New insights into Ce anomalies and mechanisms of trace metal enrichment in seep carbonates

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Authigenic carbonates formed at marine hydrocarbon seeps provide a unique geological archive of past local environmental conditions and pore fluid geochemistry. Recent works on such carbonates revealed variable Ce anomalies and anomalous enrichments of some trace metals. However, the mechanisms accounting for such anomalies remain poorly constrained. Here, we characterize the rare earth element (REE) patterns of carbonate phases and the trace metal patterns of bulk carbonate rocks sampled at three hydrocarbon seeps located at Congo Fan pockmarks (CF) and the Gulf of Mexico sites AC645 and GB425. The analyzed CF, GB425, and AC645 carbonates yielded different REE patterns, displaying positive, no, as well as negative Ce anomalies. The covariation of molybdenum (Mo) with uranium (U), including authigenic Mo (Mo_{auth}) and U (U_{auth}) enrichments and $(Mo/U)_{auth}$ ratios proved useful to obtain new insight into the applicability of Ce anomalies to constrain past redox conditions. The results suggest: 1) the CF carbonates formed in a restricted sulfidic environment; 2) AC645 site apparently experienced intermittent oxygenation causing negative Ce anomalies; 3) environmental condition at the GB425 mud volcano site were variable. Interestingly, the GB425 carbonates show significant Mo, As, and Sb enrichments with the enrichment factor of As (As_{EF}) correlating well with the authigenic Fe fraction, suggesting that Fe-oxy-hydroxides played an important role in the absorption of Mo, As, and Sb in water column and their transportation to sediment. The combination of trace metal and REE geochemistry of authigenic carbonates used here is a powerful tool to better assess past variability of redox conditions and biogeochemical processes at marine seeps.

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