Iron speciation in volcanic soils from Fogo island (Cape Verde)

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Most volcanic soils are known as fertile soils as they contain an abundance of iron which all plants need. Among the different mineral phases, iron oxides (Fe_{ox}) are soil constituents of great interest in soil chemistry and relevance to plant nutrition. They have significant effects on many processes such as sorption and redox due to their high specific surface areas and reactivity. Fe_{ox} are known to incorporate elements such as Cr and As, that can be a threat to health. The Fe speciation in volcanic soils of Fogo island (Cape Verde) where this element may occur in significant amounts is the main goal of this work, contributing to environmental and health issues.

Fe contents, its compounds and forms in topsoils of Fogo island were studied by neutron activation analysis, Mössbauer spectroscopy and X-ray diffraction (XRD). The soils were collected from all units of the island in diverse geological formations – carbonatite, nephelinite, limburgite, pyroclasts and historic lavas. Fine materials from Mota Gomes volcanic crater (the most recent eruption which occurred in 1995) were also sampled. The total Fe content varies significantly from 1.7 % (Fe_2O_3 weight) in acid sulfate topsoils (pH = 3.9), up to between 11% and 21% in the other geological contexts (pH= 7.2 to 9.1).

In the most recent volcanic materials Fe is clearly more reduced with a fraction (Fe^{2+}) / (total Fe) within the range 21%-65%. This Fe^{2+} mainly occurs in pyroxenes, phyllosilicates and pure or slightly oxidized magnetite. With increasing materials age the (Fe^{2+}) / (total Fe) ratio gradually decreases down to 4% indicating that the Fe that is still incorporated in the silicates structures is increasingly oxidized. Maghemite is detected instead of magnetite and hematite appears becoming the main Fe-containing phase in the oldest materials. These results suggest that in a first weathering step Fe^{2+} is oxidized in the silicates structure and in magnetite which gradually evolves to maghemite. With the eventual decomposition of pyroxenes Fe^{3+} is mobilized in hematite. As weathering proceeds maghemite is also replaced by hematite. Hydroxides were neither detected by XRD nor by Mössbauer spectroscopy, which may be explained by the high aridity of the island. In the superficial materials inside the Mota Gomes crater, where fumaroles are still active, hydroxisulphates such as jarosite are found. Topsoils developed on nephelinites and carbonatites are in general more oxidized than those developed from limburgites. The former soils have higher concentrations of rare earth elements and show higher amounts of hematite. This correlation may be related to the high adsorption capacity of binary Fe_{ox}. Significantly high Cr contents (>200 µg/g) are also found in hematite rich soils.

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