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Néel Temperatures of Synthetic Substituted Goethites and their Rapid Determination Using Low-Field Susceptibility Curves

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Abstract. The Néel temperatures (T_N) of synthetic goethites (α -FeOOH), substituted with diamagnetic elements (Al, Ga) have been determined from the temperature dependence of their low-field susceptibility using a Kappabridge AC bridge. These temperatures proved to be identical to those derived from more conventional measurements of high-field or remanent magnetization versus temperature, and in good agreement with those inferred from Mössbauer models. The low-field susceptibility based-technique appears to offer a precise and rapid method of determining T_N . While Néel temperature coincides with maximum unblocking temperature in Ga-goethites, supporting the assumption that antiferromagnetism and parasitic ferromagnetism have a similar origin in goethite, the lack of clear correlation between saturation remanent magnetization and increasing diamagnetic substitution suggests that the weak ferromagnetism of goethite is due to substitution independent defects induced during crystal growth.

1. Introduction

Néel temperatures (T_N) in antiferromagnetic materials are usually determined either directly by high magnetic field measurements at low temperatures, using SQUID magnetometers or superconducting susceptometers [Rochette and Fillion, 1989; Bocquet and Kennedy, 1992; Özdemir and Dunlop, 1996], or indirectly by extrapolation of Mössbauer spectra taken at various temperatures [for example, Murad and Schwertmann, 1983]. In the latter case, T_N determination requires models of magnetic ordering that are controversial, for example in goethite [Pollard et al., 1991; Bocquet and Kennedy, 1992]. Alternatively, the disappearance of a parasitic, ferromagnetic moment, mostly manifested in the maximum unblocking temperature of remanence (T_{mb}), may be an indirect way to determine T_N , provided that these temperatures can be considered equivalent, which is not always the case [Hedley, 1971; Rochette and Fillion, 1989].

The main purpose of this paper is to establish low-field susceptibility versus temperature measurements (χ -T curves) using Kappabridge AC bridge as a rapid method for accurate

and direct determination of T_N . The consistency of χ -T curves was checked by using the temperature dependence of high-field induced and remanent magnetization (M-T curves and M_r -T curves respectively) to calibrate the Néel temperature of well-characterized synthetic goethites, substituted with the diamagnetic elements Al and Ga. The temperature-dependent magnetic properties of these goethites were investigated as well, since Néel temperatures and magnetochemistry are closely related in goethite [Murad and Schwertmann, 1983; Pollard et al. 1991, Bocquet and Kennedy, 1992, Özdemir and Dunlop, 1996].

2. Samples

Our Ga-goethites comprised a set of samples with up to 38 mol%Ga in solid solution, i.e. c=0, 7, 18 and 38 mol%Ga (samples GGa0, GGa7, GGa18 and GGa38 respectively). They were synthesized from 0.1M nitrate solutions with various Ga(III)/Fe(III) ratios, precipitated at pH=12 with 1M KOH, and aged at T=60°C for 6 days. Sample GA17, with c=7 mol%Al, as determined from the X-ray diffraction pattern [Schulze, 1984], was synthesized using the same procedure, which reduces effects of variable crystallinity on T_N , due to synthesis water concentration, pH or temperature [Murad and Schwertmann, 1983; Schwertmann and Murad, 1983; Schwertmann et al., 1985]. This allows meaningful comparisons to be made regarding the influence on T_N of the different element substitution. It also allows comparisons with the T_N of Al-goethites of the same high-temperature synthesis type, (i.e. synthesis temperature above 40°-50°C [Schwertmann et al., 1985] inferred from Mössbauer models.

Conversely, sample GA14.6, with c=4.6 mol%Al, was synthesized at 25°C [Wells, 1998] and was used to investigate on the sensitivity of χ -T curve to possible effects of lower crystallinity on T_N by comparing the two Al-goethites samples which have comparable Al content.

