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Large spatial variations in redox- and diagenesis-sensitive trace metals in sedimentary carbonates: insights from micron-scale laser ablation study

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The (bio)geochemistry of sedimentary carbonates serves as an unmatched archive of Earth's past geochemical and biological history. The concentration of major and trace metals within the lattice of sedimentary carbonates measured using bulk techniques has been used frequently to reconstruct redox conditions of past oceans and diagenetic history of marine carbonates. The concern has been increasingly raised that the bulk geochemistry of sedimentary carbonates might capture a mixture of both a primary ocean signal and processes of post-depositional diagenetic alteration. To quantify the potential influences of primary versus secondary processes on paleoredox indicators in sedimentary carbonates, we mapped the geochemistry of different carbonate components using LA-ICP-MS with a 30 µm spot size to determine spatial variation in geochemical composition across different carbonate components within shallow-marine carbonate samples of Permo-Triassic and Cretaceous age. The micron-scale analysis revealed large variations in major (Sr, Fe, Mg and Mn) and trace (U, Mo) metal concentrations within and across petrographic components (micrite, oncoid, skeletal grain, cement). The micrite exhibits the largest variations in the redox-sensitive elements such as uranium (0-3 ppm) and molybdenum (0-0.5 ppm). The micritic components also contain the highest concentrations of redox-sensitive trace metals. We interpret that differences in the concentrations of redox sensitive trace elements (U, Mo, Fe) across petrographic phases within single rock samples result from microbially mediated redox reactions at and below the sediment-water interface. Additionally, we found that the variations in concentrations of diagenetically sensitive major elements (Sr. Mg, Mn) within different components is significantly larger than variations across different components. This observation of diagenetically sensitive major elements showing smaller variations across components than within components could indicate that the post-depositional diagenetic processes affect all components similarly. In contrast, the redox sensitive trace elements show large variations within and across different petrographic components thus presenting a cautionary tale while utilizing bulk concentration variations as indicator of oceanic redox conditions.