

Characterisation of Geothermal Systems Through FTIR Mineral Analysis of Drill Cuttings for Exploration, Appraisal and Development.

P. Joseph Hamilton, Carmen Harris and Sigrid Hillier

Ana-Min

joseph.hamilton@ana-min.com

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ABSTRACT

Fourier Transform Infrared (FTIR) spectroscopy, petrographic observations and X ray diffraction analyses have been used to identify key minerals indicative of hydrothermal alteration and hence geothermal potential in two samples of drill cuttings from an Indonesian geothermal field. Analysis of bulk samples, handpicked particle lithotypes and handpicked minerals together indicate the presence of xonotlite, vaterite, chlorite and epidote. Individual monomineralic grains as small as ~1 mg can be unambiguously identified by FTIR analysis. These hydrothermal minerals together indicate formation from hot aqueous fluids of neutral to alkaline pH and at temperatures greater than about 220-250°C. Hydrothermal alteration minerals that form at higher temperatures such as actinolite, biotite and garnet were sought but not identified from the FTIR analyses. Lower temperature hydrothermal alteration minerals such as smectitic mixed layer clays and water rich zeolites can be identified from their FTIR spectra but none were identified in these two samples. Additionally, minerals that form under low pH conditions such as alunite and pyrophyllite were shown not to be present by FTIR analysis. This confirms that the samples analyzed comprise propylitic assemblages.

Introduction

During the high risk and high cost phases of exploration and appraisal drilling of geothermal prospects it is of immense value to be able to undertake mineral analysis of cuttings in near real time at the well site. Cuttings descriptions by the well site geologist are of value for lithotyping but not adequate for robust distinction of many important minerals. Methods available for well site deployment include X Ray Diffraction (XRD), thin section petrography, scanning electron microscope / energy dispersive X ray spectrometry and Fourier Transform Infrared (FTIR) spectrometry. The FTIR method offers the advantages of using readily portable instrumentation with small footprint, no potential hazardous radiation or chemicals, simple and rapid sample preparation and analysis and robust mineral identification. Pre-drill mineral analysis of legacy cuttings and outcrop samples would further reduce risk and cost.

FTIR analysis is the measurement of frequency and intensity of absorption of mid-infrared light by a

sample. The bonds between atoms vibrate with different modes and different frequencies. Resonance of an interatomic bond vibration with a particular incident infrared frequency leads to absorption of that frequency which is diagnostic of that bond and its host mineral. The mid-range (400 to 4000 cm⁻¹) of infrared frequency (Figure 1) is the most useful for mineral identification as many minerals exhibit vibration modes within this range.

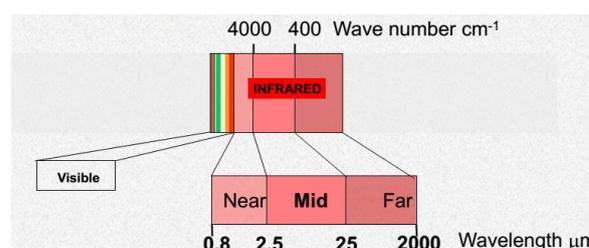


Figure 1: Illustration of mid-range of infrared frequency used for mineral identification

FTIR spectra are displayed as absorbance units against wave number (Figure 2). Absorbance (A) is defined as the natural log of the ratio of the radiant power incident on the sample (I₀) to the power transmitted from the sample (I).

$$A = \log(I_0/I)$$

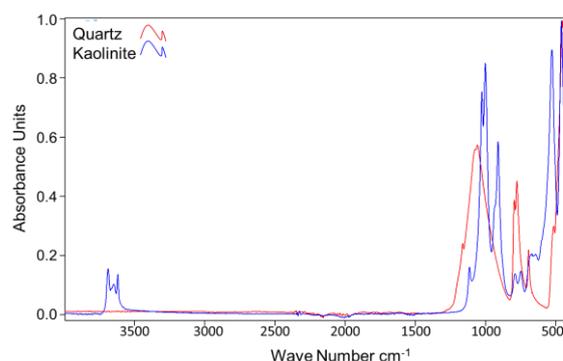


Figure 2: FTIR spectra for kaolinite and quartz.

Methodology

Sample Preparation

Two washed and dried cuttings samples (A and B) from an Indonesian geothermal field containing hydrothermal alteration minerals were provided for analysis. The samples were air dried for approximately 30 minutes to ensure they contained no excess moisture and picked for individual rock types. Each of

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these sub samples was ground to a fine powder in a pestle and mortar.

