Characterization of magnetic iron oxides in Oxisols using XRD and Fourier transform infrared spectrometry

Worachart Wisawapipat[1], Irb Kheoruenromne[1], Anchalee Suddhiprakarn[1] and Robert J. Gilkes[2]

[1]Department of Soil Science, Faculty of Agriculture, Kasetsart University, Bangkok 10900, Thailand.
worachart_b@hotmail.com
[2]School of Earth and Environment, Faculty of Natural and Agricultural Sciences,
University of Western Australia, Crawley, WA 6009, Australia.

Thai Oxisols derived from mafic rocks exhibit natural magnetization due to the presence of maghemite (γ-Fe_2O_3) and/or magnetite (γ-Fe_3O_4); however little is known of these significant mineral constituents. Eight maghemite/magnetite samples were separated with a hand magnet from surface and subsurface horizons of five Oxisols on basalt under a tropical monsoonal environment in Thailand to characterize their mineralogy using XRD and Fourier transform infrared spectrometry (FTIR) techniques. Ferrimagnetic iron oxide minerals (i.e. maghemite/magnetite) were the most abundant constituents of the magnetic fraction with appreciable amounts of antiferromagnetic iron oxides (i.e. hematite and goethite) and diamagnetic minerals (i.e. kaolinite, gibbsite and quartz) (Fig. 1). The inclusion of non ferrimagnetic impurities in all magnetic samples is interpreted as a consequence of aggregation by iron oxides creating stable silt size aggregates, which are characteristics of Oxisols.

Mean coherently diffracting length (MCD) calculated from the width of reflections at half maximum using the Scherrer formula (Schulze, 1984), for maghemite/magnetite are presented in Table 1. The MCD_{311} of maghemite/magnetite varies from 17 nm (Ti soil) to 36 nm (Nb soil). Maghemite crystal size in Nb soil that has developed under higher rainfall conditions is larger than for Ti soil, which may indicate that microclimate exerts an influence on crystal growth of the maghemite/magnetite, though differences in the nature of their parent material should also be considered. Amounts of metal substituted in the magnetic minerals were very small and small substitutions do not change unit cell dimension (UCD). MCD_{220} of maghemite/magnetite ranges from 18 – 39 nm which resemble values obtained from Chinese loess magnetite (e.g. 30 nm, Chen et al., 2005) but it is rather larger than values the reported values for maghemite formed by dehydroxylation of hydrated ferric oxides in a bush fire (e.g. ~12 nm, Grogan et al., 2003) and is smaller than values for synthesized magnetite (e.g. 62 nm, Schwertmann and Murad, 1990). There are very close positive linear relationships of MCD_{220} with MCD_{311} (R^2 = 0.80) and MCD_{511} (R^2 = 0.86) with no relationships between MCD dimensions and unit-cell dimension.
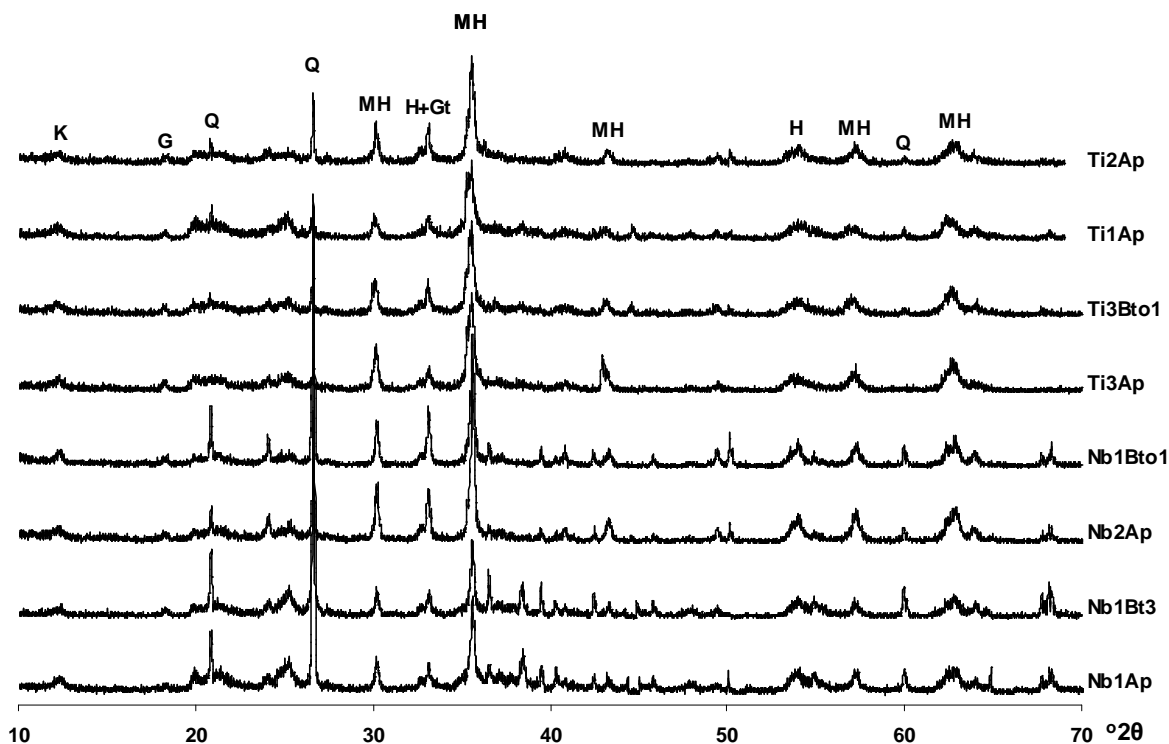
Fig. 1. X-ray diffraction patterns of randomly oriented maghemite/magnetite separates from Oxisols.
K = kaolinite, G= gibbsite, Q = quartz, MH = maghemite/magnetite, H = hematite and Gt = goethite.

