

## ANALYSIS OF IRON CONTENTS IN CARBONATE BEDROCK BY SPECTRORADIOMETRIC DETECTION BASED ON EXPERIMENTALLY DESIGNED SUBSTRATES

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### ABSTRACT:

In this study continuous spectral reflectance of experimentally designed substrates, simulating the typical sedimentary fabric of marls and carbonates was measured by an ASD FieldSpec in the range 0.4-2.5  $\mu\text{m}$ . Based on these data direct relationships between reflection features and iron content (total Fe) were calculated. Statistical analysis was done by standard procedures using characteristic primary parameters of iron absorption features and spectra derivatives. Close relations are evident between the area of the iron absorption features and the total iron content. Supplementally, the different absorption features of the varying iron oxides showed the necessity of integrating a correction factor, which is given by the position of the maximum iron absorption (wavelength). Validation of the modelling was executed by transferring the model onto a set of data generated from carbonate playa-lake-sediments. Additionally, quality of the model was proven by a set of soil samples from southern Israel; soils were developed on limestones respectively chalky bedrock.

**KEY WORDS:** iron oxide, continuous reflectance spectra, soil color

### 1 - INTRODUCTION

In surface substrates iron content yields valuable informations about present and past environmental conditions. In sediments iron content allows to draw conclusions on the synsedimentary degree of weathering and, in the best case, about the sediments' origin. Is the surface material covered by soils, iron content points to soil development and soil degradation.

Spectral reflectance of soils and bedrock is highly influenced by soil moisture, organic carbon content, and iron content (Schulze et al., 1993). Various approaches to derive iron content from spectral reflectance are already published. It is well known that iron oxides have primary reflection features (Baumgardner et al., 1985; Clark, 1997). Even trace amounts of iron oxides can cause the presence of absorption bands (Geerken, 1991). Several attempts were performed using multivariate statistics, but either relationships worked out are weak or argumentation of independent variables is not convincing (Ben-Dor and Banin, 1994).

The idea of this paper is to extract the influence of iron content in soils and bedrock on spectral reflectance by using an iron mixture series based on a marl matrix, containing varying iron contents and iron oxides. The model generated on these data, furthermore, will be validated on 'natural' soils and bedrock samples, including additional parameters to eliminate the influence of the overall albedo such as caused by organic carbon,

carbonate content, clay content, and soil moisture. In this first attempt data analysis will be limited on carbonate rich materials such as marls and limestones respectively on the soils developed in these bedrock.

## 2 - METHODS

The iron mixture series is based on a marl which is composed of 60 [weight-%] precipitated  $\text{CaCO}_3$ , 20 [weight-%] kaolinite, and 20 [weight-%] illite. Iron rich substrates of different origin (table 1) were added to this matrix in various concentrations (min. 0.4 [weight-%  $\text{Fe}_2\text{O}_3$ ], max. 10 [weight-%  $\text{Fe}_2\text{O}_3$ ]; figure 1, figure 2). Before, mineralogical composition of

Table 1: Lithofacies and mineralogical composition of iron-rich base substrate (mineral contents shown semi-quantitatively: +++ major component, ++ minor component, + trace)

	<b>Lithofacies</b>	<b>Matrix minerals</b>	<b>Predominating iron minerals</b>	<b>[weight-% <math>\text{Fe}_2\text{O}_3</math>]</b>
Fe1	sandstone	quartz +++ phyllosilicates +++ dolomite +	goethite ++ hematite ++ biotite ++	37.47
Fe2	sandstone	quartz +++ dolomite +	hematite ++	57.17
Fe3	iron sandstone	quartz ++	hornblende +++ goethite ++ hematite ++	71.69
Fe5	iron sandstone	quartz ++	goethite +++	76.37
Fe6	sandstone	quartz +++	goethite +++	44.68

