

A MINERAL ANALYSIS WORKFLOW FOR DRILL CUTTINGS AT THE WELLSITE: APPLICATIONS TO GEOTHERMAL RESOURCE EXPLORATION, APPRAISAL AND DEVELOPMENT

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ABSTRACT

Development of a workflow for mineral analysis at the well site has been developed from a comprehensive laboratory work flow for predrill analysis of legacy samples. It uses benchtop Fourier Transform Infrared spectrometry (FTIR) analysis of individual minerals sampled by handpicking and / or with a scalpel, in amounts as small as a few milligrams. Identification of scale minerals and key minerals indicative of the conditions of hydrothermal alteration is made from their FTIR spectra. Where legacy samples are available, the workflow comprises use of other methods of mineral analysis (X ray diffraction, thin section petrography, fluid inclusion geothermometry, scanning electron microscopy/energy dispersive spectrometry) in addition to bench top FTIR analysis. Some comparison of the advantages and disadvantages of some of the methods available are provided. To date, projects have been laboratory based but the well site work flow is now available for geothermal resource application.

Keywords: Minerals, Fourier Transform Infrared Spectroscopy, Hydrothermal Alteration, Scaling.

INTRODUCTION

Mineral analysis of cuttings in near real time at a geothermal drill hole adds much value to the cuttings descriptions by the well site geologist for lithotyping and can aid in the reduction of risk and cost. Recognition of, and correlation of, mineral zones can provide subsurface temperature distributions for resource assessment, locate recharge and discharge zones and define the size of the resource. Robust identification of important minerals can be undertaken at the well site using X Ray Diffraction (XRD), thin section petrography, scanning electron microscope / energy dispersive X ray spectrometry (SEM/EDS) or Fourier Transform Infrared (FTIR) spectrometry. The first well site mineral analysis work flow was developed for rapid identification of scale minerals. Of the well

site methods available, the FTIR method was chosen as it offers the advantages of using readily portable instrumentation with small footprint, no potentially hazardous radiation or chemicals, simple and rapid sample preparation and analysis and robust mineral identification. A comprehensive, laboratory based, mineral analysis work flow was then developed for legacy cuttings and outcrop samples. The ensuing results provide useful contextual data and validation for well site sample analysis. The FTIR method was again selected as being the most appropriate.

METHODS

Some of the various laboratory based and well site deployable methods of mineral analysis are described below. The work flow for laboratory based analysis of legacy samples is illustrated in Figure 1.

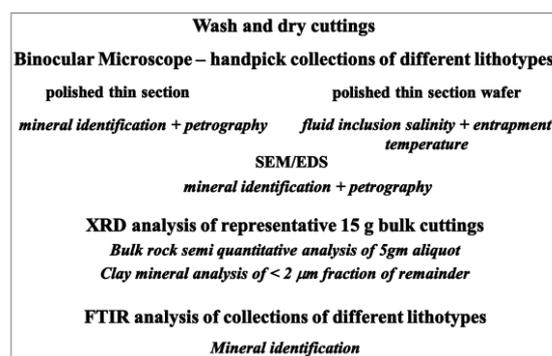


Figure 1: The workflow for laboratory based mineral analysis of washed and dried legacy cuttings.

Binocular Microscopy

A binocular microscope with variable magnification from 5 to 50 times, illumination from above and below and a trinocular attached camera is adequate for the purposes of handpicking and image capture (e.g. Figure 2). It is commonly used for well site deployment for cuttings descriptions and lithotyping. Sampling of individual mineral grains from cuttings particles is

achieved with a scalpel and/ tweezers under binocular microscope observation.

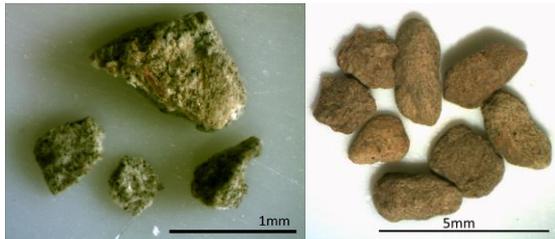


Figure 2: Images of handpicked cuttings particles.

