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## Mineral-based Free Radical Formation: Analytical Challenges, Process-Level Understanding, and Implications for Human Health

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Free radicals—atoms or molecules with one or more unpaired electrons—are typically unstable, highly reactive, cause cellular damage, and can lead to disease. Two of the more common reactive free radicals (FR) are superoxide,  $O_2^{*}$  and hydroxyl radical, OH\*, which form via stepwise reduction of  $O_2$ , itself a relatively unreactive bi-radical. Protective enzymes, such as superoxide dismutase, high levels of antioxidants, and repair systems limit the deleterious effects of FR within mamallian cells. However, inhalation exposure to particulate matter that induces FR formation can overwhelm these defense mechanisms. For example, mineral-driven FR formation is thought to contribute to silicosis and asbestosis. FR formation associated with quartz is thought to be largely driven by the presence of surface defects, which are often induced by mechanical stress.

Analyzing for FR is a challenge because of they typically react almost immediately after they form. The "gold" standard in FR analysis is spin trapping which leads to the formation of an adduct that is labile and gives rise to a specific ESR spectrum. While specific, it is not easy to use this analytical technique to study the kinetics of mineral-driven radical formation. We have adapted biomedical molecular probe techniques and developed two new techniques to study the formation of OH radical formation in aqueous mineral dispersions. In addition, we have developed a protocol to determine the effect of mineral exposure on human epithelial cells.

Using these new tools we have extensively studied an alternative mechanism to mineral defect-driven radical formation. This alternative, Fenton-like process has been shown to operate in the formation of hydroxyl radicals when iron-bearing minerals are dispersed in water or simulated lung fluid. For example, pyrite forms significant amounts of OH\* when dispersed and its presence in coal is thought to be a major factor in the development of black lung disease among coal miners. Currently we are working on the reactivity and toxicity of materials relevant to the human exploration of airless planetary bodies.