

Article

Re-Visiting the Quantification of Hematite by Diffuse Reflectance Spectroscopy

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Abstract: Hematite concentration is an important climatic proxy for environmental (climatic) studies of soils and sediments. However, the accurate quantification of naturally occurring hematite has always been a difficult question, especially for those areas with lower hematite concentrations. Diffuse reflectance spectroscopy (DRS) is an effective method for hematite identification and quantification with lower detection limits. In this study, we synthesized a set of samples with well-determined concentrations to explore the exact detectable range of hematite and propose the most effective transfer function between the DRS proxy and hematite concentration. In addition, natural sediments from Inland Asia and the Western Pacific Ocean were used to further test the feasibility of the new transfer function. Results show that the lowest DRS detection limit for hematite could reach ~0.00078%, but is affected by the natural matrix. We also find that the second derivative of the Kubelka–Munk (K–M) function is monotonically correlated with the hematite concentration (0.00078%–100%), but ambiguities exist for the first derivative. Therefore, the second derivative of the K–M function is highly suggested for the hematite quantification, especially when concentration exhibits a wide range of variations. This study provides important references for the application of hematite proxy and promotes the popularization and development of the DRS method.

Keywords: environmental magnetism; hematite; diffuse reflectance spectroscopy; detectable range; detection limit; Inland Asia; Western Pacific Ocean



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1. Introduction

Hematite (α -Fe₂O₃) is widely distributed on Earth and other planets (e.g., Mars, Moon, etc.) [1–9]. As one of the most stable iron oxides, hematite serves as a common and important paleomagnetic remanence carrier in sediments and rocks [10–14]. In addition, characterized by the distinct red color of natural hematite pigment, it can be further used to investigate the paleoenvironment conditions not only on the Earth [3,15–27], but also on the other planets, in particular on Mars [1,28–31].

Accurate detection and quantification of hematite is a prerequisite for environmental and climatic studies [6,32,33]. High coercivity (B_c , up to several Tesla) and Néel temperature (T_N , 675–690 °C) are the dominant magnetic characteristics for hematite [2,34–38]. Based on these characteristics, several magnetic parameters have been proposed to quantify hematite, e.g., “hard” isothermal remanent magnetization (HIRM) and S-ratio, which use

300 mT crudely as a conventional cutoff field. However, these parameters apparently ignore those hematite particles with remanent coercivity below 300 mT [6,39–43]. In addition, isomorphous cation substitution (e.g., Al^{3+} for Fe^{3+}) into the hematite lattice may result in the coercivity lower than 300 mT [2,3,9,19,44–49]. Furthermore, goethite and ferrihydrite contribution cannot be neglected [22,23,35,50,51].

Apart from the magnetic methods, the stepwise dissolution of natural samples with citrate–bicarbonate–dithionite (CBD) can be used to identify and trace the concentration and particle size of hematite [52,53]. However, it is difficult to simply distinguish the Fe ions contributed by hematite [54]. In addition, X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), and X-ray diffraction (XRD) can also be used for the complementary identification of hematite [32,55–58]. However, the XRD peak of hematite is difficult to identify when the proportion of hematite is lower than 1% [32]. Furthermore, poor crystallinity and lattice defects make it difficult to effectively identify hematite using these methods [6]. Microscopic examination provides a direct observation method, which can effectively identify the morphologic characteristics of hematite [18,59]. Color can also be used for the identification and quantification of hematite, but it is affected simultaneously by both visual and environmental factors [7,8,33,60–64].

In comparison, diffuse reflectance spectroscopy (DRS) is most effective to identify and quantify hematite even with rather low concentrations [16,32,65–71]. Accordingly, several data processing methods have been proposed to extract hematite information from the DRS data, e.g., first derivative curves of raw DRS data, and the first and second derivative curves of the Kubelka–Munk (K–M) function curve [66,72–75]. However, three basic questions still remain, which include (1) the lowest detection limit of hematite, (2) the best transfer function between the DRS proxy and hematite concentration, and (3) the best data processing method to retrieve hematite information from DRS.

To resolve these questions, we synthesized and tested a set of samples with known concentrations of hematite. First, we aimed to determine the lowest detection limit of hematite with an ideal matrix background. Then, we constructed and analyzed the transfer function between DRS proxy and hematite concentration with different data processing approaches. Finally, natural sediments were used to test the feasibility of the proposed DRS methods.

2. Materials and Methods

2.1. Materials

Two types of materials were used in this study—manufactured materials and natural samples. Manufactured materials have the advantage of known composition and consistent physical characteristics with no contaminants [32]. In this study, 31 manufactured samples with different hematite concentrations were made by fully mixing different proportions of stoichiometric kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, light color, CAS: 1332-58-7, Lot: P1501105, produced by the Shanghai Titan Scientific Co., Ltd., Shanghai, China) and hematite ($\alpha\text{-Fe}_2\text{O}_3$, red color, CAS: 1317-60-8, Lot: 32446800, produced by Strem Chemicals, Inc., Newburyport, MA, USA) in an agate mortar. A Mettler Toledo LE104E/02 balance (0.1 mg actual graduation value and 1 mg scale verification value) was used for weighing. To ensure the accuracy of the proportion, manufactured samples were prepared using two methods (Figure 1): (1) The weighing method. For manufactured samples with hematite content $\geq 0.2\%$, the required amounts of hematite and kaolinite were weighted separately, and then mixed to produce 500 mg samples. (2) The diluting method. For manufactured samples with hematite content $< 0.2\%$, the balance cannot weigh the required amount of hematite due to its precision limit. Therefore, a manufactured 500 mg sample with 0.2% hematite was diluted by adding 500 mg kaolinite repeatedly to obtain the manufactured samples with different proportions of hematite.

