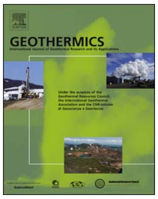
Geothermics 73 (2018) 74–90

Contents lists available at ScienceDirect

Geothermics

journal homepage: www.elsevier.com/locate/geothermics



Short-wave infrared (SWIR) reflectance spectrometric characterisation of clays from geothermal systems of the Taupō Volcanic Zone, New Zealand

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ARTICLE INFO

Keywords:
Reflectance spectrometry
Short-wave infrared (SWIR)
X-ray diffraction (XRD)
Smectite
Mixed-layered illite-smectite
Illite
Approximate mineral compositions
Geothermal

ABSTRACT

Many hydrothermal minerals including clays show zoned distributions in geothermal systems that are useful for inferring formation temperatures, fluid composition and the geohydrologic structure (i.e. upflow, outflow, influx zones) of the geothermal reservoir at the time these minerals formed. This study investigates the use of short-wave infrared (SWIR) reflectance spectroscopy to identify clay minerals in geothermal systems of the Taupō Volcanic Zone (TVZ). The study also recognises and documents that volcanic glass, a common constituent in unaltered and weakly altered volcanic rocks and reworked equivalents, and amorphous silica also have a spectral signature that overlap with some clay minerals (i.e. smectite). The spectral distinctions between smectite, mixed-layered illite-smectite and illite have been determined by calibrations of the calculated SWIR H_2O/Al-OH depth ratio against clay-separate X-ray diffraction (XRD) mineral identification and interlayering quantification. In general, a hull quotient corrected H_2O/Al-OH depth ratio of < 0.76 and > 0.96 broadly correspond to smectite and illite, respectively; however, there is overlap. In the case of mixed-layered illite-smectite it is not possible to quantify the amount of interlayering apart from making a generalisation that it is either smectite-rich or illite-rich. Care needs to be taken when evaluating the H_2O/Al-OH depth ratio since it can be perturbed by spectrally overlapping kaolinite, volcanic glass or silica. Nonetheless, in the case examples illustrated here for four geothermal wells, the H_2O/Al-OH depth ratio value was successfully used to determine clay rank that closely parallels those determined by clay-separate XRD analyses.

1. Introduction

Portable reflectance spectrometers that use short-wave infrared (SWIR) and visible/near-infrared (VNIR) electromagnetic radiation are useful for the rapid identification of many hydrothermal alteration minerals (Clark et al., 1990; Thompson et al., 1999) and are widely used for this purpose in mineral exploration (e.g. Herrmann et al., 2001; Ducart et al., 2006; Harraden et al., 2013, Swayze et al., 2014; Calvin and Pace, 2016; Wang et al., 2017) and to a lesser extent for the investigation of geothermal systems (Yang et al., 2000, 2001; Mauriohooho et al., 2014, Simpson et al., 2015; Calvin and Pace, 2016). Their portability allows for use in the field, at the drilling site, core shed or laboratory. Analyses are non-destructive, can be made on various sample types (i.e. rock outcrops, soils, drill core or chips/cuttings, or powders/pulps), and require minimal sample preparation; they simply need to be clean and dry (Thompson et al., 1999). Analyses can be acquired in as little as five seconds per sample (Chang and Yang, 2013), allowing for quick and rapid collection of a large dataset.

Reflectance spectrometry can be used to identify many minerals and mineral groups with molecular (OH, H_2O, CO_3, and NH_4) or cation-hydroxyl bonds (Al-OH, Fe-OH, and Mg-OH) and include phyllosilicates (e.g. kaolinite, montmorillonite, illite, chlorite, micas), sorosilicates (e.g. epidote), inosilicates (e.g. actinolite), carbonates (e.g. calcite, ankerite, and siderite), sulfates (e.g. alunite, jarosite, and gypsum), as well as ammonium-bearing minerals (e.g. NH_4-illite/tobelite, NH_4-feldspar/buddingtonite and NH_4-alunite). However, it is not possible to detect minerals lacking these molecular or cation-hydroxyl bonds (e.g. quartz, adularia, albite, and anhydrite) (Hunt, 1979; Hunt and Ashley, 1979; Clark et al., 1990; Clark, 1999; Thompson et al., 1999). It is effective in the identification of hydrothermal clay minerals including montmorillonite, illite, kaolinite, dickite, pyrophyllite, plus others, that can only be reliably identified for example using time consuming and relatively expensive clay-separate X-ray diffraction (XRD) analysis. These clay minerals and others can be identified by their characteristic spectral profiles mainly from the SWIR portion of the electromagnetic spectrum and are represented by a series of absorption features of specific wavelength position and absorption depth. Differences in the wavelength positions and either the slope or depth ratios of absorption