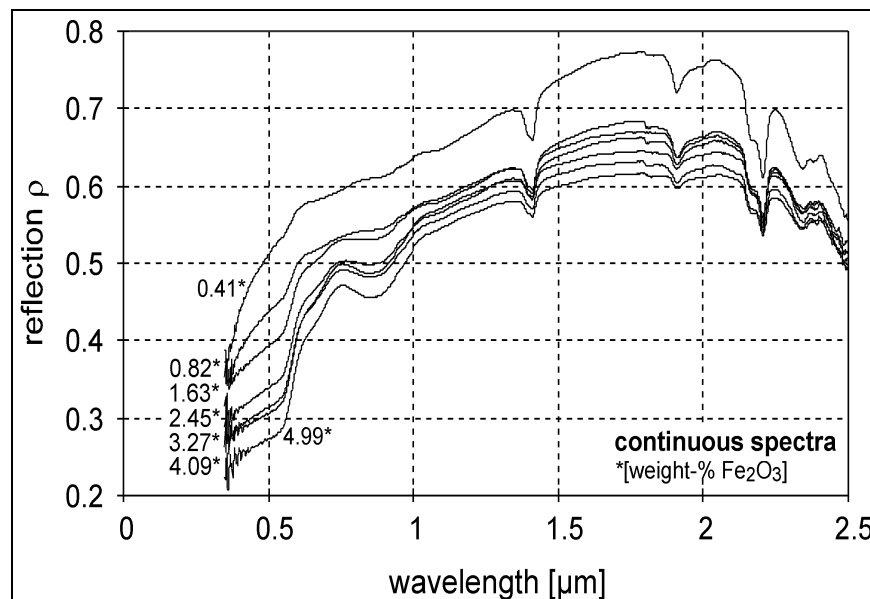


Figure 1. Continuous spectral reflectance of synthetic samples from iron mixture series generated from a hematite and goethite rich sandstone added to the marl matrix.

the iron rich substances was analysed by X-ray powder diffraction ( $2^\circ$ - $70^\circ$   $2\Theta$   $\text{CuK}_\alpha$ ). Proxy data for validation of the model were derived from carbonate rich bedrock from central Spain (18 samples) and soil samples from southern Israel (developed on limestone or chalky bedrock, partially associated with loess; 39 samples). In all samples iron content was analysed by X-ray fluorescence

analysis (SPECTRA 2000).

For the spectral measurements in the laboratory the optical head of the ASD FieldSpec II was mounted on a tripod in nadir position. The distance between optical head and sample was 10 cm. Illumination of samples and reference panel occurred with a 1000 W quartz-halogen lamp set in a distance of approximately 30 cm under an

illumination angle of 30 degrees. Absolute bidirectional reflectance spectra were obtained by multiplying the absolute reflectance of the spectralon standard into the raw measurements. Spectral reflectance of the homogenised samples was recorded in 1 nm steps.

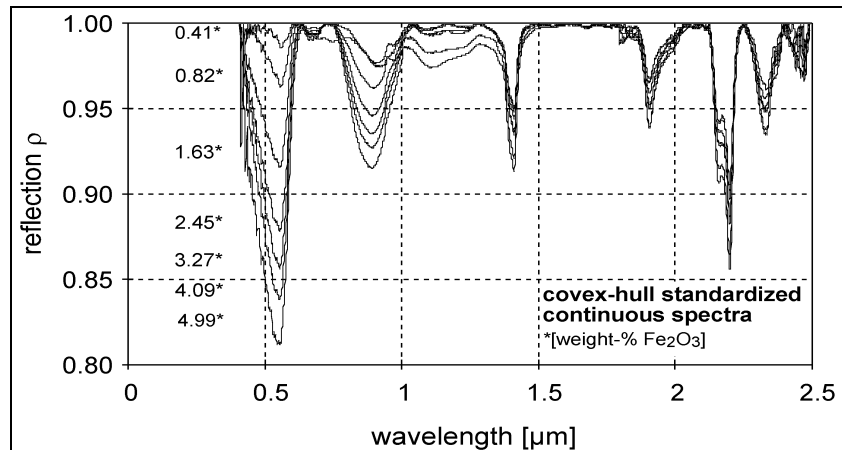


Figure 2. Convex-hull standardized continuous spectral reflectance of synthetic samples from iron mixture series generated from a hematite and goethite rich sandstone added to the marl matrix.

