Mechanism of the parasitic remanence of aluminous goethite [α-(Fe, Al)OOH]

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[1] The Néel temperature (T_N) of cation-substituted goethites is controlled by the degree of isomorphous substitution and crystal defects. In particular, the exact relationship between the $T_{\rm N}$ of the antiferromagnetism (AFM) and the unblocking temperature ($T_{\rm B}$) of the parasitic remanence is undetermined. We found that $T_{\rm B}$ is systematically higher than T_N for a set of well-characterized aluminous goethite samples. In addition, the difference between $T_{\rm B}$ and $T_{\rm N}$ increases from $\sim 8-9$ K for a pure goethite (that contains vacancies) to >20 K for Al-substituted goethites. This indicates that $T_{\rm B}$ and $T_{\rm N}$ change independently with the diamagnetic substitutions, suggesting a fundamental difference of magnetization process between parasitic remanence and AFM. A zonal distribution of the diamagnetic substitutions has been incorporated to account for the observed magnetic properties of the AFM and the parasitic remanence. Nonetheless, both parasitic remanence and AFM could exist along the goethite c axis. INDEX TERMS: 1512 Geomagnetism and Paleomagnetism: Environmental magnetism; 1519 Geomagnetism and Paleomagnetism: Magnetic mineralogy and petrology; 1540 Geomagnetism and Paleomagnetism: Rock and mineral magnetism; KEYWORDS: magnetism, aluminous goethite, low-temperature techniques

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1. Introduction

[2] Goethite (α -FeOOH) is a common iron oxyhydroxide in natural environments (e.g., soils, oceanic and continental sediments), generally as a weathering product of ironbearing minerals. Accurate knowledge of its magnetic properties is essential because goethite is sensitive to paleoenvironmental changes. The magnetic properties of goethites have been widely investigated [e.g., Banerjee, 1970; Murad and Bowen, 1997; Dekkers and Netherlands, 1988; Dekkers, 1989; Rochette and Fillion, 1989; Özdemir and Dunlop, 1996; Mathé et al., 1999]. Goethite often records the paleomagnetic information such as thermal remanent magnetization (TRM) [Strangeway et al., 1967] or chemical remanent magnetization (CRM) [O'Reilly, 1984]. Goethite has also been used to quantify variations in aeolian dust inputs into oceans [Maher and Dennis, 2001].

[3] Pure goethite is a uniaxial antiferromagnetic mineral (the Néel temperature, T_N , is ~395–400 K) [*Özdemir and*

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Dunlop, 1996]. The crystal structure consists of double chains of $[Fe(O,OH)_6]$ octahedron. The spin coupling is collinear and parallels the long crystallographic axis (denoted as the c axis) [Forsyth et al., 1968]. However, the net (or parasitic) magnetic moment along c axis is not zero and varies with the amount of defects and isomorphous substitution in the crystal lattice [Strangeway et al., 1968; Hedley, 1971]. Unlike the canting mechanism for remanences carried by hematite, this parasitic remanence is believed to be caused by preferential substitutions of cations (e.g., Al and Mn) on a particular octahedral lattice site during crystallization, or by random lattice vacancies [Özdemir and Dunlop, 1996], resulting in unbalanced numbers of spins on the A and B sublattices. On the basis of Mössbauer spectroscopy, it has been shown that most metallic ions equally occupy either the A or B lattice for <5 mol % of Al substitution [Pollard et al., 1991]. With increasing Al substitution (up to 10-15 mol %), the Al ions show preferred clustering along the same sublattice where the presubstitution of Al ion occurred [Pollard et al., 1991]. The preferred Al substitution gradually disappears as the concentrations of Al and Fe become comparable to each other [Pollard et al., 1991].

