Hematite contaminated by heavy metals

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The aim of this project is to use computational and mineralogical techniques to determine the mobility of potentially toxic metallic and metalloid elements such as lead (Pb) and arsenic (As) in pyrite ash wastes..

Contaminated soils and aquifers are often linked with industrial activities or land treatments. One example is the high levels of potentially toxic metallic and metalloid elements on sites associated with old paper mills. To produce cellulose the paper mills used to dissolve wood in sulphite SO_3^{2-} solutions, which were produced on site by oxidizing sulphur-bearing minerals (mostly pyrite) at high temperatures. The remaining ash, so called 'pyrite ash', is now found as fine-grained sand with a characteristic red-violet colour.

Pyrite ash contaminated by lead and arsenic has been found in the south-west of Sweden. Mineral characterization shows that the main components of the pyrite ash are hematite (α-Fe_2O_3), and quartz (α-SiO_2). The soils contain more than 20000 mg/kg Pb and 10000 mg/kg As. We find that Pb concentrations are independent of soil pH, but As concentrations are highest at $pH < 2$.

In order to gain a better understanding of the mobility of Pb and As in pyrite ash wastes, we are using quantum mechanic and classical inter-atomic potential calculations to study the 1) bulk structure of hematite contaminated with Pb, As and Mg and 2) Pb and As adsorbed on hematite surfaces under different pH conditions.

Traditional density functional theory (DFT) techniques cannot be applied to study α-Fe_2O_3. To deal with this problem we are using HYBRID functionals and DFT+U. We have found that the electronic and geometric structures of the hematite can be correctly described using the B3LYP functional. Our simulations show a phase transition into a spinel structure (magnesioferrite, $MgFe_2O_4$) when hematite is contaminated with higher concentration of Mg. Results for Pb and As will be presented on the poster. Initial calculations indicate that these elements might reduce iron(III) to iron(II) in hematite.

Determination of semi-volatile organic compounds adsorbed on the surface of suspended particulate matter

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Atmospheric particles, with their high surface area to mass ratio, constitute a possible sink for organics. On the other hand, semi-volatile organic compounds (SVOC), because of their molecular size and complexity, tend to become easily attached to aerosol particles. The amount in the adsorbed phase depends on several factors such as volatility and polarity of the organic, and nature of particulate components to which it might adsorb. Organics adsorbed on particles have a different fate with respect to organic compounds in the gaseous phase, as they can be long-range transported, thanks to a lifetime similar to those of aerosol particles themselves, and removed from the atmosphere by wet and dry deposition. In addition, atmospheric particles may have a catalytic role in the reactions between adosrbed VOCs and inorganic gases, leading to the formation of secondary PM. Also, it is probable that the species adsorbed on the external surface of particles are particularly available for the interaction with the human body and the ecosystem. For all these reasons, the issue of organics adsorption deserves an deep investigatiom.

A few studies, up to now, have been addressed to the determination of SVOC adsorbed on PM; these studies were generally aimed to evaluate the extent of PM sampling artefacts which are the result of the interaction between organics in the gaseous phase and the particles collected on the filter media.

We report in this paper the results of a first series of experiments aimed to develop a reliable procedure for the determination of organics adsorbed on atmospheric PM. Thermogravimetric methods, headspace analysis and thermal desorption of the filter membranes followed by GC-MS determination of the evolved species have been tested on atmospheric PM samples of different composition.

The fingerprint of the organic species thermodesorbed at different experimental conditions has been used also to evaluate the performance of the front + backup filter configuration commonly used for OC determination in atmospheric particulate matter.