Coping with Oxygen: Peroxy defects in Rocks and the survival of bacteria

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An oxygen-rich atmosphere appears to have been a prerequisite for complex life to evolve on Earth and possibly elsewhere in the Universe. The question is still shrouded in uncertainty how free oxygen became available on the early Earth. Here we study processes that introduce peroxy defects into silicate minerals which, upon weathering, result in oxygen formation in an initially anoxic subsurface environment. Reactive Oxygen Species (ROS) are precursors to molecular oxygen during this process. Due to their toxicity they may have strongly influenced the evolution of life. ROS are generated during hydrolysis of peroxy defects, which consist of pairs of oxygen anions. A second pathway for formation occurs during (bio) transformations of iron sulphide minerals. ROS are produced and consumed by intracellular and extracellular reactions of Fe, Mn, C, N, and S species. We propose that despite an overall reducing or neutral oxidation state of the macroenvironment and the absence of free O_2 in the atmosphere, microorganisms on the early Earth had to cope with ROS in their microenvironments. They were thus under evolutionary pressure to develop enzymatic and other defences against the potentially dangerous, even lethal effects of ROS and oxygen.

We have investigated how oxygen might be released through weathering and test microorganisms in contact with rock surfaces and iron sulphides. Our results show how early Life might have adapted to oxygen. Early microorganisms must have "trained" to detoxify ROS prior to the evolution of aerobic metabolism and oxygenic photosynthesis. A possible way out of this dilemma comes from a study of igneous and high-grade metamorphic rocks, whose minerals contain a small but significant fraction of oxygen anions in the valence state 1- , forming peroxy links of the type $O_3Si\text{-}OO\text{-}SiO_3$ [1, 2]. As water hydrolyzes the peroxy links hydrogen peroxide, H_2O_2, forms. As a result, microorganisms attached to mineral grains will be exposed to a constant trickle of ROS from the H_2O_2 production. Many different groups of microorganisms are able to grow or survive in the presence of ROS.

[1] Balk et al. (2009) *Earth and Planetary Science Letters* **283,** 87-92. [2] Grant, R. A. *et al.* (2011) *Int. J. Environ. Res. Public Health* **8**, 1936-1956.

Impact of fungi and bacteria on the mobility of metals (Fe, Al) in podzolic soils

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Mineral weathering is a key process in soil leading to leaching and release of essential elements (Fe, Al), which sustain plant growth and determine the chemistry of soil solutions and exchange complex. Soil microorganisms (fungi and bacteria) play a major role in the availability of nutrients in soils. They participate in weathering of primary materials through the production of low-molecular organic molecules (siderophores and organic acids). Determination of their relative contribution and understanding their interaction with soil minerals through different mechanisms is a key step toward characterization of the mobility of metals and identification of the pedogenic processes in action.

Recent techniques of *in situ* dynamic sensor have been developed to assess bioavailable fractions of metal in soil according to different relevant time scales of environmental processes. Diffusive gradients in thin films (DGT) are one of these speciation analyses [1]. This technique allows to establish a permanent flux of labile metal through a gel and then to measure the labile concentration upon its deployment time (i.e. the labile fraction corresponds to free metals in solution and metals linked to inorganic and organic ligands). In order to identify different weathering agents implied on the mobility and speciation of metals (Fe and Al) in soil solutions both in field studies and laboratory experiments, we have deployed DGT and DET (Diffusive Equilibrium in Thin Film) in different horizons of a podzol (developed on granitic rocks) on Norunda Site (Sweden) in November 2011. In parallel, we lead several experiments of geological material (granite) bioweathering to investigate the impact of fungi and bacteria on the release of Fe and Al from granite. To characterize mechanisms of dissolution, we monitored low-molecular organic molecules produced by microorganisms, microbial biomass, pH, and free and labile iron and aluminium fraction released by combining DGT and DET techniques.

The comparison of the results between field studies and laboratory experiments will permit the improvement of our knowledge of the contribution of microorganisms on the bioavailability of metals in soils and also on the podzolisation process that remains still always debated.

[1] Zhang *et al.,* (2001) *Env. Sci. Technol.,* **35**, 2602-2607.