Thin Section Petrography

Steiger et al. (2015) provide a well-documented case to support the use of rapid thin section production and description at geothermal well sites. Equipment for sample impregnation with resin, cutting and polishing are required. Also, an experienced mineralogist is essential for use of the polarizing light microscope for robust mineral identification and petrography (Figure 3). These authors have used thin section analysis in tandem with drilling and logging operations to address real time issues that are dependent to some extent on mineralogy. These issues may include positioning of casing shoes, drilling parameters such as speed and weight on bit, log interpretation and recognition of significant changes in porosity and permeability. Better decision making and risk reduction are tangible benefits even when smaller sampling intervals and slower drilling speeds are required for the optimal siting of casing points.

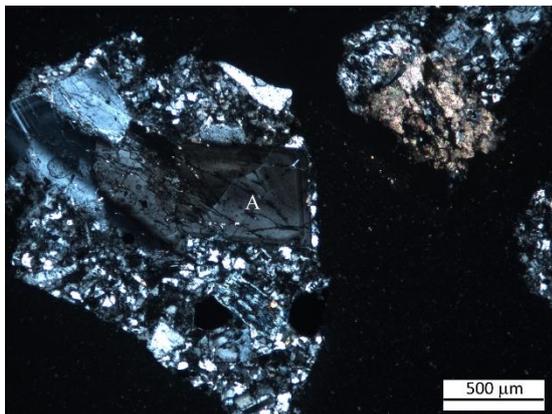


Figure 3: Thin section crossed polarized light photomicrograph of cuttings particles showing rhombic grain of hydrothermal adularia (A).

X Ray Diffraction Analysis

When a monochromatic X ray beam is incident with a crystalline lattice, parallel lattice planes of atoms cause diffraction under certain conditions described by Bragg's Law (equation 1). This relates the incident wavelength to the angle of

incidence and the lattice spacing in a crystalline sample

$$n\lambda = 2d\sin\theta \quad \text{equation 1}$$

where n = an integer, λ = x ray wavelength, d = lattice spacing and θ = the incident angle of the X ray beam.

Diffacted peak positions, expressed as 2θ , and their relative intensities are plotted as a diffractogram (e.g. Figure 4). Because the sample is analyzed as a powder, the lattice planes are in random orientations and all are detected by scanning through a wide range of incident angles. The lattice spacings can be determined from the peak positions and provide a diagnostic pattern used for mineral identification (Bish and Post, 1989; Poppe et al., 2001).

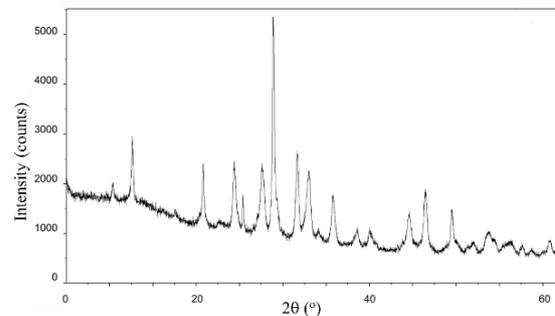


Figure 4: X ray diffractogram from a hydrothermal vein sample comprised mainly of the zeolite mineral xonotlite.

Sample preparation for well site XRD analysis is simple, rapid and occupies little space. It requires grinding, using a mortar and pestle, of about 5 gm of sample to pass through a 325 mesh sieve (less than 45 μm). Fine grain size is necessary for good signal-to noise ratio, ensuring sufficient numbers of particles contribute to diffraction and minimizing preferred orientation. Excessive grinding is avoided as this may generate amorphous material and broaden some diffraction peaks through lattice distortion.

Well site XRD analysis is limited to the provision of semi quantitative bulk rock results. Clay minerals are often underestimated in these results as many clays are poorly crystalline with consequently diminished diffraction peak intensities. Additionally, because clay minerals have layered structures diffraction is mainly from the basal layers, but this is diminished in a bulk rock sample with randomly oriented grains. Robust clay mineral XRD analysis can be undertaken on an oriented sample of a separated $<2\mu\text{m}$ size fraction. If carbonates, organic matter or iron oxy hydroxides are present their removal by chemical treatments is undertaken (Jackson, 1958).

