Micro-geology in the atmosphere: the chemical evolution of aerosolized mineral phases and their role in ice nucleation

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The roles of mineral-containing particles ejected into the atmosphere from understudied sources – biomass burning and volcanic eruptions – in atmospheric chemistry and cloud microphysics are explored. Emissions from the combustion of some types of biomass fuels have been found to contain ice nucleating particles (INPs) active at temperatures as warm as −20 °C that can catalyze the freezing of supercooled water and thus induce cloud glaciation. Combustion of tall grass fuels such as cutgrass and sawgrass were found to produce new mineral phases in the resulting bottom ash and biomass burning aerosol particles. The greater mass fraction of these simple minerals seems to explain the higher freezing ability of the bottom ash compared to ash from combustion of fuels such as birch, ponderosa pine, and fatwood. Production of mineral phases by biomass burning – especially those that are ice active – has not been previously considered by the atmospheric chemistry community, which usually attributes minerals in smoke-laden aerosol to resuspended pre-existing soil and dust particles. These mineral phases may also explain the often observed efficient ice nucleating particles (INPs) in biomass burning aerosol, while soot particles appear to make a small contribution to the INPs.

The effects of atmospheric aging on the ice nucleation properties of biomass burning aerosol were explored using the CMU smog chamber reactor to simulate photochemical oxidation. Unexpectedly, chemical aging often enhanced the freezing ability of smoke aerosol from tall grasses. The freezing ability also improved during time aging experiments where the aerosol was held in the chamber without external perturbation. Combined with the discovery of new ice-active mineral phases in bottom ash, these results have produced a new model of the ice nucleation properties of biomass burning aerosol. The produced and resuspended mineral phases likely drive most of the freezing ability, while the uncovering of preexisting ice active sites by the slow evaporation or dissolution of organic carbon components would explain the enhancement of ice nucleation properties with time or oxidative aging. This would mean that the number of effective ice nucleating particle emitted by biomass burning would actually increase as the plume dilutes from the source, in contrast to the expected dilution of INPs.

Three volcanic ash samples from Central America were found to contain efficient ice nucleants. The ice nucleation properties were largely explained by the crystalline content, such as by the presence of Ca- and Na-rich plagioclase feldspars. Pyroxene minerals were also found to play an important contribution to the freezing ability for the first time. Pyroxenes are unique to volcanic tephra and uncommon in mineral dust, potentially providing a previously unrecognized source of efficient ice nucleating particles to the atmosphere. Alteration of the freezing properties caused by chemical aging was investigated using a chamber reactor to generate sulfuric acid through gas-phase oxidation. Deposition of sulphuric acid vapor was contrasted with aqueous processing by acidic solutions. The effects of aging were unexpected, where water aging alone often reduced the freezing properties of the volcanic ash to a greater extent than sulphuric acid uptake. This may be attributable to the dissolution of ions from the mineral surfaces that is arrested by solutes.

Bio:
Ryan Sullivan is an Associate Professor at Carnegie Mellon University, with a joint appointment in the Departments of Chemistry and Mechanical Engineering, and a courtesy appointment in the Department of Civil and Environmental Engineering. He is also a faculty member in the Center for Atmospheric Particle Studies, and the Associate Director of CMU’s Institute for Green Science. He obtained his
bachelors in chemistry from the University of Toronto, and his doctorate in chemistry from the University of California, San Diego. Before moving to Carnegie Mellon University in 2012 he completed his postdoctoral research in atmospheric chemistry at Colorado State University. Ryan is the recipient of a Faculty Early Career Development (CAREER) award from the National Science Foundation, and the National Academy of Science’s Cozzarelli Prize.

His research group at CMU develops laser-based analytical techniques for real-time analysis of individual aerosol particle composition. These include laser ablation single-particle mass spectrometry, aerosol optical tweezers, and microfluidic devices for ice nucleation research. The multi-phase chemical evolution of biomass burning aerosol from wood smoke is a major current focus. Ongoing experimental investigations include the alteration of the ice nucleation properties of smoke particles induced by chemical aging; and the activation of photo-labile chlorinated gases from heterogeneous reactions of nitrogen oxides with chloride salts emitted in the smoke. As part of the Institute for Green Science he is developing advanced water oxidation technologies for micropollutant removal based around NewTAML catalytic activators of hydrogen peroxide.