Manganese oxide minerals are critical players in a number of biogeochemical processes and have the potential to be used in environmental remediation and materials science applications. These minerals are powerful oxidants of inorganic and organic species and have remarkably high adsorption capacities for trace and contaminant metals. The reactivity of layer-type manganese oxides (birnessite) is controlled by their structure and composition, including particle size, presence of structural defects in the form of vacancy sites, and the presence of adsorbed or structural Mn(III) (Simanova & Peña 2015; van Genuchten & Peña 2016).

The goal of this project was to investigate the redox properties for a suite of birnessite minerals that varied in terms of their structure (nm – µm sizes) and composition (0 – 20 % Mn(III): c-disordered birnessite (c-dis Bi), nanocrystalline δ-MnO₂ (δ-MnO₂), crystalline potassium birnessite (K Bi) and microcrystalline triclinic birnessite (Tc Bi). We hypothesized that both particle size as well as the crystallographic location and amount of Mn(III) in the mineral govern the mineral redox properties and thus reactivity. To test this hypothesis we developed analytical methods that are easily applicable to assess the redox state of these minerals. We then used mediated potentiometry (Sander et al. 2015; Gorski et al. 2016) to determine the reduction potentials (E₉) of the minerals at different pH values and concentrations of Mn²⁺. The combination of results from solid-phase characterization and electrochemical measurements will allow us to link the structure and composition of the birnessites to their oxidative capacity.

Thus far, we established two methods for the quantification of Mn(III) and the determination of the Average Manganese Oxidation Number (AMON) for a given manganese oxide. In the first method, sodium pyrophosphate (PP) is used to extract surface-bound/incorporated Mn(III) from Mn(III)-bearing MnO₂ to form Mn(III)-PP complexes. The concentration of these complexes can be quantified spectrophotometrically. In the second method, the AMON was determined by potentiometric titrations (Simanova et al. 2015): after using Mohr’s salt to achieve complete reductive dissolution of the mineral to Mn²⁺, permanganate is used to back titrate the Mn²⁺ solution to Mn(III) using excess PP. While both methods are quite accurate, the PP extraction method slightly underestimates the Mn(III) content, compared to the AMON titration method (about 5% less Mn(III)), of the minerals with a low specific surface area.
To measure the reduction potential ($E_H$) as a function of suspension pH we used mediated potentiometry in which the electron transfer mediator 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) was used to facilitate redox equilibration between the mineral and the working electrode (Pt). Initial observations suggest that the four minerals present different potentials, for the same conditions of pH and total Mn concentration, that depend on Mn(III) contents and -to a lesser extent- on parameters like specific surface area. A deeper investigation of the redox properties, especially focusing on potential equilibrium conditions and covering a broad range of environmental pH values will improve our ability to understand the role of manganese oxides in biogeochemical processes and pollutant dynamics. A more fundamental understanding of the relationship between mineral structure and redox properties will further allow for control and design of manganese oxides with specific redox properties.

REFERENCES