Proton and ligand promoted dissolution of apatites

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Phosphorous is an essential nutrient required for construction of nucleic acids, ribosomes, adenosine triphosphate (ATP), and other cell materials in all living organisms. The primary natural source of phosphorous is apatite minerals, ($Ca_5(PO_4)_3F,Cl,OH$), which are abundant soil constituents throughout the world. Although phosphorous is abundant in soils and sediments, it is a growth limiting nutrient for biological productivity in many ecosystems. Plants and microorganisms have consequently devised several strategies to obtain the phosphorous they need, and one of these strategies is to exude small organic acids that can accelerate the dissolution of minerals like apatites.

The objectives with our studies are to clarify the surface acid/base properties of apatites, as well as to elucidate the effect of three different organic polycarboxylic acids. We used citrate, malonate and mellitate as model substances. Malonate and citrate are ligands generally produced by bacteria, while mellitate is a synthetic compound included in the study to evaluate the effects of ligand charge on the release of phosphate. To distinguish the effects due to pH from those of the organic ligands, the dissolution of apatite was also studied in the absence of the organic ligands.

Results from the experiments shows that malonate only had a minor effect on the dissolution of apatite, while both citrate and mellitate enhanced the amount of phosphate present in solution at $pH > 7$. ATR-FTIR data also provided information that all three ligands were adsorbed to the apatite surface as fully deprotonated outer sphere complexes. Furthermore, there are spectroscopic evidence for the formation of Ca_3Mel (s) at $pH \leq 6.2$ in the apatite mellitate system.

The petroleum reservoir deep biosphere, new views from petroleum geology and geochemistry

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Petroleum reservoirs provide a direct portal into the deep biosphere enabling microbiological and geochemical studies of microorganisms, carbon cycling processes, microbial reaction kinetics and the spatial distribution of the organisms. Detailed mapping of oil chemical composition shows that microbially and geologically induced oil compositional gradients are ubiquitous at regional to sub-reservoir scales (m to 10^5 m) in heavy oil deposits in Alberta and elsewhere. Some oil columns show a cascading series of gradients in one through three ring alkylaromatic and thioaromatic hydrocarbons with increasingly deeper locations of complete compound removal related to increasing resistance of degrading hydrocarbon component to biodegradation and decreasing component diffusivity.

We often observe steepening compositional gradients at the base of the oil column coincident with up to 10–15 m thick, downward increasing water saturation zones, thicker than a capillary pressure controlled oil-water transition zone. These “burnout zones” represent a vertically extensive bio-reactor with increased concentrations of biogeochemical parameters of microbial processes and commonly an immobile and probably discontinuous oil phase. The degradation systematics within the transition zone appear more complicated than in the oil column probably due to more localised factors involving accessability to microbes and nutrient supply. In this zone and across an oilfield, the relative biodegradation susceptibility of different hydrocarbon components varies greatly, indicating a suite of biodegradation reaction pathways dependent in part on local mass transport controls. 1D models show that the top of the degradation zone is coincident with complete depletion of reactive components, when oil charge is active. Thus in heavy oil reservoirs, biodegradation processes extend into the oil leg well above the base of the oil leg (5-10 m) rather than just near the base of the oil column as previously proposed. Thick biodegradation zones especially develop where high oil viscosity results in high relative water mobility, enabling efficient transport of essential nutrients through the mobile water phase to microorganisms.