The 3D distribution of phyllosilicate clay minerals in western Victoria

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ABSTRACT

The mineralogy of the clay fraction of soils is a major determinant of the behavior of soil. Conventionally these clay minerals have been determined using techniques such as X-ray Diffraction (XRD), but new complementary methods such as infrared spectroscopy can be used to rapidly and economically predict these minerals. This paper presents a methodology to predict these clay minerals at high-resolution that adhere to GlobalSoilMap (GSM) standards. Mid-infrared (MIR) spectroscopic models were formulated for clay minerals kaolinite, illite and smectite using partial least squares regression (PLSR) and legacy quantitative XRD determinations. Very strong models were achieved for kaolinite, illite and smectite and the root mean square error of cross validation (RMSECV) were all <12 wt.%. Spectroscopic models were applied to 11,500 samples from western Victoria and harmonized to the GSM specified depth intervals using equal area splines. Clay minerals were then mapped using data mining model trees with a 10-fold cross validation to derive a mean prediction estimate and 90% prediction interval. Spatial models accounted for 26 to 77% of the total variation with kaolinite predictions for all 6 GSM depths ≥ 65%. Kaolinite is the dominant soil clay mineral of western Victoria for uplands and weathered volcanic terrains. Illite concentrations are higher where associated with weathered granitic plutons and in aeolian deposits of semi-arid environments. Smectite tends to occur associated with depressions of plains (volcanic and sedimentary). Further supplementation of additional sites and samples for landscapes with relatively sparse observations should contribute to refined and improved maps of these clay minerals.

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1. Introduction

The mineralogical composition of the clay fraction (<2 μm) is a key determinant of soil physical and chemical properties and the regulation of biogeochemical processes. Clay is a generic term for the fine particle size, <2 μm in soil, but the mineralogy of clay and the variability of particles < 2 μm is highly diverse depending on the source material of primary minerals, the physical and chemical weathering environment and time (Gilkes, 1990). Primary minerals (generally >2 μm) and, more so, secondary minerals that are reactive with their environment (Churchman and Lowe, 2012), support key functions of ecosystem services including the filtering and storage of water, adsorption of soil organic carbon and supply of available nutrients to plants (e.g. potassium), retention of heavy metals as contaminants and provision of a physical medium for infrastructure. The clay minerals (phyllosilicates, otherwise known as the layer silicates) comprise a single octahedral alumina sheet, linked to either a tetrahedral sheet of silica (1:1 layer

silicate) or sandwiched between two tetrahedral silica sheets as a 2:1 layer silicate. Due to the clay's dominant specific surface area characteristics for interactions with plants, nutrients, metals and organic compounds, the clay fraction is largely responsible for the chemical behavior of soils (Gilkes, 1990). The importance of phyllosilicate group minerals to organic matter storage and turnover is recognized (Torn et al., 1997; Fontaine et al., 2007; Yuan and Theng, 2012) and emphasized in global efforts to reduce greenhouse gas emissions though soil carbon sequestration (Amundson et al., 2015). In contrast, there has been a noted decline in mineralogical research (Hartemink et al., 2001) and failure to include mineralogy information with spatial modelling and mapping of soil properties (Grunwald, 2009).

1.1. Measurement of clay minerals

Crystalline clay minerals have conventionally been characterized and quantified from monochromatic X-rays using X-ray Diffraction (XRD) techniques. Quantification and identification of mineral phases in soils derived from alteration and formation processes (e.g. transformation or neoformation) such as kaolinite, illite, halloysite, smectite and vermiculite has been the mainstay of clay mineralogy determination for over 80 years (Churchman and Lowe, 2012). As a method,

XRD determination has improved significantly due to increased sensitivity and reliability of equipment (Gilkes, 1990) and advances in assessment techniques. Four common XRD analytical methods are described by Kahle et al. (2002) including full-pattern methods that trace the entire diffractogram with mean or calculated diffraction patterns (Hughes et al., 1994) and quantify phases using the Rietveld Method (Rietveld, 1969).

A complementary method is infrared spectroscopy (IR) that requires relatively little sample preparation. In contrast to XRD, IR uses assessment techniques that are quantitative and precise, and analysis is rapid and thus economic (Madejova´ and Komadel, 2001; McBratney et al., 2006; Viscarra Rossel, 2011; Mulder et al., 2013). An additional benefit of IR is that minerals with poorly crystalline structures (e.g. iron and manganese oxides) can be easily identified from their prominent absorption features, enabling their quantities to be better predicted (Viscarra Rossel et al., 2009). IR spectroscopy is a non-destructive technique that interrogates characteristic molecular bond vibrations that occur in the infrared region of the electromagnetic spectrum. The implementation of Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy for soils analysis in the visible (VIS), near-infrared (NIR) and mid-infrared (MIR), as summarized by Soriano-Disla et al. (2014), has grown rapidly leading to national (Hicks et al., 2015) and global spectral libraries being developed (Viscarra Rossel, 2009). Authors including Bellon-Maurel and McBratney (2011), Chang et al. (2001), Janik et al. (1995, 1998, 2007), Janik and Skjemstad (1995), McBratney et al. (2006), Reeves III (2010), Viscarra Rossel et al. (2006), Viscarra Rossel and McBratney (2008), have published on the application of spectroscopy for soil property determination.