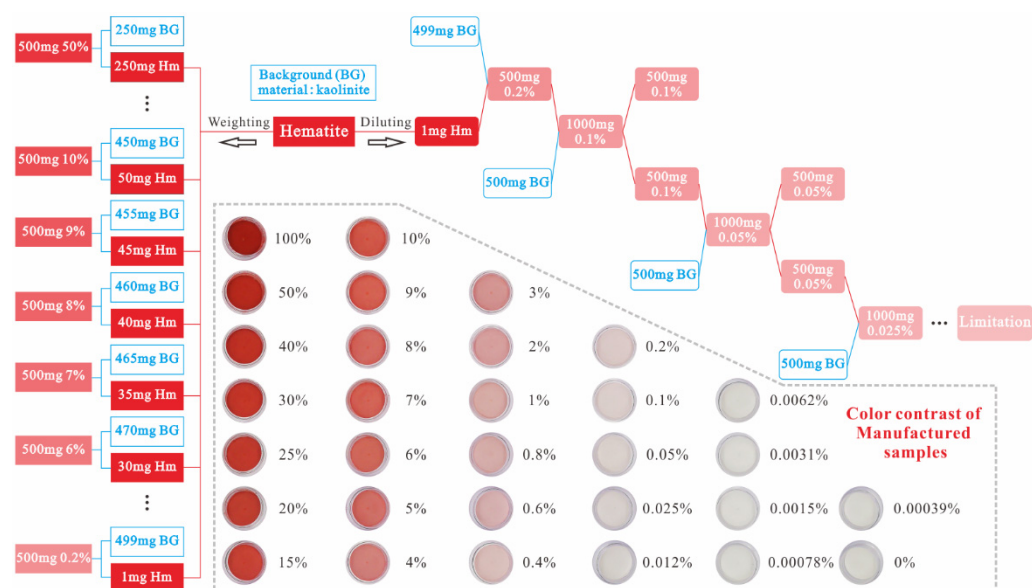


Figure 1. Synthesizing process and color contrast of manufactured samples.

Natural samples were used for testing the effect of natural matrixes. Together, 20 natural samples were collected from different areas located across 90° E–180° E, 10° N–60° N (Figure 2), which includes 10 terrestrial samples from Inland Asia (Tibet, Tsaidam, Hexi, Mongolia, Tengger, Mu Us, Kubuqi, Hami-Tulufan, Badain Jaran, and Tarim), and 10 marine sedimentary samples from the Western Pacific Ocean (Laizhou Bay, Liaodong Bay, Bohai Bay, Central Basin, North Yellow Sea, South China Sea, Subarctic Pacific, North Pacific, Equatorial Pacific, and Mariana Trench).

2.2. Methods

Manufactured and natural samples were measured using a Varian Cary 5000 spectrophotometer equipped with a BaSO₄-coated integrating sphere, and BaSO₄ was used as the standard white (calibration) [8,71]. Samples were filled and compacted into a circular sample holder with a round hole, and then placed vertically on one side of the integrating sphere. DRS measurements were recorded from 400 to 700 nm in 0.5 nm steps at a scan speed rate of 300 nm/min. After measuring the raw reflectance curve, natural samples were treated with CBD solution to remove hematite [76], and the residue was regarded as the background powder to perform DRS measurement again.

Compared with other iron oxides, the characteristic absorption of hematite is uniquely particular at 500–600 nm due to its double electron excitation of the magnetically spin-coupled Fe ions within the crystal lattice [8,21,75]. To obtain a quantitative proxy for hematite, the raw DRS data were processed three ways using the Varian instrument software (Savitzky–Golay method with a smoothing factor of 99): (1) the first derivative was calculated directly [57]; the raw data were transformed into the Kubelka–Munk (K–M) functions $((1-R)^2/2R)$ [19,66] to calculate the (2) first and (3) second derivative curves of the K–M function [66,74,75,77].

S-ratio and HIRM are commonly used magnetic proxies to trace changes in hematite concentrations and were used to compare with the DRS results presented here. In this study, S-ratio ($S_{-0.3T}$) was defined as $-IRM_{-0.3T}/SIRM$, and HIRM was defined as $(SIRM+IRM_{-0.3})/2$ [6,19,42]. Isothermal remanent magnetization (IRM) was acquired by a DC field using a 2G model 660 pulse magnetization meter. The saturation IRM_{1T} (regarded as SIRM) was imparted at 1 T, and then backward fields (−100 and −300 mT) were subsequently applied. The corresponding remanences were termed $IRM_{-0.1T}$ and $IRM_{-0.3T}$, respectively.

