# REE Evidence for elevated $pCO_2$ throughout the Boring Billion

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The rare earth elements occur in seawater as carbonate complexes (e.g. $Yb(CO_3)^{2-}$ and their stability is controlled by $pCO_2$ of the ocean and atmosphere. Recent studies show that REE in modern seafloor black muds are concentrated in the organic-rich fraction and have a REE distribution pattern very similar to post Archean shales, which in turn reflect the composition of the upper continental crust. Thus temporal variations in REE of marine black shales, are controlled by variations in composition of both the upper continental crust (UCC) and $pCO_2$ in the atmosphere. However these two factors are linked, as a change from mafic-rich UCC to felsic-rich UCC will lead to a lower flux of Ca and Mg to the oceans, causing a gradual increase in $pCO_2$ in the atmosphere.

We have measured the REE in the clay-organic matrix of 52 widely dispersed Precambrian marine black shales by LA-ICPMS. The data show that the boring billion was a period of elevated HREE compared with the Archean, likely due to elevated atmosphere $pCO_2$. This may be explained by a change from mafic-dominant UCC in the Archean, to felsic-dominant UCC during the boring billion. The middle Proterozoic is known as a period of extensive K-U-Th-rich granite intrusions and lack of komatiitic volcanics, both of which may have contributed to the change to a felsic-dominant UCC during the boring billion.