3. Methods

χ -T curves were measured at CEREGE, on an AGICO Kappabridge KLY-2 (0.4 mT), 920 Hz alternating magnetic field; sensitivity of $10^{-8} \text{ m}^3 \text{ kg}^{-1}$ for a sample mass of 0.2 g), coupled with the CS-2 (300 to 950 K) or CS-L (120 to 270 K) variable temperature attachments. Temperature accuracy is better than ± 5 K, after calibration of the platinum resistance thermal sensor with the melting and boiling points of MilliQ water for the high temperature range and a paramagnetic Gadolinium salt for the low temperature range. Empty furnace χ -T curve, measured prior to each sample analysis, was

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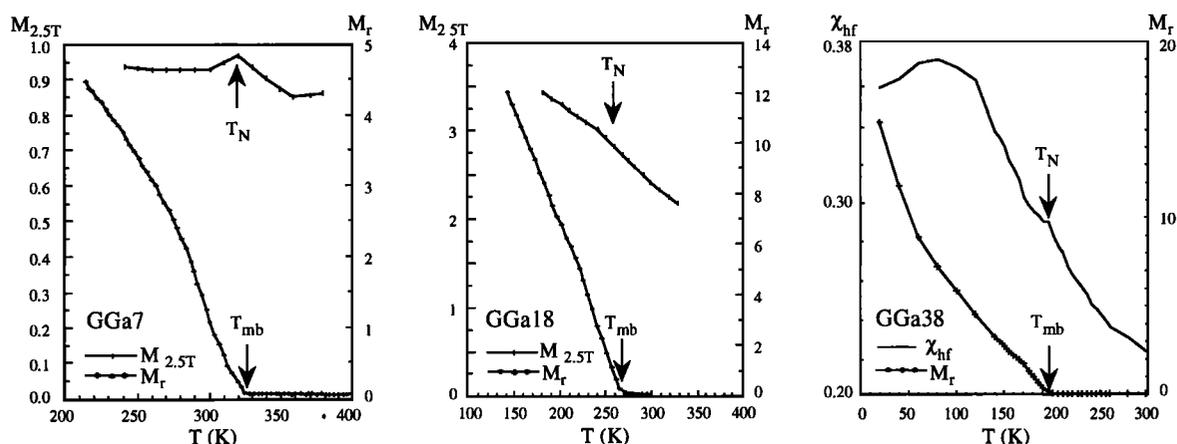


Figure 1. Temperature dependence of remanent magnetization M_r ($10^{-2} \text{ Am}^2\text{kg}^{-1}$), 2.5T-induced magnetization $M_{2.5T}$ (in $10^{-2} \text{ Am}^2\text{kg}^{-1}$) magnetizations for GGa7, GGa18 and GGa38; calculation of high-field susceptibility χ_{hf} ($10^{-6} \text{ m}^3\text{kg}^{-1}$) from 1.5 and 2T-induced magnetization curves was necessary to reveal T_N of GGa38.

subtracted from the combined curves (0.25 cm^3 or less sample powders plus empty furnace) using the CUREVAL program [Hrouda, 1994], to remove the empty furnace signal.

M-T curves and M_r -T curves were recorded around the temperature where the magnetic ordering transitions were supposed to occur (from 4.2 K to 400 K, depending on samples), using a SHE cryogenic magnetometer at the Louis Néel laboratory. Samples GGa7 and GGa18 were cooled down in steps of 10 K in an ambient field $H_0=2.5 \text{ T}$, then reheated in zero field in temperature steps of 5 K. The induced magnetization of GGa38 was recorded in steps of 5 K and measured at each step in $H_1=2 \text{ T}$ and $H_2=1.5 \text{ T}$. High-field susceptibility curves (χ_{hf} -T curves) were calculated using $\chi_{hf}=(M_1-M_2)/(H_1-H_2)$, [Rochette and Fillion, 1989]. χ_{hf} -T curves of GAl7 sample were established using the same procedure with $H_1=3 \text{ T}$ and $H_2=2 \text{ T}$, and $H_1=7 \text{ T}$ and $H_2=6 \text{ T}$.

4. Results and Discussion

M_r -T and M-T curves (Figure 1 and 2) exhibit the characteristic increase for goethite at low temperatures

