HEAT-INDUCED SOIL MINERALOGICAL CHANGES, AS MONITORED BY REFLECTANCE SPECTRAL INFORMATION

R. Lugassi[a,*], E. Ben-Dor[b], and G. Eshel[c]
[a] The Porter School of Environmental Studies, Tel-Aviv University, 69978, Tel-Aviv, Israel – rachellu@post.tau.ac.il
[b] The Remote Sensing and GIS Laboratory, Department of Geography and Human Environment, Tel-Aviv University, 69978, Israel – bendor@post.tau.ac.il
[c] Soil Erosion Research Station, Ministry of Agriculture & Rural Development, Israel – eshelgil@gmail.com

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ABSTRACT:

In this study we heated soil samples from two Israeli soils under controlled conditions from 150-1000ºC in 50ºC intervals. The soil spectral reflectance (350-2500 nm), after cooling the soil to room temperature, was measured by ASD spectrometer. The spectral changes across the entire spectral region, induced by heating, were manifested by the soil color changes (e.g. iron - oxide transformation); shifting of the absorption bands (e.g. iron oxides) and the disappearance of absorption features (e.g. calcite).

1. INTRODUCTION

Soils that have been exposed to fire events may be degraded by removal of significant amounts of organic matter, deterioration of structure and porosity, considerable loss of nutrients through volatilization, increased soil pH values, and alteration of soil minerals (Ghuman & Lal, 1989; Certini, 2005; Hatten et al., 2005). Heat-induced soil mineralogical changes may cause irreversible changes in the soil mineral structure and composition, and they occur at a wide range of temperatures. For example, dehydroxylation and structural breakdown of clay minerals occur between 460°C and 980°C (DeBano et al., 1998), and dehydroxylation of goethite occurs at 200-320°C (Schwertmann, 1984). The degree of changes is a function of temperature and heat duration. Extensive knowledge of heat-induced changes in soil minerals has accumulated over the years using a variety of laboratory techniques such as DTA (Differential Thermal Analysis) (Tan & Hajek, 1977) and XRD analyses (X-ray Diffraction) (Schwertmann et al., 1987). Reflectance spectroscopy in the VIS-NIR-SWIR spectral region is one of the emerging and most promising techniques that can extract information on soil and rock mineralogy from near and far distances (Ben-Dor, 2008). Moreover, it is probably able to recognize the heat-induced mineralogical changes of the soil's minerals. The main objective of this study was to systematically study the spectral properties of two Israeli forest soils during a controlled heating process.

2. MATERIALS AND METHODS

2.1 Heat Treatments for Soils and Minerals

Two Israeli forest soils were collected from the upper 10 cm: Loess (Camborthids) and Rendzina (Calciorthids) (according to the local and USDA 1993 classification system). Fifty kg of each soil was collected and air-dried; remains of plants were removed and gently grounded and sieved through a 2-mm sieve. The soils and the minerals (goethite, hematite, and calcite) were heated (in ceramic cups) for 20, and 120 min, in 3 replicates, to 150 - 1000ºC (at 50ºC intervals) using a laboratory furnace. The heated soil and mineral samples were allowed to reach equilibrium with the surrounding environment for 48 hours before spectral measurements took place.

2.2 Spectral measurements

The reflectance of soil samples was gently measured on the undisturbed soil surface, using an ASD Field-Pro spectrometer furnished with a contact probe. The ASD (VNIR-SWIR spectral region, 350-2500 nm) has 2151 bands with 1-nm intervals (ASD, Inc., Boulder, CO, USA). The reflectance was measured relative to a Halon white reference. Each spectral measurement represented an average of 40 spectral readings. The mineral samples were mixed well in the ceramic cups, and then were passed to a box with a diameter identical to that of the contact probe and finally reflectance was measured.

3. RESULTS AND DISCUSSION

As a result of heat treatments, the following spectral changes occurred across the optical spectral region under consideration:

- Visual VIS changes – the redness factor.
- Absorption peak shifts of iron oxides at the VIS region.
- Disappearance of absorption features of calcite at the SWIR region.