[4] The parasitic remanence along the *c* axis has long been recognized as ferrimagnetism [e.g., *Hedley*, 1971; *Özdemir and Dunlop*, 1996; *Mathé et al.*, 1999]. *Özdemir and Dunlop* [1996] investigated a centimeter-sized wellcrystallized natural goethite sample, and reported that T_N and unblocking temperature (T_B) both occur at ~120°C. Assuming the maximum T_B is close to the Curie temperature T_C , they suggested that T_N coincides with T_C . However, the generalization of this observation is limited in practice

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Table 1. Methods Used to Synthesize the Goethites

Sample	Procedure and Solutions Used	Alkali Added	Final [OH] or pH
GV3	200 mL Fe(NO ₃) ₃	2 <i>M</i> KOH	pH = 13
CB22	200 mL 0.5 M Fe(NO ₃) ₃	2 <i>M</i> KOH	0.9 - 1.35
35/3	$1.5 \text{ L} \ 0.5 \ M \text{ Al}(\text{NO}_3)_3 + 900 \text{ mL} \ 5 \ M \text{ KOH} + 225 \text{ mL} \ 1 \ M \text{ Fe}(\text{NO}_3)_3$	5 <i>M</i> KOH	
35/5	$1.5 \text{ L} \ 0.5 \ M \ \text{Al}(\text{NO}_3)_3 + 900 \text{ mL} \ 5 \ M \ \text{KOH} + 225 \text{ mL} \ 1 \ M \ \text{Fe}(\text{NO}_3)_3$	5 <i>M</i> KOH	
CB19	100 mL 1 M Fe(NO ₃) ₃ + 0 to 75 mL 0.5 M Al(NO ₃) ₃	3 <i>M</i> KOH	0.6
38/33	slow oxidation of a 3:1 mixture of $FeCl_2$ and $AlCl_3$ with air at room temperature and $pH = 11.77$		

because most natural samples contain much smaller crystals and with significant amount of substituted cations. Indistinguishable $T_{\rm B}$ and $T_{\rm N}$ were also observed for a set of Ga goethites [*Mathé et al.*, 1999]. However, the temperature uncertainty (5–10°C) was quite large [*Mathé et al.*, 1999] to confidently determine the exact relationship between $T_{\rm B}$ and $T_{\rm N}$ of the goethites.

[5] In order to precisely define $T_{\rm B}$ and $T_{\rm N}$, we determined $T_{\rm N}$ directly from a low-field magnetic susceptibility measurement and temperature dependence of zero-field cooled (ZFC) and in-field cooled (FC) curves. We also determined $T_{\rm B}$ from the temperature dependence of TRM curves. To avoid systematic errors in temperature inherited from the use of different instruments, all experiments were conducted using a Quantum Design Magnetic Properties Measurement System (MPMS). We used small sweeping rates (<2 K/min) to improve the temperature accuracy. Our aim is to precisely determine whether $T_{\rm N}$, $T_{\rm B}$ and $T_{\rm C}$ are equivalent for synthetic Al goethites.

2. Samples and Experiments

[6] Six Al goethites [α -(Fe, Al)OOH] samples were synthesized by *Schulze and Schwertmann* [1984, 1987] and *Torrent et al.* [1987]. Various synthesis procedures and properties of these samples are summarized in Tables 1 and 2. In these studies, the mol % of Al was determined by wet chemical analysis. The degree of Al substitution ranges between 0 mol % and 32.6 mol %. Samples GV3 and CB22 are pure goethites (Al mol % = 0), and are used to investigate the effects of the initial vacancies caused by different synthetic procedure.

[7] Temperature dependence of low-field magnetic susceptibility (χ -*T*) was measured by MPMS. We used AC frequency of 1 kHz and the DC field of 0.35 mT. For a ZFC and FC run (denoted as M_{ZFC-FC}), the sample was first cooled to 20 K in a zero field, then warmed up to 300 K (ZFC), and subsequently cooled down to 20 K (FC) in a field of 1 T. Total TRM was acquired by cooling from 400 K in fields of 10 mT, 100 mT and 1 T, and denoted as TRM_{100mT}, TRM_{100mT} and TRM_{1T}, respectively. All mea-

surements were made at steps of 2–5 K. The temperature sweeping rate is 2 K/min with corresponding errors less than ±0.5 K due to thermal lags when sweeping. The temperature for the maximum χ or in-field magnetization values from χ -T and ZFC/FC curves marks $T_{\rm N}$. Because blocking/unblocking occur over a range of temperatures, to obtain the maximum $T_{\rm B}$, a logarithm scale was used for TRM (see discussion section for detail). A graphic method is used to determine $T_{\rm B}$ by using the intersection of two tangents to the thermomagnetic curve that bounds $T_{\rm B}$.