Table 1. Unit-cell *a* and mean coherently diffracting length (MCD) values for maghemite/ magnetite calculated from XRD line broadening.

Sample	Maghemite/magnetite			
	MCD (220)	MCD (311)	MCD (400)	Unit-cell dimension *a*
	(-----------nm----------)			(Å)
Nb1AP	29	30	22	8.359
Nb1Bt3	41	32	22	8.356
Nb2AP	36	36	28	8.354
Nb2Bto1	39	35	28	8.351
Ti3AP	25	18	31	8.368
Ti3Bto1	21	23	17	8.358
Ti1AP	18	17	16	8.398
Ti2AP	24	24	16	8.35
Average	29	27	31	8.362
s.d.	8.6	7.3	19	0.016
Magnetite reference value[A]	-	-	-	8.3455
Magnetite reference value[A]	-	-	-	8.3967

[A]Schwertmann and Murad (1990)

Unit-cell dimension was calculated using the UnitCell program (Holland and Redfern, 1997), from corrected positions of the maghemite/magnetite (220), (311), (400) and (511) reflections. The unit-cell *a* dimension of most maghemite/magnetite samples is close to 8.35 nm indicating the dominance of maghemite rather than magnetite except for the Ti1Ap sample that has a larger unit-cell dimension (8.398 Å) that is consistent with magnetite. There is slight shift of all maghemite peaks towards lower angles as compared to the magnetite peak (Fig. 1). Our values of the unit-cell *a* dimension can be related to values for appropriate end member minerals, i.e., magnetite (8.3967 Å; JCPDS 19- 62a), maghemite (*a* = 8.3455 Å; Schwertmann and Murad, 1990).

FTIR spectra of 13-mm diameter pressed discs (1 mg sample 1:170 mg KBr) were obtained using a Perkin-Elmer Spectrum One Fourier transform infrared (FTIR) spectrometry over the range 4000–400 cm^{-1} with a 4 cm^{-1} resolution. FTIR spectra of maghemite/magnetite separate samples indicate the presence of hematite, maghemite and kaolinite (Fig. 2). The IR spectrum of magnetite is absent as it would exhibit a broad absorption band at 570 (Russell and Fraser, 1994). Maghemite show a very small broad absorption band at 694 cm^{-1}. Hematite exhibits strong absorption bands at 430, 470 and 540 cm^{-1} (Cornell and Schwertmann, 1996). The spectra show the OH-deformation bands at 914, 1010, 1035 and 1100 cm^{-1} with OH stretching bands at 3620 and 3700 cm^{-1} indicating the presence of kaolinite. The absence of quartet of OH stretching bands at 3620, 3527, 3464 and 3380 cm^{-1} for gibbsite and of strongly hydrogen-bonded OH at 3153 cm^{-1} and OH deformation bands at 893 and 794 cm^{-1} for goethite (Russell and Fraser, 1994) confirm XRD results that these minerals were not present in the magnetite separates.

