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IRON OXIDES AND COLOR OF TRIASSIC SEDIMENTS: APPLICATION OF THE KUBELKA-MUNK THEORY

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ABSTRACT. The Kubelka-Munk theory establishes that the color of any turbid medium results from the absorption and scattering of light and can be described by the so-called absorption and scattering coefficients within the visible wavelength range. We used this approach to study the colors of a group of Triassic sediments located in the Extern Zones of the Cordilleras Béticas (southern Spain). The shapes of absorption curves of goethite and hematite-containing sediments matched the shapes of the curves of synthetic goethites and hematites. This could be explained by applying the Kubelka-Munk theory to a mixture of a pale, gray Fe-oxide-free matrix with goethite or hematite. The theory permits not only calculating the "pure" color of the Fe oxide of a sediment but, if the type and color of the Fe-oxides is known, quantifying the Fe oxides in a sample.

INTRODUCTION

Many sediments and soils owe their colors to iron oxides, in particular to hematite and goethite. The effect of these pigments on the optical properties of the materials in which they are present can be studied using the Kubelka-Munk theory (Kubelka and Munk, 1931). This theory establishes that the two processes that govern the reflectance and transmittance, and therefore the color, of any turbid or translucent medium are the scattering and the absorption of light. It has been applied successfully to materials considered typically as turbid media:paints (Duncan, 1962), pigmented plastics (Davidson and Hemmendinger, 1966; Saunderson, 1942), foods (Francis and Clydesdale, 1975), ceramic systems (Hogg and Noble, 1979), and kaolinite minerals used in paper filling (Jepson, 1985). Recently Barrón (ms) has elaborated a rapid and easy method to estimate hematite and goethite in soils by assuming that soils are turbid media and applying the equations derived from the Kubelka-Munk theory. A similar treatment is followed in the present paper to study the effect of hematite and goethite on the color of Triassic sediments.

THEORY

A general relationship between the diffuse reflectance, R, at one wavelength, of a layer of material against a background of reflectance R_g, and the absorption, K, and scattering, S, coefficients, is given from the Kubelka-Munk theory:

$$R = \frac{1 - R_g\,(a - b \coth b\,S\,X)}{a - R_g + b \coth b\,S\,X} \qquad (1)$$

where coth b S X is the hyperbolic cotangent of b S X, X is the thickness of the layer, a is equal to (1 + K/S), and b is equal to $(a^2 - 1)^{1/2}$. When the thickness is such that any further increase therein produces no further

change in reflectance, R (a condition that occurs for pressed powders of sediments or soil for thicknesses of a few tenths of a millimeter), the background reflectance is negligible ($R_g \sim 0$) and the thickness, X, is given as infinite. Then the previous expression becomes:

$$R = \frac{S}{K + S + (K\,(K + 2\,S))^{1/2}} \tag{2}$$

which can be more conveniently written as

$$\frac{S}{K} = \frac{2\,R}{(1 - R)^2} = \phi \tag{3}$$

The ratio S/K has been called the "reflectivity function", ϕ (Duncan, 1940). It has been shown (Duncan, 1940) that for those opaque samples (that is, those fulfilling eq 3) that are composed of a mixture of pigments the absorption, K_M, and scattering, S_M, coefficients follow a simple additive law, that is:

$$K_M = C_1K_1 + C_2K_2 + \ldots\ldots + C_nK_n \tag{4}$$

$$S_M = C_1S_1 + C_2S_2 + \ldots\ldots + C_nS_n \tag{5}$$

where K_1, K_2, ..., K_n and S_1, S_2, ..., S_n are, respectively, the absorption and scattering coefficients of each pigment and C_1, C_2, ... C_n their concentrations. Combining (3), (4), and (5):

$$\phi_M = \frac{S_M}{K_M} = \frac{C_1S_1 + C_2S_2 + \ldots. + C_nS_n}{C_1K_1 + C_2K_2 + \ldots. + C_nK_n} \tag{6}$$