3. Results

[8] The χ -*T* and M_{ZFC-FC}-*T* curves for the pure goethite sample GV3 are shown in Figure 1a. Both of them exhibit a peak around 362 K, corresponding to $T_{\rm N}$ (see section 4.1.). Most importantly, the difference between M_{ZFC} and M_{FC}(= M_{FC} - M_{ZFC}) (Figure 1a) equals TRM_{1T} (Figure 1b), especially when temperature is well below $T_{\rm N}$:

$$TRM_{1T} = M_{FC} - M_{ZFC}$$
(1)

[9] The temperature dependence of various TRMs for sample GV3 is illustrated in Figure 2. With increasing applied field, the absolute TRM increases, but the unblocking temperature $T_{\rm B}$ is fixed at ~ 370 K. The TRM_{1T} is used for other samples to sufficiently suppress the effects of the background signal.

[10] The corresponding $T_{\rm B}$ values for samples CB22 (0%), 35/3 (4.9%) and 38/33 (32.6%) are ~357 K (Figures 3a and 3b), ~362 K (Figures 3c and 3d) and ~210 K (Figures 3e and 3f), respectively. It appears that upon a slight increase in Al substitution, $T_{\rm B}$ increases from 357 K to 362 K, and then decreases with further increase in Al substitution (Figure 3). The corresponding $T_{\rm N}$ values for CB22 and 35/3 are ~348 and 340 K, 10–20 K lower than $T_{\rm B}$ (Figure 3). It appears that $T_{\rm B}$ and $T_{\rm N}$ are not equivalent, and the difference between them varies with the amount of Al substitution. For sample 38/33, $T_{\rm B}$ is unambiguously estimated to be ~210 K, but it lacks a characteristic AFM behavior (Figures 3e and 3f).

 Table 2.
 Summary of Properties of Al Goethites

	-	-							
Sample	Al, mol %	MCD _a , nm	MCD _b , nm	SA, m ² /g	$T_{\rm B},{\rm K}$	<i>T</i> _N , K	Δ <i>T</i> , K	Method for $T_{\rm N}$	Reference ^a
GV3	0	17	62	48	370	361	9	χ /ZFC-FC	1
CB22	0	12	61	70	357	348	9	ZFC-FC	2
35/3	5	23	35	42	362	340	22	ZFC-FC	1
35/5	12	39	59	26	342	315	27	χ	1
CB19	17	25	74	64	310	286	26	X	2
38/33	33	32 ± 14	20	35	210	?	180	ZFC-FC	3

^aReferences are 1, Torrent et al. [1987]; 2, Torrent et al. [1990]; 3, Schulze and Schwertmann [1984]. For Al mol %, MCD and SA, which is surface area.



Figure 1. (a) Temperature dependence of zero-field cooling (ZFC)/field cooling (FC) curves and magnetic susceptibility of GV3. (b) Temperature dependence of TRM of GV3. The dashed arrows in Figure 1a show that $M_{FC}-M_{ZFC}$ equals to TRM in Figure 1b. The dashed lines in Figures 1a and 1b represent T_N and T_B , respectively.

[11] Temperature dependence of magnetic susceptibility for samples CB19 and 35/5 is shown in Figure 4. Similarly, $T_{\rm B}$ was determined from TRM curves. As in other samples in Figure 3, CB19 and 35/5 had $T_{\rm B}$ higher than $T_{\rm N}$ (Figure 4).