3.1. Visual VIS changes - the redness factor.

Increases in redness occurred in soils that were exposed to temperatures above 300ºC (figure 1a). A redness index of Loess soil was calculated as the ratio between the red (640nm) to the green (550nm) and was plotted versus temperature (figure 1b). A stepwise behavior was observed, as well as a positive trend of the redness index with elevated temperature. Kampf et al. (2000) and Schwertmann (1984) supported this linkage between increases in redness and transformation of iron oxides. Kämpf et al. (2000) assumed that the reddening of the soil is due to transformation of goethite to hematite. Schwertmann (1984) found that Differential Thermal Analysis (DTA) indicates that goethite dehydroxylation occurs at 320ºC. Kämpf et al. (2000) suggested that the reddish soil (5YR according to the Munsell color system) is due to the presence of hematite, masking the presence of goethite's yellow color (between 7.5YR and 2.5Y).

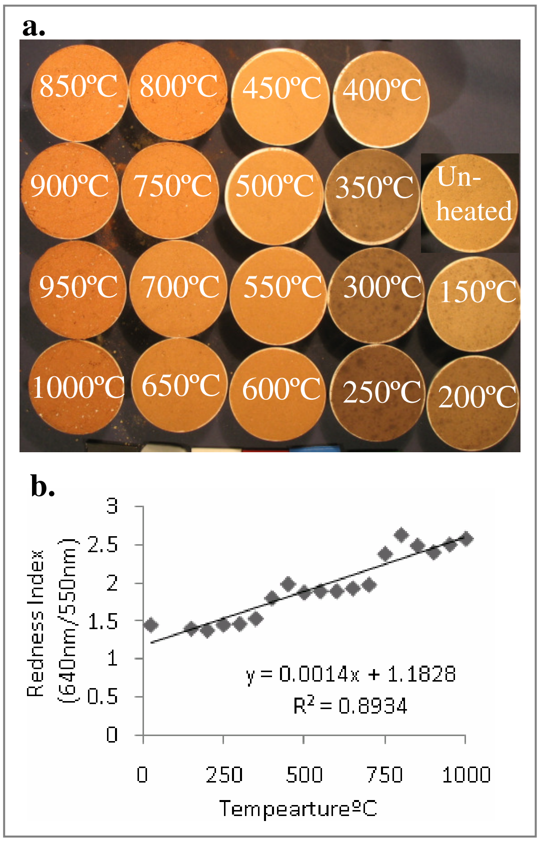

Figure 1: Redness changes in Loess soil: the true color of heated soil (a) and the redness index increased with elevated temperatures (b).

3.2 Absorption peak shifts of iron oxides at the VIS region

In order to emphasize the spectral changes, we applied a continuum removal (CR) (Clark, 1999) to reflectance at the VIS region. An absorption peak that shifted toward the longer wavelength with elevated temperatures was observed.