The oriented clay fraction is then subjected to a number of treatments (cation saturation, e.g. Mg; glycollation; heating to various temperatures) each with a subsequent diffractogram to document diagnostic structural changes evident in peak shifts. The time consuming nature of clay mineral XRD analysis renders it impractical for well site application.

SEM/EDS

Over the past ten years scanning electron microscopes with energy dispersive X-ray detectors (SEM/EDS) have become commercially available for rig site deployment specifically aimed at achieving near real time, automated analysis of cuttings (Hamilton and Ly, 2012). Samples are placed in resin blocks which, once set, are cut, polished and carbon coated prior to automated analysis.

Figure 5 below illustrates the various reactions that result from electron beam incidence on a mineral surface.

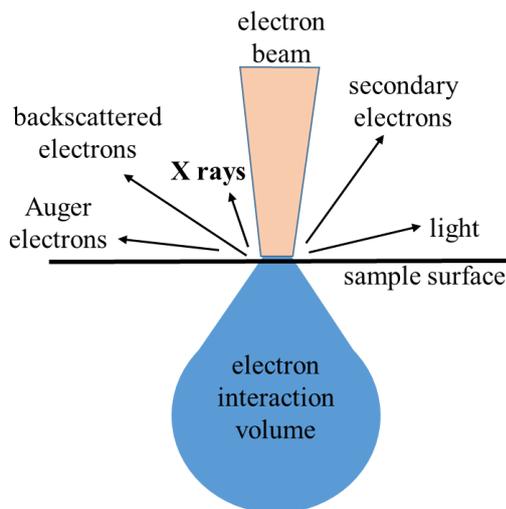


Figure 5: Interactions of an electron beam incident on a mineral surface.

SEM/EDS instruments make use of the resultant X-ray spectrum for mineral identification at each analysis point. Example spectra for illite and K feldspar, both K-bearing aluminosilicate minerals, are shown in Figure 6. They are resolvably different.

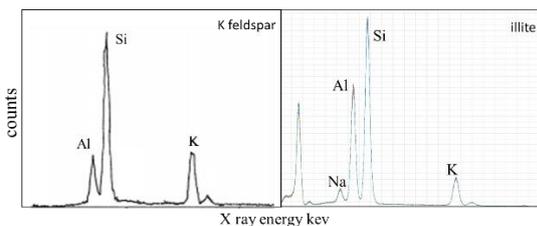


Figure 5: Comparison of X ray spectra for K feldspar and illite.

The X rays are generated at the point of incidence of the and from within an electron interaction volume

+ boundary phases – fine grained rocks

Sample preparation and analysis at point spacings of 20-30 µm takes about one hour. Lengthier laboratory analyses typically use analytical point spacings of 2-10 µm and yield mineral maps of cuttings particles with sufficient resolution to provide good textural information (Figure 5).

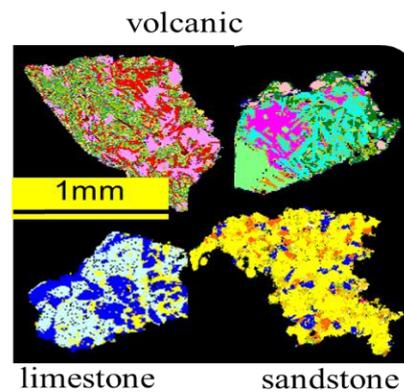


Figure 6: Minerals maps from automated SEM/EDS analysis of cuttings articles.

FTIR Spectroscopy

Bonds between atoms and groups of atoms vibrate in different ways with different frequencies. Resonance of a bond vibration with a particular incident infrared frequency leads to absorption of that frequency which is diagnostic of that bond and its host mineral. FTIR analysis is the measurement of frequency and intensity of absorption of mid-infrared light by a sample. The mid-range (400 to 4000 cm⁻¹) of infrared frequency (Figure 7) is the most useful for mineral identification as many minerals exhibit vibration modes within this range.