therefore the reflectance, at any wavelength, of any sample containing a mixture of pigments can be calculated from the absorption and scattering coefficients and the concentration of each pigment. Conversely measurements of reflectance can be used to calculate the K and S coefficients or the concentration of a pigment. The absolute values of K and S of a pigment can be calculated by different methods (Saunderson, 1942; Hogg and Noble, 1979). For most purposes, however, it suffices to obtain the relative rather than the absolute coefficient values, which facilitates their experimental determination. In the simple case of a binary mixture of a pigment (p) with a white standard (s) whose reflectance, R, is taken as the unity (and, therefore, K_s taken as zero) eq (6) leads to:

$$\phi_M = \frac{C_pS_p + C_sS_s}{C_pK_p} \tag{7}$$

whence:

$$\phi_M = \frac{S_p}{K_p} + \frac{S_s}{K_p}\,\frac{C_s}{C_p} = \frac{2\,R_M}{(1 - R_M)^2} \tag{8}$$

Hence ϕ_M is a linear function of the ratio of the concentration of standard and pigment, C_s/C_p. The slope of this line is the ratio S_s/K_p, and the intercept is S_p/K_p. Therefore K_p and S_p may be evaluated in terms of S_s, which, arbitrarily and for the sake of simplicity, can be taken as unity.

MATERIALS AND METHODS

Reference synthetic goethites and hematites.—The four referenced goethites (G51, G612, G31, G12) were synthesized according to the method described by Lewis and Schwertmann (1979). G51 was synthetized in 1 M KOH at 70°C (70 days); G612 in 0.3 M KOH at 50°C (15 days); G31 in 0.3 M KOH at 70°C (70 days), and G12 in 1 M KOH at 25°C (70 days). In one case (G12) Al^{+3} was substituting for Fe^{+3} (7.4 mole percent Al). The Munsell colors of these goethites were: 0.1Y 5.9/8 (brownish yellow) for G51; 9.6YR 5.6/7.4 (brownish yellow) for G612; 7.9YR 5.3/8.8 (strong brown) for G31 and 9.7YR 5.4/7.5 (yellowish brown) for G12.

Hematites H32 and H42 were obtained by hydrothermal synthesis in presence of tartrate (H32) and oxalate (H42) (Fischer and Schwertmann, 1975). Hematite H21 was obtained by heating a goethite similar to G31 at 400°C for one day. The "Merck" hematite was reagent grade α-Fe_2O_3 (Merck no. 3924). The Munsell colors of these hematites were: 1.4YR 3.2/6 (dark red) for H32, 3.2YR 2.8/5.9 (dark yellowish red) for H42, 0.1YR 3.7/5.4 (dark red) for H21, and 1YR 3.2/6.7 (dark red) for "Merck".

Sediments.—Samples were collected in a broad area along the Extern Zones of the Cordilleras Béticas and included, essentially, argillites, marls, and evaporites from the Keuper facies, corresponding to the Keuper, Muschelkalk, and Buntsandstein stages. Their relevant mineralogical properties are shown in table 1.

Mineralogical properties.—The free Fe oxide content was estimated by selective dissolution with dithionite–citrate–bicarbonate (DCB) using the Mehra and Jackson (1960) method but modified by increasing the time to 16 hrs and decreasing the temperature to 25°C. This modification provides, in general, a more complete extraction of Fe oxides. The residue obtained after this treatment ("deferrated" residue) was washed, dried, and stored for color study.

The minerals of the clay fractions were analyzed by X-ray diffraction (XRD). The concentration of hematite and goethite was determined by differential X-ray diffraction (DXRD) (Schulze, 1981) after concentrating the Fe oxides by a boiling 5M NaOH treatment (Norrish and Taylor, 1961). Details of this procedure are given by Torrent, Schwertmann, and Schulze (1980). In short the procedure leads to the calculation of the ratio hematite/goethite; then the absolute amounts of each of these minerals are calculated by partitioning DCB Fe accordingly.