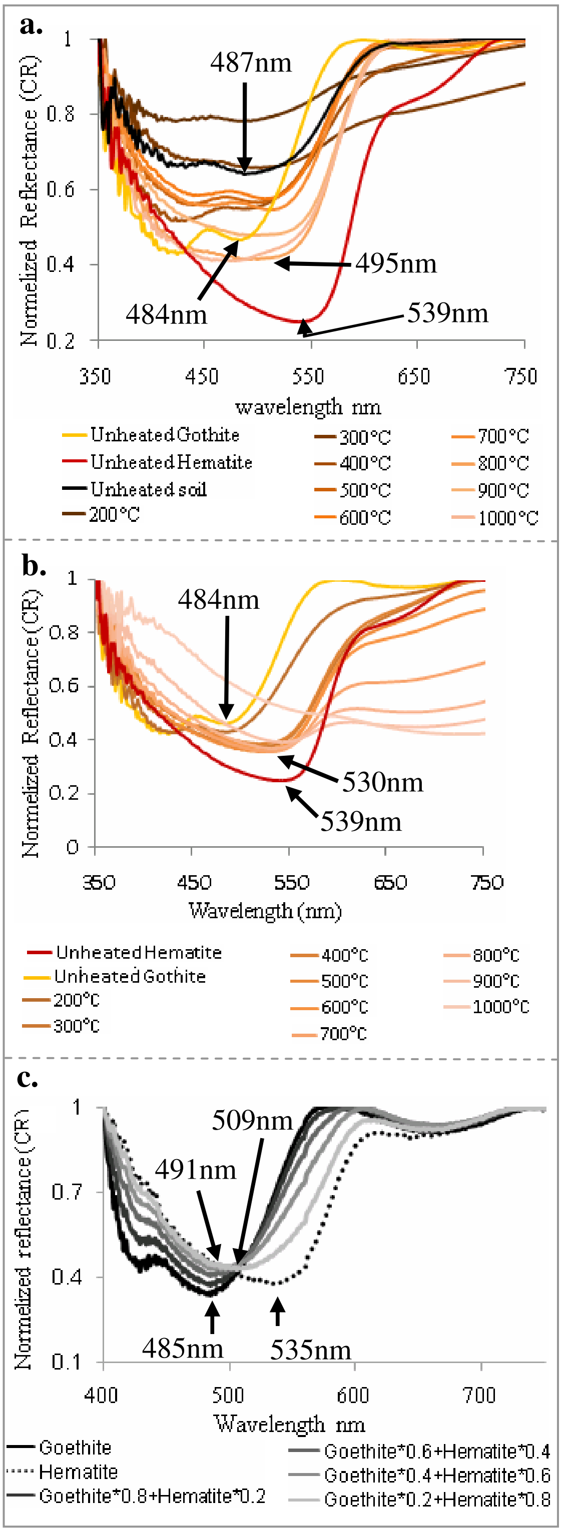

Figure 2: Absorption peak shifts toward the longer wavelength with elevated temperatures of Loess soil (a), Goethite (b), and a synthetic linear mixture of Goethite and Hematite (taken from the JPL laboratory spectra) (c).

Figure 2 shows the absorption peak shift of the Loess soil and that of the goethite mineral, which were heated from 200ºC to 1000ºC (over 20 minutes). For example, absorption peaks of unheated soil (487nm) shifted toward a longer wavelength (495nm) when soil was heated to 800ºC (figure 2a). Examination of the goethite normalized reflectance (CR) (figure 2b) revealed the same phenomenon, with an absorption shift from 484nm (unheated) to 530nm (heated to 800ºC). A similar trend was observed in an artificial spectral mixture of pure goethite and hematite spectra taken from the JPL (Jet Propulsion Laboratory) spectral library (Research Systems, 2000) (figure 2c). As shown, as the proportion of the hematite to goethite increases, the absorption peak is shifted from 485nm (the goethite peak) toward 535nm (the hematite peak) (figure 2c). The content of free iron oxides in clay fractions of Loess soil is about 2% (Ravikovitch, 1981). Thus, when dehydroxylation of goethite to hematite occurs ($2FeOOH \rightarrow Fe_2O_3 + H_2O$, Murad & Wagner, 1998), this shift is strikingly observed (figure 2a, b). Furthermore, DTA observation indicates that goethite dehydroxylation occurs at 320ºC (Schwertmann, 1984), which is in good agreement with our results.

3.3 Absorption features – the disappearance of calcite at the SWIR region

Spectral changes across the SWIR region are also obtained in calcite. The content of calcite in clay fractions of Rendzina soil is about 60% (Ravikovitch, 1981). The strong calcite band absorption at 2300-2350 nm is asymmetric, with a shoulder toward the short wavelength due to overtones ($3v_3$) of CO_3 asymmetric stretch (Hunt & Salisbury, 1971). The reflectance spectra of heated Rendzina soil and pure calcite samples from 200-1000ºC are presented in figures 3 and 4 (heat duration of 20 and 120 minutes, respectively). Significant spectral changes occur in calcite absorption peaks in both materials. The absorption at 2343nm that occurs with unheated and heated samples less than 800ºC, totally

