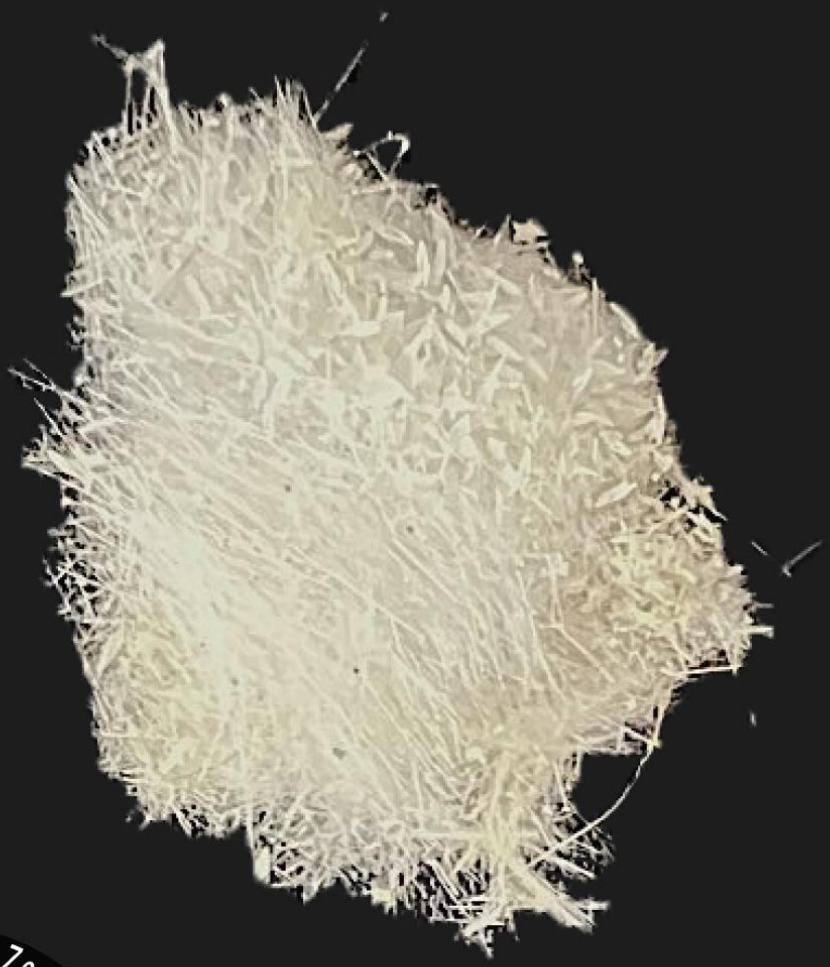
Identification, Sampling and Analyses of Erionite Rock Material
A Technical Note



Erionite in New Zealand
Assessing and Managing Risk

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Purpose

The purpose of this technical note is to provide information on how to identify, sample and analyse rock material, which may contain fibrous erionite. This document covers what is erionite, the occurrence of erionite in rock material and the different analytical techniques used to identify fibrous erionite. The health and safety protocols associated with sampling and analysis of erionite are covered elsewhere in 'Erionite Tikanga Akuaku / Health and Safety Protocols'.

Erionite

Erionite (CAS Registry No.: 66733-21-9) is a mineral that belongs to a group of hydrated aluminosilicate minerals called zeolites that occurs in a variety of elongated shapes. It's ideal chemical formula is: $(Na_2, K_2, Ca, Mg)_{4.5}Al_9Si_{27}O_{72}•27H_2O$).

Erionite is one of many zeolites that may display a fibrous and/or asbestiform (fibrous zeolites) crystal habit like mordenite and offretite. Erionite may also display crystal habits other than fibrous like other relevant zeolite species (e.g. clinoptilolite and heulandite).

Erionite Occurrence

Zeolites, including erionite, are mainly found in altered volcanic rocks, including tuffs, ash and vesicular basalt. Erionite forms when aluminosilicates are dissolved by hydrothermal fluids percolation and recrystallised into erionite within pore spaces of rocks.

Erionite and fibrous zeolites have been observed in New Zealand to occur in vuggs (cavities inside rocks), as veins and disseminated in ash layers, See Figure 1.