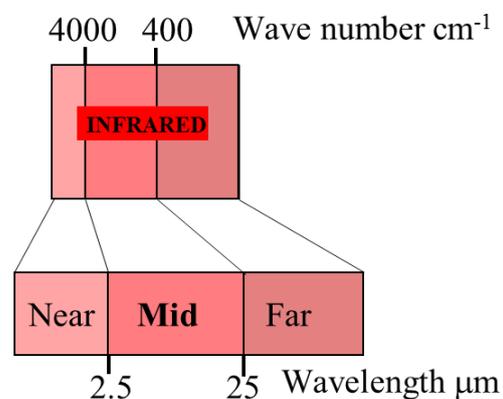


Figure 7: Illustration of mid-range of infrared frequency used for mineral identification.

An FTIR spectrum is displayed as a plot of absorbance units against wave number. Absorbance (A) is defined as the natural log of the ratio of the radiant power incident on the sample (I_0) to the power transmitted from the sample (I).

$$A = \log(I_0/I) \quad \text{equation 2}$$

By way of example the spectra for quartz and calcite are shown in Figure 8.

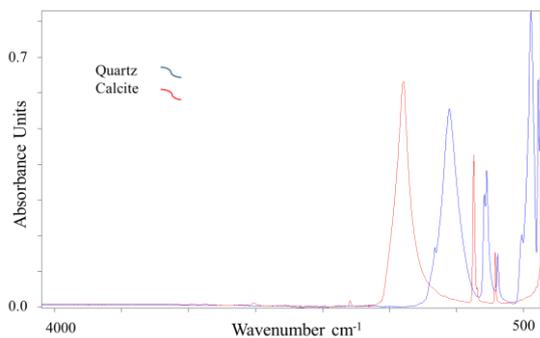


Figure 8: FTIR spectra for quartz and calcite

Sample preparation and analysis

Cuttings samples are washed with de-ionised water, oven dried at 90°C and then handpicked for collections of particles of individual rock types. Samples are then ground to a fine powder, a portion of which is placed on the analysis plate of the FTIR spectrometer. The FTIR spectrometer has an attenuated total reflection (ATR) accessory which operates as shown in Figure 9. An infrared beam enters a crystal with high refractive index and undergoes a number of total internal reflections creating an evanescent wave that extends for a few microns out of the crystal into the powdered sample with which it is in contact. The absorbance of the sample results in attenuation of the evanescent wave which returns to the infrared beam which passes out of the crystal and into a detector.

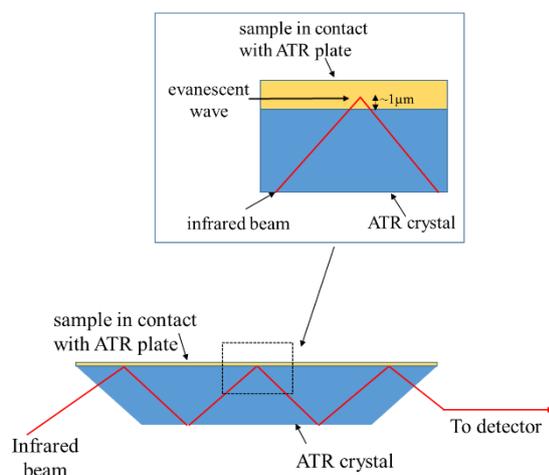


Figure 9: Mechanism of attenuated total reflection.

Occasionally it may be necessary to attempt some separation or concentration of a particular mineral in a collection of multi-mineralic particles. This can happen when such a mineral has low absorbance and is present in low abundance or a mineral is known to be present from the spectrum but cannot be matched to a library mineral. An example is provided from the analysis of a collection of carbonate bearing particles (Figure 10) from an argillic zone in an Indonesian geothermal field. A sub sample of these particles was subjected to treatment with dilute HCl until effervescence ceased and removal of any fine particles generated.



Figure 10: Particles before and after acid washing.

The spectrum for the untreated particles (Figure 11) allowed identification of calcite and a small amount of a clay mineral possibly a mixed layer chlorite-smectite. Another phase is present but could not be identified from the spectral library. The acid treatment of the particles allowed this phase to be concentrated. Its spectrum closely matches that of opaline silica except for the absorbance peak at 945 cm^{-1} indicated on Figure 11. This peak arises from vibrations of silanol (Si-OH) bonds and is characteristic of opaline silica originating from diatom frustules.