XRD Analysis of Samples

Two particle types were recognised in abundance in sample A. One is pink, soft and fine grained (AP) and the other (AV) a mottled grey colour and harder

(Figure 3). About 5 gm of each was handpicked and ground to a fine powder to be used for XRD analysis.

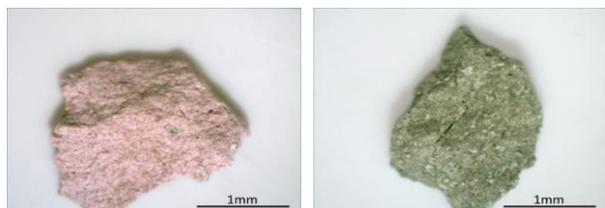


Figure 3: Particle images - AP (left), AV (right).

Each ground sample was pressed into a back-packed sample holder to minimize preferred orientation of the particles. Powder X-ray diffraction (XRD) was used to analyse the samples and a combination of matrix flushing and reference intensity ratio (RIR) derived constants were used in the semi-quantification of the minerals identified in the samples. The XRD traces were collected under the instrument conditions given in Table 1.

Table 1: Analytical details for X Ray Diffraction Analysis

XRD Instrument	Panalytical Empyrean
Radiation	Cu K α 1.5406
Generator	45 kV 40 mA
Angular Range	5° to 65° 2 θ
Time/Step	145 s
Step Size	0.0131° 2 θ
Divergence Slit	0.5 °
Anti-Scatter Slit	7.5 mm
Slit Type	Fixed
Detector	PIXcel in linear mode
Rotation Speed	60 rpm

FTIR Analysis of Samples

FTIR Analysis of Samples

An approximate 0.5 gm aliquot of each powdered sample was analysed utilising a Bruker Alpha Infrared Spectrometer through a spectral range of 380-4000 cm⁻¹. The absorbance over this range provided spectra with a resolution of 4 cm⁻¹. The resultant spectral profiles were then examined to identify minerals present that are indicative of hydrothermal alteration.

RESULTS

X Ray Diffraction Analyses (XRD)

Results of the XRD analysis of two particle types from sample A are given in Table 2 and the associated diffractograms shown in Figure 4 and Figure 5. Of note are the occurrences of zeolites, xonotlite, and

tobermorite, and vaterite. Xonotlite, Ca₆Si₆O₁₇(OH)₂, comprises almost the entirety of AP and occurs at ~12 % together with ~ 3 % tobermorite, Ca₅Si₆O₁₆(OH)₂·4H₂O, in sample AV.

Table 2: Semi quantitative XRD Results for handpicked particles from sample A

Mineral ID	wt %	
	AP	AV
Serpentine	0	4
Tobermorite	0	3
Xonotlite	<100	12
Alpha quartz	trace	53
Calcite	trace	5
Vaterite	0	23

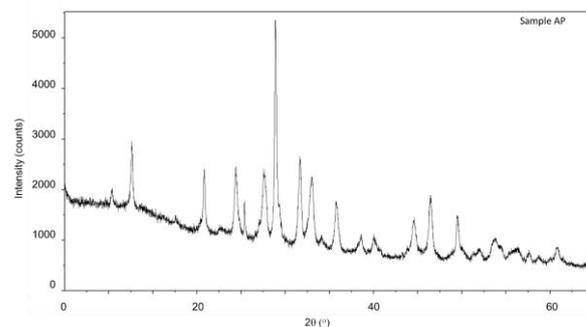


Figure 4: X Ray Diffractogram for particle type AP from sample A.

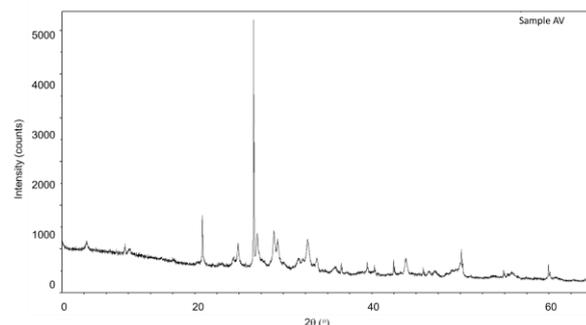


Figure 5: X Ray Diffractogram for particle type AV from sample A

FTIR Analyses

Sample A

FTIR spectra for the particle types AP and AV are shown in Figures 6 and 7. The spectrum for AP is very

