



In situ Atomic Force Microscopy (AFM) study of erionite and offretite interactions with Simulated Lung Fluids (SLFs)

Matteo Giordani (1), Georgia Cametti (1), Fulvio Di Lorenzo (1), Sergey V. Churakov (1,2)

(1) University of Bern, Institute of Geological Sciences, Mineralogy, Bern, Switzerland (matteo.giordani@geo.unibe.ch), (2) Paul Scherrer Institute, Forschungsstr 111, Villigen PSI, CH-3012 Bern, Switzerland

Erionite is a mineral belonging to zeolites group occurring with prismatic or fibrous habit. The exposure of humans to erionite fibres has been unambiguously linked to the development of several pulmonary diseases, e.g. malignant mesothelioma, and at present the erionite is classified as Group I carcinogenic mineral (WHO, 1986). Moreover, a second zeolite called offretite, typically prismatic but closely related to erionite from the chemical and structural point of view, has also been found under asbestiform habit (Mattioli et al., 2018). Despite the great number of researches, the relationships between mineralogical features and biological activity of erionite have not been fully understood. In opposite, there are no studies regarding the potential hazard of offretite fibres, and it is unclear whether the mineralogical distinction between erionite and offretite has any health implications.

Recently, the biodurability and dissolution of erionite fibres after leaching with artificial simulated lung fluids (SLFs) (e.g. Gualtieri et al., 2018) was investigated. Although these studies were extremely useful to determine the eventual response of erionite fibers in lung environment, at present, information on modifications occurring at nanometric scale at the fibres surface are still missing. Considering that the chemical reactions involved in pathogenesis mainly take place at the solid-liquid interface, this kind of information is of paramount importance. With this aim, the interactions of erionite and offretite with SLFs were investigated in real-time by means of in situ AFM.

To simulate different environments in the lungs, Artificial Lysosomal Fluid (ALF) and Gamble's solution were used (Stopford et al., 2003). Significant morphological changes on zeolite-surfaces at nanometric scale were observed. In ALF ($4.15 < \text{pH} < 4.31$) superficial dissolution of erionite and offretite crystals occurred. In particular, an evident removal of adhered particles (mainly impurities with diameter ranging from $<30 \text{ nm}$ to $\sim 2 \mu\text{m}$) from the zeolites surface was detected. Instead, a layer of an unknown phase, likely amorphous, on the surface of both zeolites, grew during interaction with Gamble's solution ($7.4 < \text{pH} < 8.48$). The thickness of this layer reached few tens of nanometers but covered all the investigated area. These results highlight how different and complex the response of fibers surface are with respect to the bulk mineral. The understanding of these aspects is crucial since they could potentially be involved in the reactions triggering the carcinogenic process.

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