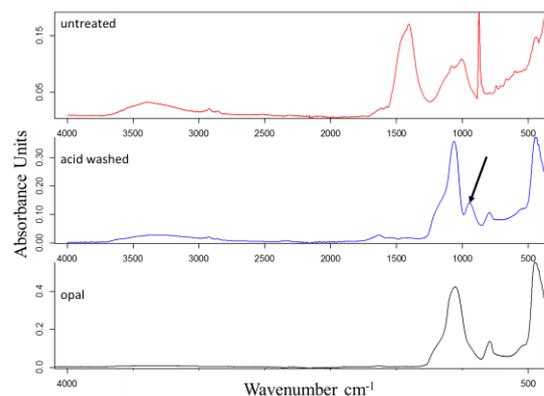


Figure 11. FTIR spectra for untreated particles, acid washed particles and standard opaline silica.

APPLICATIONS

Scale Minerals

Changes in pressure and temperature along the wells, in pipework or in the surface heat exchanger may result in scaling in turn leading to reductions of injectivity and transmissivity. Mineral deposition is caused by changes in solubility that

accompany cooling and boiling of the geothermal water. Application of preventative and remedial techniques to address this issue requires identification of the mineral or minerals present in the scaling. Some of the scale minerals recorded in the literature (e.g. Arnórsson, 1981; Browne et al., 1989; Elguedri, 1999; Gallup, 1997; Gunnarsson and Arnórsson, 2005) are listed in Table 1. With the FTIR technique scale minerals can be identified in less than a minute. The scale mineral spectrum is automatically compared to a spectral library for more than 100 minerals resulting in correct identification of all minerals of interest.

Table 1: Scale minerals.

Mineral	Formula
calcite	CaCO_3
vaterite	CaCO_3
aragonite	CaCO_3
siderite	FeCO_3
silica different forms	SiO_2
anhydrite	CaSO_4
barite	BaSO_4
celestine	SrSO_4
talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
serpentine	$(\text{Mg, Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$
prehnite	$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$
wairakite	$\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 16\text{H}_2\text{O}$
epidote	$\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})$

Chemically similar scale minerals such as the sulphates anhydrite, barite and celestine have similar but resolvably different FTIR spectra (Figure 10).

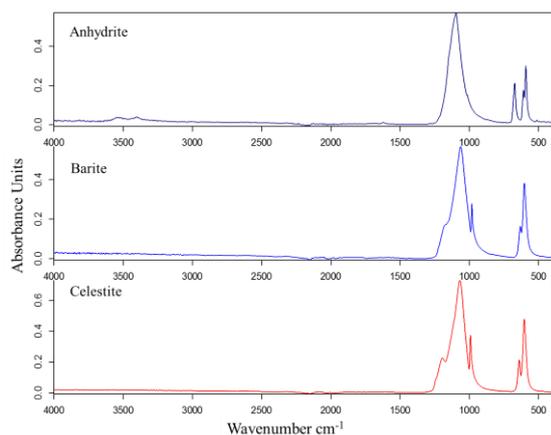


Figure 10: FTIR spectra for three sulphate scale minerals.

Shut in wells are also prone to mineral scaling Browne et al. (1989) document such an example from rock ejecta produced upon opening of a shut in geothermal well in New Zealand. Rock chips comprised wairakite, prehnite and epidote and some had surface features consistent with having formed inside the casing and liner slots of the well during the shut in period. These are minerals that

are readily and automatically identifiable from their distinct FTIR spectra (Figure 11).

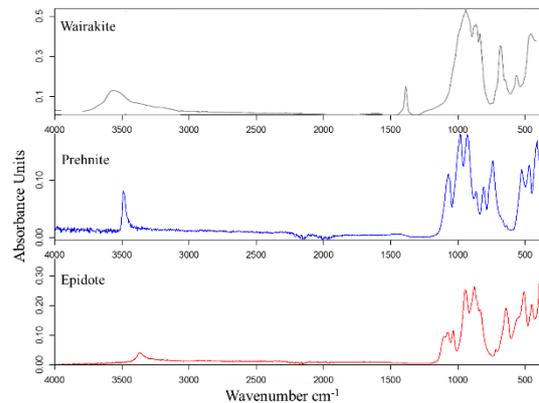


Figure 11: FTIR spectra for some minerals that may cause scaling in shut wells.