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similar to a published spectrum of xonotlite (Mostafa et al., 2009) and confirms the XRD result indicating this particle type to be almost entirely composed of this mineral. The AV spectrum is consistent with the identification by XRD of the main minerals, namely quartz, vaterite, and xonotlite, and also the minor amount of calcite. The other phases (tobermorite, serpentine) identified by XRD analysis at low abundances in AV could be neither confirmed nor discounted from the FTIR spectrum. The resolution is insufficient to allow identification of the diagnostic peaks for these minerals at low abundances of less than about 5 %. However, the presence of these minor minerals is not inconsistent with the nature of the dominant mineralogy.

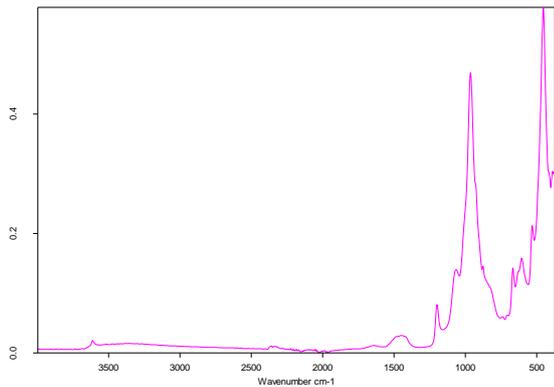


Figure 6: FTIR spectrum for particle type AP.

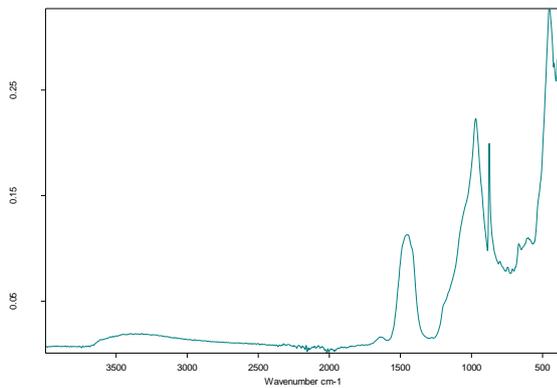


Figure 7: FTIR Spectrum for particle type AV.

Hard, red coloured crystalline particles, illustrated in 8, were also handpicked from sample A for FTIR analysis. Visually these seem to comprise mostly quartz and alkali feldspar. The FTIR spectrum (Figure 9) is consistent with this mineral identification.



Figure 8: Red coloured crystalline particles.

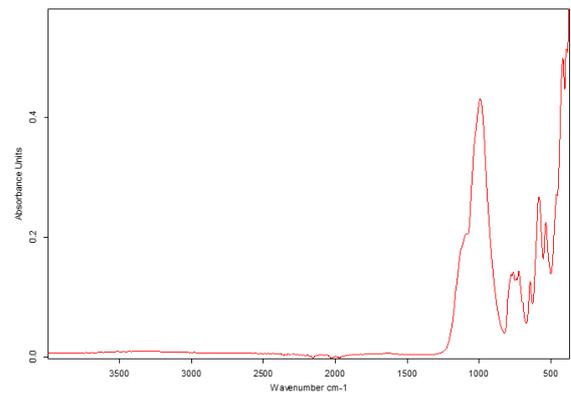


Figure 9: FTIR spectrum of red coloured crystalline particles from sample A.

Also noted in A were some particles (Figure 10) with 0.5 – 1 mm areas of a white, soft, very fine grained mineral. This was sampled in sufficient quantity with a scalpel for a FTIR analysis. The resultant spectrum (Figure 11) closely matches that of kaolinite with some minor features that indicate that illite may also be present.

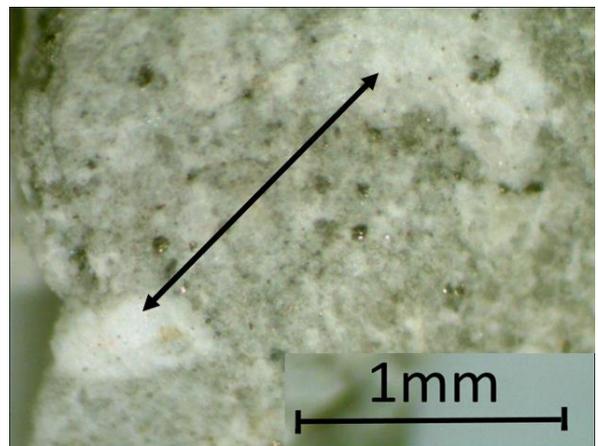


Figure 10: Illustration of areas of white mineral from sample A analysed by FTIR analysis.