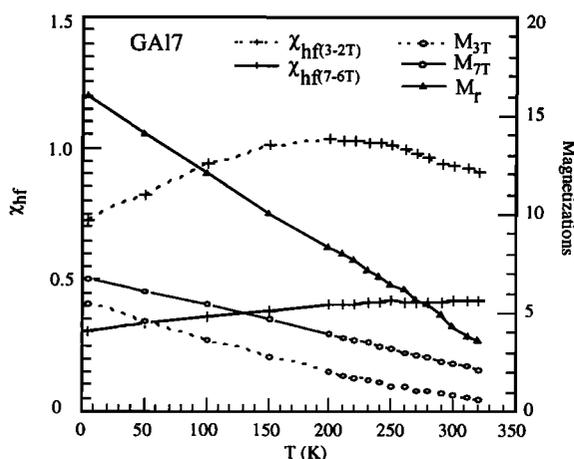


Figure 2. Temperature dependence of remanent magnetization M_r (in $10^{-2} \text{ Am}^2\text{kg}^{-1}$), 3T and 7T-induced magnetization M_{3T} and M_{7T} respectively (in $\text{Am}^2\text{kg}^{-1}$), and corresponding high-field susceptibility $\chi_{hf(3-2T)}$ and $\chi_{hf(7-6T)}$ (in $10^{-6} \text{ m}^3\text{kg}^{-1}$) for sample GAl7.

[Rochette and Fillion, 1989]. However the continuous curvature of magnetization curves up to 7 T (testified by the significant difference between $\chi_{hf(3-2T)}$ and $\chi_{hf(7-6T)}$ in Figure 2) implies that the ferromagnetic moment of goethite is better estimated by remanent than induced magnetizations. T_{mb} was defined as the intercept of the intersection between the slopes of high and low temperature parts of M_r -T curves. T_N was determined either from M-T (samples GGa7 and GGa18) or χ_{hf} -T curves (samples GGa38) as the maximum of the peak that is expected for the antiferromagnetic to paramagnetic transition under higher inducing fields [Özdemir and Dunlop, 1996]. All curves exhibit a clear downward shift of magnetic ordering temperature (Table 1), due to the increasing substitution of iron with a diamagnetic element such as Al or Ga into the goethite.

Low-field susceptibility values at 300 K (Table 1) lie in the range of synthetic or natural substituted goethites [Dekkers, 1988; Dekkers and Rochette, 1992]. The χ -T curves (Figure 3) each exhibit a marked and sharp peak, as expected in the vicinity of the Néel temperature for samples under near zero-field conditions [Bocquet and Kennedy, 1992]. Some of the peak values (GGa0 and GGa7) are of the order of the noise level, due to the small sample volumes remaining after previous experiments. However, the smooth shape of the peaks clearly contrasts with the background fluctuations. Since the temperature of the peak maximums for samples GGa7 and GGa38 corresponds, within temperature uncertainties, to those determined from the M-T curves, they must characterize T_N . None of the M_r -T, M-T and χ_{hf} -T curves of GAl7 gives evidences for T_{mb} and T_N to occur below 320K. This is confirmed by the Néel temperature observed on χ -T curves, which is also in good agreement with the one extrapolated from Mössbauer studies (Figure 4).

These results suggest that χ -T curves allow us to pinpoint T_N accurately. In the vicinity of T_N , magnetization responds to second order transitions, whereas susceptibility reflects first order transitions and diverges [Hrouda, 1994]. This leads to a better precision of low-field susceptibility in the determination of T_N from the peak maximum. M-T curves may be so smooth [Rochette and Fillion, 1989; Özdemir and Dunlop, 1996, see also Figure 1] that evidence for T_N can only often be obtained after calculating their first derivative, i.e. χ_{hf} -T

Table 1. Magnetic properties of synthetic goethites with various substitution of Al and Ga (in mol%) and synthesis temperature T_s (in °C) from this study and Rochette and Fillion [1989] denoted with *.

| sample | T_s | M_{rs} | χ | T_{mb} | T_N^a | T_N^b |
|--------|-------|----------|--------|----------|---------|---------|
| 0 | 60 | - | 0.49 | - | - | 368±5 |
| 0* | 70 | 0.29 | 0.32 | 380±5 | 380±10 | |
| 0* | 25 | 0.40 | 0.41 | 335±5 | 355±10 | |
| 7 Ga | 60 | 0.11 | 0.39 | 325±5 | 320±10 | 328±5 |
| 18 Ga | 60 | 0.25 | 0.61 | 265±5 | 250±10 | 250±5 |
| 38 Ga | 60 | 0.18 | 1.15 | 200±5 | 195±5 | 188±5 |
| 7 Al | 60 | 0.15 | 2.00 | >320±10 | - | 328±5 |
| 4.6 Al | 25 | - | 0.83 | - | - | 327±5 |

