Weathering sequence of volcanic ash soils in the Matese Mountians as evaluated by Diffuse reflectance spectroscopy (DRS)

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Summary

In recent years, soil reflectance measurements by means of spectrophotometers have been widely adopted in pedogenetic studies, and have gained relevance in the acquisition of remote sensing data at the laboratory and field scale. The goal of this work has been to establish the relationship between the chemical and mineralogical composition of soil and its spectral reflectance. Although reflectance analysis appears promising, there are no studies that have used reflectance spectroscopy to study volcanic soils. The results presented here confirm that diffuse reflectance spectroscopy (DRS) in the VIS-NIR (400-2500 nm) region of some Andisols is influenced by their specific mineral composition. In particular, the absorption band at 2200 nm was correlated to kaolinite content, and the presence of gibbsite was correlated to an absorption band at 2260 nm. These results show that laboratory spectrometric measurements can be used to rapidly acquire reliable information on the mineralogical properties of volcanic soils. These properties can then be used to evaluate how soils vary as a result of weathering and differences in parent materials. Future work can potentially involve the execution of field-level studies employing a portable spectroradiometer.

Key Words

Diffuse reflectance spectroscopy (DRS), soil genesis, volcanic soils, aluminium oxides.

Introduction

Spectroscopic analysis is a rapid and non-destructive method for determining the solid-phase constituents of a soil (Ben-Dor 2002). Laboratory spectroscopic analysis of soils requires little or no sample preparation, and when used in conjunction with more traditional mineralogical characterization methods, can identify subtle mineralogical changes that other methods alone may miss. It is a powerful tool for the identification of both crystalline and amorphous minerals and can be used to identify rock and mineral weathering products, particularly phyllosilicates and other OH-bearing materials (Viscarra Rossel *et al*. 2006). The characteristic absorption features used to identify a material are influenced not only by their chemistry but also by their structure. Consequently, subtle changes, for example a slight shift in the wavelength position of an absorption feature, can be indicative of significant changes in mineral chemistry or degree of crystallinity. As each layer in a mineral structure absorbs energy almost independently of its neighbor, the absorption of photons does not require long range crystallographic order. Reflectance spectra of soils result from the complex interaction of the mineral, organic, and liquid phases, as well as soil structure and particle size distribution (Chang *et al*. 2001). Differences in these prosperities can be recognized by variation in the wavelength position, shape, and intensity of absorption features in the 0.3-2.45 µm wavelength interval. Subtle variations in the mineral composition or structure will result in changes in wavelength position and/or shape of characteristic absorption features and allow both the identification of individual minerals and mineral mixtures (Clark *et al*. 1990). Many minerals, including clay minerals and iron oxides, can be routinely identified with FTIR even when their concentrations are less than 1% of the bulk soil (Farmer 1974).Visible near infrared reflectance spectroscopy VIS-NIR (400-2500 nm) of soils has been utilized for many years in soil studies typically as a means of relating spectra to bulk soil properties such as the kind and amount of iron oxides (Sellitto *et al*. 2009). The relationships between these broad properties of soils and reflectance spectra have been established by utilizing correlation statistics between soil spectra and independently measured soil properties. The spectral reflectance data used in this study allows for the identification of specific minerals based on the wavelength position and shape of diagnostic absorption features. Currently, there are no studies that use these techniques to study the chemical and mineralogical composition of volcanic soils. Therefore, the aim of this study was to characterize mineralogical composition of several volcanic ash soils using diffuse reflectance spectroscopy (DRS).

Methods

Sample site

We examined a total of 50 samples from 5 soil profiles from the Matese Massif in southern Italy. Each sample was air-dried, ground, sieved (<2 mm), and then split into two sub-samples. One was used for the spectroscopic measurements and the other for mineralogical analysis.

Mineralogical Analysis

Diffraction patterns were obtained using a PANalytical X'Pert PRO MPD x-ray diffraction system (PANalytical, Almelo, The Netherlands) equipped with a PW3050/60 θ-θ goniometer and a Co-target x-ray tube. Aliquots of the clay samples were saturated with 0.5 M $MgCl_2$ or 1 M, KCl solutions. The Mg-saturated samples were solvated with glycerol by adding glycerol directly onto the moist clay, then x-rayed. The air-dried, K-saturated clay fractions were x-rayed at room temperature and after heating to 100, 300, and 550° C for 2 h at each temperature. The <2 µm fraction was used for X-ray diffraction (XRD) and differential X-ray diffraction (DXRD), as well as for selective dissolution by acid ammonium oxalate (Schulze 1981).

