

A notable incorporation of isotopically heavy U(IV) species into carbonates under the modern marine environment

YAN YUAN¹, TIANYU CHEN¹, DR. FEIFEI ZHANG, PHD¹,
YUANYUAN LIU¹, GUOLIN XIONG¹, GUANGYI WEI¹,
TAIS W. DAHL², WEN YAN³, HONG-FEI LING¹, HAI
CHENG⁴ AND SHUZHONG SHEN¹

¹School of Earth Sciences and Engineering, Nanjing University

²University of Copenhagen

³South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou

⁴Institute of Global Environmental Change, Xi'an Jiaotong University

Presenting Author: dg21290021@smail.nju.edu.cn

Carbonate associated uranium (U) isotope ratio ($^{238}\text{U}/^{235}\text{U}$, reported as $\delta^{238}\text{U}$) is an important proxy for understanding changes in past oceanic redox states. It is generally believed that U dominantly presents as U(VI) in carbonates such as shallow-water carbonate deposits formed within oxic marine environments. Yet the valence state of U in marine carbonates has not been studied systematically, due to the analytical challenges on samples with low U concentration (i.e., less than a few $\mu\text{g/g}$) using spectroscopic methods.

In this study, we have calibrated an ion exchange chromatographic method to separate trace amounts of U(IV) and U(VI) from geological carbonates and determined their contents respectively by mass spectrometry. The method has then been applied on various types of carbonates, i.e., speleothems, cold-seep carbonates, corals, as well as drill core (NK-1) samples from Meiji Reef in the Nansha Islands of the South China Sea. The $\delta^{238}\text{U}$ and trace elemental concentrations of these samples have also been reported. While U in primary carbonates (e.g., modern coral, speleothems) formed in oxic aqueous environments is indeed dominated by U(VI), with the proportion of U(IV) ($\text{U(IV)}/\text{U}_{\text{carb}} < 3\%$), the diagenetic samples from NK-1, fossil coral and veins of cold-seep carbonates all show presence of various proportion of U(IV) (from 5% to 65%). The U isotopes of NK-1 samples are traditionally considered not affected by diagenetic alteration as inferred from conventional diagenetic proxies (e.g., Mn/Sr). However, a significant positive correlation has been found between $\delta^{238}\text{U}$ and $\text{U(IV)}/\text{U}_{\text{carb}}$ for NK-1 samples, which suggests that the U(IV) is present in the marine carbonates and drives $\delta^{238}\text{U}$ toward higher values than that of seawater. Our study indicates that local reducing environment in diagenetic fluid could result in direct incorporation of significant amount of U(IV) into marine carbonates. Therefore, coupled valence and isotopic analyses of carbonate associated U would provide critical constraints toward reliable reconstruction of past ocean evolution.