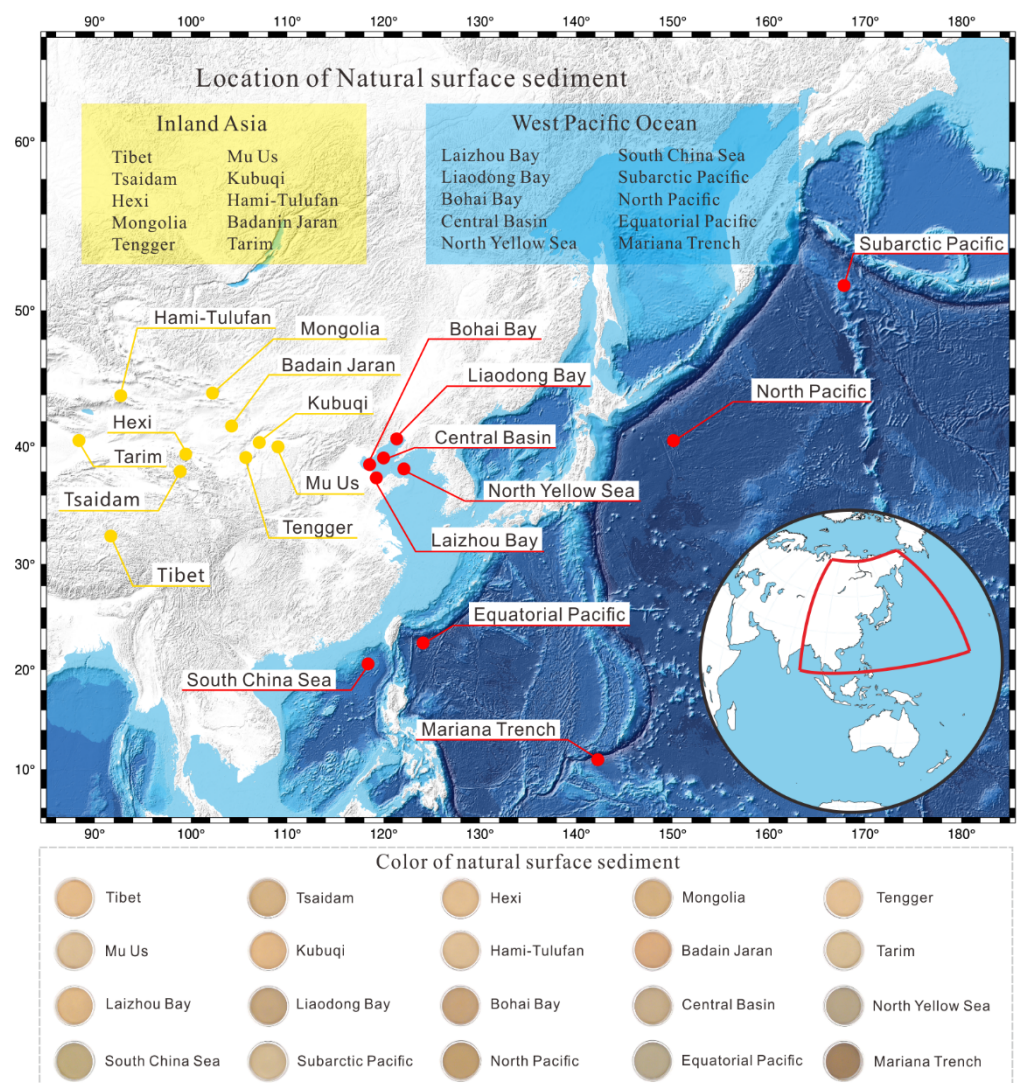


Figure 2. Locations and colors of natural samples (surface sediments from Inland Asia and the Western Pacific Ocean).

All experiments were performed at the Centre for Marine Magnetism (CM²), Southern University of Science and Technology (SUSTech), China.

3. Results and Discussion

3.1. The DRS Detection Limit of the Hematite Concentration

3.1.1. The Technical DRS Detection Limit

Raw reflectance curves of manufactured samples with various hematite concentrations display several obvious features. The slope of reflectance (i.e., absorption band) changes at 550–600 nm. The concentration of hematite increases (decreases), the inflection is more obvious (more subtle), and the characteristic band shifts to a longer (shorter) wavelength (Figure 3(a₁)). In addition, the reflectance curves are smoother at higher concentrations while approaching instrumental noise signal at lower concentrations (Figure 3(a₂,a₃)). All these variations corroborate that the content change can be identified qualitatively from the raw reflectance curve. However, the patterns of change (e.g., stratification of overall reflectance, tilt degree at 550–600 nm) lack strict quantitative parameters, which make it difficult to estimate hematite concentration quantitatively.