Rock material that contains zeolites is often cemented or zeolitised and harder than the surrounding material. In tuff / sedimentary layers zeolites are often observed at the basal contact.

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The majority of erionite crystals are very small and are difficult to identify even with a microscope. The crystals can occur individually, or as "bundles", "radiating clusters", or as a "woolly mass".

A global review of the geological occurrence and character of erionite has recently been published by the authors of this guidance note (Patel et al., 2022)

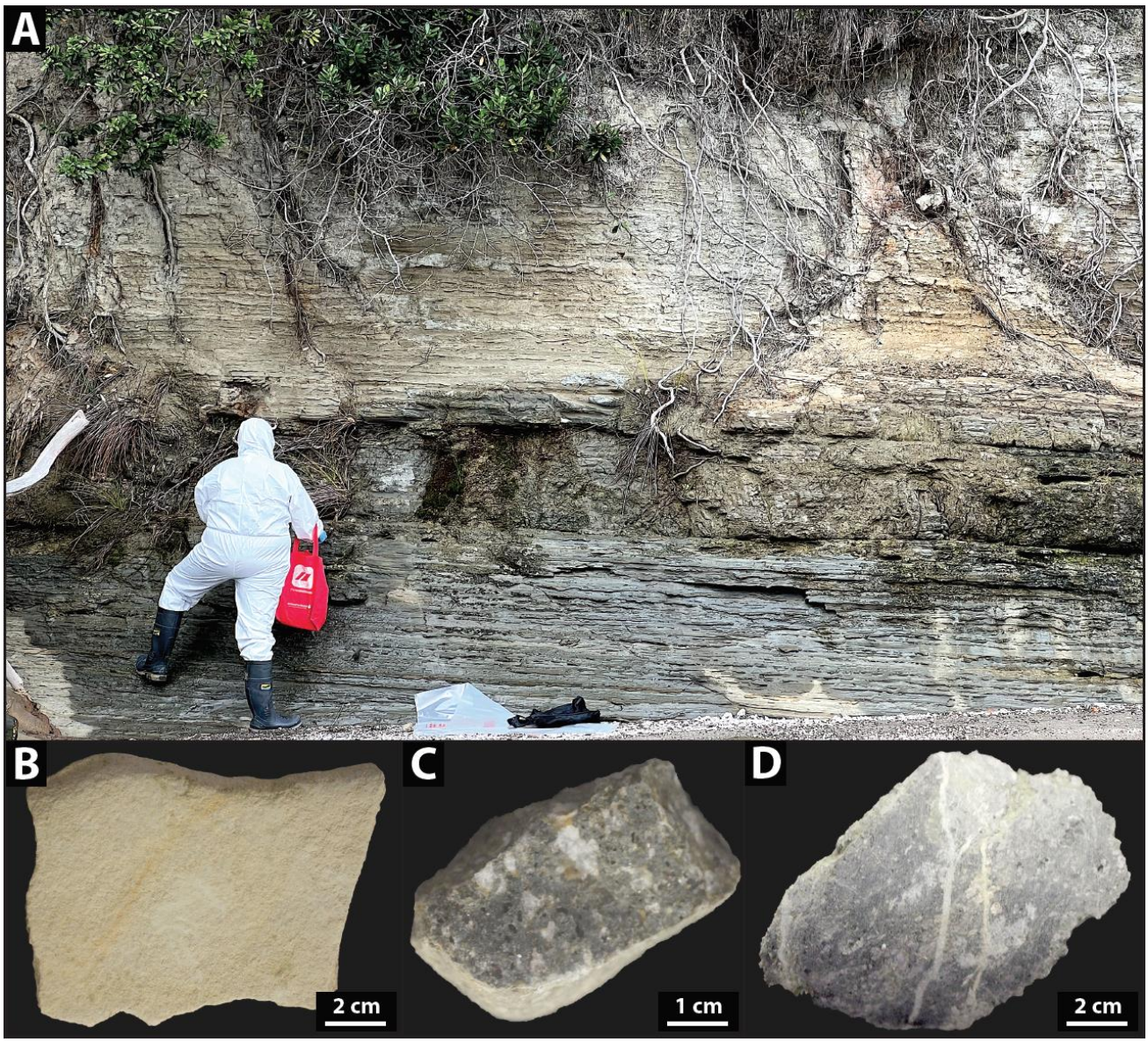

Figure 1: Occurrence of erionite, A) Timber Bay Formation, Puketotara peninsula, Kaipara area. Showing cemented layer at base of ash unit. B) Cemented ash layer that contains disseminated erionite, Timber Bay Formation. Erionite has been detected at 75% in this material. C) Erionite (white) in vesicles within basalt, Waitakere. D) Fibrous zeolites veins (white) in rhyolite, Coromandel Peninsula.