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https://doi.org/10.1016/j.geothermics.2018.01.006
Received 16 October 2017; Received in revised form 31 December 2017; Accepted 10 January 2018
0375-6505/

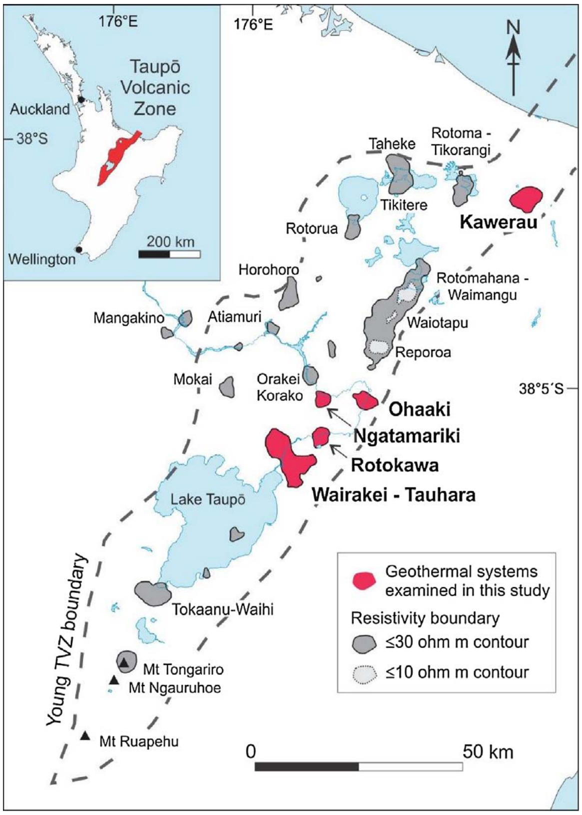

Fig. 1. Simplified map of the Taupō Volcanic Zone (TVZ) showing the general near surface outlines for geothermal systems as approximated by resistivity (Bibby et al., 1995) and the Young TVZ boundary (Wilson et al., 1995). Reflectance spectral analyses were made on drill cuttings from the Kawerau, Ohaaki, Ngatamariki, Rotokawa and Wairakei geothermal systems (highlighted). Inset shows the location of the TVZ within the North Island of New Zealand.

features can be further used to approximate the composition and 'crystallinity' of certain minerals. For example, differences in wavelength position can be used to determine the approximate compositions of Fe- versus Mg-chlorite (McLeod et al., 1987; Doublier et al., 2012), Na- versus K-rich alunite (Thompson et al., 1999; Bishop and Murad, 2005; Chang et al., 2011), as well as the Al, Fe, Mg and inferred K content of illite/muscovite (Post and Noble, 1993; Duke and Lewis, 2010; Yang et al., 2011). Furthermore, the slope or the depth ratio of absorption features can be used to approximate the 'crystallinity' of kaolinite and illite/muscovite (Pontual et al., 1997).

In high temperature (> 225 °C) geothermal systems of the Taupō Volcanic Zone (TVZ), New Zealand (Fig. 1), there is a common zonation of clay minerals with increasing rank into the hottest part of the reservoir (Fig. 2). On the margins and at shallowest depths, the clays present are typically smectite (montmorillonite) and kaolinite. With increasing temperature towards the centre and hottest part of the reservoir, smectite grades into mixed-layered illite-smectite with increasing amounts of interlayered illite until at temperatures greater than ~230 °C, illite dominates (e.g. Browne and Ellis, 1970; Reyes, 1990; Simmons and Browne, 2000). Accordingly, the identification of these clays minerals during the drilling of a geothermal well can be used to infer temperature conditions and fluid composition when these minerals formed. Furthermore, mapping clay distribution both laterally and vertically across numerous wells offer useful insight into the inferred thermal structure of the geothermal reservoir (i.e. zones of fluid upflow, outflow, boiling and mixing), during clay formation and when compared to modern reservoir temperatures can provide information of how the reservoir may have changed over time. Thus, reflectance spectroscopy offers a rapid means to identify clay minerals and their occurrences in addition to other minerals of significance in geothermal systems such as kaolinite, alunite and epidote (Browne and Ellis, 1970; Reyes, 1990).

