Rare Earth Elements and authigenic 'coatings' in the service of palaeoceanography: a microanalysis approach

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Rare Earth Element (REE) distributions in the ocean bear the fingerprints of several key environmental processes, including vertical particle/organic carbon fluxes, water column/pore-water oxygenation and ocean transports. The use of 'fossil' REE analyses in the service of palaeoceanography as redox, water transport or nutrient cycling 'proxies' has long been a tantalizing possibility. Here we demonstrate the application of a novel laser-ablation microanalysis approach for investigating the REE composition of early diagenetic 'coatings' on fossil foraminifera and their variability over time. Our pilot work demonstrates the fidelity of sedimentary core-top REE analyses with respect to global pore-water and seawater REE trends, including the typical HREE/LREE enrichment along dominant water flow trajectories in the modern ocean. However, we also find that REE patterns in foraminifer 'coatings' near the sediment-water interface evolve away from seawater properties exactly as expected for pore-waters influenced by e.g. anoxic diagenesis. 'Fossil' REE signatures in foraminifer surface enrichments therefore record the impacts of early diagenetic processes operating near the sediment-water interface, and not only the initial seawater composition. Nevertheless, down-core measurements on more deeply buried sediments from the last deglaciation are found to track independent palaeoceanographic proxy reconstructions of deep-water ventilation, suggesting that down-core REE variability may preserve the influence of changing deep-water hydrography despite early diagenetic impacts. A viable 'palaeoceanographic REE proxy' may therefore be a possibility, if we can fully understand exactly how 'fossil' REE compositions are 'locked in' on foraminifer surfaces during deposition.