4. Discussion

4.1. Are T_N , T_B , T_C , and $T_{\chi-max}$ Equivalent?

[12] For AFM material, below T_N , χ depends on the orientation of the applied field with respect to the spin axis (*c* axis for goethite). Parallel to the *c* axis, χ_{\parallel} is theoretically zero. However, thermal energy will deflect the spins in A and B sublattices out of perfect parallelism or antiparallelism. Therefore χ_{\parallel} reflects the combined action of thermal fluctuations and the applied field against the AB interaction, and is proportional to temperature. As a result, χ_{\parallel} reaches its maximum at T_N . On the other hand, perpendicular to the *c* axis, χ_{\perp} is solely due to the rotation of the spin sublattices by the torque of the applied field. Thus χ_{\perp} is almost temperature independent [*Nagamiya et al.*, 1955]. In addition, χ_{\perp} is always larger than χ_{\parallel} . For an ensemble of goethite grains without preferential orientation of spins,

$$\chi_{\text{powder}} = (2/3)\chi_{\perp} + (1/3)\chi_{\parallel}$$
 (2)

which also exhibits a maximum at T_N or a minimum for the reciprocal χ (χ^{-1}). Above T_N , goethite becomes paramagnetic and follows the trend of $c/(T + \Theta)$, where Θ is the asymptotic point.

[13] The critical point for ferrimagnetism or ferromagnetism to become paramagnetism is the Curie temperature $(T_{\rm C})$. $T_{\rm C}$ is also an intrinsic property determined by the AB interactions, and is independent of other physical properties such as grain volume and coercivity. Unlike $T_{\rm C}$, $T_{\rm B}$ strongly depends on the given physical setting including the grain volume, applied field, or cooling rate. As a result, $T_{\rm B}$ is always $\leq T_{\rm C}$. When temperature approaches $T_{\rm B}$, remanence gradually decreases to zero, but χ steadily increases and reaches its maximum at $T_{\chi-\rm max}$ (the temperature for the maximum χ) around $T_{\rm B}$. $T_{\chi-\rm max}$ generally represents the

upper limit of $T_{\rm B}$ for an assemblage of ferrimagnetic material.

[14] Among $T_{\rm N}$, $T_{\rm C}$, $T_{\rm B}$, and $T_{\chi\text{-max}}$, the latter two can be accurately determined by TRM ~ T and χ -T curves, respectively. We observe that $T_{\chi\text{-max}}$ is always less than $T_{\rm B}$ (Figures 1, 3, and 4). This strongly indicates that $T_{\chi\text{-max}}$ is not caused by the blocking of the parasitic remanence, but represents the $T_{\rm N}$ of goethite [*Mathé et al.*, 1999]. Because $T_{\chi\text{-max}} = T_{\rm N}$ and $T_{\chi\text{-max}} < T_{\rm B} \leq T_{\rm C}$, then $T_{\rm N} < T_{\rm C}$. Therefore $T_{\rm N}$ and $T_{\rm C}$ do not coincide, indicating a different physical origin.

[15] $T_{\rm B}$ has been previously proposed to represent $T_{\rm N}$ [Strangeway et al., 1967; Banerjee, 1970; Mathé et al., 1999]. However, we found that they are significantly different. The difference between $T_{\rm B}$ and $T_{\rm N}$ (ΔT) is $\sim 8-$ 9 K for pure goethite (Figures 3a and 3b) and > 20 K for the Al-substituted goethite (Figures 3c, 3d, and 4 and Table 1). Therefore the nominal $T_{\rm N}$ estimated from $T_{\rm B}$ will be systematically higher than the true $T_{\rm N}$ for the Al-substituted goethites. The coincidence of $T_{\rm B}$ and $T_{\rm N}$ is probably valid



Figure 2. A distinctively different temperature dependence observed for a set of TRMs that are produced in a different bias field (10 mT, 100 mT, and 1 T) for sample GV3. The vertical gray bar represents $T_{\rm B}$.



Figure 3. Temperature dependence of the ZFC-FC (gray) and TRM (black) curves for samples (a) CB22, (c) 35/3, and (e) 38/33, associated with M^{-1} versus (b, d, f) temperature curves for comparison.

only for a coarse-grained pure goethite with insignificant amount of crystal defects [e.g., *Özdemir and Dunlop*, 1996].

[16] Above T_N , AFM of goethite becomes paramagnetic, showing a linear trend of χ^{-1} with temperature (Figures 4b and 4d). However, with further increasing temperature (above T_B), χ^{-1} shows a linear segment with a smaller slope, which is caused by the parasitic remanence (Figures 4b

and 4d). In principal, susceptibility of the ferrimagnetic mineral above $T_{\rm C}$ is not linear, but is convex upward. In contrast, χ^{-1} is perfectly linear for ferromagnetism.

