Quantification of hematite from the visible diffuse reflectance spectrum: effects of aluminium substitution and grain morphology

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ABSTRACT: Hematite exists ubiquitously in soils and sediments, and is commonly aluminium (Al)-substituted. This study investigated systematically the effects of Al substitution on the visible diffuse reflectance spectrum (DRS) of hematite by using several sets of synthetic samples. We found that the position and amplitude of the characteristic absorption band of hematite (estimated from the first- and second-order derivative curves of the Kubelka-Munk remission function spectrum derived from the DRS) was significantly affected by the degree of Al substitution as well as by sample grain morphology. Therefore, there are ambiguities in quantifying the degree of Al substitution and the mass concentration of hematite using DRS. Nevertheless, if hematite forms under similar environmental conditions, it is possible to establish a transfer function between the DRS parameters and hematite concentration as discussed here for a Chinese loess-palaeosol sequence.

KEYWORDS: hematite, diffuse reflectance spectroscopy, aluminium substitution.

Hematite is an important antiferromagnetic mineral in natural environments on both Earth (Schwertmann, 1987) and planetary surfaces (Christensen et al., 2000, 2001; Morris et al., 2005). As a major remanence carrier, hematite carries stable natural remanent magnetization over the geological time scale (Kletetschka et al., 2000; Dunlop & Kletetschka, 2001). In addition, the formation and preservation of hematite is sensitive to the ambient environment (Schwertmann, 1987, 1989, 1993) and therefore various proxies related to hematite have been widely used to track palaeo-environmental changes, e.g. recorded by marine sediments (Yamazaki & Ioka, 1997; Maher & Dennis, 2001; Larrasoana et al., 2003, 2006) and by terrestrial aeolian deposits (Ji et al., 2001; Carter-Stiglitz et al., 2006; Liu et al., 2004, 2006).

There are several approaches to quantifying the concentration of hematite in natural samples. First, hematite has coercivity values significantly higher than magnetite and maghemite, and thus hard (or high-field) isothermal remanent magnetization (HIRM) and the corresponding S-ratio has been used to trace the ‘absolute’ and relative variations in the concentration of hematite, respectively.

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(Thompson & Oldfield, 1986). However, the remanence carried by hematite is affected by multiple factors: the degree of foreign ion substitution, grain size and morphology. Liu et al. (2007) showed that HIRM is also related strongly to its coercivity. In addition, large errors could mask the weak HIRM values when the magnetic background is high (Liu et al., 2002). Mössbauer spectroscopy (Eyre & Dickson, 1995) and X-ray diffraction (XRD) (Pomies et al., 1998) are conventional methods to detect the presence or even quantify the concentration of hematite in samples. However, these methods are time-consuming, costly and need enrichment by prior separation (Liu et al., 2002).

The visible diffuse reflectance spectrum (DRS) serves to characterize iron oxides in natural samples (Kosmas et al., 1986). In particular, the concentrations of hematite and goethite in soils and sediments have been estimated using appropriate standards and different parameters derived from the spectrum of the reflectance (R) itself but also the spectra of the absorbance (A = log 1/R) or the Kubelka-Munk (K-M) remission function \[ F(R) = \left(1 - R^2/2R\right) \]. Thus, Torrent et al. (1980, 1983) and Ji et al. (2001) used colour parameters derived directly from the DRS; Deaton & Balsam (1991) used the first derivative of the DRS, and Scheinost et al. (1998) and Torrent et al. (2007) used the second derivative of the K-M remission function.

Hematite in soils and sediments is usually Al-substituted (Schwertmann, 1987, 1989, 1993). Al substitution, which can reach up to ~16 mol.%, strongly influences the magnetic properties (de Grave et al., 1982; Van San et al., 2001; da Costa et al., 2002; Liu et al., 2007), IR absorption spectrum (Barrón et al., 1984), colour parameters (Torrent & Barrón, 2003), visible DRS (Kosmas et al., 1986; Van San et al., 2001; da Costa et al., 2002; Torrent & Barrón, 2003) and the unit cell dimensions of hematite (Kosmas et al., 1986; Schwertmann, 1993).

Kosmas et al. (1986) found that the position of the characteristic absorption band of hematite at ~545 nm, which is marked by a minimum in the second derivative of the K-M remission function spectrum, was negatively correlated with Al substitution \(r = -0.86; P < 0.01\) for a group of nine synthetic samples. Torrent & Barrón (2003) found this correlation to be much weaker \(r = -0.36; P < 0.01\) for a group of 55 synthetic and natural samples. In any case, this negative correlation does not support the postulates of the crystal field theory if this band is attributed to the \(2(6A_1) \rightarrow 2(^4T_{1g}(^4G))\) electron pair transition (Sherman & Waite, 1985). Torrent & Barrón (2003) also observed that colour was related to the position of this band so that the hue becomes more purple when the band shifted to longer wavelengths. In addition, the amplitude of this band in the second derivative of the K-M function spectrum (taken as the difference in ordinate between the minimum marking the position of the band and the next maximum at a longer wavelength) ranged widely and was uncorrelated with Al substitution and only weakly and positively correlated \(r = 0.40; P < 0.01\) with the specific surface area (i.e. negatively correlated to particle size). Therefore, linking hematite concentration and Al substitution in natural samples to the parameters obtained from the DRS is far from straightforward.

