# Impact of radiation on the microbial reduction of iron oxides

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The microbial reduction of Fe(III) in geodisposed nuclear waste or radwaste contaminated land can play a significant role in controlling the mobility of a range of long-lived radionuclides, including U(VI), Np(V) and Tc(VII). As such environments are likely to receive large radiation doses, radiation induced changes to the iron mineralogy may impact upon microbial respiration and subsequently alter the stability of the radionuclide inventory. Hence, characterization of radiation damage to Fe(III) mineralogy and the resultant impact upon microbial respiratory processes is essential in the preparation of a geological waste disposal safety case. In this study aerobic irradiation (1 MGy gamma) of hematite and ferrihydrite led to an increase in the rate of Fe(III) reduction by the Fe(III)-reducing bacterium *Shewanella oneidensis* MR-1 in the presence of an electron shuttle, riboflavin. Sequential extractions of iron in microbial cultures containing irradiated ferrihydrite suggested a 10% increase in ferrous iron partitioned into an operationally defined iron carbonate phase. A 15% increase in microbially reduced iron in irradiated hematite systems was incorporated into a combination of a putative carbonate phase, an easily reducible fraction and also increased dissolved Fe(II). Mossbauer spectroscopy of irradiated ferrihydrite suggests conversion to a more crystalline phase similar to akaganeite, whilst anoxically irradiated hematite appears to show a decrease in Fe coordination. This study suggests that structural changes in the mineralogy by irradiation lead to an increase in bioavailabilty of ferric iron. This may have positive implications to the geological disposal of nuclear waste, as reducing conditions may be accelerated by radiation-induced microbial iron reduction, potentially mediating the enhanced stability of key radionuclides.

# Geochemical insights from accessory phases in a sanukitoid-like suite: Towards understanding temporal changes in subduction style

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Crustal evolution is governed by plate tectonics and it has been shown that between the Archean and the Phanerozoic major changes in subduction style occured. Among others, the chemistry of different plutonic rocks through time and the understanding of their petrogeneses have helped to define different stages in the evolution of plate tectonics on Earth. Although TTG, the direct product of melted oceanic lithosphere, were the main plutonic rocks generated during the Archean, an important change around 2.7 Ga led to the genesis of rocks that are the result of melting of a metasomatized mantle wedge: the sanukitoids. This observation is often interpreted as the result of a change from shallow to steep subduction. Modern plate tectonics generally generates calc-alkaline suites but exceptions can occur such as the Caledonian (Paleozoic) high Ba-Sr plutons in Northern Scotland. The latter have been interpreted as a "modern" analogue of sanukitoids [1].

In this contribution, we present a study of accessory minerals from this Caledonian sanukitoid-like suite (ultrabasic to acidic). Whole-rock chemistry (trace elements, radiogenic and stable isotopes) is well constrained [1] but the study of accessory phases reveals additional petrogenetic constraints [2]. Indeed, accessory phases are important beyond their modal proportion because they commonly contain elements that are not incorporated easily into major rock forming minerals. The incorporation of trace elements and more particularly rare earth element (REE) in their structures make them ideal to delineate petrogenetic processes. In particular, the study of apatite, titanite and zircon will test the ability of accessory phases to retain the signature of their tectonic affinity. We present a detailed petrographic study and the systematic analysis of trace elements and O isotopes of these phases in a range of fractionated plutonic rocks from appinitic (ultrabasic) to granitoid composition. These results have an important impact in the understanding of accessory phases saturation during the magma genesis and thus offer another way to study the petrogenesis of these sanukitoid-like rocks. This approach will be extended to other magma compositions to further our insight into petrogenetic processes and tectonic affinity that may be available from accessory phase studies.

[1] Fowler et al. (2008) *Lithos* **105**, 129-148. [2] Hoskin et al. (2000) *Journal of Petrology* **41**, 1365-1396.