[17] For micron-sized samples (CB22 and GV3), we anticipated that $T_C \approx T_B$. On the contrary, χ^{-1} versus *T* curves show convexities when $T > T_C$ (Figures 3 and 4), indicating that the parasitic remanence is more ferrimagnetic-



Figure 4. Temperature dependence of susceptibility (solid dots) for samples (a) CB19 and (c) 35/5. (b) and (d) Comparison of TRM (open circles) and the reciprocal susceptibility versus *T* curves. Dashed lines mark $T_{\rm N}$ and $T_{\rm B}$.

like (the spin structure is composed of two opposing but unequal magnetic sublattices) than ferromagnetic-like (the spin structure composes of parallel equal magnetic sublattices).

4.2. Role of Vacancy and Al Substitution

[18] The magnetic properties of goethite are strongly affected by particle volume [*Dekkers*, 1989], the amount of defects or vacancies [*van Oosterhout*, 1965; *van der Woude and Dekkers*, 1966; *Yamamoto*, 1968; *Bocquet and Kennedy*, 1992; *Bocquet and Hill*, 1995], isomorphous

substitutions [*Hedley*, 1971; *Mathé et al.*, 1999] (see Table 1), and crystallite size (so called "mean crystallite dimension," MCD). Note that MCD reflects the average size of the coherently scattering domains within crystals [*Schulze and Schwertmann*, 1984] and is much smaller than the particle volume. Unfortunately, most of these parameters covary with the amount of Al substitution (Table 3).

[19] Schulze and Schwertmann [1984, 1987] showed that the parameter Δa (defined as $a_{obs} - 0.00212*A1\%$, where a_{obs} is the measured lattice parameter) was positively correlated with mol % Al, indicating that the crystal

Table 3. Summary of the Effects of Al Substitution and Structural Defects on Goethite Properties

	Effect					
Properties	Al substitution	Structural Defects	Reference ^a			
Unit cell dimensions	decrease	a dimension dilates	1			
Crystal size	laths become shorter and narrower but thicker	decreases	1			
Temperature of dehydroxylation	increases	decreases	1			
T _N	decreases	decreases	1			
T _B	decreases	decreases	1, 2			

^aReferences are 1, Schulze and Schwertmann [1984]; 2, this study.



Figure 5. Compilation of the estimated $T_{\rm N}$ and $T_{\rm B}$ of goethites as a function of the mole percent of the substituted diamagnetic element (Al or Ga). Crosses are from Mössbauer models [*Fleisch et al.*, 1980; *Pollard et al.*, 1991] and temperature dependence of 2.5 T magnetization and susceptibility curves [*Mathé et al.*, 1999]; solid circles indicate $T_{\rm B}$ [this study]; open circles indicate $T_{\rm N}$ (this study); star indicates $T_{\rm N}$ and $T_{\rm B}$ for a centimeter-sized natural goethite sample [*Özdemir and Dunlop*, 1996].

defects increase with increasing Al mol % [Schulze and Schwertmann, 1987]. The grain size of Al goethites has also been investigated by transmission electron microscopy (TEM) studies [Schulze and Schwertmann, 1984, 1987; Torrent et al., 1990], showing that a different synthetic condition causes a substantial difference in particle size and shape. In general, samples with low Al mol % are lath-shaped and have large $(1-2 \mu m \log)$ jagged lath-shaped ends. With increasing Al mol %, the Al goethites become shorter, narrower and thicker [e.g., Schulze and Schwertmann, 1984, 1987; Torrent et al., 1990]. However, no systematic relation between MCD and Al mol % has been reported. Therefore it is apparent that MCD is not a dominant factor in controlling magnetic properties of Al goethites, although we cannot completely rule out the possibility. By the same token, Dekkers [1989] proposed that the magnetic interactions among crystallites could account for the grain size dependence of magnetic properties.