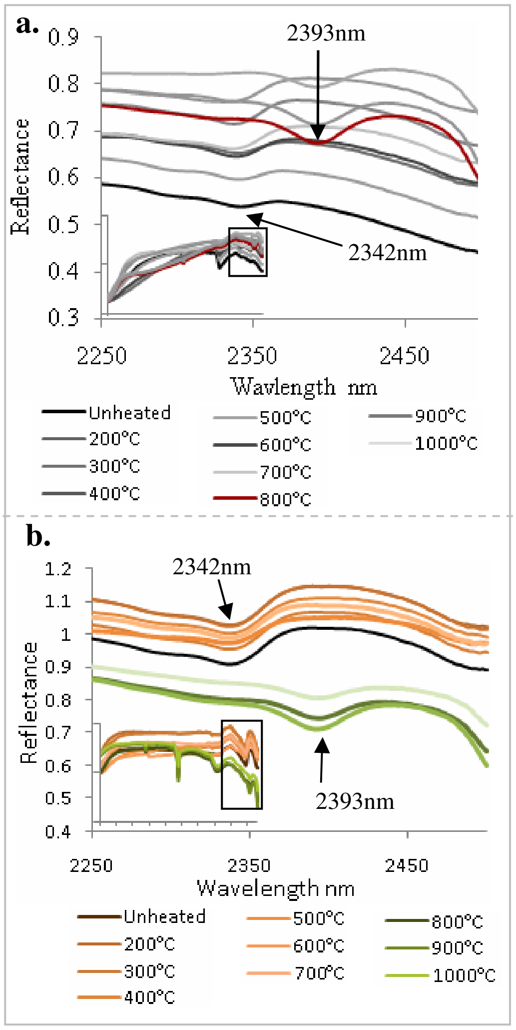

Figure 3: Spectral changes in the SWIR region of heated Rendzina soil (a) and Calcite minerals (b) from 200 to 1000°C for 20 minutes.

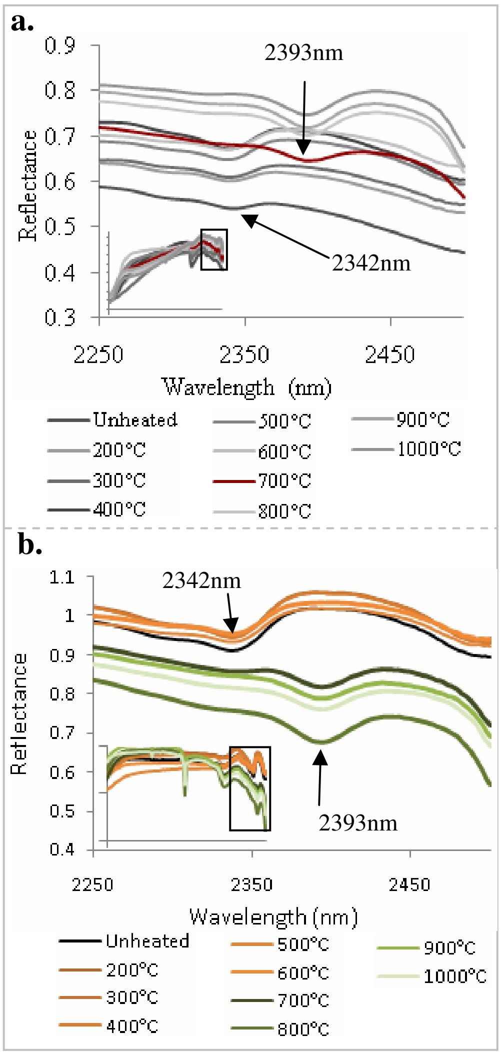

Figure 4: Spectral changes in the SWIR region of heated Rendzina soil (a) and Calcite minerals (b) from 200 to 1000°C for 120 minutes.

disappears with soil that was heated from 800-1000ºC, where a new absorption peak emerged at 2393nm (figure 3a). An identical phenomenon coincides in pure heated calcite from 200-1000ºC (figure 3b). Calcium carbonate decomposes into calcium oxide and carbon dioxide according to Rodriguez-Navarro et al. (2009), by the following process: $CaCO_3 \rightarrow CaO + CO_2$ and the decarboxylation usually take place at temperatures above 800ºC (Ben-Dor & Banin 1990, Gibbs et al. 2000). This explains why the absorption feature at 2343nm vanishes at 800ºC and above (figure 3a).

In addition, the heat duration was found to affect the rate of spectral changes in the heated soils and pure calcite. Whereas the discussed new absorption peak at 2393 nm occurred at 800ºC for 20 minutes heat duration (fig. 3a,b), it occurred at a lower temperature (700ºC) when the soil and calcite were exposed to heat for 120 minutes (fig. 4a,b).

4. CONCLUSIONS

Several spectral changes were observed when two Israeli soils underwent controlled heating: color changes that were caused by transforming iron oxide from Goethite to Hematite; a shift in the absorption band at the VIS range due to the above transformation and the vanishing of the major calcite absorption peak at the SWIR region. The heat duration was also found to be responsible for the rate of possible spectral changes.

This study shows the potential of reflectance spectroscopy to serve as an additional tool for thermal analysis of soil minerals. Importantly, it enables scientists to monitor thermal processes after the fire event occurred.

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