1.2. Prediction of clay minerals using IR (VIS, NIR and MIR)

Few IR studies have quantitatively predicted the mineral phases of soil. Janik et al. (1995) found general correspondence between MIR and qualitative XRD mineral estimates from surface samples that were ground to <200 μm. Viscarra Rossel et al. (2009) using VIS-NIR reflectance spectra processed using continuum removal techniques, and Clark and Roush (1984) also achieved good agreement with XRD phase estimates from samples ground to <50 μm. Yitagesu et al. (2011) using continuum removed spectra for the 3–5 and 8–14 μm wavelength region for <2 μm achieved useful results for quantifying clay minerals from spectrally distinct bands. Malone et al. (2014a) applied a shape-fitting algorithm to estimate clay mineral abundance using mineral reference spectra and diagnostic wavelengths prior to digital soil mapping. Both Janik et al. (1995) and Viscarra Rossel et al. (2009) used whole soil samples in qualitative XRD analysis; but overall, there has been little research on the prediction of mineral composition for whole soil or separated fractions (e.g. clay) using DRIFT spectroscopy. Furthermore, there is little published information on the application of MIR spectroscopy to quantitatively predict major phyllosilicate minerals including kaolinite, illite and smectite.

1.3. Mapping of clay minerals

Viscarra Rossel (2011) highlights a global absence of soil mineralogy maps that would benefit assessments of soil functions supporting ecosystems services. Mineralogical maps, based upon soil association mapping for England and Wales and results from samples characterized for soil clay mineralogy at Rothamsted (now Rothamsted Research), have been derived for Great Britain (Loveland et al., 1999), and recent application of VIS and NIR spectroscopy using Digital Soil Mapping (DSM; McBratney et al., 2003) approaches have delivered the first digital maps of soil mineral distribution at national scales (Viscarra Rossel et al., 2010; Viscarra Rossel, 2011) and regional scales (Mulder et al., 2013).

The occurrence of clay minerals and their relative abundance are attributed to the five genetic factors of soil formation described by Jenny (1941): climate, relief, parent material, living organisms and time. These soil forming factors are primary influences on soil and the association of clay mineralogy with other properties, e.g. structure, cation exchange and water characteristics. For clay mineralogy: climate (current and past) affects weathering rate, erosion and deposition of soil; relief often produces localized leaching and weathering effect through interaction with hydrological regimes; parent material provides the host lithology from which primary minerals are inherited, with the weathering sequence acting on it to produce secondary clay minerals; living organisms contribute to dissolution of primary and secondary silicates (Jackson, 1957), the production of biomass and ground cover that shelters soil from erosional events; and time influences all the aforementioned soil forming processes. These factors and processes form a pedogenic framework that can be applied to prediction of the occurrence of clay minerals based on environmental correlation principles (McKenzie and Ryan, 1999).

This paper presents an approach to quantify clay mineral abundance using quantitative XRD analysis with MIR spectroscopy to formulate predictive models. This was implemented using an MIR spectral library, linked to georeferenced soil sites, to map the spatial occurrence and quantity of clay minerals (kaolinite, illite and smectite) in western Victoria, Australia. Spatial covariates used to derive maps according to GlobalSoilMap specifications (Arrouays et al., 2014) are appraised for their connections with clay mineral distribution and relationship to soil forming factors.

2. Methods

2.1. Study area

The study area of 135,000 km² (western Victoria, Australia) is characterized by a Mediterranean climate with mean annual rainfall varying between <300 mm in the north and over 2000 mm in the south. Landscapes are diverse, reflecting their geomorphic origins, from marine shoreline deposition, structural faulting and uplift, lacustrine and alluvial deposition, widespread aeolian accession of calcareous loess, periodic volcanic eruption and drainage displacement. The geomorphology has been mapped using a hierarchical classification of landforms and landscapes, known as the Victorian Geomorphology Framework (VGF) (Rees et al., 2010) with five tier-one (Fig. 1) and twenty tier-two units. The tier-one divisions (North Western Dunefields and Plains, Northern Riverine Plains, Western Uplands, Western Plains and Southern Uplands) serve as a spatial system to classify areas with common processes and land types while simplifying the immense range of geological, landform, climate, soils and vegetation variation encountered (Rees, 2000). Comprising a range of sedimentary, igneous and metamorphic source lithologies, soil types are dominated by calcareous uniform to gradational profiles (Northcote, 1979) or Calcarosols, (Isbell, 2002) in the north to texture contrast soils (Chromosols, Sodosols and Kurosols), uniform clays (Vertosols) and sands (Podosols and Tenosols) in the south. Primary agricultural industries include wool, red meat (lamb and beef) and dairy, and extensive cereal and pulse production across the northern plains that continue to extend further south into traditional pasture-based farming systems in response to drying conditions of the past two decades.

2.2. Soil sites

Soil samples used for MIR spectroscopy were sourced from the Victorian Soil Archive (VSA) (Johnstone et al., 2010) and are georeferenced to sites in the Victorian Soil Information System (VSIS). In total, 2795 sites (11,532 samples) from soil and land surveys of different scales undertaken during the last 80 years by various state and federal government agencies were used (Fig. 1). Samples with associated clay mineralogy predictions from MIR calibration models for kaolinite, smectite and illite (described in Section 2.5) were harmonized to the