Mapping Subsurface Mineral Zones

Exploration and appraisal drilling of geothermal prospects are necessarily high risk and high cost activities. Acquisition in a timely and inexpensive manner of information that relates to the size of the geothermal resource is of immense value. Knowledge at the well site of the distribution with depth, and between wells, of key minerals indicative of down hole temperatures allows rapid identification of recharge and discharge zones, thermal gradients and permeability barriers. For this purpose, the FTIR method should be the one of choice as it 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.

A key development with the FTIR application is the incorporation into the well site workflow of the ability to analyse individual mineral grains amounting no more than a few milligrams. Grains such as illustrated in Figure 12 contain minerals of potential interest and can be readily and rapidly identified from their FTIR spectra. Mineral veins such as the anhydrite illustrated in Figure 12 are testament to fluid flow events and often provide minerals useful for other analyses (e.g. stable isotopes and fluid inclusions) subsequent to drilling. Mineral vein samples and monomineralic grains such as the muscovite grain in Figure 12 can be placed directly on the ATR crystal for analysis. Vug lining crystals such as the epidote illustrated in Figure 12 and soft minerals such as clay mineral pseudomorphs can be scrapped with a scalpel directly onto the ATR crystal for analysis. The intensity of absorbance is often diminished with such small sample volumes but with monomineralic samples the spectra produced still provide robust identifications.

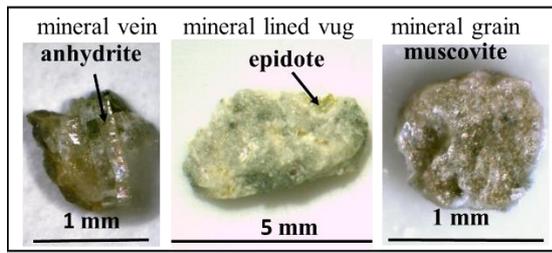


Figure 12: Images of particles suitable for single mineral identification.

At temperatures greater than about 250°C albite, adularia, epidote, chlorite, calcite, hydrogrossular, muscovite and water-poor zeolites (e.g. xonotlite, analcime) are common. At lower temperatures water rich zeolites (e.g. wairakite, mordenite) and clay minerals (illite, smectite, halloysite) are common. All of these can be identified from small volumes of sample. Some are diagnostic of minimum temperatures of formation and indicative of the fluid chemistry from which they formed (Legat, 2010; Reyes, 1990).

In a pilot study of two cuttings samples from a geothermal field in Indonesia (Hamilton et al., 2016) the minerals identified included kaolinite, epidote, chlorite, vaterite, tobermorite and xonotlite. Figure 13 illustrates the interpretation of the observed mineralogy. Most of these minerals form under neutral to alkaline conditions. Epidote forms at temperatures greater than about 220°C. Coexistence of a water poor zeolite (xonotlite) with a more water rich precursor zeolite (tobermorite) is consistent with a transition between the two at about 220 - 240°C.

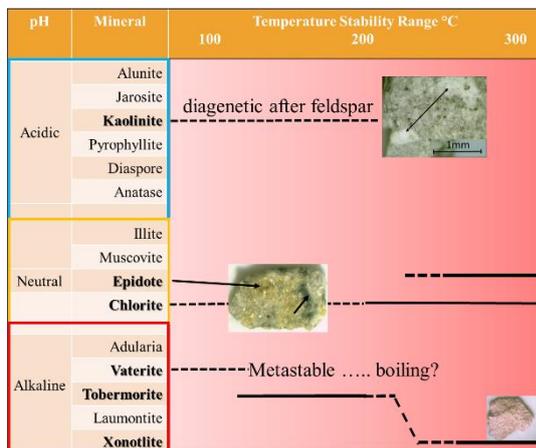


Figure 13: Indications of hydrothermal fluid composition and temperature from identified minerals.

SUMMARY

The FTIR method of mineral analysis provides a relatively simple, rapid and low cost reconnaissance tool to both provide near real time information to guide decision making and to direct later and more detailed studies.

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