

## Secondary weathering phases and apatite (U-Th)/He ages

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Apatite (U-Th)/He dating provides unique constraints on low-*T* thermal histories of rocks, but in some settings produces anomalous ages. Possible (nonanalytical) origins of this include complications arising from alpha ejection and implantation or reheating. Here we present observations from several settings suggesting a role for secondary grain-boundary phases with high parent nuclides.

Detrital apatite from Paleogene clastic sediments that have not been heated above ~30-40 °C from the Sierra Nevada, the Bighorn Basin, and the Pyrenees shows anomalous ages that are often younger than depositional age and inversely correlated with U and Th across large ranges of U-Th concentrations. In several cases, single-grain analyses from individual conglomerate clasts show correlations that are distinct from those of other clasts, suggesting parent nuclide mobility at the cm-scale.

Many apatites in these samples are similar to those in soils, showing several features distinct from those in most unweathered crystalline rock. These include secondary clay-oxyhydroxide phases on grain exteriors and filling cleavage fractures and c-axis-parallel dissolution pits. Induced fission-track distributions indicate that the secondary weathering phases often have high U relative to apatite.

Given relatively low U-Th concentrations (~10s of ppm) in most apatite and often high concentrations in oxyhydroxides, late-stage addition of secondary phases may have a significant influence on the parent nuclide budget and therefore age of a grain. If the secondary phases have higher U-Th than the grain on which they precipitate, then regardless of when they form relative to cooling-age closure, measured ages will be “too-young” and U-Th concentrations relatively high. If, however, the secondary phases are not analyzed with the grain (e.g., due to removal during mineral separation), apparent ages will be “too-old” due to He implantation. The U-Th concentration of secondary phases is likely to vary by setting, but may be higher in old (e.g., Precambrian) rocks with radiation-damaged U-Th-rich phases such as zircons. In such cases grain boundary secondary phases may have the potential to implant significant amounts of He into apatite.

## Oxidative weathering and the Fe-S balance of the late Archean ocean

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Archean ocean chemistry is thought to have been characterized by extremely low levels of both oxygen and sulfate, and as a result Archean seas are presumed to have been rich in dissolved Fe<sup>2+</sup>. The most striking consequences of this are the presence of abundant marine siderite and the episodic deposition of banded iron formation (BIF), which attests to temporally extended sourcing and transport of dissolved Fe<sup>2+</sup> across wide oceanic distances. With the notable exception of a transient pulse of BIF deposition following Neoproterozoic low-latitude glaciation, BIFs are absent from the rock record after ~1.8 Ga. This observation has been interpreted to reflect an increase in the oxidation state of the atmosphere and surface ocean, which resulted in the removal of dissolved Fe<sup>2+</sup> via iron (oxyhydr)oxide precipitation and/or FeS<sub>2</sub> formation. The latter may have occurred in marine environments supporting microbial sulfate reduction or inorganically during the venting of hydrothermal fluids charged with oceanic sulfur.

We present a case study focusing on iron mineral speciation in the late Archean Mt. McRae Shale and the underlying Mt. Sylvia Formation (Hamersley Basin, Western Australia). Data for the Mt. Sylvia Formation and lower Mt. McRae Shale show sulfur limitation of pyrite formation and are consistent with reducing, iron-rich aqueous chemistry. However, data for the upper Mt. McRae Shale indicate iron-limited pyrite formation during deposition, and primary authigenic enrichments in molybdenum suggest free sulfide concentrations in excess of 10 μM. Both observations imply oxidative weathering and transport of SO<sub>4</sub><sup>2-</sup> and MoO<sub>4</sub><sup>2-</sup>, although a photolytic source for SO<sub>4</sub><sup>2-</sup> cannot be ruled out and the presence of small but significant non-mass-dependent sulfur isotope anomalies indicates very low oxygen levels. More broadly, the data speak to the possibility of reactive iron limitation and vacillations between the dominance of iron and sulfur in Archean oceanic environments as a function of secular or sporadic changes in the input and output fluxes of both elements to/from the ocean.