



Quantifying mineral abundances of complex mixtures by coupling spectral deconvolution of SWIR spectra (2.1–2.4 μm) and regression tree analysis



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ARTICLE INFO

Article history:

Received 6 November 2012

Received in revised form 29 April 2013

Accepted 14 May 2013

Available online 21 June 2013

Keywords:

Soil minerals

Spectral unmixing

Exponential Gaussian optimisation

Regression trees

SWIR reflectance spectroscopy

ABSTRACT

This paper presents a methodology for assessing mineral abundances of mixtures having more than two constituents using absorption features in the 2.1–2.4 μm wavelength region. In the first step, the absorption behaviour of mineral mixtures is parameterised by exponential Gaussian optimisation. Next, mineral abundances are predicted by regression tree analysis using these parameters as inputs. The approach is demonstrated on a range of prepared samples with known abundances of kaolinite, dioctahedral mica, smectite, calcite and quartz and on a set of field samples from Morocco. The latter contained varying quantities of other minerals, some of which did not have diagnostic absorption features in the 2.1–2.4 μm region. Cross validation showed that the prepared samples of kaolinite, dioctahedral mica, smectite and calcite were predicted with a root mean square error (RMSE) less than 9 wt.%. For the field samples, the RMSE was less than 8 wt.% for calcite, dioctahedral mica and kaolinite abundances. Smectite could not be well predicted, which was attributed to spectral variation of the cations within the dioctahedral layered smectites. Substitution of part of the quartz by chlorite at the prediction phase hardly affected the accuracy of the predicted mineral content; this suggests that the method is robust in handling the omission of minerals during the training phase. The degree of expression of absorption components was different between the field sample and the laboratory mixtures. This demonstrates that the method should be calibrated and trained on local samples. Our method allows the simultaneous quantification of more than two minerals within a complex mixture and thereby enhances the perspectives of spectral analysis for mineral abundances.

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1. Introduction

Soil mineralogy is an important indicator for soil formation and parent material characterisation. Among other minerals in soils like quartz, feldspars and carbonate minerals, clay minerals are the main secondary phases formed by the weathering of the parent material. The abundance of different clay minerals and their structural features become useful indicators in defining the evolutionary stage of a soil (Egli et al., 2008; Hong et al., 2007; Mavris et al., 2011; Sedov et al., 2003). In environmental and geological studies, the characterisation (and quantification) of soil mineralogy is typically achieved using X-ray diffraction (XRD). XRD is broadly acknowledged as the essential tool for mineral determination of mono- or multi-mineral mixtures (Bish and Plötze, 2011; Gomez et al., 2008; Mulder et al., 2011; Omotoso et al., 2006). The basic limitation of XRD is that the analysis must be carried out indoors, basically due to

sample preparation requirements and specific laboratory treatments necessary for some clay minerals, such as glycolation and heating after various cation saturations. Visible Near Infrared and Shortwave Infrared (VNIR/SWIR) spectroscopy has proven to be an efficient method for the determination of various soil properties since measurements can be done with little effort and in situ (Ben-Dor et al., 2009; Viscarra Rossel et al., 2006). In this paper, we propose and demonstrate its use for simultaneous quantification of mineral abundances from complex mixtures.

Some minerals such as quartz, and low iron feldspars do not show absorption features in the 0.350–2.500 μm wavelength range except for the features arising from $\text{Fe}^{2+/3+}$ related to their weathering products (Clark et al., 1990). Detection of minerals having absorption features within the 0.350–2.500 μm range have been successfully obtained using linear spectral unmixing techniques (Dennison and Roberts, 2003). However, these analyses were limited to estimating the main component within a sample having the most distinct absorption feature (Mulder et al., 2012b). Linear mixing behaviour of spectra, however, is highly unlikely

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in soils because the mineral constituents are typically in intimate association with one another. Influencing factors are e.g. the opaqueness of minerals and coating by other minerals. Furthermore, simultaneous retrieval of multiple mineral abundances from reflectance spectra in the 0.350–2.500 μm region is affected by the co-occurrence of absorption features at similar wavelengths arising from overtones and combinations of the fundamental absorptions of OH, H₂O and CO₂ which occur at wavelengths greater than 2.500 μm , nonlinear mixing (or scattering) phenomena (Singer, 1981; Sunshine et al., 1990), and measurement noise (Stenberg et al., 2010). Hence, reflectance spectra of mixtures are typically a complex result from the combinations of the spectral characteristics of the constituents (Clark et al., 1990), as illustrated in Fig. 1. A comparison of the diagnostic features of pure calcite with the continuum removed reflectance (Clark, 1998) of samples containing an spectrally dominant mineral shows that e.g. in the presence of quartz the double absorption feature near 2.300–2.350 μm is present but much less distinct while it is absent in mineral mixtures of calcite with kaolinite or dioctahedral mica at approximately 15% abundance. Note also that the absorption near 2.150 μm is absent in the smectite and dioctahedral mica mixtures while it changes the typical absorption of kaolinite. Depending on the composition, the abundance and the spatial arrangement of the minerals, the total reflectance resulting from the scattering of the minerals within the intimate mixture produces positional shifts, changes in intensity, disappearance of absorption features or changes in their shape.