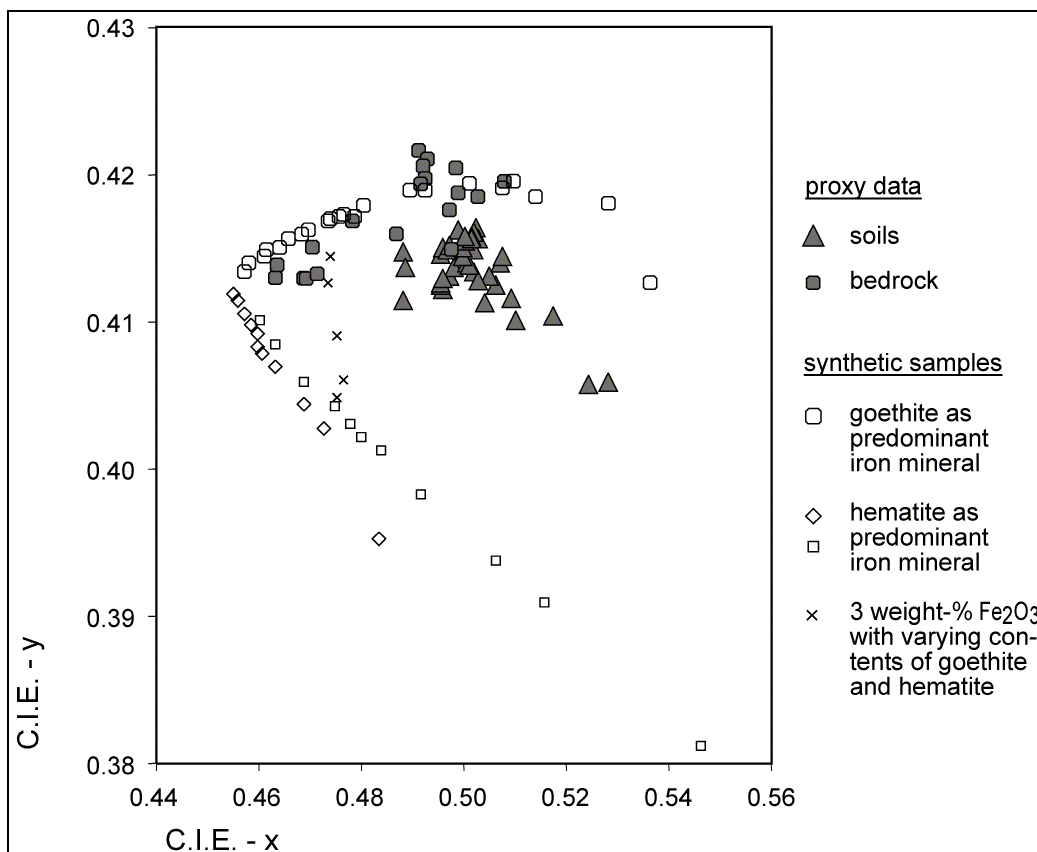


Figure 3. C.I.E. colour values of synthetic samples and proxy data. Synthetic samples show the iron mixture series with increasing x values corresponding to rising  $\text{Fe}_2\text{O}_3$  content ( $\diamond \square$ ). Transition from goethite regions to hematite regions is fluid depending on the goethite-hematite ratio ( $\times$ ). Proxy data are predominated by goethite as iron oxide ( $\blacktriangle \blacksquare$ ).

Additionally, for the calculation of color parameters the reflectance measurements were converted to trichromatic specifications, and then the results were expressed in terms of C.I.E. color notation (Y, x, y) (computer code kindly provided by R. Escadafal, JRC Ispra/Italy). In this color scheme, x and y are the chromaticity coordinates while the color intensity is characterized by the luminance Y, which represents the brightness of color (figure 3).