Erionite Sampling

Due to the various ways erionite may occur in rock material, as described above, sampling should be carried out to collect all material that potentially may contain fibrous erionite.

Where zeolites are observed in veins or vuggs these areas should be preferentially sampled.

Where zeolites are potentially disseminated within rock material that is outcropping, channel samples that include fresh (unweathered) material should be sampled perpendicular to bedding. See Figure 2A.

Where zeolites are potentially disseminated within core material, sampling cuttings or a continuous linear layer should be taken down the length of the core intercept. See Figure 2B.

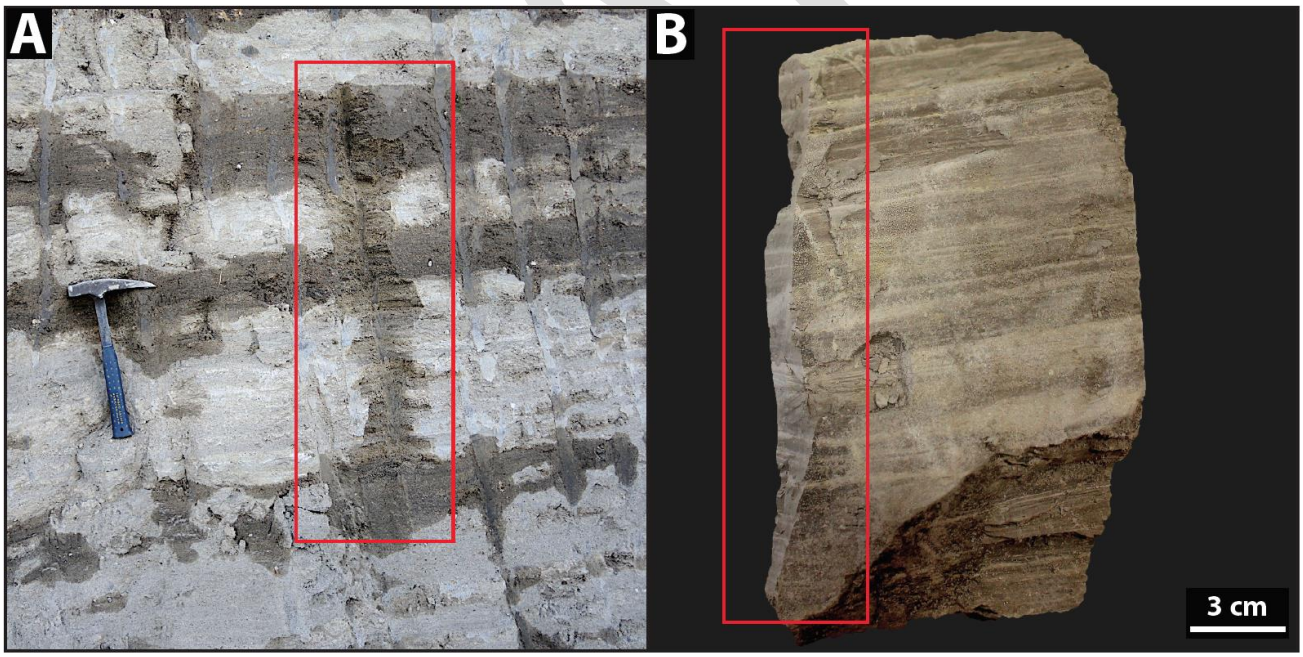

Figure 2: Sampling of erionite, A) Example of channel sampling of zeolites within ash beds, perpendicular to bedding (in red rectangle). B) Example of core sampling, of a half core of lacustrine sediments, perpendicular to bedding (in red rectangle).