Calculation of unit-cell dimension is highly suitable for the characterization of maghemite/magnetite but conventional XRD is not the optimum procedure. We will next use the synchrotron XRD technique that offers high precision, improved resolution of reflection and much greater sensitivity.
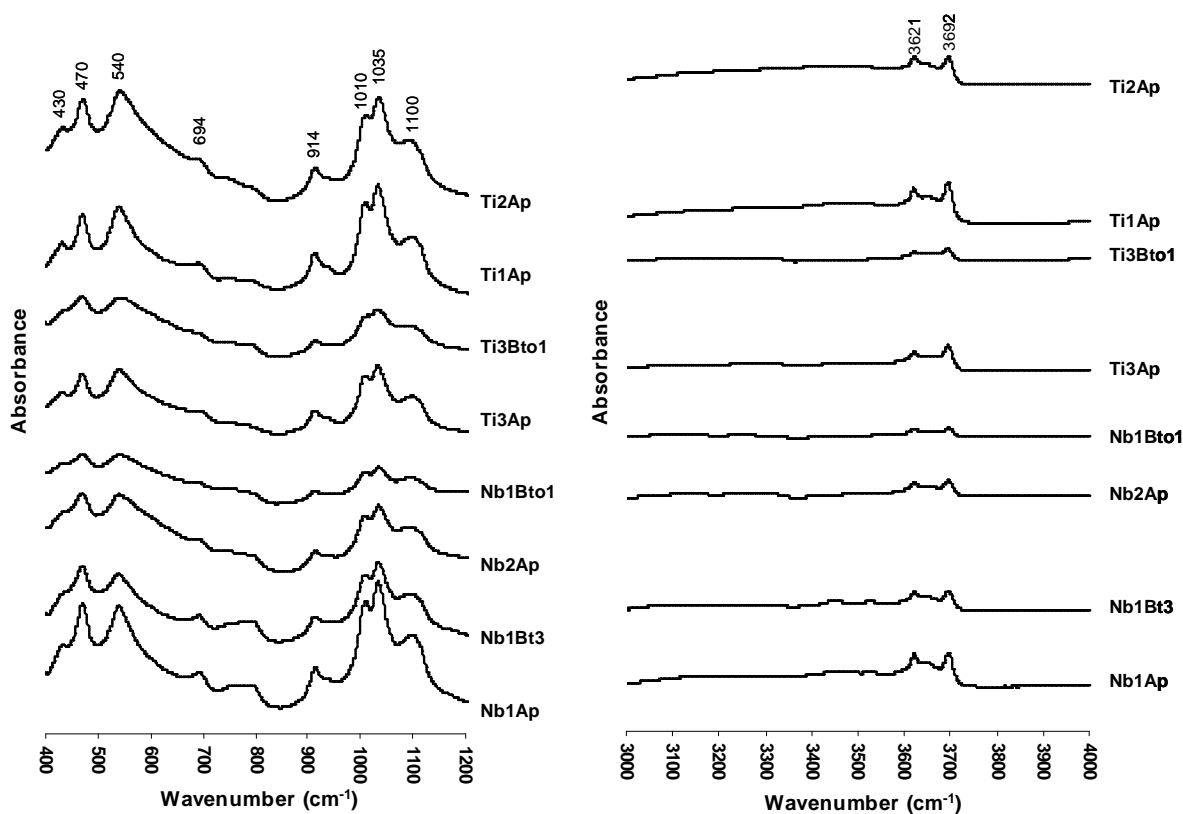
Acknowledgments

Fig. 2. FTIR spectra of maghemite/magnetite separates from Oxisols.

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