

Rare Earth Element Chemistry of Jurassic Seawater Inferred from Fish and Reptile Apatite (Paris Basin, France and England)

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Modern biogenic apatites in open marine basins acquire sea-water-like REE spectra with concentrations enriched by a factor of 10^6 - 10^7 at the sediment-water boundary, during extremely early diagenetic processes. However, the faithful preservation of the paleoceanographic signal, potentially recorded in fossil apatite, mainly depends on the composition of the REE flux released by the host sediment during early diagenesis and on the possible REE addition and fractionation during post-depositional recrystallization during late diagenesis. The Rare Earth Element (REE) chemistry of Jurassic shelf seawater from the western Tethys (Paris basin) was investigated by analyzing fish and reptile teeth deposited in shallow and deeper water (< 200 m) environments. No enrichment in middle-REE relatively to both light REE and heavy REE was observed in our Jurassic vertebrate apatite, indicating a general absence of a typical late diagenetic alteration signal. A relationship was sought between the depositional environments varying from shallow coastal to deep and distal, the REE budget in sedimentary matrix and, the REE pattern in bio-apatite. Vertebrate remains sampled from siliciclastic sediments (calcareous sandstones and shales) show flat REE patterns that reflect the dominant influence of the continental source from which the REE in the sediments were derived. Carbonate deposits, protected from clastic sources, contain fish and reptile apatite whose REE patterns reflect more accurately the REE composition of the overlying water column. These specific bio-apatites can be used for paleoenvironmental studies. Samples of marine vertebrate teeth were selected from limestones of Bajocian through to Oxfordian age in the Paris basin. Variations in the REE patterns and ratios through time were sought and interpreted in terms of evolution of the REE chemistry and oxidation state of seawater. The REE patterns are similar through the Bajocian to the Oxfordian. They are characterized by a depletion in Heavy Rare

Earth Elements ($Dy/Yb_N = 1.8$ to 4.6) compared to modern seawater compositions ($Dy/Yb_N = 0.8$ to 0.9). Our results suggest that a specific mechanism of HREE subtraction relatively to LREE occurred that was more efficient than modern HREE removal processes. Examination of these Jurassic data combined with those published for the Paleozoic and Cretaceous, indicates that the efficient heavy REE depletion process operated until the Late Cretaceous. The fractionation of HREE relative to LREE is correlated with the increasing depth of the basin as indicated by the oxygen isotope composition of co-existing brachiopods. The $(Dy/Yb)_N$ ratios of fish and reptile apatite increase from 1.8 to 4.6 as bottom water temperatures, derived from the brachiopod data, decrease from 30°C to 15°C . This decrease of bottom temperatures reflects an increase of water depths from shallow to deeper (200 m) environments, assuming that the thermal structure of Jurassic seas was similar to modern seas. We propose that the Dy/Yb_N ratio of marine biogenic phosphates can be used as a proxy of paleo-water depths at the scale of a water mass. Ce anomalies (Ω_{Ce}) in biogenic apatite-bearing limestones are systematically negative and variable ($\Omega_{Ce} = -0.74$ to -0.13). A maximum negative value ($\Omega_{Ce} = -0.74$) is observed for the Bathonian and is within modern surface seawater values ($\Omega_{Ce} = -0.8$ to -0.3 for Pacific and Atlantic Oceans). Minimum negative values occur in the Callovian and Oxfordian (mean $\Omega_{Ce} = -0.21 \pm 0.09$). In well oxygenated waters, a significant fraction of $Ce\Omega^{3+}$ is oxidized to Ce^{4+} that is incorporated into insoluble metal-oxide coatings, explaining the negative Ce anomaly observed in water and apatite REE spectra. Thus, the less negative Ce anomalies for Callovian-Oxfordian bio-apatites imply that Callovian-Oxfordian seawaters were more reducing than Middle Jurassic or modern water. These weak negative Cerium anomalies are contemporaneous with the deposition of organic rich-layers in the western Tethys during the Middle Callovian.