

Evidence for the formation of a fluorapatite surface layer on nano-sized hydroxyapatite after the exposure to an aqueous solution

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Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAP) is the main constituent of bones and teeth [1]. Its ability to take up fluoride is applied in dental care [2] but also for drinking water purification [3]. Even though much research has been performed on fluoride uptake on HAP [e.g. 4], it is not fully understood how deeply fluoride incorporates into the HAP crystal.

It is believed that fluoride adsorbs to the HAP surface and exchanges for the hydroxide to form the less soluble fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$; FAP) [5]. The uptake capacity of fluoride on the HAP crystal is controlled by the exposure time and pH of the system [4]. A simultaneous formation of fluorite (CaF_2) cannot be ruled out when calcium and fluoride achieve saturation concentration [6]. However, a dissolution of CaF_2 in favour of FAP recrystallization is likely.

Batch studies were performed at 25 °C to investigate the uptake of fluoride as function of pH and initial fluoride concentration on synthetic HAP over an equilibration time of 28 days.

The reacted solids were investigated by Fourier Transform Infrared Spectroscopy (FTIR), which provided estimates on weight percentages on FAP formation on HAP after 28 days. Nano Secondary Ion Mass Spectroscopy (NanoSIMS) and Transmission Electron Microscopy (TEM) analysis gave additional information for a thin layer of FAP on HAP crystals.

To our knowledge it is the first time that the presence of a fluoridated surface layer on a nano-sized HAP crystal was qualitatively *and* quantitatively determined by micro- and spectroscopic analyses.

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Ice formation on atmospheric mineral dust particles

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Mineral dust particles are known to be efficient catalysts for the formation of ice in clouds. In recent field studies by our group at the Jungfrauoch in the Swiss Alps a good correlation of the concentration of ice nuclei with the concentration of large particles during Saharan Dust events at this location was found [1]. Similar results are available from other groups as well e.g. [2].

However, the influence of size, shape, chemical composition, and the modifications of some of these parameters through anthropogenic emissions of pollutants to the atmosphere on the formation of ice is still mostly unknown and needs to be investigated further. This is complicated by the fact that ice in clouds may form via different pathways or mechanisms (immersion freezing, deposition freezing, contact freezing) and the parameters determining their efficiency in forming ice are different.

In our lab we investigate these different ice nucleation mechanisms with individual experiments for the different mechanisms using mineral dust aerosols. In this paper, our recent results on the ice nucleation properties of mineral dust particles for immersion freezing, and contact freezing are presented and compared.

The analysis of the immersion freezing data is done by calculations based on classical nucleation theory (CNT) assuming different assumptions regarding the properties of the mineral dust aerosols. From this analysis, the presence of so-called active sites can be deduced at which the nucleation process takes place preferably [3]. CNT also predicts that ice nucleation is a statistical process and therefore time dependant. To proof this, we conducted a special set of experiments where the residence time in the nucleation chamber is varied between 3 and 19 seconds. The results are again analysed and compared against CNT calculations as explained above and suggest, that immersion freezing is indeed time dependant where the frozen fraction increases with residence time.

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