Reflectance Measurements

Diffuse reflectance measurements were obtained by using a Jasco 560 UV-visible spectrophotometer, equipped with an integrating sphere, according to the method proposed by Torrent and Barrón (1993). Briefly, air-dried soils, previously sieved at <2 mm, were vigorously ground in an agate mortar for at least 10 minutes in order to exclude the influence of micro-aggregation. Then, the samples were gently pressed into a special circular sample holder (diameter of 10 mm) against unglazed white paper in order to avoid undesired particle orientation, and also to prevent material from falling into the integrating sphere. The integrating sphere has a geometry that simultaneously allows the measurement of the sample and a white standard (polytetrafluorinethylene), which was assumed to have 100% reflectance at all wavelengths.

Results

The reflectance measurements show substantial homogeneity of the mineraological composition from sample to sample. The absorption at 1400 nm is due to vibrations of the water molecules and OH^- groups (O-H stretching), whereas absorption at 1900 nm is due to water absorbed into 2:1 minerals (bending process). . (Figure 1).

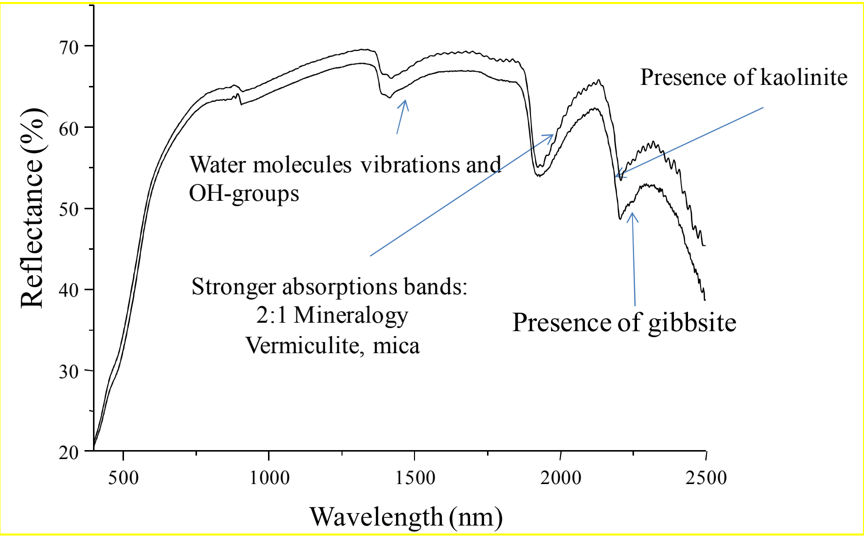

Figure 1. Comparation of the mean spectral reflectance curve from clay fraction of the MAT8 pedon BC6 and BC7 horizons.

The absorption at 2200 nm indicates the presence of kaolinite and is due to O-H stretching and Al-OH bending. These vibrations are present in both expandable and non-expandable mineral structures. The presence of kaolinite in most of the analyzed soils was confirmed by the presence of absorption bands at 2208, 2160, 2242, and 2290 nm. All these absorption bands are due to vibrational processes (bending Al-OH).

