

LA-ICP-MS analysis of isolated phosphatic grains indicates selective rare earth element enrichment during reworking and transport processes

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Rare earth elements (REE) are a commonly used proxy to reconstruct water chemistry and oxygen saturation during the formation history of authigenic and biogenic phosphates in marine environments. In the modern ocean REE exhibit a distinct pattern with enrichment of heavy REE and strong depletion in Cerium. Studies of ancient phosphates and carbonates, however, showed that this ‘modern’ pattern is only rarely present in the geological past. Consequently, the wide range of REE enrichment patterns found in ancient marine phosphates lead to the proposition that water chemistry had to have been radically different in the earth’s past. A wealth of studies has already shown that both early and late diagenesis can strongly affect REE signatures in phosphates and severely alter primary marine signals. However, no previous research was conducted on how alteration processes occurring prior to final deposition affect marine phosphates.

Herein we present a dataset of multiple LA-ICP-MS measurements of REE signatures in isolated phosphate and carbonate grains deposited in a carbonate ramp setting in the central Mediterranean Sea during the middle Miocene “Monterey event”. The phosphates are represented by authigenic, biogenic and detrital grains emplaced in bioclastic grain- to packstones dominated by bryozoan and echinoderm fragments, as well as abundant benthic and planktic foraminifers. The results of 39 grain specific LA-ICP-MS measurements in three discrete rock samples reveals four markedly different REE patterns (normalized to the Post Archean Australian Shale standard) in terms of total enrichment and pattern shape. Analyses of REE diagenesis proxies show that diagenetic alteration affected the samples only to a minor degree. Considering grain shape and REE patterns together indicate that authigenic, detrital and biogenic phosphates have distinct REE patterns irrespective of the sample.

Our results show that the observed REE patterns in phosphates only broadly reflect water chemistry under certain well constrained circumstances of primary authigenesis. Are these conditions not met, REE patterns are more likely to reflect complex enrichment processes that likely already started to occur during reworking over geologically relatively short time frames. Similarities in the REE patterns of clearly detrital and biogenic phosphate further suggest that the often observed ‘hat-shaped’ pattern in biogenic phosphates can easily result from increased middle REE (Neodymium to Holmium) scavenging during taphonomic processes prior to final deposition. Finally, cluster analysis coupled with sedimentological considerations proved a valuable tool for the characterization of REE patterns of phosphates in terms of their formation conditions and depositional history, such as the distinction of phosphates formed in situ from reworked and transported phosphate grains.