Erionite Analysis

The identification of erionite is notoriously difficult for a range of reasons (laboratory equipment, training, lack of accepted standards, disagreements about erionite chemistry etc). Binocular microscopy may be used to determine if fibrous minerals are present within a sample, but it is unreliable when discriminating amongst different mineral fibres.

For the identification of fibrous erionite using a combination of analytical techniques, including the following as part of a staged approach (Figure 3), is usually recommended: x-ray diffraction (XRD), scanning electron microscope (SEM), with energy dispersive x-ray spectroscopy (EDS) and transmission electron microscopy (TEM) equipped with EDS. These analytical techniques provide chemical composition, distinguishing erionite from other minerals that maybe misidentified, and morphology, with the morphology of erionite is the primary reason the mineral is toxic .

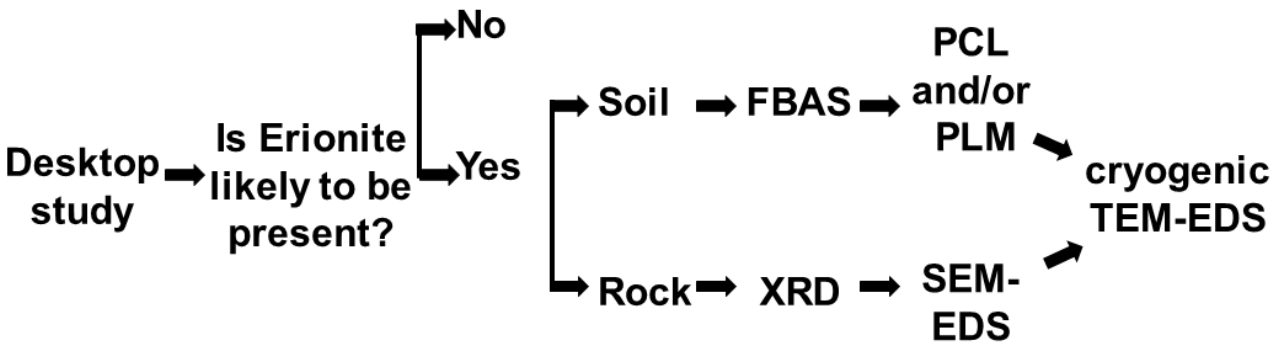

Figure 3: Flow diagram of suggested staged approach to managing erionite hazards.

This section covers each of these analytical procedures in detail, including what each method measures, the size and type of sample required, the operational requirements and the data output.

X-Ray Diffraction

X-Ray Powder Diffraction (XRD), is used to identify the crystallography of the material. This can be used on a single mineral, if enough of the mineral is available, or bulk samples, providing information on the individual minerals that are within a sample.

Sample Type: Approximately 10 g of sample powdered in a mortar and pestle, ground to < 250 µm is required.

Sample Preparation: The powdered sample is loaded into a Zero Diffraction Plate using a clean glass slide. Care needs to be taken, by applying forces in different directions, to ensure the powder is randomly oriented. A random orientation is necessary for the X-rays to have an equal chance of diffracting off any of the mineral crystal lattice faces within the sample, particular mineral fibres.

Sample Analysis: Samples should be analysed on a rotating stage and not a fixed stage to ensure random orientation. Moreover, the divergence slit size should be set as 1 and using a beam knife to reduce scattering, typically for geological samples a slit size of 2 degrees is used. Operating conditions for the acquisition of XRD data can be found in Table 1.

Data Output: XRD provides spectral data that can be analysed with software, such as HighScore Plus. See Figure 4 for typical erionite spectra from XRD analysis. Bulk samples can be semi quantitative of the proportions of each mineral, as shown in Figure 4B pie chart.

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Table 1: Acquisition parameters and values used to conduct XRD analysis.