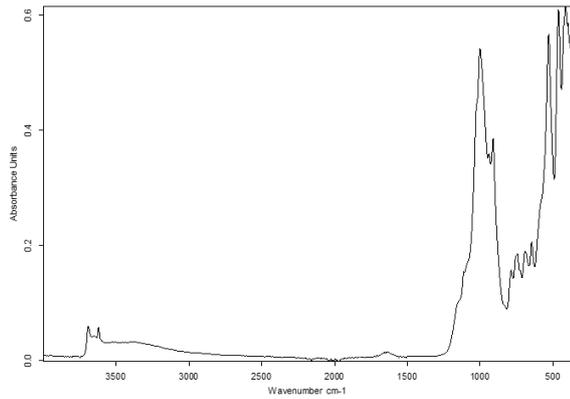


Figure 11: FTIR spectrum of white mineral(s) from sample A illustrated in Figure 8

Sample B

Examination of the FTIR spectrum (Figure 12) for a bulk sample of B indicates the presence of quartz, alkali feldspar, and a clay mineral that is probably chlorite as well as some minor phase(s).

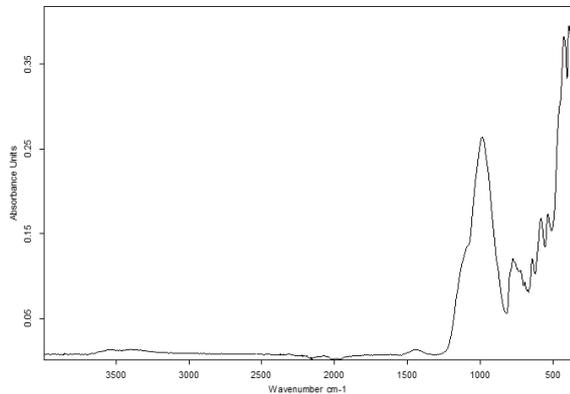


Figure 12: FTIR Spectrum for bulk analysis of sample B.

Some particles of B were observed to have small amounts of fine needle shaped crystals of a yellow green colour tentatively identified as epidote (3). Some particles also have a more abundant dark green, soft and platy mineral identified as chlorite (3).

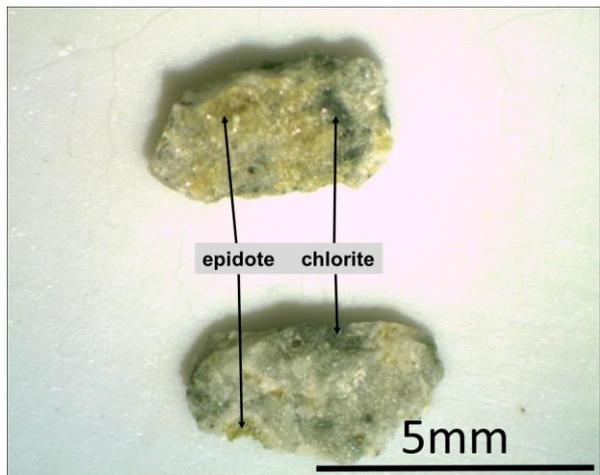


Figure 13: Green minerals in sample B.

Sufficient amounts of these green minerals were obtained with a scalpel and tweezers for FTIR analysis. The spectra obtained match published spectra for epidote (Figure 14) and chlorite (Figure 15) as well as those of our library standards.

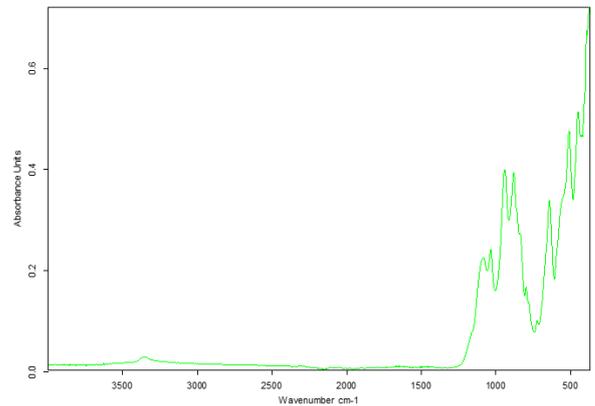


Figure 14: FTIR spectrum of yellowish green mineral identified as epidote from sample B.