Color measurement and Kubelka-Munk analysis.—Air-dry sediment samples were ground in a ball mill equipped with a container and balls of agate to obtain powders passing a 300 mesh sieve. The color changed rapidly in the first minutes becoming stable after 40 to 60 min. In general the final colors were lighter and had lower chromas than the initial ones. It was also observed that the colors become less purple with increasing grinding time. This fact is assumed to be due to destruction of clusters of hematite particles (Torrent, personal commun.). For color measurement these dry powders as well as the white standard were back-filled into 8x17mm aluminum frames and gently pressed against filter paper to mini-

TABLE 1
Mineralogical properties of the sediments

Sample code	Clay Content (%)	Silicate clay*	DCB extractable Fe (%)	Fe oxides Goethite (%)	Fe oxides Hematite (%)	WHH** of the hematite peaks (104) (°2θ)	WHH** of the hematite peaks (110) (°2θ)	Munsell Color***	
ALC31	70	M	7.2	11.5	--	--	--	brigth yellowish brown	0.2Y 5.9/6.0
BAE21	80	CHL, M	5.1	8.1	--	--	--	brigth yellowish brown	9.9YR 6.1/5.1
AHI6	40	M	1.6	2.5	--	--	--	light yellow	3.2Y 6.6/2.6
BAE22	30	M	2.3	--	3.3	0.34	0.20	dull reddish brown	3.4YR 5.0/4.7
ALC2	60	M	2.4	--	3.4	0.34	0.22	dull reddish brown	3.3YR 4.7/5.0
CAS1	60	M	1.9	--	2.7	0.50	0.24	dull reddish brown	3.7YR 4.9/4.3
GUI3	80	M	1.6	--	2.3	0.27	0.22	dull reddish orange	0.8YR 5.8/3.2
OLV1	70	M	1.5	--	2.1	0.26	0.20	dull reddish brown	8.3R 5.7/3.2
AGU13	70	M	1.0	--	1.4	0.25	0.19	grayish red	3.7YR 6.1/1.8
BAE0	--	-	66.5	--	95.0	0.25	0.21	dark red	9.6R 3.5/5.2
MOR78	80	K, M	1.6	1.7	0.7	0.35	0.25	dull brown	6.9YR 5.4/4.3
AGU02	80	M, CHL	0.6	--	--	--	--	gray	9.3RP 6.5/0.6

* Listed in order of abundance; M = Mica, CHL = Chlorite, K = Kaolinite.
** Width at half height.
*** In the ground sediment.

mize preferred orientation (and specular reflection). With this technique no cover glasses are needed since the powder mounts (which are about 1 mm thick) are self supporting. The measurement of the diffuse reflectance (400-700 wavelength range, 10 nm increments) of these mounts was carried out in a double beam Perkin-Elmer Lambda 3 spectrophotometer equipped with a reflectance (integrating sphere) attachment. Pure barium sulfate (Din 5033, Merck no. 1748) was used as the white standard (reflectance = 1) in the reference beam.

The diffuse reflectance values were converted to tristimulus values (X,Y,Z) (Judd and Wyszecki, 1975), and these were transformed to the Munsell Hue (H), Value (V), and Chroma (C) using the method given by the ASTM (1980).

The absorption and scattering coefficients (K_p and S_p) of both synthetic iron oxides and sediments at different wavelengths were obtained from mixtures, at different proportions, with the $BaSO_4$ standard (in general, five mixtures containing about 1, 4, 10, 40, and 100 percent of the sample studied). After measuring the reflectance of these mixtures, K_p and S_p were calculated according to eq (8).

RESULTS AND DISCUSSION

Absorption and scattering coefficients of synthetic iron oxides.—In the mixtures of each of the synthetic Fe oxides with different amounts of the white standard the reflectivity function (ϕ_M) was highly and linearly correlated with the C_s/C_p ratio used in eq (8) ($r^2 > 0.999$) indicating that the Kubelka-Munk theory holds in this case. These high correlations were also observed for the sediment-white standard mixtures which will be considered later.