While the distinction between smectite (montmorillonite) and illite by SWIR is well established (e.g. Clark et al., 1990), the spectral characterisation of mixed-layered illite-smectite, which shares absorption features with both smectite and illite, is not. This paper is in two parts with a focus on the identification of clay minerals by reflectance spectroscopy in reverse circulation drill cuttings for geothermal systems of the Taupō Volcanic Zone (Fig. 1). The first part details the spectral distinctions between smectite, mixed-layered illite-smectite and illite that have overlapping absorption features, but different absorption depth ratios. This is addressed by comparing the depth ratio of the H_2O/Al-OH features (Pontual et al., 1997) against a reference set of cuttings for which the clay mineralogy and amount of interlayering has been determined by clay-separate XRD analysis. The second part details the spectral identification of clays from closely spaced cuttings in four geothermal wells and documents clay types, occurrences, and approximate compositions and what these indicate about the geohydrological structure of the geothermal reservoir.

2. Geological and hydrogeological settings of TVZ geothermal systems

The TVZ represents the continental portion of the largely oceanic Tonga-Kermadec volcanic arc system that, at its southern termination, intersects continental crust in the Bay of Plenty region of the North Island, New Zealand (Fig. 1). Behind the volcanic arc is a region of crustal rift extension that forms the oceanic back-arc rifting Havre Trough, and the continental Taupō Rift Zone (e.g., Cole and Lewis, 1981; Mortimer et al., 2010). Volcanism in the TVZ rifted arc extends ~250 km from White Island in the north to Ruapehu in the south. Both the northern and southern arc segments are dominated by cone-building eruptions of andesite, whereas the central segment is dominated by explosive caldera-forming eruptions of rhyolite that have produced at least 6000 km^3 of magma during the last 1.8 Ma (Cole, 1979; Houghton et al., 1995; Wilson et al., 1995; Wilson and Rowland, 2016).

Associated with this volcanism are some twenty-one high temperature (> 225 °C) geothermal systems, seven of which are utilised for electricity generation (Bibby et al., 1995; Simpson and Bignall, 2016). Most of these geothermal systems are hosted by thick sequences (~0.8 to > 3.2 km) of rhyolitic pyroclastics and lavas intercalated with lacustrine and fluviatile units (Wilson and Rowland, 2016). At two geothermal fields (Rotokawa and Ngatamariki), deep drilling shows andesite (≥1.1 km) can underlie the rhyolites (Browne et al., 1992; Chambefort et al., 2014; McNamara et al., 2016). These volcanic rocks unconformably overly Mesozoic *meta*-sediments (greywacke and argillite) that form the basement rocks of the North Island. At Ngatamariki there is also an intermediate intrusive complex at < 2 km depth (Browne et al., 1992; Chambefort et al., 2014).

The geothermal systems of the TVZ have deep (> 5 km) convection cells of magmatically-heated, modified hot meteoric water (Henley and Ellis, 1983) that at near surface (< 600 m) are typically expressed in 10–40 km^2 fields (Bibby et al., 1995). The dominant geothermal fluids are near-neutral pH chloride waters that in the main reservoir (220°–335 °C and 600–3,200 m depth) have variable amounts of chloride (500–2,200 ppm), dissolved CO_2 (< 100–10,500 ppm) and H_2S (10–245 ppm); in most fluids, CO_2 concentrations exceed those of dissolved salts (Giggenbach, 1995). Above and peripheral to the chloride-water, plume-localised steam-heated acid sulfate condensates/waters form in the vadose zone via the oxidation of H_2S to H_2SO_4 (Schoen et al., 1974), and marginal CO_2-rich steam-heated waters form via condensation of steam and absorption of CO_2 into cool ground waters (Mahon et al., 1980; Hedenquist and Stewart, 1985; Hedenquist, 1990).

Interaction of these hot chloride waters and associated shallow and