Acquisition Parameter	Value
Scanner	PANalytical Empyrean Xray Diffractometer
Scan Axis	Gonio
Start Position (°2θ)	3.0021
End Position (°2θ)	64.9941
Step Size (°2θ)	0.0070
Scan Step Time (s)	198.6450
Scan Type	Continuous
PSD Mode	Scanning
PSD Length (°2θ)	3.35
Offset (°2θ)	0
Divergence Slit Type	Fixed
Divergence Slit Size [°]	1.0000
Irradiated Length (mm)	14
Specimen Length (mm)	10
Measurement Temperature (°C)	25
Anode Material	Cu
K-Alpha1 (Å)	1.5406
K-Alpha2 (Å)	1.54443
K-Beta (Å)	1.39225
K-A2 / K-A1 Ratio	0.5
Generator Settings	40 mA, 45 kV
Diffractometer Type	11147379
Diffractometer Number	0
Goniometer Radius (mm)	240
Dist. Focus-Divergence Slit (mm)	100
Incident Beam Monochromator	No
Spinning	Yes

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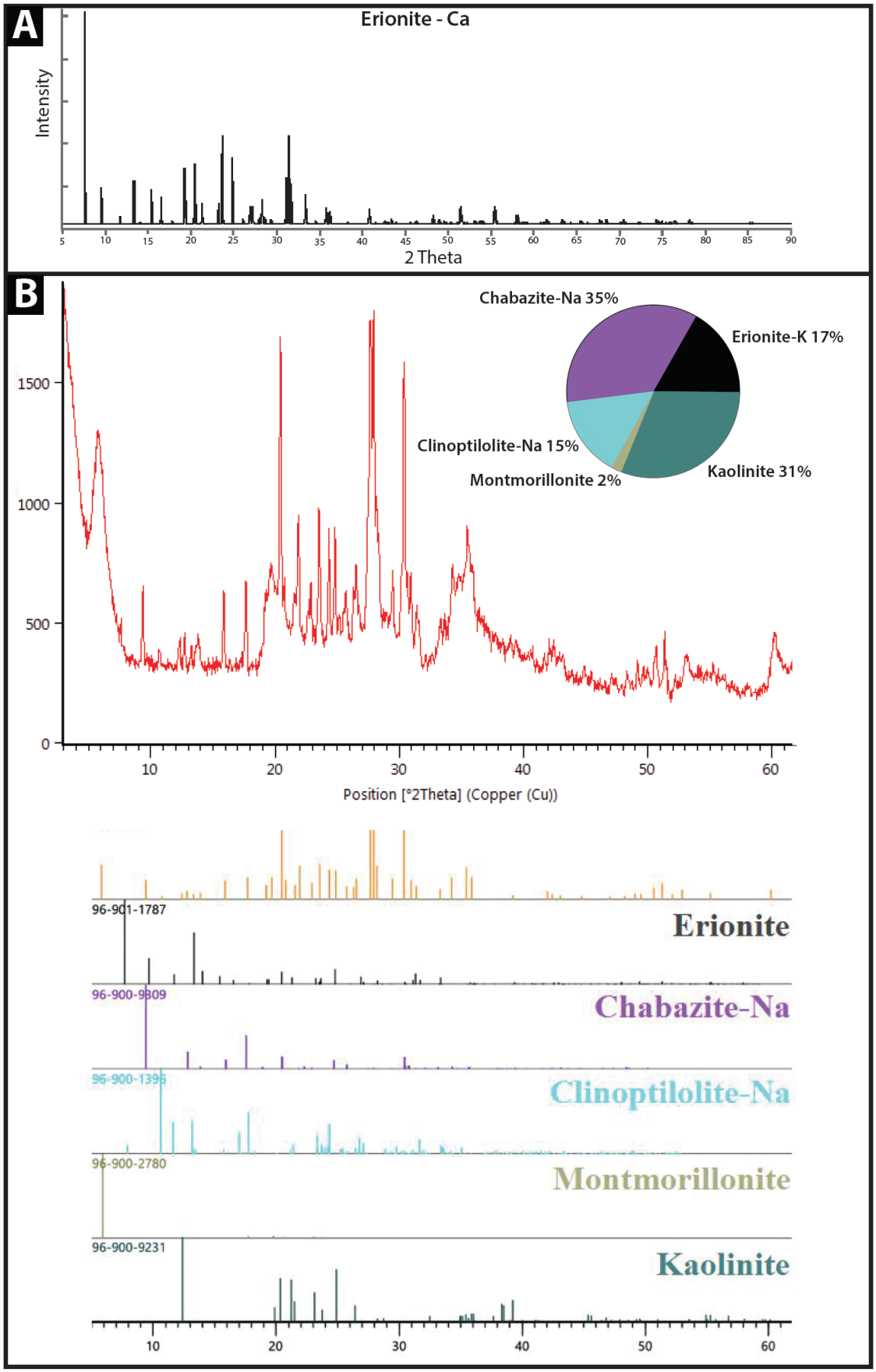

Figure 4: Typical erionite spectra from XRD analysis. A) Spectra for erionite-Ca single Crystal. B) Spectra of bulk XRD analysis of sample containing erionite from Riverhead, Auckland.

