

Role of acid mobilization in projected response of soluble iron supply to improvement of air quality in the future

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Acidification of dust aerosols may increase aerosol iron (Fe) solubility, which is linked to mineral properties (e.g., crystallinity, grain size and impurity content). The mixing of the mineral dust with combustion aerosols can also elevate iron solubility when aerosol loading is low. Here, we use a process-based chemical transport model [1, 2] with improved treatment of Fe in mineral dust and proton-promoted dissolution scheme to investigate the deposition of soluble iron and its response to changes in anthropogenic emissions of both primary particles and precursor gases.

Comparisons of modeled Fe dissolution curves with the measured dissolution rates show overall good agreement under acidic conditions. The improved treatment of Fe in mineral dust and the proton-promoted dissolution scheme results in reasonable predictive capability for iron solubility over the oceans in the Northern Hemisphere. Our model results suggest that iron included in aluminosilicate dust can be released in the form of ferrihydrite colloids, nanoparticles and aqueous species during the long-range transport and thus provide an important bioavailable source of iron to the oceans. As a result of considering both the atmospheric processing of mineral dust and source composition of combustion aerosols, soluble iron deposition to the subarctic North Pacific is projected to respond nonlinearly to changing emissions of fly ash and air pollutant gases (e.g., SO₂, NO₂ and NH₃). These results could have important implications for iron fertilization of phytoplankton growth, and highlight the necessity of improving the process-based quantitative understanding of the response of the chemical modification in iron-containing minerals to environmental changes.

[1] Xu, & Penner (2012) *Atmos. Chem. Phys.* **12**, 9479–9504, doi:10.5194/acp-12-9479-2012. [2] Ito (2013) *Global Biogeochem. Cycles* **27**, 1–10, doi: 10.1029/2012GB004378.

Spin transition of Fe²⁺ in ringwoodite (Mg,Fe)₂SiO₄ at high pressures

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Electronic spin transitions of iron in the Earth's mantle minerals are of great interest to deep-Earth researchers because their effects on the physical and chemical properties of mantle minerals can significantly affect our understanding of the properties of the deep planet. Polycrystalline samples were synthesized in a multi-anvil apparatus using ⁵⁷Fe-enriched starting material ((Mg,Fe)O-SiO₂ mixture) at conditions of approximately 22 GPa and 2000 K. Energy dispersive x-ray elemental mapping and electron diffracton study of the sample showed that Fe predominantly presents in the ringwoodite phase γ -(Mg_{0.75}Fe_{0.25})₂SiO₄.

The electronic spin states of iron in ringwoodite were studied at high pressures up to 82 GPa using synchrotron Mössbauer spectroscopy (NFS) in a diamond anvil cell (HPCAT, Sector 16, APS, ANL). At ambient conditions, the NFS spectra reveal two non-equivalent iron species (Fe²⁺)₁ and (Fe²⁺)₂ which can be attributed to octahedral and tetrahedral sites in the cubic spinel structure of ringwoodite, respectively. High-pressure NFS spectra showed the disappearance of the hyperfine quadrupole splitting of the Fe²⁺ ions in both sites at approximately 45-70 GPa, indicating an electronic high-spin to low-spin transition. The spin transition exhibits a continuous crossover nature and is reversible at decompression.

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