Open-system behavior of U-series in carbonates: what we can learn from old limestones

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Conventional U/Th age determination assumes closed-system behavior. This criterion is violated in most Pleistocene fossil corals as evidenced by unreliable ages, ^{226}Ra offsets with respect to radioactive equilibrium with parent ^{234}U, as well as variable initial coral ^{234}U/^{238}U ratio, that are in most case substantially higher than that of modern seawater. The source of excess ^{234}U (and ^{230}Th) in fossil corals and its relationship to U-series age determinations remains an open issue in U-Th geochronology. Many investigators [2,3] consider that open-system behavior results from an enhanced alpha-recoil mobility of U-series nuclides (^{230}Th, ^{234}Th and consequently ^{234}U).

The premise of this study is that alpha-recoil-related processes evoked for open-system behavior of fossil corals, should also be active in "old" carbonates. Here we illustrate this issue with precise and accurate measurements of ^{234}U/^{238}U ratios in borehole core samples from deep, low-permeability Mesozoic formations of the Paris basin, France [3]. The initial objective of the study was to investigate the behavior of naturally occurring uranium isotopes as a means to assess the long-term safety of radioactive waste disposal in a clayey formation of Callovo-Oxfordian age targeted by the French Agency for nuclear waste management (ANDRA). Special attention was paid to U-series disequilibria within over- and underlying Mesozoic carbonate formations. All samples associated with pressure-dissolution features (stylolites) depicted systematic ^{234}U/^{238}U disequilibria at the centimetric scale, thus illustrating some uranium mobility during the last 2 Ma. This finding illustrates an unusual and unexpected mechanism of uranium remobilisation implying relocation and fractionation processes, since U was supposed to be practically immobile under the reducing conditions and low porosity and permeability characterizing the host sedimentary formations. We intend to discuss here the mechanisms responsible for uranium mobility in such deep sedimentary rocks and will make a comparison with mechanisms that have been proposed to drive U mobility in fossil corals.

[1] Thompson et al. (2003). *EPSL*, **210(1-2)**: 365-381.

[2] Villemant et al. (2003). *EPSL*, **210(1-2)**: 105-118.

[3] Deschamps et al. (2004). *HESS*, **8(1)**: 35-46.

Impact of remediation design on arsenic leaching from historic gold mine tailings

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Secondary As minerals can reduce metal(loid) mobility in mine wastes, but may dissolve under changing geochemical conditions during or after remediation. The objective of this study is to optimize remediation strategies for As-bearing tailings from abandoned gold mines in Nova Scotia. A logical clean up plan at these publicly accessible sites would be to place a cover on the tailings, a method often successful at limiting sulphide oxidation and thus, preventing acid production and metal(loid) release. However, due to the heterogeneous nature of these strongly weathered mine wastes, this may lead to dissolution of some As-bearing minerals and an influx of As to local waters. The challenge of remediating such tailings lies in the different Eh-pH niches in which Fe-arsenates (oxidizing, acidic), Ca-Fe-arsenates (oxidizing, alkaline), and sulfides (reducing) are stable. Since these mine wastes are mineralogically complex and associated with variable pH and redox conditions, a one-size-fits-all remediation approach will be difficult to achieve.

To assess the geochemical changes induced by various remediation scenarios, the following options have been tested: (1) unremediated tailings in the field, (2) unremediated tailings in the lab, (3) a simulated limestone cover, (4) a simulated vegetative cover, and (5) a soil cover. For scenario 1, four field bins were filled with one of each tailings end member (hardpan tailings, oxic surface tailings, wetland tailings, or high Ca/As tailings). Leachate from the bins was sampled bi-weekly for two years. Scenarios 2-4 involved a set of three columns per tailings end member that were leached weekly with one of three input solutions: synthetic rainwater, synthetic rainwater equilibrated with $CaCO_3$, or a weak organic acid solution, respectively. Scenario 5 consisted of one column of each tailings end member topped with a 30-cm-thick soil cover that was leached with synthetic rainwater.

Results from Scenarios 1-4 show the As mineralogy in the tailings is the primary control on As mobility. Under field conditions, both hardpan and wetland tailings produced acidic, metal(loid)-rich drainage over time, and only the high Ca/As tailings remained near-neutral throughout the tests. In the lab, column leachates for a given tailings end member showed similar pH values and concentrations of sulphate, As and Fe despite the range in input solution pH (from 4.6 to 10). The scenarios tested so far have not proven to be effective mitigation strategies against As leaching. Reducing water and oxygen availability may be the best way to minimize As release and prevent acid generation.