Methods aiming to match diagnostic absorption features with spectra from a large spectral library include the Tetracorder (Clark et al., 2003) and the CRISM Analysis Tool (CAT) (Flahaut et al., 2012). While the extended library enables application to unknown areas without the need of calibration on local samples, the retrieval of the mineral composition of complex mixtures remains limited because spectral mixing effects may yield diagnostic features not distinct enough to be matched to minerals in the spectral library. Theoretically the spectra could be matched to the corresponding spectra with known abundances in the library. However the spectra to be included in the library of various minerals and the possible variation in mixtures of these would follow combinatorial logic (Mulder et al., 2012b). So, the methods are commonly applied to characterising mineral composition in terms of presence or absence but not quantifying mineral abundances (Clark et al., 2003). Non-linear models, such as the single scattering albedo model of Hapke (Hapke, 2002; Warell and Davidsson, 2010) have been successful in predicting the abundances of minerals in intimate mixtures. The main reason why such a nonlinear approach is not widely adopted is the amount of detailed information on the scattering properties of all endmembers needed to perform the calculations (Keshava and Mustard, 2002). Alternatively, the modelling of reflectance and the inference of absorption components within complex features can be done by fitting Gaussian curves or modified Gaussian curves to the

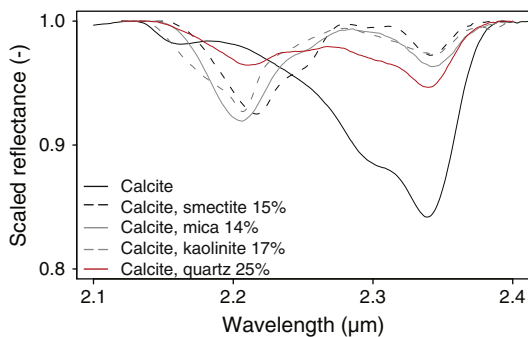


Fig. 1. Continuum removed reflectance of calcite and mixtures containing calcite. The mixtures contain minerals of which the additional mineral with absorption features has an abundance of approximately 15% and a sample of calcite with 25% quartz (spectra originate from field samples measured in this experiment, the calcite spectra contain a small trace of mica).

absorption features and absorption components in reflectance spectra of minerals also referred to as spectral deconvolution (Burns, 1993; Noble et al., 2006; Roush and Singer, 1986; Singer, 1981). Sunshine et al. (1990) provided the explanation for Gaussian behaviour of absorption features. The signal sensed by a spectrometer corresponds to the mean response from massive amounts of electronic and vibrational processes that cause absorption around specific wavelengths (absorption bands). Owing to the Central Limit Theorem, an absorption feature closely resembles a Gaussian distribution. Alternatively, the exponential Gaussian optimisation (EGO) of Pompilio et al. (2009) has been designed to model absorption components which are not Gaussian in shape and accounts for saturation and asymmetry effects. The use of such a quantitative deconvolution method for a spectrum of a specific composition is dependent only on the spectra and absorption of the minerals themselves rather than the detailed information on the scattering properties required for the Hapke model (Shepard and Helfenstein, 2007). It provides the means to study the individual absorption components in spectra and interpretation of these can then be analysed in terms of composition (Sunshine et al., 1990).

Modified Gaussian models have been demonstrated in laboratory experiments by mixtures with two constituents of interest using either multiple linear regression techniques (Bishop et al., 2011; Singer, 1981) or the ratio between intensities of absorption components (Kanner et al., 2007; Sunshine and Pieters, 1993). It has thus been assumed that the model parameters vary as a linear function of the relative proportions of the constituents in the mixture (Pompilio et al., 2009; Sunshine and Pieters, 1998). Samples with similar mineralogy but unknown abundance can then be predicted by the calibrated mixtures models. However, such approach is insufficient for the prediction of mixtures with more than two minerals. Model parameters might vary linearly over a short range of the mixture possibilities but over the complete range of mixture possibilities, non-linearity dominates. As a result, a different type of analysis is required to relate the EGO parameters to the mineral content in order to determine abundances of three or more minerals within a mixture. We propose a recursive partitioning of the data by regression tree analysis (Breiman et al., 1984). Regression tree analysis allows to deal with nonlinearity and interactions between the EGO parameters. Regression trees can be trained by setting decision rules based on the predictive structure of the dataset with mineral mixtures (Breiman et al., 1984). This approach is an often used data mining technique in several disciplines (De'Ath and Fabricius, 2000; McBratney et al., 2003; Yang et al., 2003).

Below we give details on combining the deconvolution by EGO and the use of regression trees on the EGO parameter values for quantifying mineral abundances of mixtures having more than two constituents. The approach is demonstrated on a range of prepared samples with known abundances of kaolinite, dioctahedral mica, smectite, calcite and quartz and on a set of field samples from Morocco, which were quantitatively analysed by XRD analysis.

2. Methods

2.1. Spectral deconvolution by Gaussian modelling of absorption components

Deconvolution of the spectra by fitting Gaussian curves needs to be concerned with partly overlapping absorption components (Sunshine and Pieters, 1993) as well as the presence of amorphous materials and impurities that may modify absorption band shapes and contribute to saturation and asymmetry of spectral features (Burns, 1993; Pompilio et al., 2009). The Modified Gaussian Model (MGM) describes absorption components as modified Gaussian distributions that are parameterised by a band centre, band width (full width at half maximum) and band strength (amplitude intensity), for more details see Sunshine et al. (1990) and Kanner et al. (2007). In several studies MGM has been successfully used to model overlapping absorptions components (Bishop et al., 2011; Kanner et al., 2007; Lane et al., 2011; Ogawa et al., 2011; Pinet

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