The curves of the absorption and scattering versus wavelength for the four synthetic goethites are shown in figure 1. At low wavelengths (violet-blue) the absorption coefficients are high in accordance with the yellow color of goethite. All samples show a broad shoulder in the absorption curve at 440 to 500 nm wavelength which has been used for the goethite characterization by means of second-derivative curves (Kosmas and others, 1984).

In the hematites the shape of the absorption coefficient curve (fig. 1) varies with their mode of formation. Samples H32 and H42 are hematites synthetized hydrothermally at low temperature (< 100°C) and have small particle sizes (< 0.1 μm) as seen under the electron microscope. In contrast the two others were obtained at high temperature (> 400°C) and have larger particle sizes (> 1 μm). The latter have sharper diffraction lines (corrected width at half height of less than 0.1° 2θ against values of 0.2 to 0.4° 2θ for the former) indicating a higher crystallinity and have, to the common observer, a more "purplish" red color in contrast with the yellowish red color of the former. This fact is congruent with their smaller absorption coefficient values at low wavelength (violet-blue range). Absorption curves for hematites have higher values in the yellow wavelength range as compared to the curves for goethites, in agreement with the typical red color of hematite.

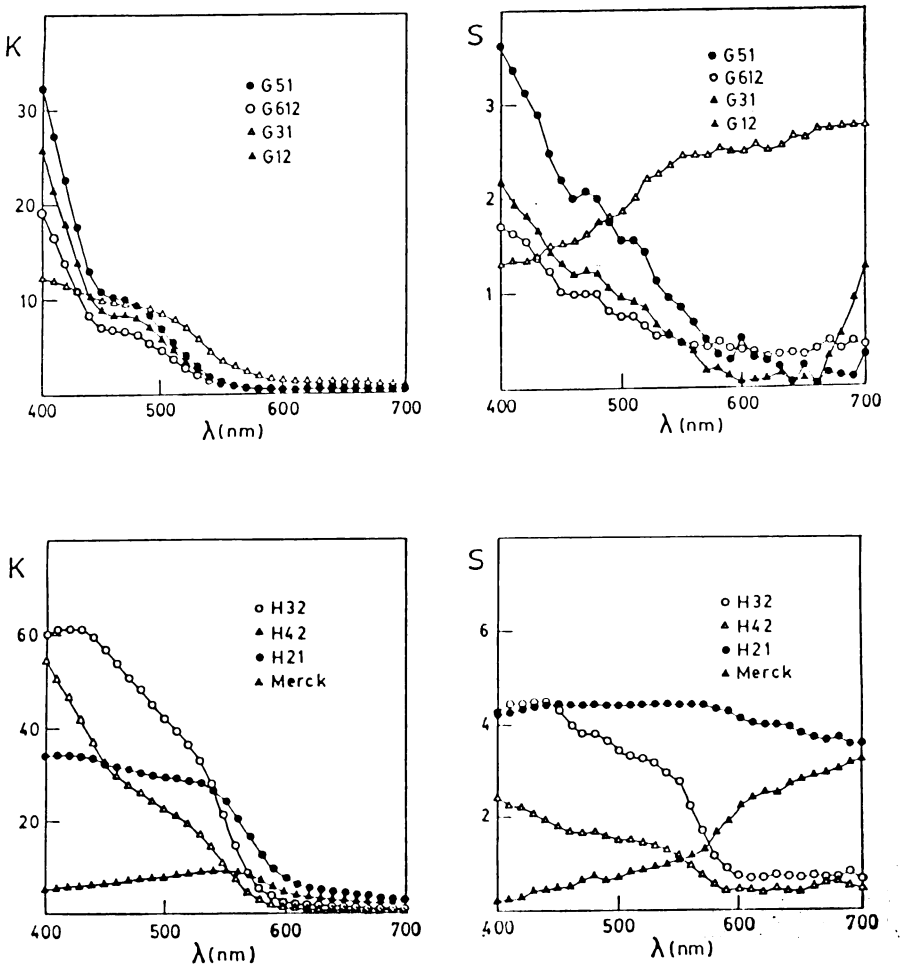

Fig. 1. Absorption (K) and scattering (S) coefficients for synthetic goethites (upper figures) and hematites (lower figures).

