Defining spatial and temporal variations in biogeochemical processes governing arsenic mobility

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Dissolved concentrations of arsenic within pore-waters of soils and sediments are controlled by a composite of biogeochemical reactions which typically vary in space and time. Collectively, and coupled with hydrologic processes, they are responsible for contaminating groundwater with arsenic that is presently impacting approximately 100 million people—'the largest mass poisoning in history'. Generally, arsenic binds strongly to soil/sediment solids under aerated conditions where the arsenate anion prevails, with the exception of conditions having a high pH (>8.5) or competing ligand concentration(s). Anaerobiosis, however, often results in increased concentrations of arsenic within the aqueous phase, but the processes and ultimate fate of arsenic remain unresolved. Here we use a multifaceted approach, ranging from microspectroscopic analysis of laboratory-based experiments to reactive transport modeling of field systems, to evaluate the fate and transport controlling processes of arsenic, with a specific focus on the large deltaic environments of Southeast Asia.

Arsenate reduction nearly universally increases the lability of arsenic within surface and subsurface environments, while, in contrast, iron reduction can either increase or decrease the retention of arsenic depending on the initial iron phase, the rate of reaction and resulting Fe(II) concentration, and the extent of reduction. For short-range order ferric (hydr)oxides such as ferrihydrite, rapid reduction initially decreases dissolved concentrations of arsenic relative to abiotic controls, but continued reduction ultimately results in progressively increasing arsenic concentrations until complete liberation of arsenic. Within physically complex media, release of arsenic is dependent on mass transfer coupled with biogeochemical reduction, which exhibits extreme heterogeneity even in simplified porous networks. Within SE Asian deltas, arsenic is mobilized by a convolution of biologically induced reduction processes, ensuing geochemical reactions, and mass transport limitations.

Rare earth element of cold seep carbonates: A comparative study

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We report rare earth element (REE) of seep carbonates collected from modern seeps of Gulf of Mexico, Congo Fan, Black Sea, and South China Sea, ancient seeps of Morocco (Devonian), Germany (Carboniferous), France (Oxfordian, J_3), USA (Oligocene), and Italy (Miocene). Our fucos has been on 5% HNO_3-treated solution (carbonate minerals) of the carbonates, in which different carbonate facies has been selected to do analyses using VG Plasma-Quad Excell ICP-MS. Our aim has been to trace the variation in redox conditions during seep carbonates precipitation.

The total concentration of REE ($\sum$REE) in seep carbonates varies widely, from 0.07 to 75.59 ppm, but common trends is that the $\sum$REE in micrite is of the highest and in sparite is of the lowest, suggesting that the REE concentration of seep carbonates may be a function of diagenesis. The shale-normalized REE patterns of the seep carbonates show varied Ce anomalies across multiple geographic areas and even within individual study areas. Based on the Ce anomalies, it is suggested that Congo Fan and South China Sea seep carbonates formed under anoxic conditons, Black Sea seep carbonates formed under oxic (130 m water depth) and anoxic (190 m water depth) conditions, Italy seep carbonates formed under oxic condition, while Gulf of Mexico, Morocco, Germany, France, and USA seep carbonates formed under both anoxic and oxic conditions. This suggests that the formation condition of the seep carbonate is variable and complex, which is possibly controlled by fluid flux and may also be related to the hydrocarbon source (e.g. oil and/or methane) of seeps.

Overall, our results show that apart from anoxic, oxic formation conditon is also common at hydrocarbon seep environments, especially at oil seeps.

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