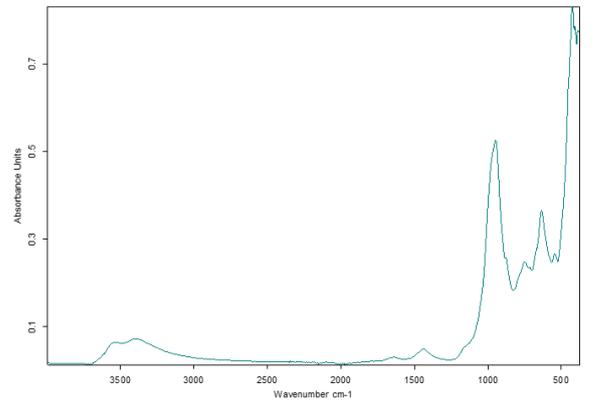


Figure 15: FTIR spectrum of dark green crystals identification as chlorite from sample B.

SUMMARY

With respect to FTIR identification of minerals in drill cuttings that are indicative of hydrothermal alteration and geothermal potential the following minerals were identified:

- Xonotlite and tobermorite. These are both zeolite minerals.
- Vaterite
- Epidote
- Chlorite

Other minerals identified from FTIR spectra include quartz, alkali feldspar, and kaolinite. The latter may be present as a mixed layer illite/kaolinite of low illite content.

In geothermal systems, secondary (hydrothermal alteration) minerals can form and potentially these may indicate the conditions of their formation. Mapping of such minerals in the subsurface can indicate the extent and temperature conditions prevailing in the geothermal reservoir. Figure 16

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below shows the potential geothermometric application of some common hydrothermal minerals.

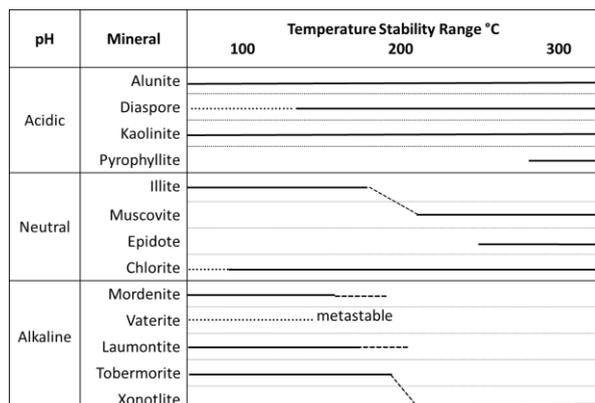


Figure 16: Indicative pH and temperature stability ranges for hydrothermal minerals.

Zeolite minerals are particularly indicative of temperatures of formation with water rich varieties such as tobermorite prevalent at <150-200°C and less water rich varieties such as xonotlite common at hotter levels in the hydrothermal system (Corbett and Leach, 1997). Speakman (1968) documented that at saturated steam pressures tobermorite is unstable relative to xonotlite with but with further increased pressure the decomposition temperature could be raised to about 285°C.

Xonotlite often occurs in association with the hydrothermal alteration that leads to serpentinisation of ultrabasic rocks (Esteban et al., 2003; Kaye, 1953; Smith, 1954). The co-existence of serpentine and xonotlite indicated from the XRD analysis of sub-sample AP is consistent with a similar association for this sample.

Vaterite is a CaCO₃ polymorph stable at one atmosphere pressure at temperatures less than about 15-20°C. Nevertheless, hydrothermal occurrences of vaterite have previously been reported (McConnel, 1955; Bantor et al., 1963). If the vaterite in subsample AV is hydrothermal in origin, it would not have formed by inversion from calcite or aragonite but rather as a metastable precipitate from aqueous solution in the calcite stability field.

Epidote in well crystalline form as in sample B is indicative of temperatures greater than about 220-250°C (Figure 14 and Reyes, 1990).

Chlorite formation may occur over a range of temperatures from upwards of about 100°C but its coexistence with epidote would suggest similar formation temperatures of greater than about 220-250°C (Lagat, 2010).

Hydrothermal minerals indicate subsurface temperature distributions, thermal gradients, cooler vs hotter regions, zones of upwelling and recharge, and permeable zones and barriers.

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