Neither goethite nor hematite shows scattering coefficient curves with definite shape, probably because other factors such as particle size are more important than whether the particles are goethite or hematite (Kortüm, 1969).

Absorption and scattering coefficients of the sediments.—The sediments differed widely in their color and Fe oxide content (table 1). Figure 2 shows the absorption and scattering coefficient curves for the ground sediments and their corresponding DCB-treated (deferrated) residues. In the samples containing goethite but not hematite (fig. 2A-C) the absorption curves are similar to those of synthetic goethites, but the absolute values of the absorption coefficients are lower (compare fig. 2A-C with fig. 1). The

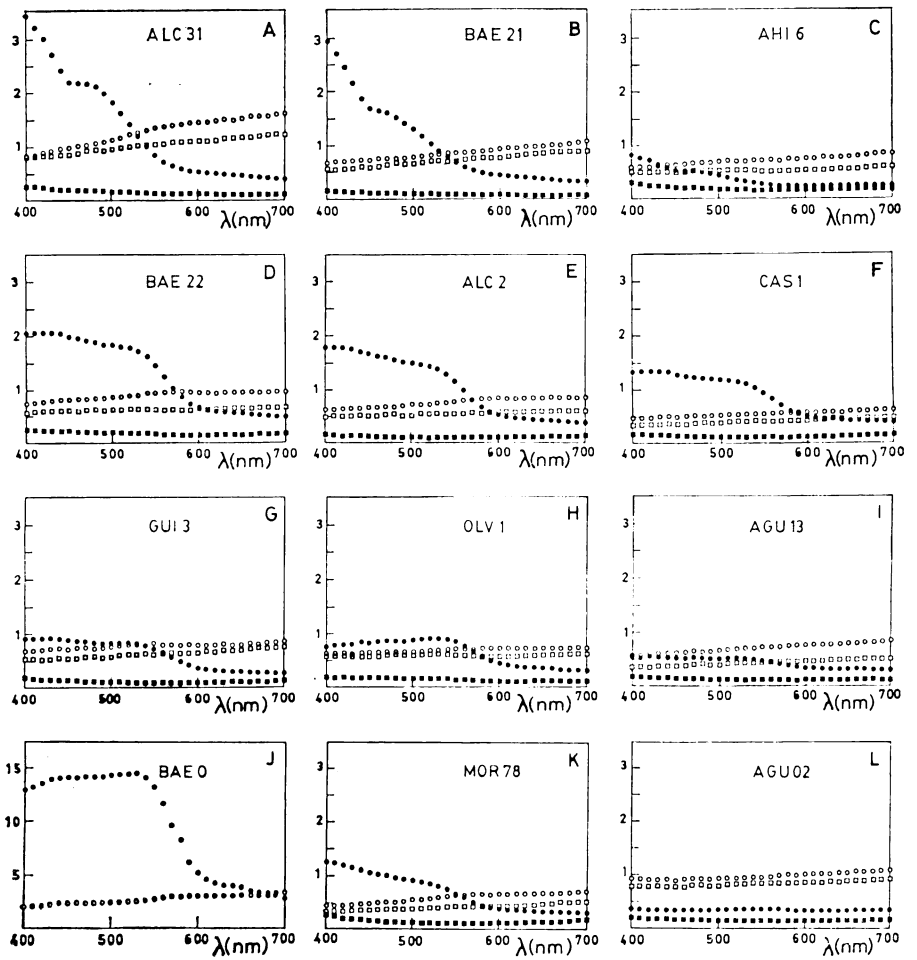

Fig. 2. Absorption (●) and scattering (○) coefficients for sediments and absorption (■) and scattering (□) coefficients for deferrated residues.

values of the absorption coefficients increase with increasing goethite content in accordance with eq (4), since the absorption coefficients for the goethite-free matrix, that is, the deferrated residue, are low through the 400 to 700 nm wavelength range, and, consequently, the matrix terms in that equation can be neglected. The scattering coefficients of sediment and deferrated residue are similar for each sample showing the small effect of goethite on these coefficients.