Scanning Electron Microscope

Scanning Electron Microscopy (SEM) uses a focused beam of electrons to create a magnified image of a sample. This technique is used to image the morphology of the rock samples.

Sample Type: Dried, freshly fractured samples <10 mm^3 are required.

Sample Preparation: Samples are glued onto SEM pin mounts using epoxy resin. The resin is cured overnight. Samples are sputter-coated with Platinum using a sputter coater.

Sample Analysis: Ideal conditions for SEM imaging erionite are a beam size of 3 or 4, Voltage of 10 – 20 kV and a working distance of ~10 mm.

Data Output: This method produces an image that can identify erionite mineral fibres as shown in Figure 5.

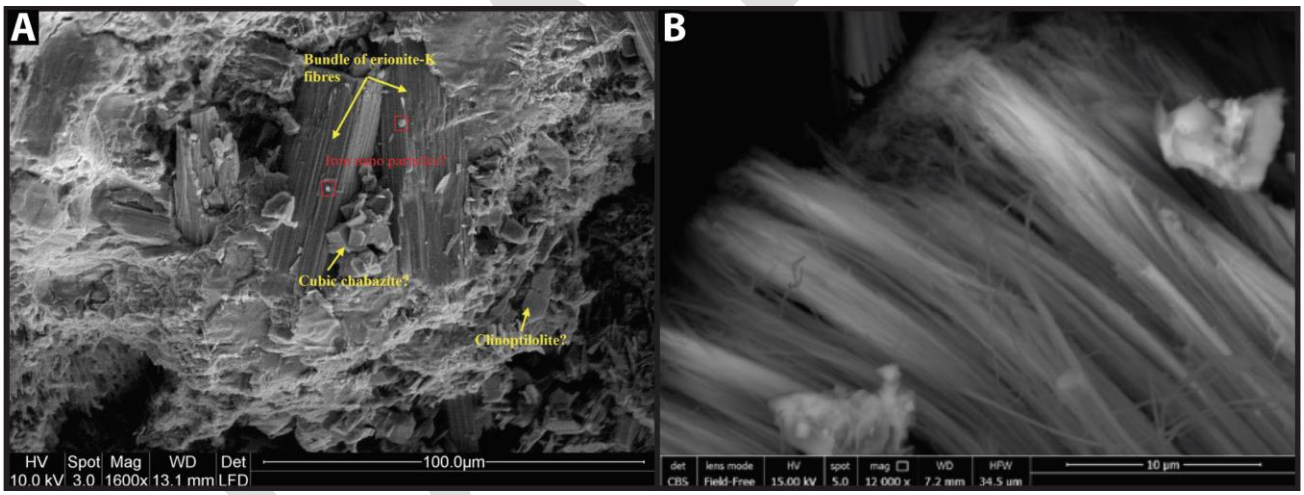

Figure 5: SEM image of erionite. A) Erionite Fibre bundles from Riverhead, Auckland. B) Fibrous erionite from Te Henga Quarry, Auckland.

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Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is similar to SEM by using an electron beam to create a magnified image of the sample. In particular, TEM is used to image the morphology of individual mineral fibres of fragile zeolites, such as erionite, that are less likely to be damaged by the electron rays. This method can determine the length and width of mineral fibres.

Sample Type: A minimal amount of the crushed rock sample <10 g is required for this procedure.

Sample Preparation: The sample is placed into a microcentrifuge tube, using a spatula, and 50 µl of 100% ethanol is pipetted into the tube. Ethanol is used as a solvent as it is unlikely to react with the sample and will quickly evaporate, leaving only the sample behind. After the grid had dried, it is placed into a cryogenic sample holder to observe the morphology of the sample. The cryogenic holder prevented the electron beam from damaging the fragile erionite fibres as the liquid nitrogen worked to cool the sample and keep it stable.