To examine the sensitivity of the DRS method to the Al content in hematite further, and therefore to reduce the ambiguity of this method, this study investigated several series of synthetic samples ranging widely in the degree of Al substitution. In addition, the environmental significance of the position of the major hematite band is discussed and applied to a Chinese loess-palaeosol sequence.

MATERIALS AND METHODS

Two types of hematite samples were investigated in this study (Fig. 1). The first set of samples, which ranged widely in the degree of Al substitution, had been synthesized by reacting \(\text{Fe(NO}_3\text{)}_3\) and \(\text{Al(NO}_3\text{)}_3\) solutions with KOH at different concentrations in the presence of different additives (e.g. low molecular weight organic acids) (Barrón et al., 1988; Colombo et al., 1994). These samples had been characterized previously in terms of their crystallochemical properties (Barrón et al., 1988; Colombo et al., 1994), grain size (Roberts et al., 2006) and magnetic properties (Liu et al., 2007). These hematites had formed via dehydration and rearrangement of precursor ferrihydrite as is the case with soil hematites (Schwertmann, 1989); therefore, their properties somewhat resemble those of soil hematites, although the average grain size of the synthetic hematites studied (~100–400 nm) is larger than that of most natural counterparts (Barrón et al., 1988; Roberts et al., 2006). In total, this group includes 16 samples (in five series: OX, TR, CLB, HE, CT and HC).
The second set, which consisted of pure hematite samples of coarser grain size (up to several μm), was synthesized using similar procedures but different initial chemical conditions. These samples have distinct morphologies and can be classified into two major groups: well-defined platy samples (H180, S7, and S8) and cubic or non-platy samples (H3, H33, J12, K2, and L3) (Fig. 1). Their magnetic properties and the corresponding relationships to the inherent vacancies were recently studied by Liu et al. (2010). The purpose of using this set of samples was to detect those major factors other than Al that control the position of the characteristic band of the hematite DRS.

The Chinese loess-palaeosol samples were collected from the Luochuan sequence on the central Chinese Loess Plateau. The sequence covers samples from the palaeosol units S7 to S4, which span a major palaeoclimatic transition from the 41 ky to 100 ky periodicity (Raymo & Nisancioglu, 2003). These samples have been previously well investigated using both magnetic (Liu et al., 2006) and geochemical proxies (Bloemendal et al., 2008); in particular, Ji et al. (2001) and Balsam et al. (2004) estimated the goethite and hematite contents from the reflectance values in colour bands and related them to the magnetic stratigraphy and palaeoclimatic conditions. Thus, sufficient background information is available for understanding the palaeoenvironmental settings. Generally the loess units (denoted as L), which were deposited during glacial periods, exhibit low magnetic susceptibility; in contrast, during interglacial periods, pedogenesis resulted in the
Fig. 2 (this and facing page). The first- and second-order derivatives of the K-M functions for the first set of hematite samples. The dashed vertical lines mark the peak positions. For CT1, CT4, HC2 and HC3 the maxima instead of the minima of the second derivative are marked. Labels with numbers indicate the sample name with the degree of Al substitution (unit in mol.%).
neoformation of hematite and fine-grained maghemite and the consequent magnetic enhancement in the soils (denoted as S).

The DRS values were recorded from 420 to 980 nm in 2 nm steps using a Varian Cary 1E spectrophotometer equipped with a BaSO₄-coated
integrating sphere and using BaSO₄ as the white standard. The scan speed was set to 30 nm per minute. From the DRS, the first- and second-order derivative curves of the Kubelka-Munk (K-M) remission function were calculated using the Savitzky-Golay algorithm provided by the Varian instrument software.