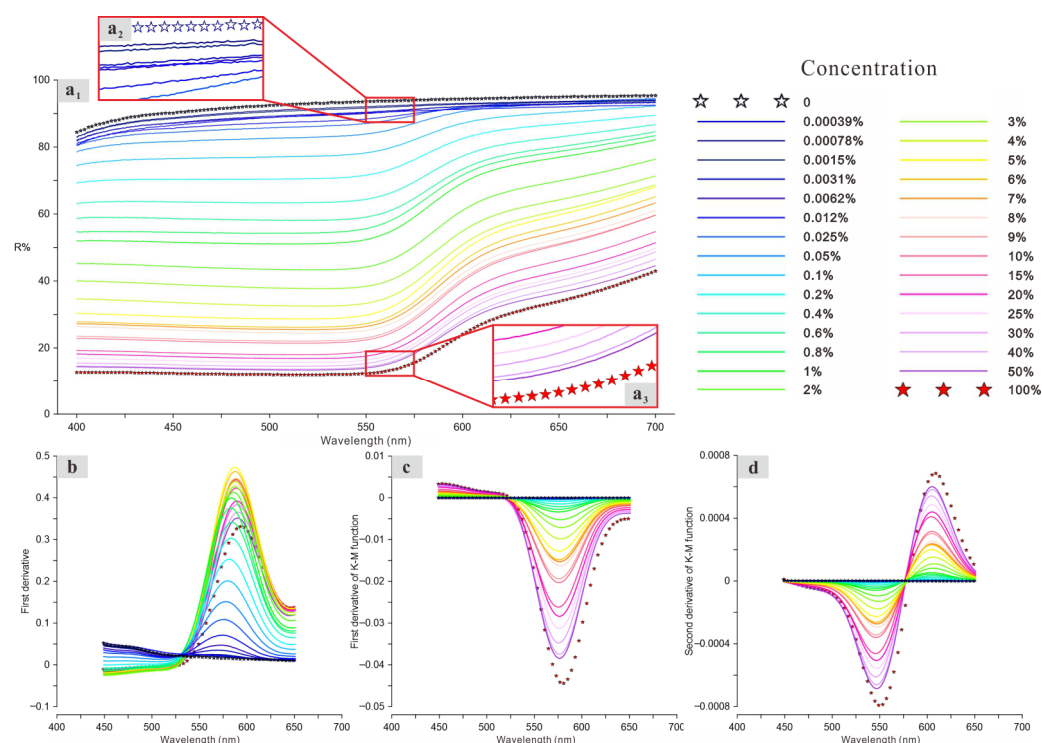


Figure 3. Reflectance spectra and processing results of manufactured samples with various hematite concentrations. (a₁) The raw reflectance response. Local amplified reflectance curves of manufactured samples at low (a₂) and high (a₃) concentrations. The first derivative of raw reflectance curves (b), the first (c) and second (d) derivatives of the K–M function.

To quantify the characteristic reflection more effectively, raw reflectance curves were processed with different methods. Distinctive signatures of hematite are manifested after different procedures. The signature (proxy) of hematite in the first derivative curve is represented by a peak at 500–600 nm, the value of which increases systematically with increasing hematite concentration. However, a clear overlap exists after reaching a certain height (Figure 3b). In contrast, the signature (proxy) of hematite in the first derivative of the K–M function curve is manifested as a valley at 500–600 nm, which is more obvious as the hematite concentration increases (Figure 3c). For the second derivative of the K–M function, the signature (proxy) of hematite is characterized by a valley and a following peak at a longer wavelength at 500–600 nm. As hematite concentration increases, amplitudes between the peak and valley increase synchronously and show a symmetrical tendency (Figure 3d).

Previous studies indicate that the DRS detection limit of hematite can reach 0.01% (for the first derivative processing) and 0.1% (for the first and second derivatives of the K–M function) [32]. However, it is unknown whether the DRS technique can detect hematite with a lower concentration, which is of great significance for the application range (region) of hematite information. To explore the potential limit of DRS for hematite detection, we designed continuous sample sequences with ultralow concentrations (as low as 0.00039%). In addition, samples were scanned with more precise steps (0.5 nm), and then more detailed spectral information could be detected for hematite. Our results suggest that the DRS method has the potential to detect a much lower concentration of hematite, as low as 0.00078% (Figure 4), which is at least two orders of magnitude smaller than the previous result (e.g., 0.1% and 0.01%).

