

Nucleation and growth of nano-apatite: Insights into bone formation

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The formation of atomic clusters is the first step in the process of nucleation of a new phase in supersaturated aqueous media. Calcium phosphate cluster formation leads to the nucleation of apatite, an important biomineral (bone, tooth), industrial mineral (scale formation, wastewater treatment) and a phase controlling phosphorus availability in soils. Formation of apatite at the atomic scale is believed to take place via the formation of a $\text{Ca}_3(\text{PO}_4)_2$ precursor. It is currently uncertain whether single or multiple $\text{Ca}_3(\text{PO}_4)_2$ units give rise to the hydroxylapatite proto-nuclei but ab initio calculations suggest the Posner's cluster: $[\text{Ca}_3(\text{PO}_4)_2]_3$ is the energetically most stable configuration (Treboux et al., 2000). It is currently unknown how the transition from Posner's clusters (Ca:PO₄ ratio of 1.50) to hydroxylapatite (Ca:PO₄ ratio of 1.67) occurs in solution, and how this may be affected/controlled by the presence of organic ligands.

The nucleation and growth of apatite has a number of important applications; the focus here is biomineralisation, specifically of bone. In bone, bioapatites are arranged with their [0001] axis parallel to the long axis of collagen (Landis, 1996). The precipitation of bioapatite is likely to be controlled by a template imposed by collagen. The way this template influences crystallite precipitation and growth ("bone mineralisation") is not known, but a control by carboxylate terminal groups is suspected (Robey, 1996). Carboxylate ligands (e.g. citrate) are also present in tissue fluid in contact with bone, and may have a significant effect on bioapatites (Eanes & Hailer, 2000).

Ex-situ TEM observations (van der Houwen et al., 2003) of precipitated apatite suggest that crystallite size and crystallinity is affected by small organic ligands (such as citrate). However, it is, at present, unclear whether this is due to the organic ligands enhancing multiple nucleation (more crystallite formation) or inhibiting growth, via, perhaps, binding on active sites. Further experimental work will be presented that explores the mechanisms of nucleation and growth of a synthetic apatite, as a proxy for bioapatites, thus elucidating the mechanisms that control nucleation, growth, particle size, shape and, perhaps, strength of bioapatites.

References

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Biogeochemical processes at the fringe of a landfill leachate plume

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Various redox reactions may occur at the fringe of a landfill leachate plume, involving oxidation of dissolved organic carbon (DOC), CH₄, Fe(II), Mn(II), and NH₄ from leachate and reduction of O₂, NO₃ and SO₄ admixing from pristine groundwater. Knowledge on the relevance of these processes is essential for the simulation and evaluation of natural attenuation (NA) of pollution plumes. The occurrence of such biogeochemical processes was investigated at the top fringe of a landfill leachate plume (Banisveld, the Netherlands). Previously, degradation of organic carbon was observed to be coupled to reduction of iron oxide within this leachate plume (Van Breukelen, 2003). Hydrochemical depth-profiles of the top fringe were captured via installation of a series of multi-level samplers at 18, 39 and 58 m downstream from the landfill. Ten-cm vertical resolution was necessary to study NA within a fringe as thin as 0.5 m.

The plume fringe rose towards the surface from a depth of around 5 m over a vertical distance of about 1-3 m in the course of three years, possibly as a result of soil excavation in the area. This rise invoked cation-exchange including proton-buffering, and triggered degassing of methane. The hydrochemical depth-profile was simulated well in a 1D vertical reactive transport model using PHREEQC-2. Optimization using the non-linear optimization program PEST showed that solid organic carbon and not clay minerals controlled retardation of cations. Cation-exchange resulted in spatial separation of Fe(II), Mn(II) and NH₄ fronts from the fringe, and thereby prevented possible oxidation of these secondary redox species. Degradation of conservative DOC seemed to happen in the fringe zone. Re-dissolution of methane escaped from the plume and subsequent oxidation could be an explanation for absence of previously present nitrate and anaerobic conditions in pristine groundwater above the plume. Stable carbon isotope (d¹³C) values of methane suggested that anaerobic methane oxidation occurred. Methane was the principle reductant consuming soluble electron-acceptors in pristine groundwater, thereby limiting NA for other solutes including organic micro pollutants at the fringe of this landfill leachate plume.

References

- Van Breukelen B.M., (2003), PhD Thesis, Vrije Universiteit, Amsterdam, 140 pp.