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The role of melanin in fungal Fe uptake, mineral weathering and metal corrosion

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Melanins are organic pigments produced by most fungi. These organisms either fix these pigments in their cell wall or secrete them into their extracellular environment to protect themselves against an array of physicochemical stresses (e.g., UV irradiation, desiccation, ...). Melanin can adsorb metals like Fe. How this affects fungal uptake of Fe and deterioration of Fe-containing minerals and metals is however less known. To study this, we use the model fungi *Knufia petricola* A95, a rock-inhabiting fungus known to deteriorate minerals and have melanised cell walls, and *Amorphotheca resinae*, able to contaminate fuel tanks, secrete melanin and corrode metals. In *K. petricola*, we have deleted genes involved in melanin production and Fe uptake using CRISPR/Cas. Through comparison of the geochemical signatures of these gene deletion mutants with those of the wild type (WT), we explore the specific mineral/metal deterioration mechanisms of melanised fungi.

Fe isotope signatures of the biomass of melanin- and Fe uptake-deficient mutants of *K. petricola* revealed that Fe adsorbed either directly onto melanin or after being reduced by Fe reductases. Importantly, once adsorbed to melanin, Fe could not be mobilised and taken up into the cell: both the WT and its melanin-deficient mutant, previously grown at Fe replete conditions, showed similar growth at Fe deficient conditions.

Olivine dissolution experiments revealed that Fe oxidation inhibits dissolution. *K. petricola* was able to enhance dissolution when this inhibition is strongest (at pH 6) and prevented dissolution when this inhibition is weakest (at pH 4). The fungus therefore dissolves olivine by interacting with the oxidised Fe at the olivine surface. However, Fe uptake did not seem to be involved: mutants deficient in various Fe uptake mechanism dissolved olivine at the same rate as the WT. This indicates that Fe adsorption onto melanin might play a key role. This is also shown by *K. petricola*'s ability to enhance olivine dissolution even further if secreting a melanin precursor and *A. resinae*'s corrosion of carbon steel whilst secreting melanin. Combined, our results imply that the Fe adsorbed to melanin cannot be taken up but enables fungi to deteriorate Fe-containing substrates at a higher rate.