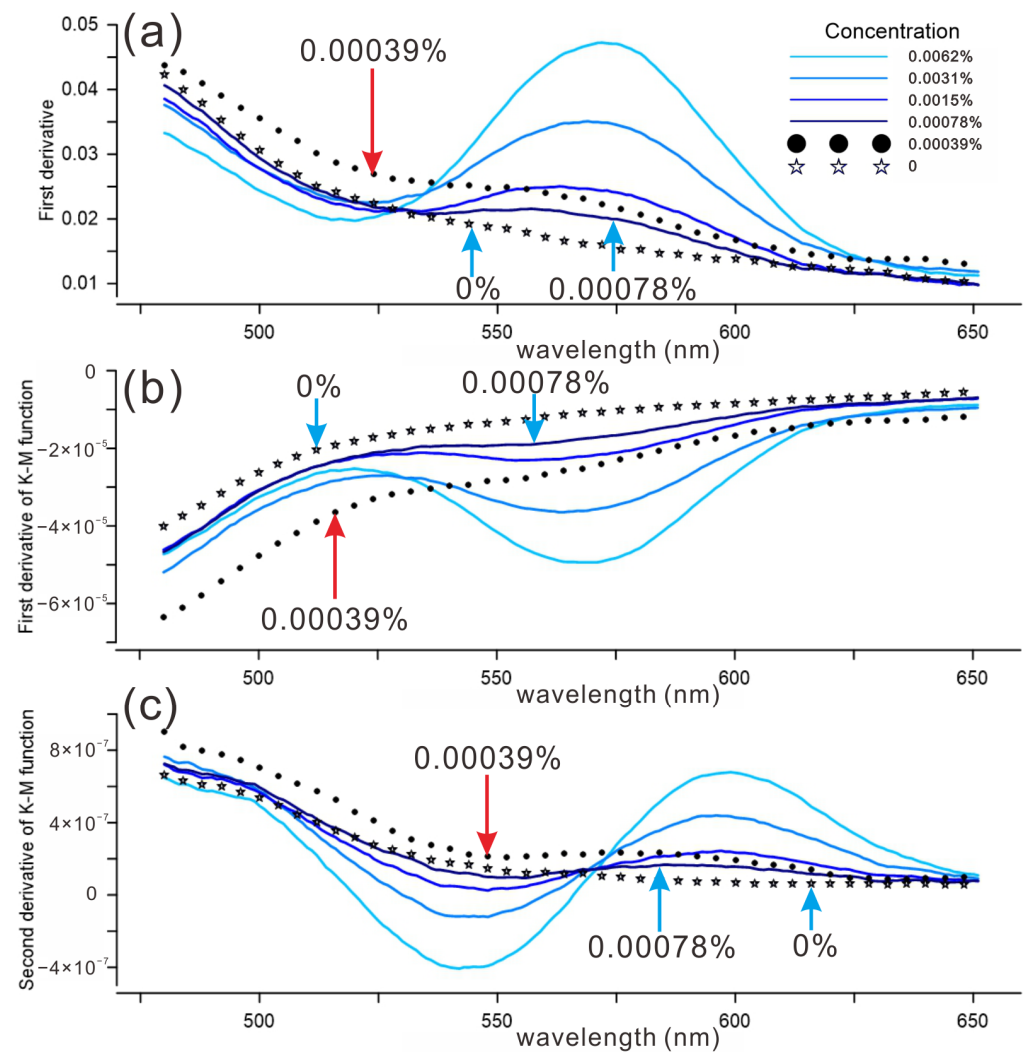


Figure 4. Technical level of lower limit for processing methods: (a) first derivative, (b) first derivative of the K–M function, and (c) second derivative of the K–M function.

3.1.2. The DRS Detection Limit for Natural Samples

For natural samples, the hematite detection limit of the DRS method can be affected by the characteristics of background (matrix) and the calculation methods of the DRS proxy [32,60,72]. Therefore, it is necessary to test the effects of natural matrixes from different locations to provide a realistic evaluation of the DRS methods.

Thus, we used the CBD method to dissolve hematite and facilitate the comparison of DRS before and after the CBD process. Results show that the characteristic signals of hematite in the original DRS curve (Figure 5a) are highly attenuated after the CBD processing for all samples (Figure 5b).

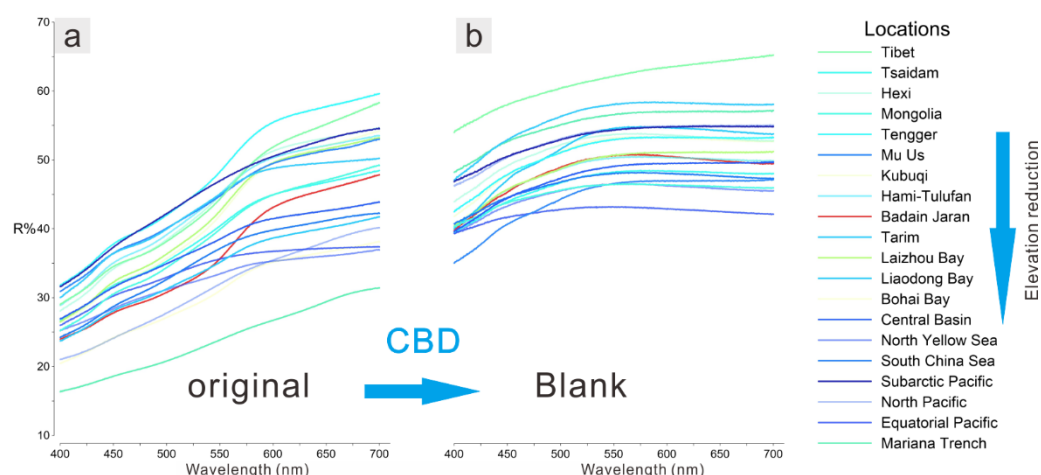


Figure 5. Reflectance spectra of natural samples before (a) and after (b) CBD processing.

Therefore, values at the characteristic wavelength after the CBD processing can be regarded as background values. Peak values of the first derivative and valley values of the first derivative of the K–M function are extracted to represent the hematite proxy (Figure 6(a₁,a₂)). However, matrix effects can shift the baseline and hide signals of low-concentration hematite. The statistical results of natural matrixes indicate that the background values are basically below 0.00078% (rarely above 0.0015%) after the first derivative (Figure 6(b₁)), and mostly exceeded 0.025% (some close to 0.15%) after the first derivative of the K–M function (Figure 6(b₂)), but has an insignificant effect to the detection limit for the second derivative of the K–M function method (Figure 6(a₃)), which is thus highly suggested for future studies.

