French Polytech network form for PhD Research Grants from the China Scholarship Council

This document describes one of the PhD subjects proposed by the French Polytech network. The network is composed of engineering schools/universities. The document also provides information about the supervisor.

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PhD information

Title	Intercalation of phosphate into green rust and potential implications on the environmental conditions permetting life to emerge
Main topics regards to CSC list (3 topics at maximum)	IV-7 Matériaux pour l'Environnement et l'Ecologie
Required skills in science and engineering	Good knowledge of Materials Chemistry Skills in Materials characterization (XRD and vibrational spectrocospies)

Subject description (two pages maximum including biblio)

Green rust (GR) is a member of the layered double hydroxide family (LDH) following the general formulae $[M^{II}_{(1-x)}M^{III}_{x}(OH)_2]^{x+\cdot}$ $[(x/n)\ A^{n-}, m\ H_20]^{x-}$ with M as Fe and A^{n-} as an anion situated in the interlayer. GR was also identified for the first time as a natural mineral called fougerite in a hydromophic soil of Fougères (Britany, France) [1]. Fougerite has been approved as a new mineral by the International Mineralogical Association (IMA) with the number 2003-057 [2]. The interaction of GR with phosphate (PO4) was studied in previous studies; a first study was devoted to the interaction of GR with PO4 in anoxic conditions [3] and a second work concerned the influence of PO4 during GR air oxidation [4]. Noteworthy, Hansen and Poulsen suggested the existence of an intermediate state of GR where a part of the SO_4^{2-} species was replaced by PO4 anions [3]. On the contrary and according to the study of Liping Fang *et al* [5], only the anions present on the outer surfaces of GR were exchanged by PO4 anions. Another very intriguing research topic developed recently concerned the potential role of GR as an inorganic membrane that could have played a role in the origin of Life [6]. In the model proposed in this study, proton phosphate and pyrophophate transfers into GR were hypothesized.

The first goal of this pHD proposal will be devoted to find a way to stabilize in anoxic condition a single phase of hydroxyphosphate GR (GRPO4) and hydroxypyrophosphate (GRPyroPO4). To the best of our knowledge, these compounds were not synthesized up till now. New synthesis methods will be proposed and GRCl will be chosen as an initial material due to its high exchange capacity. Moreover, the XRD pattern of the hypothetical GRPO4 is expected to be similar to the one of GRSO4 and should be easily distinguished from the XRD pattern of GRCl. Indeed, both compounds, GRCl and the hypothetical GRPO4 should crystallized in different structures (GR of type 2 and type 1, respectively according to the nomenclature of Bernal). A multi-technique approach combining the detailed analysis of various pH titration curves, solid characterization by XRD, Raman/Mössbauer spectroscopies will be used to

understand the pathway of formation of GRCl and the anionic exchange between GRCl and GRPO4/GRPyroPO4.

The second goal of this pHD proposal will be to study the anionic exchange properties and oxydo-reduction properties of GRPO4 and GRPyroPO4. The work will be devoted to find the Eh-pH conditions that favors either the release of phosphate and pyrophosphate species in solution or. their re-incorporation into the oxidation products of GR, *e.g.* ferrihydrite or "ferric green rust" [7]. In a final step, the PhD student will study the potential implications of the obtained results on the early Earth's biogeochemical cycle of iron, more precisely at the Fe^{II}-Fe^{III} redox frontiers that can be found in iron rich hydromorphic soils or in hydrothermal vents [6]. An estimation of the phosphate sorption and desorption capacities in such environment will be obtained in function of the Eh-pH conditions. Therefore, the pHD work will be of upmost importance for supporting the recently proposed model for which GR was hypothesized to be involved in the origin of life [6].

References

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[7] Ruby, C.; Upadhyay, C., Géhin, A., Ona-Nguema, G., Génin, J.-M. R. In Situ Redox Flexibility of FeII-III Oxyhydroxycarbonate Green Rust and Fougerite, Environ. Sci. Technol. 2006, 40, 15, 4696–4702, https://doi.org/10.1021/es0606834