M_s : saturation remanence (in $\text{Am}^2\text{kg}^{-1}$) extrapolated to 0 K from the linear part of M_s - T curves [Rochette and Fillion, 1989]; χ : low-field specific susceptibility (in $10^{-6} \text{m}^3\text{kg}^{-1}$) at 300 K; T_{mb} : maximum unblocking temperature (in K); T_N^a : Néel temperature (in K), determined from M - T curves; T_N^b : χ - T curves.

curves [Bocquet and Kennedy, 1992]. This was attempted for sample GGa38 (Figure 1) but even then, T_N is barely distinguishable. The magnetic transition appears as a minor kink, which could be confused with the more dramatic peak observed below 100 K, which however have been also evidenced in Schwertman's pure goethite standards [Rochette and Fillion, 1989].

Rock magnetic properties can be separated into a part that is due to fine grain size effects and a part that is linked to the intrinsic bulk properties. In pure goethites, the former account for differences in M_{rs} and M_s as well as T_{mb} and T_N . Hedley [1971] reports a T_{mb} 20 K lower than T_N for a poorly crystallized sample. Such differences are not observed in the whole series of Ga-goethites.

The Néel temperatures of the Ga-goethites and GAl7 are in overall agreement with those reported in Mössbauer studies (Figure 4). This suggests that the reduction in T_N with increasing diamagnetic substitution is not dominated by the weakening of magnetic interactions due to cell-parameters differences, as suggested in the case of pure goethites [Bocquet and Hill, 1995]. If this was the case, the differences

in ionic radius between Fe, Ga and Al ($r_{\text{Fe}^{3+}}=0.645 \text{ \AA}$, $r_{\text{Ga}^{3+}}=0.620 \text{ \AA}$ and $r_{\text{Al}^{3+}}=0.530 \text{ \AA}$ [Shannon, 1976]- would imply lower T_N in Ga-goethites, whereas they are identical for GGa7 and GAl7. As remarked earlier for pure goethites, T_{mb} and T_N are identical within uncertainties for Ga-goethites (Table 1), indicating that ferromagnetism and antiferromagnetism have a similar origin [Hedley, 1971; Rochette and Fillion, 1989; Özdemir and Dunlop, 1996]. The presence of vacancies was pointed out to explain both the reduction in T_N observed in pure goethites of the low temperature synthesis type (see table 1) and the weak ferromagnetism of goethite [Rochette and Fillion, 1989; Pollard et al, 1991; Bocquet and Hill, 1995; Özdemir and Dunlop, 1996]. The lack of clear increase of M_{rs} at 0 K with increasing substitution (Table 1), supports the assumption that the weak ferromagnetism in goethite is due to the presence of point defects induced during crystal growth, not related to substituted elements.

The bulk crystal chemistry of Ga-goethites is homogeneous from particle to particle. Ga is randomly distributed into the goethite structure, which implies a diversification of Fe^{3+} ions neighbouring sites as substitution increase [Martin et al., 1997; Mathé et al., in press]. On this basis, the broadening of T_N -associated peaks with increasing substitution, occurring under high- and low-field conditions (samples GGa7 and GGa18, Figure 1; GGa38, Figure 3), is assumed to arise from an increasing distribution of Néel temperatures. Such a distribution would illustrate a range of magnetocrystalline anisotropy energies linked to the crystallographic distribution of non-magnetic defects at the local scale. This would also explain the enhanced distribution of Mössbauer hyperfine magnetic field [Rice et al., 1994].

The Néel temperature of sample GAl4.6 lies below the trend exhibited by all the others samples of the high-temperature synthesis type, including the samples from Pollard et al. [1991]. This clearly indicates that χ - T curves are also sensitive to changes in crystallinity.

According to Bocquet and Hill [1995], T_N is correlated with vacancy content in increasingly poorly crystallized iron oxides, i.e. linked to the magnetochemistry of the grains themselves. A vacancy concentration less than $c=8\%$ would explain the Néel temperature of GGa0. Thus, it is worth noting that both the Néel points of GAl4.6 and GGa0 would fit the trend observed for the other goethite samples, by adding