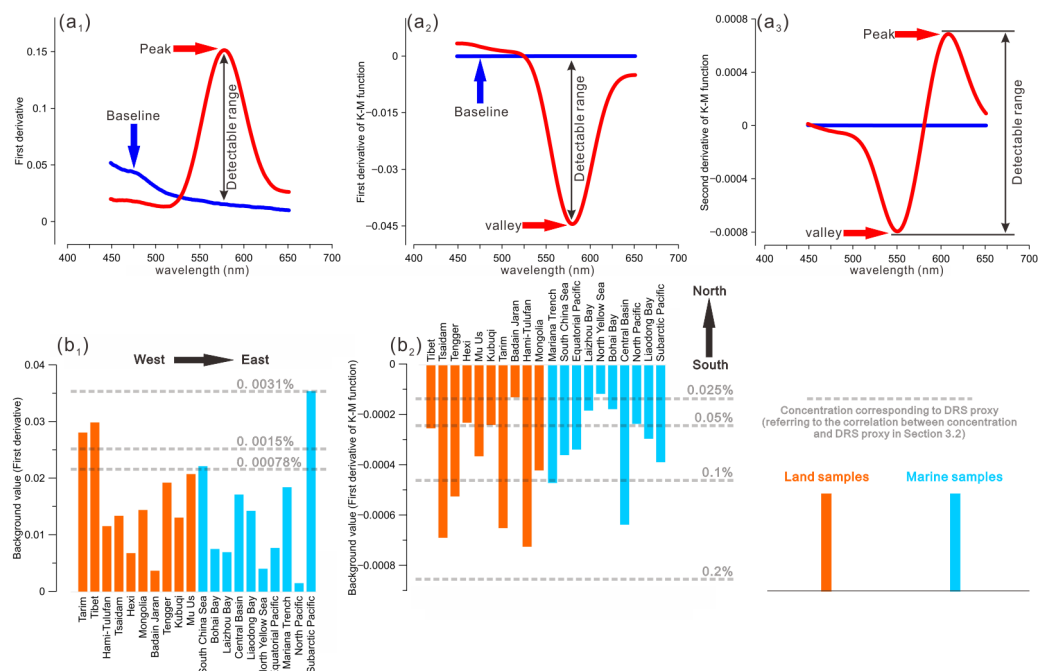


Figure 6. Extracting mechanism (of DRS proxy) and background influence of (a₁,b₁) the first derivative, (a₂,b₂) the first derivative of the K–M function, and (a₃) the second derivative of the K–M function.

3.2. Transfer Function between the DRS Proxy and Hematite Concentration

Apart from the detection limit, the correlation between the DRS proxy and hematite concentration is the key factor for DRS data interpretation and the establishment of a spe-

cific empirical formula [16,26,33,75]. Therefore, we constructed the relationship between DRS parameters of synthetic samples with known concentration and hematite concentration (Figure 7(a₁,b₁,c₁)). As hematite concentration increases, the amplitude of first derivative rises ($\leq 5\%$, positive logarithmic fitting) to reach a peak at 5% (Figure 7(a₂)) and then decreases ($>5\%$, negative logarithmic fitting) (Figure 7(a₃)). Thus, ambiguities exist in interpreting the first derivative of the DRS data as the hematite concentration is higher than 0.5% (red shadow in Figure 7(a₄)). In contrast, the proxy of (first and second) derivatives of the K–M function changes in a monotonic way for the whole range of hematite concentrations (Figure 7(b₁,c₁)), and the relationship between the proxy and hematite concentration can be further described by linear ($\leq 10\%$) (Figure 7(b₂,c₂)) and logarithmic fittings ($>10\%$) (Figure 7(b₃,c₃)), respectively. This allows for accurate hematite detection in a wide range of hematite concentrations (Figure 7(b₄,c₄)).

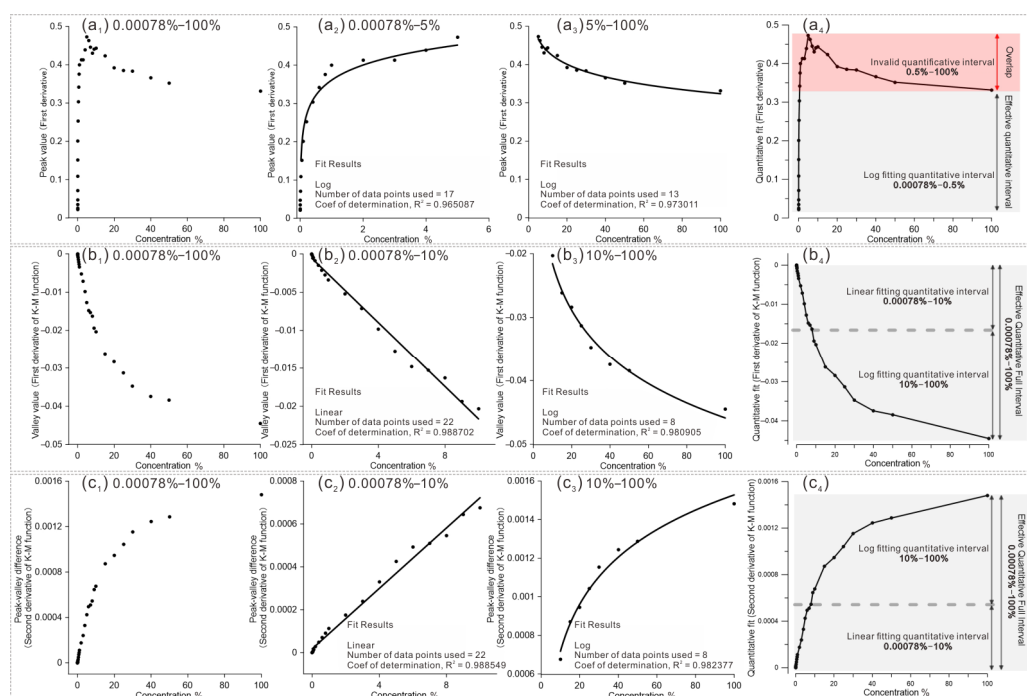


Figure 7. Correlation analysis between DRS proxy and hematite concentration: (a₁–a₄) the first derivative, (b₁–b₄) the first derivative of the K–M function, and (c₁–c₄) the second derivative of the K–M function.