[20] In summary, Al substitution decreases $T_{\rm N}$ of Al goethites through a dilution process of AB interaction both by Al contents and by the crystal defects. Undoubtedly, $T_{\rm C}$ of the parasitic remanence could also decrease due to the same mechanism. $T_{\rm B}$ will simultaneously decrease with decreasing $T_{\rm C}$, and can be further lowered by shrinking the grain size (or volume) of the particles. However, for the micron-sized grains, we expect $T_{\rm B} \approx T_{\rm C}$. Despite the similarity in purity and grain size, we observed that sample GV3 has higher $T_{\rm B}$ and $T_{\rm N}$ than CB22. The main reason for such a difference is the presence of vacancies (or defects), implying that GV3 has a lower vacancy concentration than CB22.

[21] Systematic variations in T_N versus the diamagnetic contents (Al or Ga) are summarized in Figure 5. The

maximum values of $T_{\rm N}$ and $T_{\rm B}$ (~393 K or 120°C) are from a centimeter-sized natural goethite [*Özdemir and Dunlop*, 1996]. Note that the synthetic goethites used in this study have $T_{\rm B}$ and $T_{\rm N}$ about 20–40 K lower than the maximum reference value due to higher concentrations of vacancies (Figure 5). Estimated values of $T_{\rm N}$ are systematically higher than the compiled results from the literature [*Fleisch et al.*, 1980; *Pollard et al.*, 1991; *Mathé et al.*, 1999], probably caused by a resolution difference of the instruments used and/or by a different degree of vacancy inherited from a different synthesis procedure.

[22] The magnetization peak for sample 38/33 occurs at \sim 30 K (Figures 3e and 3f), which is too low to be $T_{\rm N}$. Above 40 K, the $M^{-1} \sim T$ curve does not show AFM behavior (Figures 3e and 3f), probably indicating a superantiferromagnetism (SPAFM) phenomenon [*Néel*, 1949; *Gilles et al.*, 2002]. In a very small size of goethite (nanometer range), AFM starts to acquire large magnetic moments from uncompensated spins of the unpaired sublattices. Then, it becomes a superparamagnetic ferrimagnet with very high coercivities. If so, a strong SP moment will mask the AFM behavior, as observed in sample 38/33 (Figures 3e and 3f).

4.3. Magnetism of the Parasitic Remanence

[23] We observed that $T_{\rm N}$ and $T_{\rm C}$ are not equivalent for Al goethite. We are testing a tentative conceptual zonal model to explain the key three observations: (1) In all samples, $T_{\rm N} \leq T_{\rm C}$ (Figures 1, 3, and 4); (2) the ΔT (difference between $T_{\rm B}$ and $T_{\rm N}$) increases as the amount of Al substitution increases (Figure 5); and (3) the parasitic remanence is more ferrimagnetic-like than ferromagnetic-like (Figures 3 and 4).

[24] It has been generally regarded that both AFM and parasitic remanence of Al goethites lie along the *c* axis. However, our observation contradicts this common assumption. *Gasser et al.* [1999] investigated a series of Mn goethites by spot analytical electron microscopy (AEM). Their results revealed that the Mn distribution within individual crystals is highly inhomogeneous, and exhibits zonal features so that the Mn mol % increases from the tip to the core. For example, for the two needles (M6.4 and M6.5) for sample M6 (the average Mn mol % is ~8.8%), Mn mol % values increase from ~7% to 12% for M6.4 and from ~8.5% to 10% for M6.5, as the microscopic sensors sweep from the edge to the interior.

[25] Such a zonal distribution can be reasonably extended to Al goethites. For example, for Al goethite sample with an average 4% Al substitution, the core of the crystal could have a Al mol % higher than 4%, and the Al content could gradually decrease toward the crystal surface. On the basis of the model of *Pollard et al.* [1991], the core will have more unbalanced spins, resulting in a ferrimagnetism while the surface maintains an AFM. Therefore the whole crystal will gradually change from ferrimagnetism (core) to AFM (tip).

[26] Both $T_{\rm C}$ and $T_{\rm N}$ are critical temperature points, where the thermal energy (*kT*; where *k* is Boltzmann's constant and *T* is absolute temperature) can provide the energy necessary to rotate one spin vector against the other and the disordering effects of thermal energy will dominate the ordering force of exchange. Therefore, for Al goethites, the ordering force of spin exchange energy for ferrimagnetism is higher than that for AFM because $T_{\rm C}$ is always higher than $T_{\rm N}$.

