

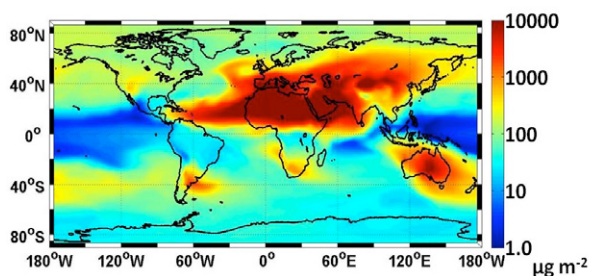
## Updated dust-iron dissolution mechanism: Effects of organic acids, photolysis, and dust mineralogy

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Aeolian dust deposition to remote oceanic regions is a major atmospheric supply pathway of essential nutrients (e.g. iron (Fe) and phosphorus (P)) which have a controlling effect on marine primary productivity. The soluble/bioavailable fractions of Fe and P in mineral dust are minor at the source regions and increase during the transport. Nutrient mobilization from mineral dust is a complex process; in the atmosphere it is thought to be controlled by dust mineralogy, atmospheric chemical composition, and meteorological variables. Therefore, quantitative predictions for the formation of these important nutrients should be included in global-scale coupled biogeochemical cycle models for improved prediction of future climate.

Here, the global 3-D chemistry transport model GEOS-Chem with a state-of-the-art Fe- and P-dissolution scheme is used to generate comprehensive global datasets for nutrient concentrations and deposition (Fig. 1). The model improvements include source-specific dust-mineralogy, organic ligand-promoted Fe dissolution, the photolytic redox cycling of Fe (II)/Fe (III), and acid-based P dissolution. Preliminary results indicate that Fe bound in clay minerals and the presence of oxalate significantly increases soluble Fe production in mineral dust. Photolysis can further increase the amount of soluble Fe by converting Fe (III)-species into the more bioavailable ferrous Fe (Fe (II)) form. Model predicted diurnal variations in Fe (II)/Fe (III) are consistent with available data.



**Figure 1:** Model-predicted total column burden of soluble Fe ( $\mu\text{g m}^{-2}$ ) between June-August 2009.

## Adsorption of organic ligands on silicate mineral surfaces in the presence of CO<sub>2</sub> and water: Insight into olivine dissolution rates

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The dissolution of magnesium silicates releases magnesium cations ( $\text{Mg}^{2+}$ ) into solution, which in the presence of dissolved carbon dioxide ( $\text{CO}_2$ ) can, under certain conditions, precipitate as magnesium carbonates. This process results in the mineralization of  $\text{CO}_2$ , a safe, long-term storage strategy to control rising  $\text{CO}_2$  concentrations in the atmosphere. However, the kinetics for these processes are slow and the mechanisms are not fully understood. Previous work by this group and others has found the dissolution rates of silicates to be enhanced by the presence of organic acids in some cases, but reduced in other cases. This study seeks to understand the factors that determine whether an organic compound acts as an activator or an inhibitor. Organic ligands may adsorb to silicate surfaces as outer-sphere complexes, likely passivating active sites and reducing dissolution rates, or as inner-sphere complexes, drawing electron density away from the mineral surface, weakening near-surface bonds, and increasing dissolution rates. The nature of the adsorbed complexes depends on mineral surface charge and ligand charge, both of which are controlled by pH. X-ray photoelectron spectroscopy has been used to examine the organic carbon adsorbed on olivine and quartz surfaces after reaction with organic acids, water, and  $\text{CO}_2$ . Initial results show additional carbon on the surfaces exposed to the organic-containing aqueous phase but none on surfaces exposed only to the supercritical  $\text{CO}_2$ - $\text{H}_2\text{O}$  phase. Mineral surfaces exposed to both the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  phases also showed increased superficial carbon.