### 3 - SPECTRAL PARAMETRISATION FOR MODELLING IRON OXIDE CONTENT

The type and relative amount of iron oxides are known to influence soil color substantially. An increase of iron oxides leads to a decrease of overall reflection in the Visible and Near Infrared.

Obukhov and Orlov (1964) found the reflection intensity in the range of 0.5  $\mu\text{m}$  to 0.64  $\mu\text{m}$  to be inversely proportional to the iron content. Karmanov (1970) reported that the soil reflection with predominantly hydrous iron oxides increases most strongly between 0.5  $\mu\text{m}$  and 0.54  $\mu\text{m}$  while soils containing ferric hydroxides with low water content show an increase of reflection in the region from 0.554  $\mu\text{m}$  to 0.596  $\mu\text{m}$ . Moreover, spectral absorptions in the Visible and Near Infrared carry important information about the presence of iron oxides. Typically, the ferrous ion is responsible for the absorption band near 1.0  $\mu\text{m}$  while the ferric ion causes absorption bands at 0.7 and 0.87  $\mu\text{m}$ . Higher iron contents reveal a broader absorption band at 0.87  $\mu\text{m}$  (Hunt, Salisbury and Lenhoff, 1971; Karmanova, 1981; Baumgardner et al., 1985).

Thus, in a first approach to determine iron content from the synthetic samples, a model was generated based on multiple regression with the area of the convex-hull standardized spectrum between [0.451; 1.27]  $\mu\text{m}$ , and maximum absorption depth of the convex-hull standardized spectrum (1-hq) at  $\lambda=0.884$   $\mu\text{m}$  to determine hematite and at  $\lambda=0.929$   $\mu\text{m}$  to determine goethite as variables (figure 4) (Morris et al., 1985; Hauff and Kruse, 1990):

#### model 1

$$\text{Fe}_2\text{O}_3 \text{ [weight-\%]} = -204.856 + 203.250 \cdot \text{area}_{[0.451;1.27]\mu\text{m}} + 186.051 \cdot (1\text{-hq})_{\lambda 0.884} + 20.644 \cdot (1\text{-hq})_{\lambda 0.929} \quad (\text{eq. 1})$$

n=42, multiple r=0.9555, adj.r<sup>2</sup>=0.9109

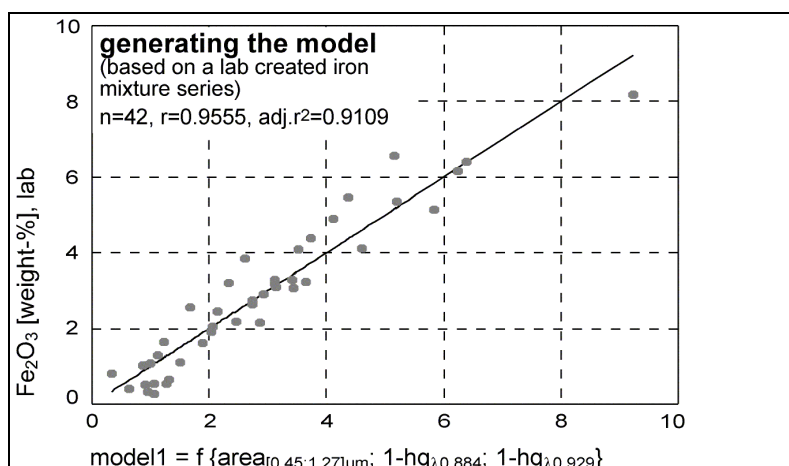


Figure 4. Scatter-plot for iron contents of synthetic samples derived from parametrized reflectance features and iron content determined by lab analysis (cf. eq. 1).

