## Discovery and dangerous human health ramifications of incidental Magnéli phase generation and release from coal burning power plants - C.C. Patterson Medal Lecture

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Coal, as one of the most economic and abundant energy sources, remains the leading fuel for producing electricity worldwide. Yet, burning coal produces more global warming CO<sub>2</sub> relative to all other fossil fuels, and it is a major contributor to atmospheric particulate matter known to have a deleterious respiratory and cardiovascular impact in humans leading to an estimated 3.3 million premature deaths per year worldwide. Recently and through serendipity, we discovered that burning coal also produces large quantities of otherwise exceptionally rare Magnéli phases (Ti<sub>x</sub>O<sub>2x-1</sub>;  $4 \le x \le 9$ ) in the nanoparticle sizerange, this from TiO<sub>2</sub> minerals (rutile and anatase) naturally present in coal. Our discovery provides a new tracer for tracking solid-state emissions worldwide from industrial-scale coalburning. We estimate that on the order of a billion metric tons of Magneli phase nanoparticles have been produced by coal burning in the last few centuries, primarily since the Industrial Revolution. In addition, shortly after our discovery, we suspected that Magneli phases may be biologically active due to the catalytic activity of TiO2, a UV absorbing wide band gap semiconductor. On the other hand, Magneli phases have been synthesized by materials scientists for many years, and they are known to be narrow band gap semiconductors. Therefore, they can promote reactions with much lower energy inputs (i.e., in the absence of light). Thereafter, we confirmed that Magneli phases were significantly toxic to dechorionated zebrafish embryos without photostimulation. Finally, this led to our next discovery that Magnéli phases are biologically toxic to human lung epithelial cells (primarily macrophages) in vitro without photostimulation, resulting in reactive oxygen species production, cell death, and the initiation of gene expression profiles consistent with lung injury. Subsequently, we exposed mice to the most frequently found Magneli phase from power plant coal burning, Ti<sub>6</sub>O<sub>11</sub>, at 100 parts per million (ppm) via intratracheal administration. Chronic exposure and accumulation of Magnéli phases ultimately results in significantly reduced mouse lung function, impacting airway resistance, compliance, and elastance. Together, these studies demonstrate that Magnéli phases, now found worldwide, are toxic in the mammalian airway and are very likely a significant nanoscale environmental pollutant.