Impact of microbial Fe^{3+} and SO_4^{2-} reduction on arsenic solid-phase cycling in Fe- and As-rich sediment

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Defining microbially induced As mobilization or binding in heterogeneous Fe and sulphide mineralogical contexts is of considerable importance to understanding the complexities of As solubility in sediments, including those of aquifers in arsenic-affected countries such as Bangladesh. This study examines the effect of microbial respiration on As-cycling in an Fe (50%; x-ray amorphous Fe and goethite) and As (400 ppm) rich model system (hydrothermal sediment, Santorini, Greece). Slurries of suboxic to anaerobic transition zone sediment were incubated under a range of biogeochemical regimes for periods of up to 111 days at 25°C, with intermittent sampling for solid and aqueous phase analyses. Analytical techniques included sequential As and Fe extraction, Ferrozine assay for Fe(II), pH, Eh, IC, ICP-AES, XRD, XANES, EXAFS, Mössbauer spectroscopy, and microbial community analysis by the clone library method, targeting general 16S rRNA and DSR (SO_4^{2-} reducer) genes. Fe(III) and SO_4^{2-} reduction in sediments amended with acetate as an electron donor corresponded with significant compositional shifts in the overall and SO_4^{2-}-reducing bacterial consortia, and substantial solid-phase redistribution of As(III) from $\geq$60% binding within the bioavailable Fe fraction to approximately 30-35% sorbed, and approximately 40% binding within crystalline-Fe and sulphide/organic phases. The effect was reversed by NO_3^- or air re-oxidation. Results provide mechanistic implications for similar As associations in aquifer systems.

Integrated biomarker records reveal complex and dramatic changes in high latitude climate during the Paleogene

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Recent work on well preserved foraminifera and organic matter from tropical (Tanzanian) sediments indicates that, contrary to previous work, tropical SSTs were relatively constant in the Paleogene. We have now determined SSTs for well preserved New Zealand sediments using a combination of TEX_{86} indices and foraminiferal $\delta^{18}O$ values and Mg/Ca ratios. In contrast to tropical records, the high latitude records reveal dramatic (>15C) SST changes from 60 to 40 Ma and, combined with the tropical data, indicate that the latitudinal SST gradient changed dramatically. We have measured other biomarker proxies as tracers for mean annual air temperature over the adjacent land, soil pH, and terrigenous organic matter delivery to the ocean (BIT index). These records reveal a clear link, on both long (Ma) and short (Milankovitch) timescales, between a weak land-air temperature gradient, low soil pH (high rainfall) and elevated runoff. Together, these proxies reveal that the warm climate of the Early Eocene was associated with aridity and low runoff at these latitudes; however, precipitation and runoff increased as climate cooled during the Eocene. The Paleocene sediments exhibit different characteristics, however; a dramatic increase in the BIT index at the Paleocene Carbon Isotope excursion is associated with no supporting evidence for precipitation change, and we propose that changes in the BIT indices at this time reflect changes in sea level. In total, these data indicate that the early Paleogene was not characterised solely by subtle temperature variations in a greenhouse climate, but also by dramatic changes in the mean climate state.