

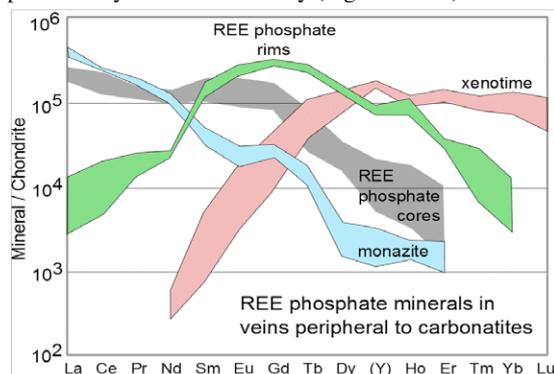
REE fractionation at the Bear Lodge REE+Au deposit, USA: Evidence from mineral chemistry

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The Bear Lodge alkaline intrusive complex hosts one of North America's largest REE deposits. Carbonatites in the central Bear Lodge have REE patterns similar to other carbonatites worldwide, with concentrations decreasing slightly from La to Lu, typical for partial melts from the mantle. Recent exploration reveals zones of HREE- and HFSE-enrichment, much of it hosted by hydrothermal veins peripheral to the LREE-enriched carbonatites. A district-wide zonation from LREE to HREE is reflected by mineralogy. The central carbonatites host REEs in the fluorocarbonate minerals, bastnäsité, synchysite, and parisite, and the carbonate minerals ancylite and carboxenite. Monazite, xenotime, and hydrated REE-phosphates of the rhabdophane group are common in the peripheral veins. New electron microprobe data show typical REE patterns for monazite and xenotime. Hydrated REE phosphates show a zonation similar to that observed district-wide (LREE to HREE), with rims particularly enriched in Eu-Dy (Figure below).



Recent experimental studies show HREEF²⁺ complexes are less strongly associated than LREEF²⁺ complexes at hydrothermal temperatures (>150°C), suggesting the fluids cooled below 150°C or that a different ligand, such as phosphate or chloride was involved. REE-phosphates (monazite) are known to be highly insoluble, suggesting phosphorous was important during precipitation, but not necessarily during transport. Potential external sources of phosphorous include Paleozoic sedimentary units containing abundant phosphatic microfossils or detrital apatite.

Uranium isotopes in anoxic sediments

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Elemental and isotopic proxies in marine archives are important tools for reconstructing the chemical evolution of the ocean through time. One sought-after parameter is past ocean redox, for which the Mo isotope tool is relatively mature [e.g., 1]. Uranium's redox sensitive behaviour has also served as a useful indicator for redox conditions in marine sediments [2]. Recent improvements in our ability to measure the ²³⁸U/²³⁵U ratio has also highlighted the potential for significant redox-induced isotopic variability at the Earth's surface [3,4]. However, the ground-truthing of any such tracer requires knowledge of the singularity of the signal, potential diagenetic overprinting and local vs. global processes, all of which have to be addressed.

To advance our understanding of ²³⁸U/²³⁵U in marine archives, and its response to ocean chemistry, we have measured U isotopes in anoxic marine sediments from modern euxinic settings (Black Sea and the Cariaco Basin) and in organic-rich Mediterranean sediments (sapropels) formed during the last glacial cycle. The sediments from euxinic settings are characterised by high U enrichment factors and all show ²³⁸U/²³⁵U moderately heavier than seawater (~0.4 ‰), consistent with published Black Sea data [4]. In contrast, U incorporation into the Holocene Mediterranean sapropel (S1), likely formed under anoxic but non-euxinic conditions, shows lower U enrichment but significantly heavier ²³⁸U/²³⁵U signatures (~1 ‰) compared to the euxinic sediments.

The ²³⁸U/²³⁵U signatures suggests different U incorporation into the two types of anoxic sediments likely linked to the specific mechanism of U reduction or the ocean setting. This observation suggest that the ²³⁸U/²³⁵U in marine archives can potentially fingerprint anoxic versus euxinic water conditions and may provide a paleo-redox proxy to be used in tandem with, for instance, Mo isotopes.

[1] Arnold *et al* (2004) *Science*, **304**, 87-90. [2] Barnes & Cochran (1990), *EPSL*, **97**, 94-101. [3] Stirling *et al* (2007), *EPSL*, **264**, 208-225. [4] Weyer *et al* (2008), *GCA*, **72**, 345-359.