Sample Analysis: Acquisition parameters and values used to analyse sample for erionite fibres with a TEM are shown in Table 2.

Table 2. Acquisition parameters and values used to analyse a sample using TEM-EDS

Acquisition Parameter	Value
Holder	Single Tilt Cu
Voltage (kV)	200
Tilt (°)	15
Spot Size	7
Acquisition Time (s)	30
Magnification	110,000
Resolution (eV)	128.3

Data Output: This method produces an image that can identify the internal morphology of erionite mineral fibres, as shown in Figure 6.

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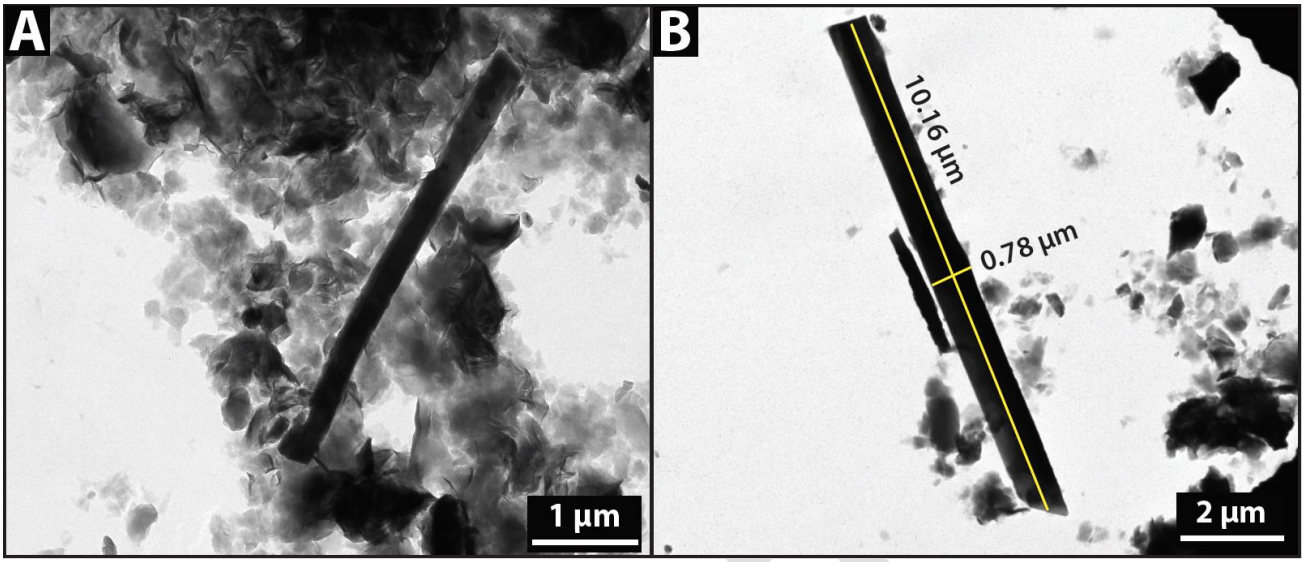

Figure 6: TEM image of mineral fibres from Riverhead, Auckland. B) Shows length and width measurements of mineral fibre.

Energy Dispersive X-Ray Spectroscopy

Energy Dispersive Spectroscopy (EDS) provides chemical composition of the sample and can be coupled with SEM or TEM imaging. EDS can be used to help accurately identify between different minerals with similar morphology, as certain zeolites such as erionite and offretite can appear visually alike; however, have varying geochemical signatures.

Sample Type: Same as SEM or TEM analysis dependant on which the EDS is coupled with.

Sample Preparation: Same as SEM or TEM analysis dependant on which the EDS is coupled with.

Sample Analysis: For EDS with SEM a beam size of 3 or 4, Voltage of 10 – 20 kV and a working distance of ~10 mm (exact image specific measurements are located at the bottom of each image, see Figure 7A). For morphological imaging, a gaseous detector was used with a pressure of 0.6 Torr, and for EDS a Backscatter (BSE) detector was used with the pressure at 0.08 Torr.