3.3. Application to Natural Samples

Given the advantages of the second derivative of the K–M function, we used it as a standard method for the natural samples (Figure 8). Our results show that hematite concentrations in sedimentary samples from Inland Asia are relatively high (0.45% on average and up to 0.91%), and decrease systematically from Inland Asia to the Western Pacific Ocean (0.29% on average and as low as 0.03%). This phenomenon accords with the variation trend of natural hematite concentration in these regions, which is possibly controlled by the source–sink effect in the first order: the oxidizing environment of Inland Asia is more conducive to the generation of hematite [17,19,23,26,78], while hematite in the Western Pacific Ocean is detrital and mainly transported from Inland Asia via the monsoonal or westerly winds, and river runoff [27,68]. Therefore, the average concentration of hematite in the Western Pacific Ocean is lower than that in Inland Asia. For the detection results of marine sediments, hematite concentrations for samples from high latitudes (as low as 0.03%) are much lower than that from low latitudes (up to 0.45%), which may be caused by the difference of source areas at different latitudes. Overall, our hematite quantification on these natural samples is consistent with the expected distribution of hematite and

conforms to the source–sink process in this region, which provides an important basis for further application of the DRS proxy.

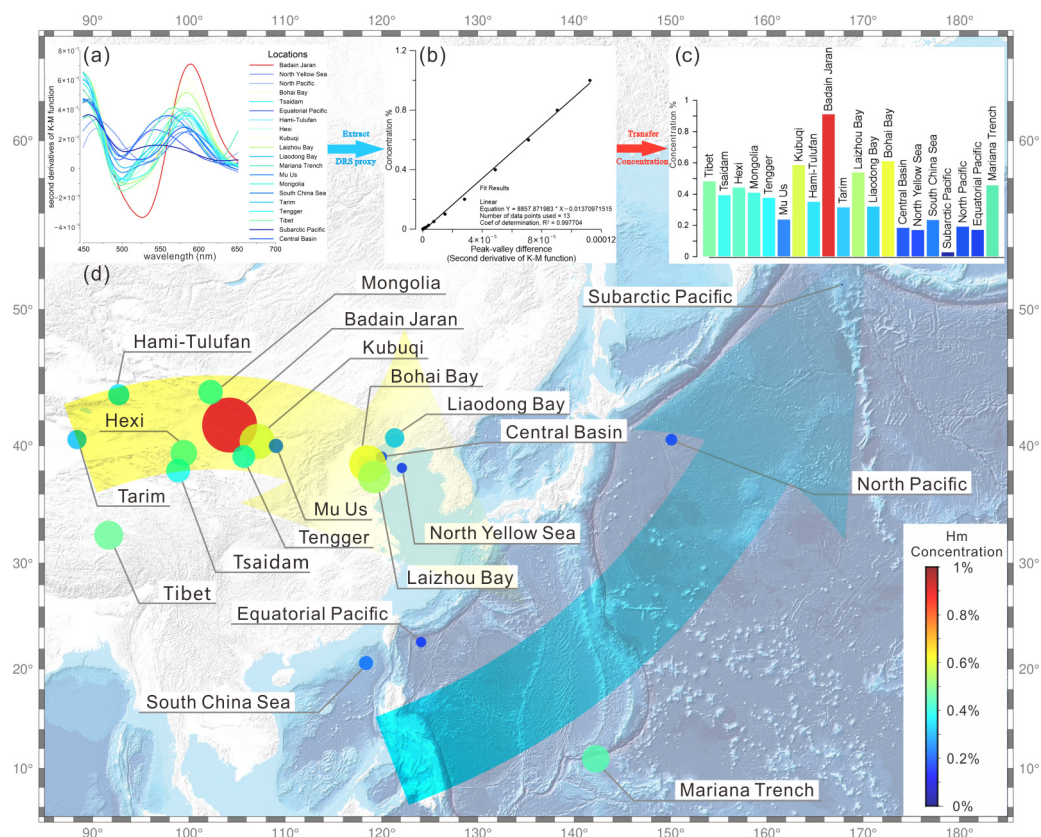


Figure 8. Estimated hematite concentration of natural samples (color and size of the circle both reflect the concentration of hematite). (a) The second derivative of the K–M function processing natural DRS curves. (b) Correlation between concentration and DRS proxy (referring to Section 3.2). (c) Statistical results of estimated hematite concentration for natural samples. (d) Location and estimated hematite concentration for natural samples (variations of concentration are indicated by the color bar).

3.4. Comparison between DRS and Magnetic Methods

In addition to the DRS method, hematite can also be semiquantified by magnetic methods, such as S-ratio and HIRM [6,19,42]. Comparisons between DRS and magnetic proxies of natural samples exhibit generally linear correlation for a broad range of hematite concentrations (Figure 9). However, discrepancies also exist due to the inherent complicated properties of hematite in natural samples.

Synthetic samples with known concentrations can be used to evaluate the estimated results of low hematite concentrations more accurately. Results show that the correlation between the DRS proxy and low hematite concentration can still be well fitted by a linear relationship (Figure 10a), but fail for the correlation between magnetic proxy (S-ratio and HIRM) and low hematite concentration (Figure 10b,c). Furthermore, the DRS proxy provides better estimations for the low hematite concentration than the magnetic proxy (Table 1).

