and Early-Triassic age sediments where U-rich aragonite is the primary carbonate polymorph. Congruence of δ^{238} U trends recorded in multiple widely spaced early Triassic carbonates suggests that early diagenetic behavior of U isotopes deposited during periods of aragonite seas is consistent between sites and relatively wellunderstood.

In contrast, U isotope records from carbonates deposited during periods of calcite seas show increased sample-to-sample variability as well as increased variation between corelative sections. Here, we use an isotope-enabled early diagenetic model of uranium geochemistry to demonstrate that the diagenetic behavior of U isotopes in shallow-water calcite sediments differs significantly from that in aragonite, necessitating a qualitatively different paradigm for the interpretation of δ^{238} U records spanning large portions of the Paleozoic and Mesozoic Eras. Over a broad range of depositional conditions, low initial concentrations of U(VI) in calcite are overwhelmed by the addition of early diagenetic U(IV). Rather than reflecting the U(VI) composition of seawater and primary calcite, the bulk composition of these sediments is expected to predominantly reflect the isotopically heavy reduced U(IV) component similar to black shales. We show that the variability of δ^{238} U observed in shallow-water calcite sediments most likely reflects variations in depositional conditions during the deposition which result in changes in the apparent fractionation factor for the reduction of U(VI) to U(IV) in porewater.