In the samples having hematite but not goethite (fig. 2D-1) the absorption curves have shapes that can be related to the shapes of the synthetic hematites. For the more purplish samples (GUI3 and OLV1) shapes are close to the more purplish, high temperature hematites (H21 and "Merck"); the yellowish red samples (BAE22, ALC2, CAS1, AGU13) have

shapes intermediate between H21, H32, and H42, that is, they are closer to the more yellowish hematites.

A further example of the chromatic resemblance between natural and synthetic samples is given in figure 2J which shows the absorption coefficients curve of a naturally occurring hematite concentrate (95 percent hematite) in a sediment. This absorption curve is intermediate between those of hematites H21 and "Merck".

For samples having goethite and hematite the absorption curves have shapes intermediate between those that contain only goethite or hematite, that is, the absorption curves for these samples are influenced by the content of each pigment according to eq (4). Figure 2K is an example of this situation.

The shapes and the absolute values of the absorption and the scattering curves for the deferrated residues do not differ much from one sample to another; in addition they are similar to the curves of the sediments without a significant amount of Fe oxides (for example, fig. 2L). This suggests that the DCB treatment does not produce chromatic artifacts capable of interferring with the color of the Fe-oxide-free matrices.

The former results indicate, in summary, that the color of the sediments can be explained by the Kubelka-Munk analysis applied to a mixture of strongly colored Fe-oxides and a weakly colored, gray matrix.

Differential coefficients and colors.—For any wavelength the absorption and scattering coefficients of a sediment can be expressed, respectively, as a linear combination of the absorption and scattering coefficients of each of its components, according to eqs (4) and (5). A good approximation can be obtained assuming that only three different pigments make up the sediment: hematite, goethite, and Fe-oxide-free matrix. The latter includes all the compounds of the sediment different from Fe oxides. Then eqs (4) and (5) can be written:

$$K_{sed} = K_{hm}C_{hm} + K_{gt}C_{gt} + K_{def}C_{def} \tag{9}$$

$$S_{sed} = S_{hm}C_{hm} + S_{gt}C_{gt} + S_{def}C_{def} \tag{10}$$

where K and S are, respectively, the absorption and scattering coefficients, C are concentrations, and sed, hm, gt, and def indicate, respectively, sediment, hematite, goethite, and Fe-oxide-free matrix (deferrated).

The values of the absorption and scattering coefficients for hematite and goethite (K_{hm}, S_{hm}, K_{gt}, and S_{gt}) are the unknowns of eqs (9 and (10), because C_{hm}, C_{gt}, and C_{def} can be known from the chemical and diffraction analysis (table 1), and K_{sed}, S_{sed}, K_{def} and S_{def} can be measured as specified in the methods section. This gives four unknowns and two equations. Eqs (9) and (10) can be solved if either goethite or hematite is absent. If both are present one can obtain "combined" K and S coefficients for the Fe oxides, K_{fe} and S_{fe}, by using the following equations:

$$K_{hm}C_{hm} + K_{gt}C_{gt} = K_{fe}(C_{hm} + C_{gt}) \tag{11}$$

$$S_{hm}C_{hm} + S_{gt}C_{gt} = S_{fe}(C_{hm} + C_{gt}) \tag{12}$$

Substitution of eqs (11) and (12) in (9) and (10) gives only two unknowns (that is, K_{fe} and S_{fe}). In summary eqs (9) and (10) can give "differential" K and S coefficients for the hematite of a sediment (if no goethite is present) or for the goethite (if no hematite is present) or for the mixture of hematite and goethite (if both are present).

The differential K and S coefficients obtained in this way (fig. 3) are similar to those of synthetic goethites or hematites (compare fig. 3 with fig. 1) or mixtures of the two minerals according to the type Fe oxide present in the sample. This gives support to the validity of eqs (9) and (10).