Data Output: EDS provides spectral data of the elemental compositional data of a sample. See Figure 7 for typical erionite spectra from EDS analysis.

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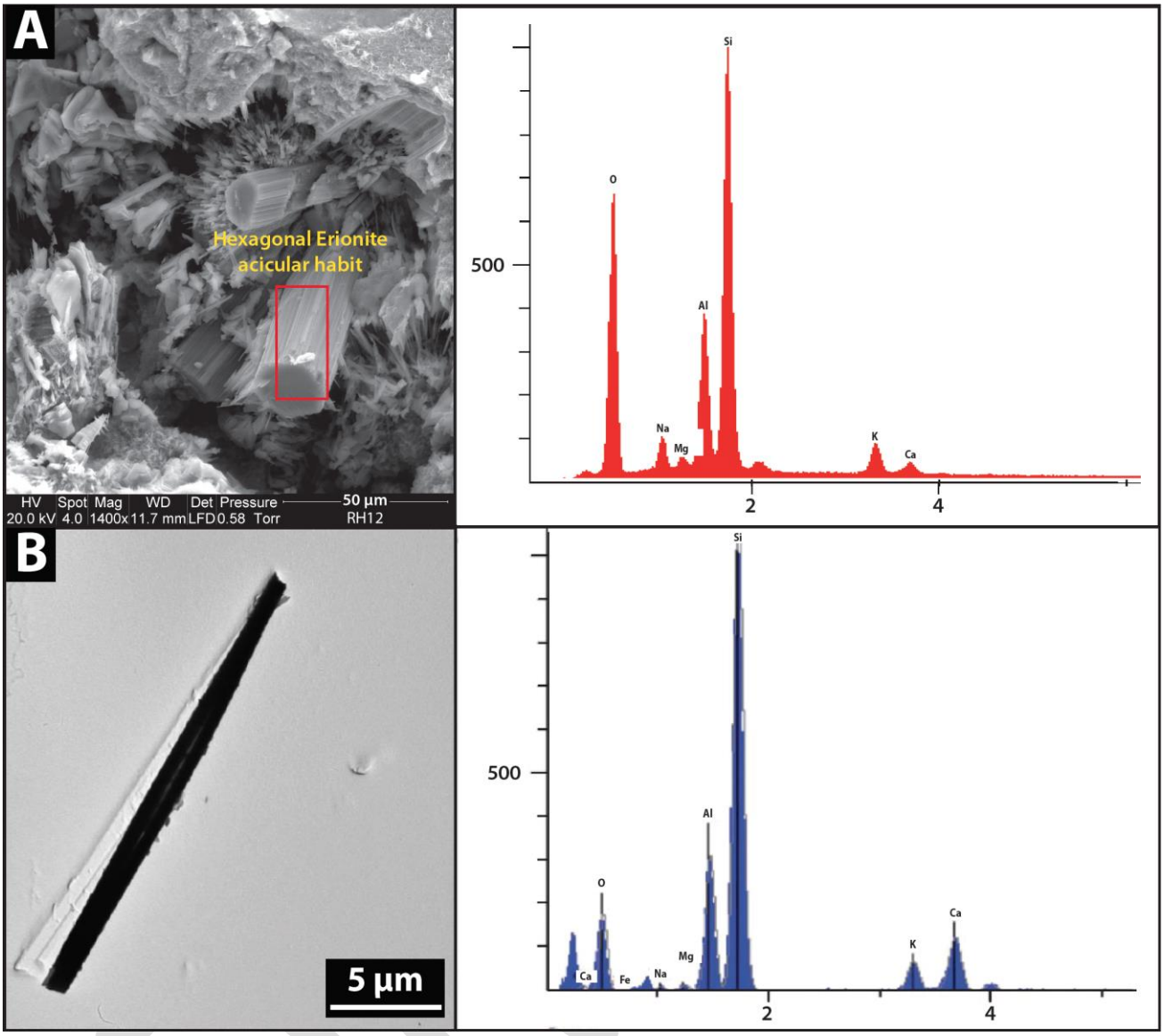

Figure 7: Typical erionite spectra from EDS analysis. A) EDS from SEM from Riverhead, Auckland. B) EDS from TEM (Ray, 2020).

References

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