

Kinetic Citrate-Bicarbonate Extraction of Green Rust Fougerite and Mineralogical Controls by XRD and Mössbauer Spectroscopy

TROLARD, F.¹, FEDER, F.², BOURRIÉ G.¹,
KLINGELHOEFER, G.³

¹ INRA, UMR 1114 Emmah, Domaine St Paul, F-84914
Avignon cedex 9, France, fabienne.trolard@inra.fr and
guilhem.bourrie@inra.fr

² CIRAD, UPR Recyclage et Risque, LMI IE SOL, BP 1386,
18 524 Dakar, Sénégal, frederic.feder@cirad.fr

³ Institut für Anorganische und Analytische Chemie,
Johannes Gutenberg - Universität Mainz, Staudinger Weg
9, D-55099 MAINZ, Germany, klingel@uni-mainz.de

Fougerite (IMA 2003-057) is a layered double hydroxysalt, the natural mineral of green rusts (GRs) and has been observed as a major iron phase in hydromorphic soils and several reductive environments. Its general formula is $[Fe_{1-x}^{2+} Mg_y^{2+} Fe_x^{3+} (OH)_{2+2y}]^{x+} [(x)OH^-, mH_2O]^{x-}$ where

$x=Fe^{3+}/Fe_{tot.}$. Natural GRs in the environment are difficult to study due to their reactivity and their small concentration. Chemical extractions with citrate-bicarbonate (CB), and mineralogical controls by XRD and Mössbauer spectroscopy (MS) were performed at different times of contact (0, 1, 6, 48, 168 and 504 h). This protocol was applied on soil samples taken in a reductive horizon at 80 cm depth of the Gleysol where fougerite was originally characterized. Kinetic extraction of Si by CB reached slowly 1.8% of absolute total concentration in the soil after 504 h. Al extracted by CB increased quickly to 9.4% until 6 h and then gradually until 48 h to reach 12% and stayed constant until 504 h. Fe and Mg increased quickly respectively to 23% and 56% after 6 h and then gradually and linearly to 97% and 69%. Kinetic extractions by CB reveal two distinct mineral compartments:

- a first mineral form of Si-Al with Fe and Mg as minors;
- then fougerite with a very nice congruence with Mg, showing that fougerite contains about 10% of Mg. After 168 h, CB extraction on the initial sample did not affect significantly any of the main peaks of the XRD patterns. MS on initial soil sample before CB treatment showed characteristic hyperfine interaction parameters of fougerite-GR, with $x=Fe^{3+}/Fe_{tot.}$ mole ratio of 0.43. After 6 and 48 h of CB extraction, x mole ratios were respectively 0.406 and 0.346. After 168 and 504 h of CB treatments, spectra did not show any peak. This disappearance of fougerite-GR, attested by MS, and the dynamics of iron extraction by CB in kinetics proved the selectivity of CB procedure to dissolve fougerite.