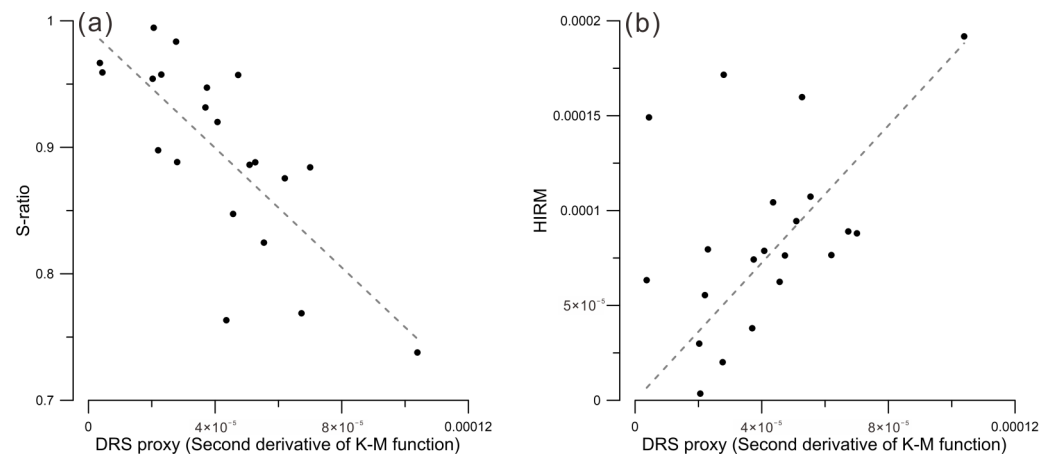


Figure 9. Comparison between DRS and magnetic methods in detecting natural samples. (a) S-ratio versus DRS and (b) HIRM versus DRS.

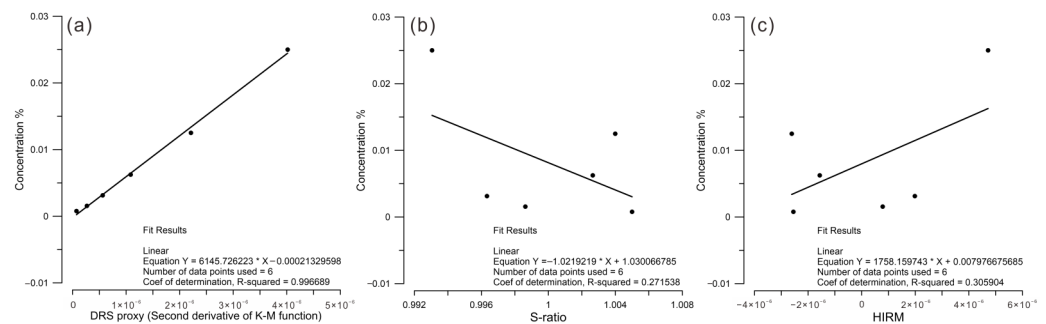


Figure 10. Comparison between DRS and magnetic methods in detecting synthetic samples with low hematite concentrations. Detection results of (a) DRS, (b) S-ratio, and (c) HIRM.

Table 1. Comparison of the estimated hematite concentration between DRS and magnetic methods.

Concentration %	0.025	0.012	0.0062	0.0031	0.0015	0.00078
DRS estimation %	0.024	0.013	0.0064	0.0032	0.0014	0.00024
Relative error %	4	8.3	3.2	3.2	6.6	69.2
S-ratio estimation %	0.015	0.004	0.0054	0.0118	0.0095	0.00303
Relative error %	40	66.6	12.9	280.6	533.3	288.4
HIRM estimation %	0.016	0.003	0.0052	0.0114	0.0093	0.00349
Relative error %	36	75	16.1	267.7	520	347.4

In summary, the DRS method is more effective in detecting low concentrations of hematite. However, limitations still exist for the application of DRS technology. For example, hematite formed in natural environments are complex due to particle size differences, the presence of lattice defects, and different sediment (soil) matrices, which may introduce quantitative uncertainties for the individual application of the DRS technique [5,19,32]. The combination of DRS and other detection methods (such as magnetic, chemical analysis, and microscopic examination) can reflect the various properties of hematite more comprehensively [6]. Apart from hematite, there are many other iron-oxide phases in the natural environment, such as ferrihydrite, lepidocrocite, and goethite [63]. These magnetic minerals also have their own characteristic absorption bands in the diffuse reflectance spectrum [75], which makes DRS a potential method to detect their spectroscopic and physical properties.

4. Conclusions

This study demonstrates that the DRS technique has the potential to detect hematite concentrations with a lower limit at least two magnitudes less than found previously. We also find that natural matrixes from different locations may affect the detection limit to varying degrees. Within the detectable range, the transfer function between the DRS proxy and hematite concentration depends on data processing methods. Based on comprehensive evaluations, we suggest that the second derivative of the K–M function has a superior performance with stable correlation, wide detecting range, and relatively weaker background effect. This method has also been successfully applied to natural samples and identified hematite information from Inland Asian and Western Pacific Ocean sediments, which conforms to the regional source–sink process.

Author Contributions: Conceptualization, supervision, Q.L.; methodology, V.B. and J.T.; formal analysis, investigation, writing—original draft preparation, W.C.; writing—review and editing, Z.J., C.G. and Y.Z. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are contained within the article.

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