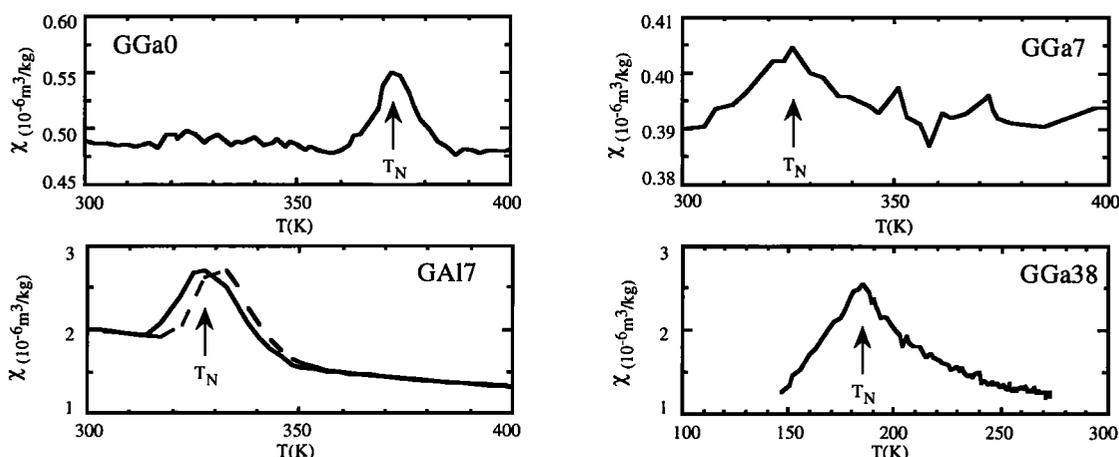


Figure 3. Temperature dependence of low-field susceptibility of GGa0, GAl7, GGa7 and GGa38 in the vicinity of their Néel temperature. Full lines: heating curves; dashed lines: cooling curves.

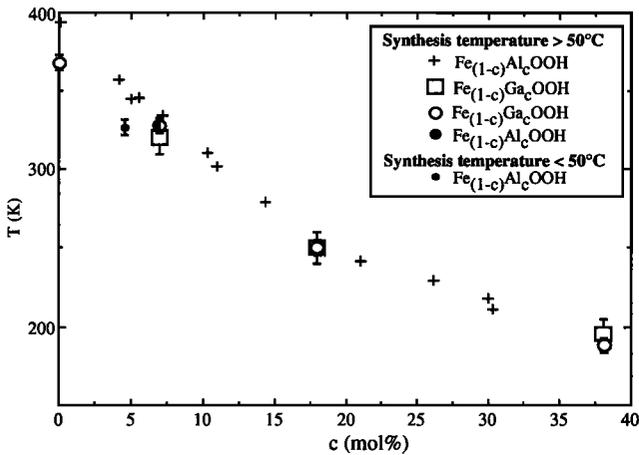


Figure 4. Néel temperatures of goethites versus c , the mol% of the substituted diamagnetic element (Al or Ga). Crosses: from Mössbauer models [Fleisch et al., 1980; Pollard et al. 1991]; squares: from M-T curves; circles: from χ -T curves.

roughly the same vacancy content to their metallic element concentration c (Figure 4).

Ferromagnetism and antiferromagnetism in goethite are highly anisotropic, thermoremanence (TRM) and M_s both strictly lying along the c -axis [Banerjee, 1970; Hedley, 1971; Özdemir and Dunlop, 1996], which also corresponds to the long axis of goethite particles. Since Al-substitutions and poorer crystallinity inhibit crystal growth in this direction [Murad and Schwertmann, 1983], changes in shape anisotropy resulting from changes in particle morphology might influence the ordering temperatures to some extent. However, arguing on the weak-ferromagnetism of goethite, Bocquet and co-authors state that effects of shape anisotropy are unimportant with regard to changes in magnetocrystalline anisotropy on the bulk magnetic properties of poorly crystallized goethite.

5. Conclusions

The regular decrease of Néel temperatures with increasing substitution is confirmed up 38 mol% substitution of Ga, with no difference between Al and Ga. The coincidence between T_N and maximum unblocking temperature of remanence T_{mb} in Ga-goethites supports the idea that both parasitic ferromagnetism and antiferromagnetism have a common origin in goethite. The ferromagnetic moment of goethite depends on synthesis temperature rather than amount of substitution, suggesting that this parasitic moment is linked to the bulk defect content induced during crystal growth. The presence of such defects may also account for the reduction in T_N observed in samples of low crystallinity, although effects of shape anisotropy have to be further investigated in diamagnetically substituted goethites.

