

## Biogeochemically induced mineral transformations controlling the fate of arsenic

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Dissolved concentrations of arsenic within pore-waters of soils and sediments are controlled by a composite of biogeochemical reactions. Generally, arsenic binds strongly to soil/sediment solids under aerated conditions; under anaerobic condition, aqueous concentrations generally increase, a phenomenon attributed to reduction of iron or arsenic. We show that reduction of arsenate to arsenite nearly universally increases the lability of arsenic, thus stimulating its migration within surface and subsurface environments. Iron reduction, conversely, can either increase or decrease the retention and lability of arsenic depending on the initial iron phase, the surface composition, the rate of reaction and resulting Fe (II) concentration, and the extent of reduction.

Whether arsenic is released to solution or incorporated into secondary transformation products during microbial reduction of Fe (III) is firstly dependent on the host phase. Ferrihydrite is particularly prone to Fe (II) induced transformation to thermodynamically more stable phases that include goethite and magnetite. Upon formation of these secondary phases, particularly magnetite, arsenic (III) (which is also produced by biological reduction) can be incorporated into the surface structure, and thus decrease (rather than increase) aqueous concentrations of arsenic. However, the secondary hosts may be short-lived and themselves undergo reductive dissolution (without reprecipitation), ultimately leading to an increase in dissolved arsenic. Moreover, both surface moieties (e.g. phosphate) as well and structural dopants (e.g. Al) modify the transformation pathway of ferrihydrite and may therefore limit formation of secondary phases that can host arsenic. Here we illustrate that structural incorporation of Al within ferrihydrite, along with the surface coverage of arsenate and phosphate, diminish ferrihydrite transformation to magnetite or goethite and thus promote arsenic release to solution.

Within the complex structure of natural soils and sediments, biogeochemical conditions (and associated reactions) will vary over small (sub-micron) scales, thus leading to micron-scale variation in reactions involving arsenic. Using constructed and natural aggregates, we illustrate variations in biogeochemical conditions and the resulting fate of arsenic.

## U/Th dating of cold-seep carbonates: Timing and duration of fluid seepage

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Authigenic carbonates from hydrocarbon seeps are unique archives of past seepage and environmental parameters. Here, we report U/Th ages of such carbonates from Gulf of Mexico, Congo Fan, and Black Sea. Our aim was to investigate the timing and duration of fluid seepage on continental margins.

In order to acquire U/Th ages of cold-seep carbonates, it is important to choose proper sample to test and evaluate the amount of initial <sup>230</sup>Th accurately. The obtained U/Th ages suggest that environmental conditions must have been favorable for enhanced methane-rich fluid seepage during the time interval of 10 to 1.7 ka for Atwater Valley 340, 11.7 to 8.6 ka, and 53 to 45 ka for Alaminos Canyon 645 of the Gulf of Mexico, 45 to 3 ka for Congo Fan, and 1.7 to 0.5 ka for Black Sea sites.

Overall, our results indicate that hydrocarbon seepage was discontinuous at the investigated sites. The short life span of seepage at a particular locality is probably controlled by the exhaustion of the hydrocarbon sources, and/or clogging of the plumbing system due to extensive carbonate formation. It seems that vigorous seepage initiated at the end of the last deglaciation in the Gulf of Mexico, reflecting a time of sedimentary loading and associated salt diapirism that activated the fault conduits to the seafloor. Seepage in the Congo Fan and Black Sea may have been a function of the stability of the gas hydrate reservoirs, which probably were affected by environmental change in the course of Late Quaternary climate change, including variations in bottom-water temperatures.

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