Sulphate formation on Mars by radiolytic oxidation of sulphide minerals

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Recent data from Mars Exploration Rovers provide multiple lines of evidence indicating the extensive presence of sulphates on Mars surface. Near-infrared spectral data on Mars Express provides additional evidences of hydrated sulphate salt deposits in the Martian tropics. Sulphates have been identified in SNC meteorites, which contain salt minerals including sulphates, up to 1% by volume. These evidences taken together strongly suggest that sulphate minerals are on the Mars surface and within the upper lithosphere. Various scenarios have been proposed for sulphate formation on Mars, including hydrothermal alteration, precipitation from evaporating brines, and volcanic aerosols. However, to date, there is no comprehensive understanding of the oxidative mechanism which satisfactory explains all the observed features.

Ionizing radiation is an energy source capable of dissociating water with the production of a complex, highly reactive combination of oxidizing (e.g., H_2O_2, $HO^{\bullet}$, and O_2) and reducing (e.g. H atoms and H_2) species [1]. Previous work done by us have shown that under anoxic conditions, radiolysis of water coupled to oxidation of sulphide minerals is an efficient mechanisms in producing partially to fully oxidized sulphur species [2, 3]. On Mars, radiolytic processes will largely depend on the presence of water, rock porosity, abundances of radioactive elements, and sulphide concentration. Although the concentration of radioactive minerals on Mars is expected to be two orders of magnitude lower than those on Earth, higher sulphur concentration in the martian rock and a water-rich crust makes radiolysis effective on the period of 10^7 – 10^9 years. Additionally, significant radiolytically-induced sulphide oxidation probably has occurred on Martian surface where ionizing cosmic radiation constantly interact with ice or even with rising groundwater producing a plethora of highly reactive oxidants.

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Cu and Zn speciation in pig slurry impact on their mobility in soil

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The agricultural recycling of pig slurry, though beneficial in some instances, needs to be controlled in order to avoid organic and inorganic contamination of natural resources. Cu and Zn, oversupplied in the feed and thus in the slurry, represent a risk of pollution of the soils.

To decipher the behaviour of Cu and Zn, we decided to use a multiscale approach: from *field scale* to study the impact of intensive application of pig slurry on volcanic soil (Cu and Zn accumulation, profile distribution and transfer of Cu and Zn in soil solution) to *molecular scale* to study Cu and Zn speciation within pig slurries (X-Ray Absorption Spectroscopy, etc.)

Concentrations of Cu and Zn in soil solutions were measured each week during 2 years after intensive pig slurry spreading. The concentrations always remain very low (50 and 240 $\mu g.l^{-1}$ respectively) and comparable to the control which underlies the very low mobility of Cu and Zn. To understand the factors which govern Cu and Zn accumulation, the speciation of the elements in pig slurry was performed. Prior analysis, a size fractionation of pig slurry which is a complex matrix was performed.

The majority of the Cu and Zn (respectively 78 and 75 % of total concentration) was detected in the smallest fraction with particle size from 0.45 to 20 µm. The first unexpected result concerns the oxidation state of copper: Cu^{1+}. Moreover, the similarity with CuS reference spectra indicates that Cu is surrounded by sulfur atoms. For Zn, we described a double contribution in the first shell: Zn-O contribution with a peak at 1.9 Å and Zn-S contribution with a second peak at 2.3 Å. Oxydation state of Cu and sulfur-linked of Cu and Zn were unexpected and are described for the first time.

The origin Cu and Zn sulfur-linked within pig slurry could be explained by a bacterial form of these metals and this bacterial form would have a very low mobility in soil.