[27] With increasing the average mol % Al, the dilution effects of the Al contents will decrease both $T_{\rm N}$ and $T_{\rm C}$, but follow a different trend. When Al mol % < 4-5%, the internal stress (caused by Al substitution, and hence lattice mismatched at a microscopic level) of Al goethites significantly increases, and can possibly overwhelm the dilution effects. A higher internal stress can increase the microscopic coercivity, in turn increase $T_{\rm B}$ for mol % Al < $4-5 \mod \%$ (Table 1). With further increasing Al mol %, the preferred Al substitution gradually disappears. Then the inner part of the crystal becomes more AFM-like and the rim becomes more ferrimagnetic-like. Because the exterior always has a lower concentration of Al mol % than interior, the dilution effects of Al on the outer part will be higher than on the inner part. Thus $T_{\rm N}$ decreases faster than $T_{\rm C}$.

[28] In summary, the AFM and the parasitic ferrimagneticlike remanence could still have the same origin. The differences between the corresponding $T_{\rm B}$ and $T_{\rm N}$ are due to the zonal structure of Al goethites. This conclusion is further supported by the results of *Scheinost et al.* [1999], who reported that Al goethites could exhibit diaspore clusters rather than a homogeneous distribution of Al.

4.4. Paleomagnetic and Paleoclimatic Implications

[29] $T_{\rm N}$ of Al goethites strongly depends on Al mol % (Table 3 and Figure 5). For example, Al mol % of ~20% can sufficiently suppress $T_{\rm N}$ below the room temperature (300 K). Around $T_{\rm N}$, Al goethites have maximum susceptibility but lose abilities in carrying remanences. Therefore Al goethites with Al mol % larger than ~20% could significantly contribute to the bulk susceptibility.

[30] The concentration of AFM minerals is usually quantified by high-field remanence magnetization (HIRM, defined, e.g., as $IRM_{1T} + IRM_{-0.3T}$). However, this parameter may fail to detect the contribution of Al goethite because its T_B could be lower than 300 K. The paleoclimatic and paleoenvironmental analysis solely based on the room temperature magnetic parameters may fall short in its intended purpose. In terrestrial environments, Al-substituted goethite is ubiquitous. Studies show that the hematite/goethite ratio in soils is a useful indicator of climate change [*Tite and Linington*, 1975; *Balsam et al.*, 2004]. It is thus important to identify a presence of Al goethite in natural environments in order to extract its paleoclimatic signals.

5. Conclusion

[31] Contrary to the common view, values of $T_{\rm N}$ of AFM and $T_{\rm B}$ of the parasitic remanence for a series of Al goethites are found to be not equivalent. Values of $T_{\rm B}$ were always larger than $T_{\rm N}$. The difference between $T_{\rm N}$ and $T_{\rm B}$ increases from ~8–9 K for pure goethites to >20 K for Al goethites, indicating that AFM and the parasitic remanences are controlled by a different mechanism. In addition, the parasitic remanence is more ferrimagnetic-like than ferromagnetic-like. Even for pure synthetic goethites without Al substitution, $T_{\rm N}$ and $T_{\rm B}$ were still different due to the existence of crystal defects. [32] Acknowledgments. This study was supported by the NSFC grants 40325011 and 40221402, by the Spanish Ministerio de Ciencia y Tecnologia Project AGL2003–01510, and by NSF-0311869. We thank S. K. Banerjee, M. Jackson and P.-E. Mathé for their useful suggestions. Thanks are also given to Tatsuro Fukuchi, Bernie Housen, and Phil Wannamaker (Associate Editor) for their constructive reviews. All the rock magnetic measurements were carried out at the Institute for Rock Magnetism (IRM), which is supported by the W. M. Keck Foundation, the Earth Science Division of the U.S. National Science Foundation, and the University of Minnesota. C. Deng acknowledges further support from the Royal Society in the form of a BP Amoco Fellowship. U. Schwertmann, Technische Universitaet Muenchen, kindly donated samples for use in this study. This is IRM publication 0410.

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