RESULTS

The first- and second-order derivative curves of the K-M function of the DRS for the synthetic hematite samples are shown in Fig. 2. The first- and second-order derivative minima in the K-M curves ranged between ~550–580 nm and between ~530–560 nm, respectively. For convenience, the positions of the two minima are defined as P₅₈₀ and P₅₆₀, respectively; it must be noted that these minima are only surrogates for the actual position of the characteristic hematite band. The minimum in the first derivative curve is substantially displaced to a longer wavelength, as can be mathematically demonstrated by derivation of a Gaussian curve representing an absorption band (Kosmas et al., 1984). Also, in the simulated spectra of a mineral mixture, it can be mathematically demonstrated that the position of this minimum is influenced by the presence of absorption bands pertaining to other

![Fig. 3](image-url)

**Fig. 3.** Correlation between the DRS proxies and the Al substitution for the first set of hematite samples. (a) peak position P₅₇₅, (b) P₅₈₀, (c) I₅₇₅, and (d) I₅₈₀. The dashed lines are the linear regression lines. All the regression lines have a slope significantly (P < 0.05) different from zero.
minerals and the concentration of hematite, as is
often the case with natural samples (W. Balsam, pers.
comm.). In contrast, as can also be mathematically
demonstrated, the position of the minimum in the
second-order derivative curve is influenced neither
by other constituents nor by the concentration of
hematite in a mixture. One should also take into
account that the derivative curve obtained via any
mathematical algorithm from data points separated
by a certain step is slightly and systematically
displaced from the true derivative curve. In
summary, in the case of pure hematite samples,
both the first and second derivative curves are useful
for comparative purposes but the second derivative
curve should be used for soils or mineral mixtures.

The difference between the minimum corre-
sponding to the band and the next associated
maximum at a longer wavelength in the derivative
curve is considered as a proxy for the true band
amplitude (Torrent et al., 2007). Thus the
corresponding band amplitudes for P580 and P560
are defined as I580 and I560, respectively.

Consistent with other authors (Kosmas et al.,
1986; da Costa et al., 2002; Torrent & Barrón,
2003) P580 and P560 were shifted to shorter
wavelengths with increasing Al substitution, with
the exception of samples HE1 (Fig. 2e) and CLB5
(Fig. 2k). In addition, Al substitution seems to
influence the amplitude of the band. Specifically,
with increasing Al content, the amplitudes of the
hematite bands were significantly depressed.

The correlations between Al substitution and the
DRS proxies (P580, P560, I580, and I560) are shown in
Fig. 3. Overall, there is a negative correlation
between the Al content and both P580 (Fig. 3a)
and P560 (Fig. 3b). Such a negative correlation is
better defined for each series of hematite samples,
but the discrepancies among different series are
obvious. For example, for the OX series, P580 and
P560 sharply decrease from 577 nm down to 561 nm
when the Al mol.% increases from 1 mol.%
(sample OX1) to only 5 mol.% (sample OX3),
and then remain relatively stable with the Al mol.%
increasing to ~8 mol.% (sample OX5). In contrast,
for the TR series, P580 decreases more linearly but
slightly from ~571 nm (sample TR2, pure hematite)
to ~566 nm (sample TR6, Al = ~13 mol.%). The
band amplitudes and the Al content also show
negative correlations (Fig. 3c, d). Specifically, the
absolute value of the correlation coefficient
between I560 and Al ($r = -0.73$) is larger than
that between P560 and Al ($r = -0.57$).

Figure 4 shows the second derivative of the K-M
function for the second group of micro-sized pure
hematite samples. These samples can be classified
into two distinct groups. Samples H180, S7, and S8
have relatively lower band position (P560 = ~560 nm),
but larger band amplitude. In contrast,
samples H3, H33, J12, K2, and L3 have much
reduced band amplitude, but the band positions are
shifted to higher values.

DISCUSSION
Factors controlling the DRS pattern for
hematite

So far, there remain arguments about the effect
of Al substitution on the peak position of the
second derivative of K-M functions. As mentioned
above, the significant linear correlation between
these proxies observed by Kosmas et al. (1986)
was not confirmed by the results of Torrent &
Barrón (2003), which were based on a larger
number of samples. Torrent & Barrón (2003) also
observed a significant correlation between the peak
position and the specific surface area (SSA). It is
difficult, however, to separate the effects of
different factors (Al content, grain size, SSA,
crystal shape) because these factors co-vary. Our
study supports the conclusion of Torrent & Barrón
(2003) that the band position is determined by
multiple factors, as evidenced by the non-linear
correlation for each hematite series, and large
discrepancies among different groups. The results of Torrent & Barrón (2003) also support a statistically significant negative correlation between the Al content and the band peak position. In particular, our new results also indicate that for hematites synthesized under similar conditions (e.g. for each series), such a negative and nonlinear correlation is significant.

