

Is Ce anomaly in carbonates real ? A perspective from leaching experiments

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Variations in Yttrium and rare earth elements (REY) concentrations in marine carbonates, such as Cerium (Ce) anomaly paleoredox proxy, are powerful paleoenvironmental indicator of oceanic conditions. However, recent studies revealed that contaminations from non-carbonate phases are nonnegligible when reconstructing seawater signatures from marine carbonates, and multiple dissolution protocols were proposed to eliminate these effects. Yet, there is no systematic study on how each non-carbonate phases contributes to the REY concentrations and patterns in pure marine carbonates. Here we report REY results from a series of dissolution experiments. Multiple standards including NOD-A-1 (Manganese nodule), SBC-1 (Brush creek shale), and Montmorillonite are selected to represent non-carbonate contamination end-members and a Key Largo limestone (i.e., 100% calcite) is used as a pure carbonate endmember. First, we preclude using ammonium acetate to remove exchangeable ions, because leaching results show less than 3% of total REY were extracted from contaminative phases, and tetravalent Ce was left in residues. We used acetic acid at pH range of 2.2-3 and a sodium acetate buffer at pH=5 to leach NOD-A-1, SBC, and Montmorillonite. Results were compared to batch experiments using nitric acid from 0.05M to 0.3M. For NOD-A-1, a negative Ce anomaly in leachates using acetic acid versus a positive anomaly using 0.3M nitric acid suggests nitric acid may introduce fake positive Ce anomaly into samples. Lastly, we conducted same leaching experiments on mixed samples consisting 80% Key Largo limestone and 20% standards, and we conclude acetic acid with a molarity lower than 0.5M is able to avoid contaminations from Mn oxides, clay minerals, and siliciclastic phases. The amount of acid must be calculated to only dissolve less than 80% of the total CaCO₃, and leachates must be filtered to remove floating particles.