Néel points, identified by sharp peaks on low-field susceptibility versus temperature curves, coincide with those estimated by high-field measurements and Mössbauer models. The determination of Néel temperature using high-field measurements has proven to be cumbersome and time-consuming, especially at high substitution rates where magnetic transition are hardly distinguishable on magnetization curves. With regard to such experiments, the temperature dependence of low-field susceptibility appears to

offer a rapid and effective method to determine Néel temperatures in goethites.

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References

- Banerjee S. K., Origin of thermoremanence in goethite, *Earth Planet. Sci. Lett.*, **8**, 197-201, 1970.
- Bocquet, S., and A.J. Hill, Correlation of Néel temperature and vacancy defect in fine-particle goethites, *Phys. Chem. Min.*, **22**, 524-528, 1995.
- Bocquet, S., and S.J. Kennedy, The Néel temperature of fine particle goethite, *J. Magn. Mat.*, **109**, 260-264, 1992.
- Fleisch, J., R. Grimm, J. Grüber, and P. Güttlich, Determination of the aluminum content of natural and synthetic aluminogoethites using Mössbauer spectroscopy, *J. Phys. (Paris)*, **41**, C1, 169-170, 1980.
- Dekkers, M.J., Some rockmagnetic properties parameters for natural goethite, pyrrhotite and fine-grained hematite, *Ph.D. Thesis, Univ. Utrecht*, 231+xxi pp, 1988.
- Dekkers, M.J., and Rochette P. Magnetic properties of Chemical Remanent Magnetization in Synthetic Goethite: Prospects for a Natural Remanent Magnetization/ Thermoremanent Magnetization Ratio Paleomagnetic Stability Test?, *J. Geophys. Res.*, **97**, 17291-17307, 1992.
- Hedley, I.G., The weak ferromagnetism of goethite, *Z. Geophys.*, **37**, 409-420, 1971.
- Hrouda, F., A technique for the measurement of thermal changes of magnetic susceptibility of weakly magnetic rocks by the CS-2 apparatus and KLY-2 Kappabridge, *Geophys. J. Int.*, **118**, 604-612, 1994.
- Martin, F., P. Ildefonse, J.-L. Hazemann, P.-E. Mathé, Y. Noack, O. Grauby, D. Beziat, and P. de Parseval, Gallium Crystal Chemistry in Synthetic Goethites, *J. Phys. IV, France 7 (Suppl. to J. Phys III, April 1997)*, C2, 821-822, 1997.
- Mathé, P.-E., F. Martin, Y. Noack, S. Petit, A. Decarreau, and P. Rochette, Characterization of gallium substitution and magnetic ordering in synthetic goethites, *Clays Clay Min.* (in press).
- Murad, E., and U. Schwertmann, The influence of aluminum substitution and crystallinity on the Mössbauer spectra of goethite, *Clay Min.*, **18**, 301-312, 1983.
- Özdemir, Ö., and D.J. Dunlop, Thermoremanence and Néel temperature of Goethite, *Geophys. Res. Lett.*, **23**, 921-924, 1996.
- Pollard, R.J., Q.A. Pankrust, and P. Zientek, Magnetism in aluminous goethite, *Phys. Chem. Min.*, **18**, 259-264, 1991.
- Rice, D.A., J.D. Cashion, and S. Bocquet, Crystallographic and magnetic order analysis of a banded limonite, *Hyp. Inter.*, **91**, 697-701, 1994.
- Rochette, P., and G. Fillion, Field and temperature behavior of remanence in synthetic goethite: Paleomagnetic implications, *Geophys. Res. Lett.*, **16**, 851-854, 1989.
- Schulze, D.G., The influence of Aluminium on iron oxides. VIII. Unit-cell dimensions of Al-substituted goethites and estimation of Al from them, *Clays Clay Min.*, **32**, 36-44, 1984.
- Schwertmann, U., and E. Murad, Effect of pH on the formation of goethite and hematite from ferrihydrite, *Clays Clay Min.*, **31**, 277-284, 1983.
- Schwertmann, U., P. Cambier, and E. Murad, Properties of goethites of varying crystallinity, *Clays Clay Min.*, **33**, 369-378, 1985.
- Shannon, R.D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr.*, **B26**, 1046-1048, 1976.
- Wells, M.A., Mineral, chemical and magnetic properties of synthetic, metal-substituted goethite and hematite, *Ph.D. Thesis, U. Western Australia, Perth, Australia*, 400 pp, 1998.

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