However, there are two exceptions: samples HE1 and CLB5 do not follow the overall trend. In addition, the band positions and amplitudes for Al-free hematite samples (TR2 and CT1) are different. This indicates that the DRS of hematite is controlled by multiple factors. On the basis of the crystal and ligand theories, Scheinost et al. (1998), using 176 synthetic and natural Fe oxide samples, showed that the spatial linking, structure, occupation and distortion of Fe(O,OH)₆ octahedra, and differences in the Fe-O-Fe distance significantly affect band position and amplitude. For example, Al substitution will affect unit cell parameters and, hence, the DRS pattern of hematite. For our samples, Al-substitution is undoubtedly the major factor controlling the position and amplitude of the characteristic hematite band in the DRS.

The effects of grain morphology cannot be neglected for well-oriented samples because these samples will yield regular reflections and break the laws of diffuse reflection (Torrent & Barrón, 2008). This can be well demonstrated by the second group of hematite samples examined in this study. These pure samples have a similar diameter but distinct morphology. The platy samples exhibit enhanced band amplitude and lower band position.

In summary, it is difficult to separate the effects of Al-substitution, grain morphology, vacancies and other factors. Therefore we tentatively interpret the ‘abnormal’ behavior of samples HE1 and CLB5 in terms of the combined effects of all of these factors.

**Feasibility of quantifying hematite using DRS**

On the basis of our analyses, it is difficult in practice to quantify accurately the degree of Al-substitution of hematite using the derivatives of K-M functions. Moreover, it is also impossible to construct a single function to translate band amplitude or colour parameters to the absolute concentration of hematite on the basis of external synthetic standards. This is mainly because hematites of different origin can have wide differences in the DRS pattern.

Nevertheless, if hematite originates under similar environmental conditions, little variation can be expected in its degree of Al-substitution and morphology. Then, the relative variations in band amplitude can still be used to trace variations in the concentration of hematite in a mineral mixture. Moreover, if the mass concentration of hematite can be quantified by using alternative methods, e.g. differential XRD combined with chemical analysis (Torrent et al., 2007), a transfer function is feasible to translate band amplitude into hematite concentration.

To examine the significance of spectral differences in natural hematites, the DRS spectra of a set of Chinese loess-palaeosol samples were systematically measured. The corresponding results (Fig. 5) show several features. First, the distinct second-order derivatives of the K-M functions for samples between the loess and palaeosol units are consistent with the fact that the hematite particles in loess and palaeosol units have different origins (Fig. 5d, e). The hematite particles in the unaltered loess (usually designated as ‘aeolian’ hematites) were generated by weathering of Fe-bearing minerals in the various source areas, so the wider second derivative spectrum of the loess samples could indicate a wider range of values of Al substitution. In contrast, band amplitude is strongly enhanced for the palaeosol sample, which indicates pedogenic production of hematite, and the spectrum is centred at ~535 nm, a value lower than that for pure hematite. On the basis of Fig. 2a, this suggests that pedogenic hematite might contain more Al than aeolian hematite. Second, by comparing all palaeosols (S8–S4), the band position is rather consistent (~535 nm) (Fig. 5c). This might reflect an essentially constant pedogenic environment at this site in the past ~1 Ma, which would result in a relatively constant degree of Al substitution in pedogenic hematite. Nevertheless, it seems that band peak positions shifted subtly (by 1–3 nm) but systematically to shorter wavelengths from S6–S8 to S4–S5. This suggests that the pedogenic hematites in S4 and S5 might have incorporated more Al than those in S6–S8. Such a pattern is consistent with the total Al content for the bulk sample (Fig. 5a), which exhibits a step around 40 m. It can be speculated that the higher Al content of the silicates present in the loess might contribute to enrich the solution in Al³⁺ during pedogenesis, and in turn increase the Al content in hematite. Also, differences in pH during pedogenesis could have
caused differences in the degree of Al substitution in hematite.

The quantitative estimation of hematite in natural samples relies on the band amplitude (Torrent et al., 2007). Because band amplitude is not only determined by the concentration of hematite, but also by other factors (e.g. Al substitution and matrix effects), potential ambiguities exist for quantitatively estimating the hematite concentration using the DRS approach (Ji et al., 2001; Torrent et al., 2007). Nevertheless, this study shows that the Al content in pedogenic hematite for the Luochuan section is seemingly uniform, and thus relative variations in band amplitude are likely to represent variations in hematite concentration, as shown in other DRS-based studies (Balsam et al., 2004). We therefore propose that variations in band position should be tracked in order to evaluate the fidelity of the DRS method for quantifying hematite concentration.

CONCLUSIONS

This study shows that the position and amplitude of the DRS band for hematite is controlled mainly by the degree of Al substitution. The negative but non-linear correlation between these two parameters is significant, especially for most hematite particles synthesized under similar conditions (e.g. for the same series). We therefore propose that the position of the DRS band still provides useful information about the inherent properties of hematite. The case study for the Luochuan loess/palaeosol sequence demonstrates that the DRS can help to discriminate between hematites of aeolian and pedogenic origin.

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