

Monitoring of mineralogical transformations of ferric oxides into magnetite by Mössbauer spectroscopy

Mustapha Abdelmoula*, Muhammad Usman, Asfaw Zegeye, Jean-Paul Moulin and Christian Ruby

LCPME, UMR7564 CNRS, Université de Lorraine, 405 rue de Vandoeuvre, 54600, Villers-lès-Nancy, France
Email*: mustapha.abdelmoula@univ-lorraine.fr

Keywords: Ferrihydrite, Lepidocrocite, Goethite, Magnetite, Mössbauer

Among the Iron oxide, magnetite is the principal constituent of iron ore deposits and one of the most common. Its origin has been matter of substantial debate during long time and several fundamentally different modes of formation have been suggested (magmatic origin, hydrothermal precipitation). Magnetite is often associated with clays and can have an effect on their properties. However, besides stoichiometric Fe_3O_4 , there is a whole range of isostructural compounds, i.e., the nonstoichiometric $\text{Fe}_{3-\delta}\text{O}_4$ and $\gamma\text{-Fe}_2\text{O}_3$ phases, which have remained relatively unexplored. Implicitly the conditions under which these phases formed should be well known and therefore can serve as genetic indicators. In this study, we will focus on the formation of magnetite obtained by mineralogical transformation of ferric oxides. The Mössbauer spectroscopy was used to monitor the mineralogical transformations of ferrihydrite (F), lepidocrocite (L) and goethite (G) into magnetite as a function of ageing time. Ferric oxyhydroxides were reacted with soluble FeII and OH^- in stoichiometric amounts to form magnetite at an initial pH of 9.7. This value is significantly higher than the pH of precipitation (~ 7) of $\text{Fe}(\text{OH})_2$ corresponding to the initial FeII concentration. As the reaction proceeded, a decrease in pH was observed as the OH^- species were consumed to form magnetite. Decrease in pH could positively be correlated to the dissolution of the initial $\text{Fe}(\text{OH})_2$ precipitates into hydroxylated FeII species adsorbed on the ferric oxyhydroxides. After 1 month, the pH observed for F and L suspension was ~ 5.5 while pH was higher (~ 7.5) for partially transformed goethite. Observed transformation extent into magnetite followed the order: $F > L > G$ with almost 30 % of untransformed G after 1 month. The departure from stoichiometry, δ , of magnetite ($\text{Fe}_{3-\delta}\text{O}_4$) generated from F ($\delta \sim 0.04$) and L ($\delta \sim 0.05$) was relatively low as compared to that in magnetite from G ($\delta \sim 0.08$). In the case of goethite, it is more striking as observed by Mössbauer spectroscopy over ageing time. The results suggests a solid-state transformation of goethite into magnetite with an electron transfer driving the spinel ordering between adsorbed FeII and the ferric oxide (substrat). On the other hand, biogenic magnetite was stoichiometric with $\delta = 0$ when the mineralogical transformation of (L) was investigated in a *Shewanella putrefaciens* culture under anaerobic conditions using methanoate as the electron source for almost 1 month (Zegeye *et al.*, 2011). Thus, stoichiometry of final magnetite could vary according to the nature of initial ferric oxyhydroxide, ageing time and the pathway of magnetite formation. Stoichiometric magnetite may form directly by coprecipitation (Jolivet *et al.*, 2004) or bioreduction of lepidocrocite (Zegeye *et al.*, 2011), while topotactic formation from ferric oxyhydroxide leads to non-stoichiometric phases. Stoichiometry of magnetite is an important characteristic as it can influence its reactivity.

References

- Jolivet, J.P. , Chanéac, C. and Tronc E. (2004) Iron oxide chemistry. From molecular clusters to extended solid networks. *Chemical Communications*, 481-487.
- Zegeye, A. Abdelmoula, M., Usman, M. , Hanna, K. and Ruby C. (2011) In situ monitoring of lepidocrocite bioreduction and magnetite formation by reflection Mössbauer spectroscopy, *American Mineralogist*, **96**,1410-1413.