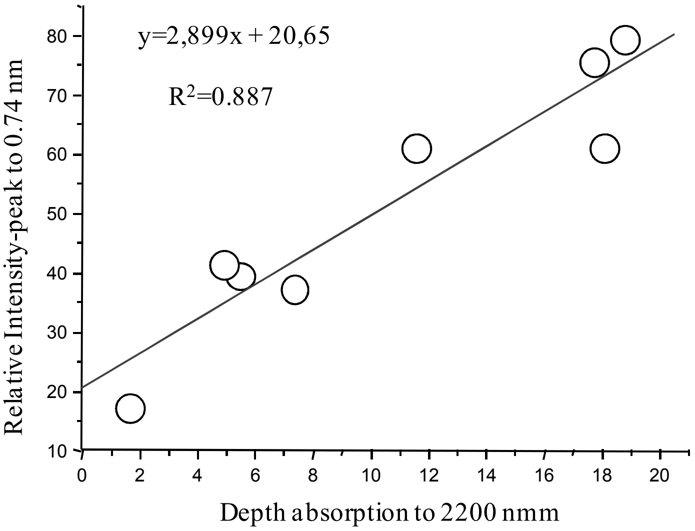

Figure 2. Relation between relative intensity of the diffraction peaks at 0.70 nm and the depth of the absorption at 2200 nm in the reflectance spectra.

The characteristic absorption bands obtained from the reflectance spectra were compared to the relative intensities of the diagnostic x-ray diffraction peaks found in the clay fraction. In particular, the depth of the bands centered at 1400, 1900 and 2200 nm was related to the relative intensity, the full width at half maximum (FWHM) and the symmetry of mineral-specific peaks of clay minerals in the x-ray patterns. Statistical analysis showed that none of these bands were significantly correlated with the relative intensities of peaks derived from diffractograms. The only significant correlation observed was between the relative intensity of the kaolinite 0.72 nm peak and the absorption depth at 2200 nm in the reflectance spectrum (Figure 2).

This correlation is present only in soils having a narrow symmetric peak at 0.72 nm that is associated with greater kaolinite crystallinity. Moreover, this correlation indicates that both kaolinite crystallinity and abundance influence the reflection band at 2200 nm. A second band at 2260 nm (Figure 3) is associated with the presence of gibbsite (Demattê and Garcia 1999; Demattê *et al.* 2004). However, soils that have shown the presence of gibbsite have an absorption band at 2226 nm in their horizons. Moreover, the presence of this type of band was found in some horizons even though gibbsite was not found by x-ray diffraction analysis. This results leads to two considerations: the first is that the reflectance measurements are very sensitive and as precise as x-ray diffraction analysis; second, the presence of large amounts of exchange-Al could affect the absorption band at 2260 nm.

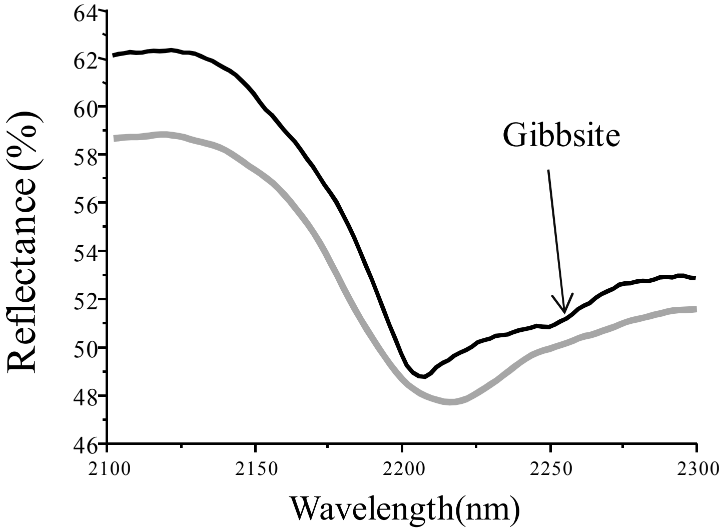

Figure 3. The absorption bands around 2200 and 2260 nm, the band at 2260 nm is associated with the presence of gibbsite.

Conclusions

Diffuse reflectance spectroscopy (DRS) in the VIS-NIR (400-2500 nm) region can be used as a rapid screening method to study the clay mineralogy of volcanic soils. Diffuse reflectance of some Andisols sampled in southern Italy is influenced by specific mineral composition. In particular, the absorption band at 2200 nm is correlated to kaolinite content, and the presence of gibbsite is correlated to an absorption band at 2260 nm. These results show that laboratory spectrometric measurements can be used to rapidly acquire reliable information on the mineralogical properties of volcanic soils. The evaluation of diffuse soil spectra obtained in the laboratory suggests that this approach for soil aluminum oxide estimation is comparable to other more well known techniques such as x-ray diffraction.

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