A refined dissolution method to extract primary seawater rare earth element signal from ancient marine carbonates

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Yittrium and rare earth elements (REY) in carbonates have been intensively studied due to their potential as paleoenviromental proxies. Recent studies revealed that non-carbonate contaminations are nonnegligible when reconstructing seawater signatures from marine carbonates, and multiple dissolution protocols were proposed to reduce these effects [1-3]. Yet, these protocols are designed for different geochmical signatures in specific carbonate samples, and there is no systematic study on how each non-carbonate phase contaminates REY of pure marine carbonates. Here we report REY results from a series of dissolution experiments in various modern and ancient carbonate powders to exam and refine the published protocols. Firstly, when prewashing four Proterozoic and one Pleistocene carbonates, ammonium acetate is more efficient than Milli-Q water in extracting exchangeable ions absorbed on the negative charged mineral surfaces and interlayers, and the amount of ammonium acetate should be adjusted based on the minerology of the specific sample. In addition, we tested a revised step-wise leaching procedure reported in Liu et al., (2013) [4]. 0.1% v/v acetic acid only dissolves less than 5% of total carboantes, while acid over 5% v/v tends to diminish both the Ce and Y anomaly. It illustrates 5%v/v acid dissolves non-carbonate phases and the REY signature is altered. On top of that, we also tested nitric acid on the same set of samples, and the result is not as consistent as acetic acid. Lastly, enriched REY concentration and a flat shale normalized pattern are observed when we perform whole-rock digestion, similar to the chemical signatures of the residuals after acetic acid leaching, suggesting that contamination from silicates can be minimized through step-wise weak acid leaching.

[1] Bayon et al. (2002), *Chemical Geology*, **187**, 179-199. [2] Zhang et al. (2015), *Chemical Geology*, **412**, 82-91. [3]Tostevin et al. (2016), *Chemical Geology*, **438**, 146-162. [4] Liu et al. (2013), *Chemical Geology*, **351**, 95-104.