

Revisiting the Role of Authigenic Clays in Ocean Rare Earth Element Cycling

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The formation of authigenic clays is an important control on marine elemental budgets through the preferential exclusion or inclusion of specific elements during reverse weathering. While the impact of clay minerals on rare earth element cycling in the ocean has been inferred using pore water REE patterns [1], these efforts have been hindered by a near-complete lack of compositional constraints on the newly formed clays due to the obstacles associated with isolating these minerals given their commonly small size and co-occurrence with clay size sediments of other origins. Here, we used a refined separation technique to isolate authigenic green clays from their host sediment. We check the resulting separates for inclusions or other unintentional phases using SEM-EDS and compare the composition of these newly formed clays to their precursor sediment, using immobile Zr to correct for the volumetric increases associated with clay authigenesis.

These clay separates primarily consist of glauconite and smectite, the most abundant and widespread authigenic clays of the Phanerozoic, making them particularly relevant to understanding the fractionation between detrital and authigenic phases in marine sediments [2]. Using clays from several locations representing a range of depositional ages and surrounding sediment compositions, we demonstrate that authigenic green clays typically exclude rare earth elements during authigenesis with no consistent fractionation between the rare earth elements during this process. The dominantly light REE enriched pattern sometimes associated with authigenic green clays [1,3] may be due to accessory phases (e.g. phosphates; [4]) not removed during purification processes, incorporating the light rare earth elements. This suggests that while clay authigenesis may be an important source of REE elements to the surrounding pore fluid, the rare earth fractionation driving a heavy rare earth element enriched flux to seawater is dominated by other authigenic phases acting as sinks.

[1] Abbott et al. 2019, *Frontiers in Marine Science*, 6, 504

[2] Baldermann et al. 2022, *Nature Communications*, 13, 1527

[3] Huggett et al. 2017, *Clay Minerals*, 52, 25-50

[4] Bayon et al. 2023, *Minerals*, 13, 1081