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Influence of reworking and transport processes of phosphatic grains on rare earth element signatures

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Rare earth elements (REEs) 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 REEs exhibit a distinct pattern with enrichment of heavy REEs 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 has been distinctly different in the earth's past. However, 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. So far, no research was conducted on alteration processes that may occur prior to final deposition.

We present a dataset of a series of 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 of primary authigenesis. These patterns 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 information 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.