Model 1 was validated by using proxy data. First of all, samples of carbonate rich bedrock from the central Iberian Peninsula (calcareous marl, limestone, chalk; > 60 [weight-% CaCO<sub>3</sub>]) were tested on their iron oxide content determined from continuous spectral reflectance. Bedrock samples, in general, have organic carbon contents below the detection limit. But as they are highly variable in clay and carbonate content albedo of the sample is not anymore constantly influenced by the iron oxide content as shown for the synthetic samples. To compensate this effect iron oxide content of the bedrock samples was generated from model 1 (eq. 1) adding the ratio of C.I.E. colour values x and y to parametrize the goethite-hematite ratio of the sample (cf. figure 3) and C.I.E. brightness value Y, which is corresponding to the panchromatic reflection ( $\alpha < 0.001$ ) and, thus, represents the overall albedo:

model 2 (bedrock samples)

$$\text{Fe}_2\text{O}_3 \text{ [weight-\%]} = 23.717 + 0.184 \cdot \text{model 1} - 0.863 \cdot Y^{-2} - 14.060 \cdot x\text{-}y\text{-ratio} \quad (\text{eq. 2})$$

$$n=18, \text{ multiple } r=0.932, \text{ adj. } r^2=0.840$$

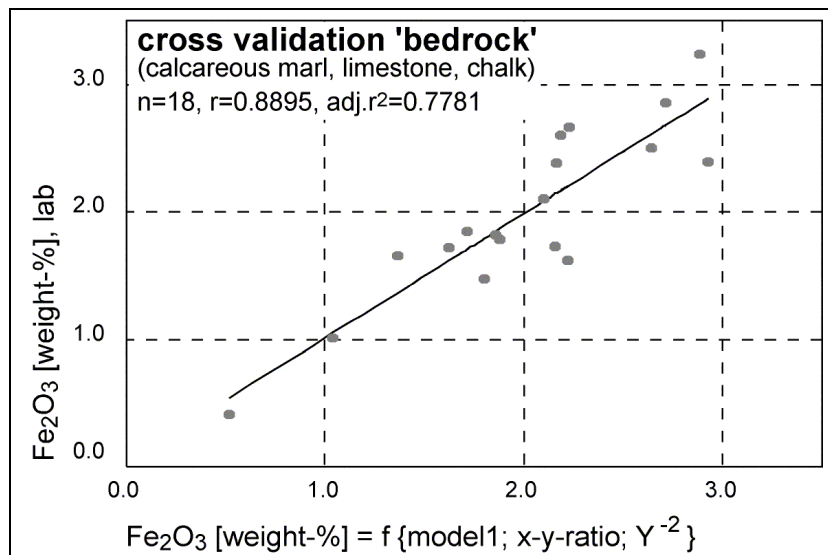


Figure 5. Scatter-plot and correlation coefficients for for cross validation of model 2 (bedrock samples: calcareous marl, limestone, chalk).

The quality of this model has been proven by cross validation as shown in figure 5.

The same procedure was practised with the soil samples. In the soil samples organic carbon contents increase up to 4 [weight-%] ( $\mu=2.55$  [weight-% C<sub>org</sub>], std.=1.82, n=39) and carbonate contents are highly variable ( $\mu=2.81$  [weight-% C<sub>inorg</sub>], std.=1.69, n=36, min.=0.67, max.=8.21). Thus, importance of brightness value Y increases to compensate albedo effect as shown in the increased negative Y-value in eq. 3 comparing to eq. 2. Correspondingly, importance of model 1 for determining soil's iron content decreases:

model 3 (soil samples)

$$\text{Fe}_2\text{O}_3 \text{ [weight-\%]} = -8.173 + 0.112 \cdot \text{model 1} - 1.138 \cdot Y^{-2} + 14.017 \cdot x\text{-}y\text{-ratio} \quad (\text{eq. 3})$$

