Nitrate reduction by Fe(II)-Fe(III) green rust: the key role of phosphate anions

C. Ruby*, M. Etique, B. Gregoire, A. Zegeye and C. Carteret

LCPME, UMR 7564 CNRS/Université de Lorraine, 405 rue de Vandœuvre, 54600 Villers-lès-Nancy, France (*correspondence: christian.ruby@univ-lorraine.fr, marjorie.etique@univ-lorraine.fr, brian.gregoire @earth.ox.ac.uk, asfaw.zegeye @univ-lorraine.fr, cedric.carteret univ-lorraine.fr)

Green rust (GR) is a mixed FeII-FeIII layered double hydroxides related to the mineral fougèrite found hydromophic gleysols. The crystallographic structure consists of positively charged hydroxyde sheets containing both Fe^{II} and FeIII species separated by anionic layers containing water molecules. The coexistence of an hydrated interlayer and Fe^{II} species induces a high reactivity of GR towards inorganic anions such as nitrate; the kinetics of reaction being much faster than the reduction rate observed for other Fe^{II} containing minerals [1]. The reactivity of hydroxycarbonate GR towards nitrate anions is studied as a function of the pH and Fe^{II}, NO₃ and PO₄ concentrations in the framework of a full factorial design. The results show that phosphate anions play a key role : (i) for a ratio [PO₄³⁻]: [Fe^{II}] higher than 2 %, the reduction of nitrate is completely inhibited, (ii) for a ratio [PO₄³⁻]: [Fe^{II}] < ~ 1 %, nitrate anions are reduced and the ammonium production rate can be as low as ~ 10 %. These effects are attributed to a full or a partial saturation of the lateral surface sites of the GR hexagonal crystals, respectively [2] (Figure 1). If GR is intended to be used for a denitrification process, a dephosphatation pre-treatment should be performed.



Figure 1: Effect of the phosphate adsorption on the ammonium production rate when GR reacts with nitrate.

[1] C. J. Matocha *et al* (2012) *Adv. Agron.* **115**, 182-207 [2] F. Bocher *et al*. (2003) *Solid State Sci.* **6**, 117-124.