

Effect of hydroxycarbonate green-rust particle size on ferrous denitrification

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Green-rusts are mixed Fe(II,III) layered double hydroxides commonly found in anoxic zones of natural environments such as sediments and hydromorphic soils, in which they control the concentration of dissolved iron in the soil solutions. In such anoxic environments, green-rust minerals play an important role in the biogeochemical redox cycling of Fe, and can affect the speciation and mobility of many organic and inorganic contaminants. Therefore, an improved understanding of the processes and/or parameters controlling the formation and growth, the particle sizes and reactivity of green-rust in natural and engineered systems may help to better managing contaminant fate. Indeed, previous laboratory studies have reported that synthetic green-rusts are capable of reducing for instance nitrate [1] and nitrite [2], selenate [3], chromate [4], Ag(I), Au(III), Hg(II) [5] and halogenated hydrocarbons [6].

In the present study, we have prepared synthetic Fe(II,III) hydroxycarbonate green-rusts [GR(CO₃)] under various conditions, using various chemical procedures. Among the abiotic GR(CO₃) obtained from these synthesis pathways, the most stable were aged, leading to significant particle growth. The reactivity of nano-sized and micro-sized GR(CO₃) was studied in the presence of either nitrite or nitrate. X-ray diffraction and scanning electron microscopy were used to characterize solid phases of time-series samples obtained after interaction with nitrite or nitrate and show major influence of the particle size on the mass balance and the kinetics of the redox reactions investigated.

[1] Hansen, H.C.B *et al.* **1994**, *Geochim. Cosmochim. Acta* **58**, 2599-2608.; [2] Hansen, H.C.B *et al.* **1996**, *Environ. Sci. Technol.* **30**, 2053-2056.; [3] Myneni, S.C.B. *et al.*, **1997**, *Science*, **278**, 1106-1109.; [4] Loyaux-Lawniczak, S. *et al.* **2000**, *Environ. Sci. Technol.* **34**, 438-443.; [5] O'Loughlin, E.J. *et al.* **2003**, *Chemosphere* **53**, 437-446.; [6] Erbs, M. *et al.* **1999**, *Environ. Sci. Technol.* **33**, 307-311.

Quantitative color mapping of a brown altered granite by means of dark field reflection visible micro-spectroscopy

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Reddish brown zones often extend from fractures toward interiors of granites (Fig.1a). Such colored zones are considered to be due to the presence of iron (hydr)oxides formed by weathering and/or hydrothermal alteration. However, their chemical forms and distributions have not been well characterized by conventional analytical methods.

In this study, microscopic visible dark field reflectance spectroscopy equipped with a color mapping system has been developed and applied to a brown-colored Rokko granite sample (Fig.1b). Sample reflectance spectra show similar features to goethite, lepidocrocite and ferrihydrite. Raman micro-spectroscopy on the granite sample surface confirm the presence of these minerals. L*a*b* color values (second CIE 1976 color space) were determined from the sample reflection spectra.

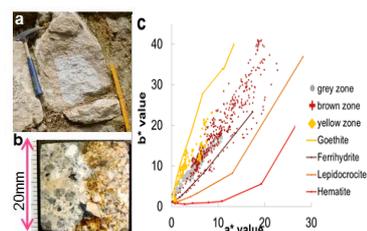


Figure 1: Brown-colored Rokko granite (a) and its hand specimen with a brown front (b). Color values by microscopic visible reflectance spectra in the a*-b* diagram (c).

Grey, yellow and brown zones of the granite show different L* a* and b* values. In the a*-b* diagram (Fig.1c), a* and b* values in the grey and brown zones are between the goethite and ferrihydrite trends, but their values in the brown zone are larger than those in the grey zone. The yellow zone shows data points close to the goethite trend. Iron (hydr)oxides rich areas can be visualized by means of large a* and b* values in the L*, a* and b* maps. The visible dark field reflectance spectroscopy with the color mapping system can be an useful method for studying distribution of colored-minerals such as iron (hydr)oxides.