

New insights into iron mineralogy and geochemistry in Saharan dust precipitated over Greece

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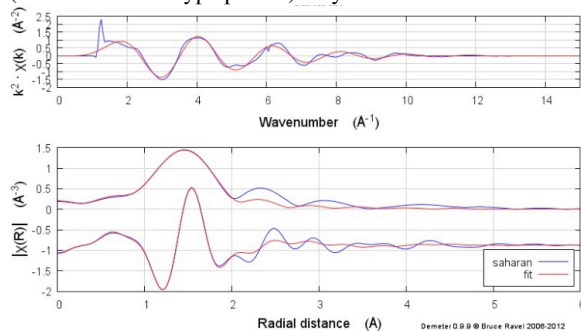
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The Saharan dust samples were collected on membrane filters after intense “red rain” episodes over the Greek megacity Athens. Characterization by means of bulk powder-XRD and SEM-EDS showed quartz, calcite and dolomite, as major crystalline phases and minor phyllosilicates (mostly clays). Detailed Synchrotron μ -XRF study proved that many trace elements are intercorrelated with Fe in microparticles of potential anthropogenic origin (e.g. Fe-Mn-V-Cu), as well as the presence of very hazardous elements such as Pb and As. Moreover, it was concluded that Fe also forms individual Fe-oxide and/or oxyhydroxy phases (sole Fe spots in μ -XRF maps) and besides it is frequently associated to Ca-containing phases and particularly carbonates (frequent Ca-Fe overlap in μ -XRF maps without Si or any other metal). However, Synchrotron μ -XRD study gave no clear evidence of crystalline Fe-oxides and/or -oxyhydroxides. Subsequent Mössbauer spectroscopic study showed abundant Fe³⁺-containing constituents and minor Fe²⁺-phases (ca. 5% paramagnetic component having Mössbauer parameters characteristic of a Fe²⁺ state). The investigation of the μ -XANES and -EXAFS (Figure below) indicated that Fe³⁺ most probably corresponds to ferrihydrite-type -XRD-“amorphous”- phases, but structural units from other Fe-oxyhydroxides, like akaganeite, and Fe³⁺-oxyhydroxy-sulphates (schwertmannite-type phases) may also contribute.



Sequential leaching experiments, using appropriate acids and ICP-MS analyses, revealed a significant percentage of extractable Fe (and also Zn, Mn and Pb), fundamentally due to carbonate phases comprising ~60% of the material according to bulk XRD. It is herein stated that Fe in Saharan dust precipitated over eastern Mediterranean, and particularly Greece, is predominantly related to Fe³⁺-oxyhydroxy (most probably ferrihydrite-type) phases, and to a lesser extent to Ca-(Mg)-carbonates hosting possibly the Mössbauer-detected minor Fe²⁺ component.

Direct observations of structures developed on fluorite surfaces after contact with an aqueous solution

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In this study we used an atomic force microscope equipped with a fluid cell to observe the surface dynamics during the first minutes of contact between a solution and polished fluorite surfaces with orientations (115), (334), (104), (110) or (102). 3-D confocal profilometry was used to analyze the surface topography developed on the same surfaces for dissolution times up to 3200 hours.

The surfaces studied, with an initially high density of defects, showed fast changes during the first seconds in contact with solution. Different types of structures were observed on the surface depending on its initial orientation and the solution composition. These structures dissolved slower than the main surface persisting for at least 1620 hours of continuous dissolution. The inhibition of dissolution on the areas of the surface where the structures developed induced the growth of crystallographically controlled topography, which was linked to a variation of the surface reactivity and measured dissolution rate.

A new interpretation of traditional kinetic and thermodynamic models of dissolution applied to surfaces with high density of defects is proposed to explain the observations. It is proposed that the structures developing rapidly during the first contact with the fluid are a fluorite phase more stable than the initial surface. A new dissolution model is suggested to include the following steps: a) fast initial dissolution at defect sites; b) formation of a fluid boundary layer at the interface mineral-solution enriched in the dissolving ions; c) precipitation of a stable phase on surface defects. This model highlights the importance of considering surface defects for advancing our understanding of processes happening at the interface mineral-solution and for developing more accurate kinetic dissolution models essential in Earth and material sciences.