It is evident that the differential K and S coefficients can be used to calculate the "pure" Munsell color of the Fe oxides of a sediment. The result of this calculation for the sediments studied is given in table 2. These calculated colors of goethites and hematites can be reasonably matched to those of their synthetic counterparts, although in some sediments having low amounts of hematite (GU13, AGU13) the calculated Munsell chromas are lower than expected.

In summary the Kubelka-Munk theory can be used and provides a useful tool to analyze the color and hence the Fe-oxide mineralogy of sediments. Color measurements can give qualitative information on the type of Fe oxide present. Conversely if enough information is available on the type (and color) of the ferric pigments the theory allows estimating their

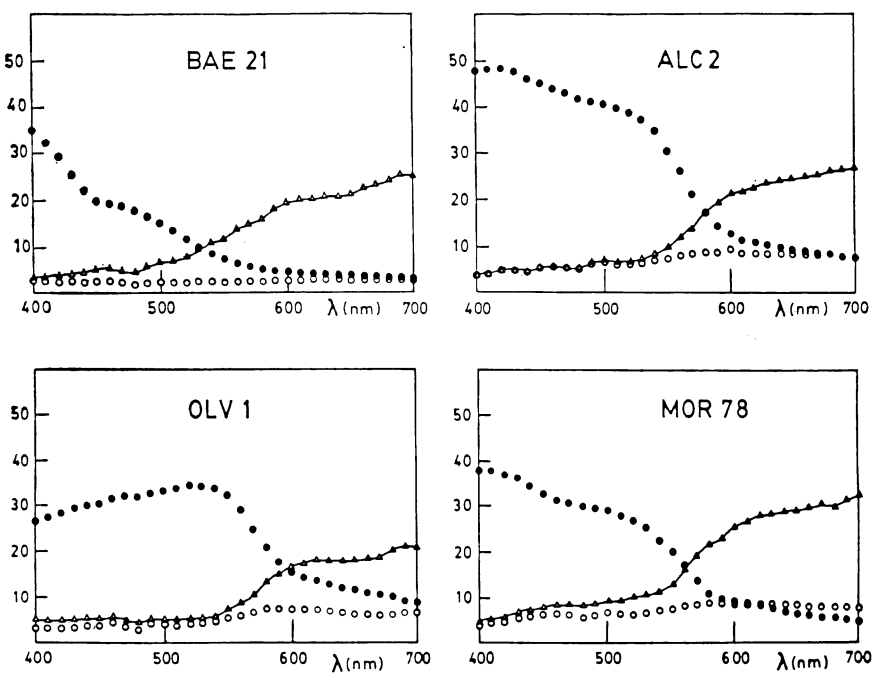

Fig. 3. Differential absorption (●) and scattering (○) coefficients and percent reflectance (△) of the Fe oxides in four selected sediments.

TABLE 2
Calculated Munsell color of the iron oxides in sediments

Sample	Iron oxide present	Munsell Color	
ALC31	Goethite	Yellowish brown	9.7YR 5.0/7.1
BAE21	Goethite	brown	8.1YR 4.1/4.8
AHI6	Goethite	bright yellowish brown	1.6Y 6.5/5.3
BAE22	Hematite	dull reddish brown	4.4YR 4.1/4.9
ALC2	Hematite	dull reddish brown	3.9YR 4.1/5.6
CAS1	Hematite	dull reddish brown	2.7YR 3.6/3.6
GUI3	Hematite	grayish red	1.9YR 4.2/2.5
OLV1	Hematite	grayish red	1.6YR 3.6/3.3
AGU13	Hematite	grayish red	2.0YR 5.6/2.3
BAE0	Hematite	dark red	9.6R 3.5/5.2
MOR78	Goethite, Hematite	reddish brown	5.6YR 4.7/5.0
AGU02	—	gray	2.7RP 5.1/2.0

proportion according to eqs (9) and (10). This is an interesting alternative to the more tedious and costly procedures (for example, XRD, chemical analyses, Mössbauer spectroscopy) of quantifying Fe oxides.

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