$$n=39, \text{ multiple } r=0.954, \text{ adj. } r^2=0.903$$

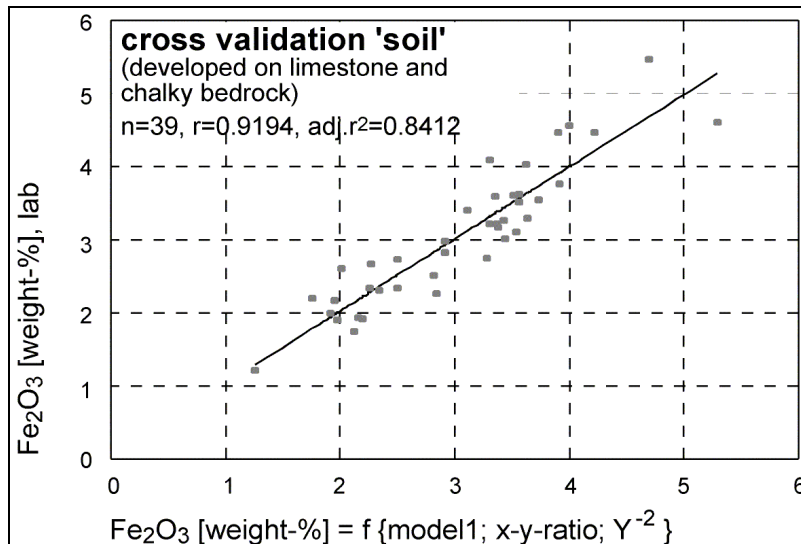


Figure 6. Scatter-plot and correlation coefficients for cross validation of model 2 (soil samples: soils developed on limestone and chalky bedrock).

The quality of model 3 has also been proven by cross validation, shown in figure 6.

## 4 - DISCUSSION OF PARAMETERS

### 4.1. Generating the Key Model

The key model is developed on lab generated data varying in iron oxide type and content based on a marly matrix. As it is well documented in literature that goethite and hematite have characteristic absorption features at 0.929 $\mu$ m and 0.884 $\mu$ m (Hauff and Kruse, 1990) the maximum absorption depth at these wavelengths were included in the model. Reflectance spectra show that these absorption features become deeper with increasing iron content but without linear relationship (figure 1, figure 2). While it is known that higher iron contents cause broader absorption features the area of the convex-hull standardized spectrum in the Visible and Near Infrared integrated in the model to compensate for this effect. Various area intervals were analysed for this purpose and highest significance was achieved for the range [0.451; 1.27]  $\mu$ m.

### 4.2. Transformation of the Key Model to Proxy-Data

As described above the key model is based on a homogeneous matrix which, overall, is not common in nature. Supplementally, the reflectance of proxy data is influenced by other properties of soils and sediments such as organic carbon or amorphous iron. All these factors are affecting the overall albedo of a substrate. Therefore, the square root of the C.I.E. brightness value Y (Y<sup>-2</sup>) was integrated into validation of the key model to recalibrate these effects (Sudduth and Hummel, 1991). Furthermore, the key model is based exclusively on varying hematite and goethite contents, not taking into consideration other iron minerals also affecting soil reflectance such as ferrihydrite, lepidocrocite, and maghemite (Schwertmann, 1993). As figure 3 shows, x-y-ratio of the C.I.E. values, as corresponding to the chromaticity values, gives a clue to the sample's predominating iron mineral composition. This ratio allows to define 'provinces' of predominating iron minerals of the proxy data and, thus, to reassess the key model according to iron mineral composition.

Using this approach for validation of the key model shows that for the sediment samples overestimation of iron contents caused by a decreased brightness value is smaller than for the soil samples. In this context it has to be considered that the sediment samples are composed of more than 60% carbonates and the content of organic carbon is close to detection limit, which causes a matrix similar to the lab generated samples. In opposite to this, the soil samples vary in carbonate content (10-50%), organic matter content (0.3-4 %) and many other properties such as composition and content of pedogenic iron or clay minerals. Due to these factors, the weight of the brightness value in the model for the sediment samples (eq.2) is low while it is many times higher for the soil samples (eq.3).

## 5 - CONCLUSIONS

It was demonstrated that the prediction of iron content using spectral absorption features and C.I.E. color coordinates shows promising results. Overall, the experiment should be extended to a data base covering additional relevant matrix characters (analysis is in progress). Beside this, it has to be evaluated whether the differences between the models for the proxy data are exclusively due to variations in chemical and mineralogical composition or whether the convex hull normalisation is the source of error using different base points for interpolation in relation to changing soil composition.

## 6 - ACKNOWLEDGEMENTS

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