DISTINGUISHING LIGHTER SHADES OF GREY: THE USE OF PORTABLE XRF TO DEFINE CHEMOSTRATIGRAPHY IN THE GREYWACKE BASEMENT OF NEW ZEALAND GEOTHERMAL SYSTEMS

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ABSTRACT

Several geothermal resources in New Zealand are hosted in the greywacke basement rocks. The basement lithologies are characterized by interlayered meta-sandstone and meta-mudstone (argillite) and can be grouped into two distinct terranes (e.g. Torlesse and Waipapa). The basement may appear grossly homogeneous (particularly for Torlesse Terrane) making the recognition of changes in lithology challenging, particularly when inspecting rock cuttings from geothermal drilling. A more detailed understanding of the basement lithologies is deemed useful in providing insight on the influence of lithology on fluid flow within the basement, in delineating possible locations and/or displacement of faults as well as in evaluating possible chemostratigraphic controls on geothermal reservoir processes. While recognising that visual changes in basement lithologies can be challenging, there is the potential to define lithology changes on a chemical basis (i.e. chemostratigraphy).

In this study, we collected systematic portable x-ray fluorescence (pXRF) chemical data from the greywacke basement of the Kawerau Geothermal Field in an attempt to define the greywacke and argillite lithologies. Approximately 1700 samples were analysed across 12 geothermal wells, with samples collected on every interval of drill cuttings (typically 5 metre intervals). The quality of pXRF data was assessed by comparing a subset to full laboratory wavelength dispersive x-ray fluorescence spectrometry on fused beads and pressed pellets.

The pXRF data collected for Kawerau could be the most comprehensive chemical data available for the greywacke basement rocks to date. The results were then compared to existing visual classifications of the basement rocks which had been previously published for the well KA50 by Wallis et al. (2012). It was demonstrated that argillite-rich intervals can be recognised on the basis of elevated K, Rb and Al concentrations, which are likely related to elevated clay content expected for argillite. Thresholds for selected chemical parameters were defined for argillite (meta-mudstone), meta-sandstone and mixed argillite/meta-sandstone. This classification was applied across the Kawerau field to reveal the distribution of argillite and meta-sandstone layers within the greywacke basement.

1. INTRODUCTION

The Taupo Volcanic Zone (TVZ) hosts numerous geothermal systems (Figure 1). The Kawerau Geothermal Field (KGF) is the northernmost of the currently active high-temperature geothermal fields in the TVZ. KGF is found in the North Island shear belt, an area located at the conjunction of the TVZ and the southern end of the Whakatane graben (Wood, et al., 2001). The geothermal reservoir in KGF is mainly hosted in the greywacke basement.

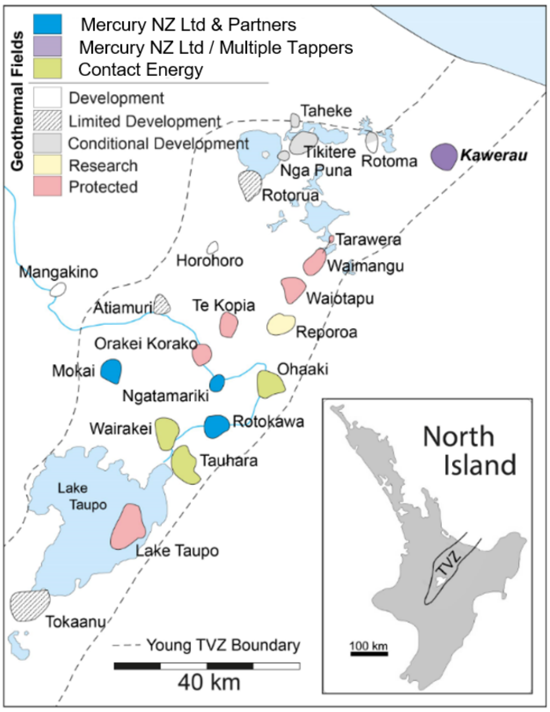

Figure 1: Location of Kawerau and other high-temperature geothermal fields within the Taupo Volcanic Zone (TVZ), New Zealand (modified from Bibby et al. (1995).

The greywacke basement at KGF is characterized by medium-grained sandstone dominated by subangular volcanic clasts (mainly andesite lava, rare rhyolite lava and ignimbrite), with minor argillite beds (Milicich et al., 2013; Wood et al., 2001). Wood et al., (2001) further described it as mostly moderately hydrothermally altered (30-60% vol.% replacement by hydrothermal minerals), although some are intensely altered (60-80%). Moderate alteration is defined by the presence of chlorite as the dominant mineral, calcite, fine-grained epidote and minor titanite and pyrite. In intensely altered rocks, plagioclase within andesite clasts is replaced by illite and totally replaced by adularia in most intensely altered rocks (Wood et al., 2001).

The KGF greywacke basement has been classified as belonging to Torlesse Terrane by Wood et al. (2001), although Adams et al. (2009) ascribed this to Waipapa Terrane. There is no known exposure of the Waipapa and Torlesse boundary but it is thought to be close to or under the KGF (Milicich et al., 2013 and Adams et al., 2009).

Figure 2: Drill cuttings from the Kawerau greywacke basement; change in color reflects argillite/meta-sandstone compositions.

Broadly, the KGF greywacke basement is stratigraphically homogeneous and is typically represented as a single unit in geological logs and cross sections (e.g. Milicich et al., 2013). Chemically, major element abundances tend to overlap between meta-sandstones and meta-mudstones in basement rocks of the North Island (Price et al., 2015). However, this study captured a large chemical data set in order to differentiate chemical boundaries within the greywacke basement (i.e. chemostratigraphy). The proof of concept for defining the chemostratigraphy of geothermal fields was provided by Mauriohooho et al. (2016).

2. METHODS

Portable X-Ray Flourescence (pXRF) is a hand-held technique which can provide a rapid analysis (~60 seconds per run) of a wide range of elements; but does not require the preparation of fused beads or pressed pellets as needed for the conventional laboratory XRF. This technique has been used for various applications, for example the analysis of superficial sediments (Liao et al., 2017), heavy metal contamination in soils (Jang, 2010) and mapping hydrothermal alteration in geothermal systems (Mauriohooho et al., 2016).

A 40 kV Olympus Delta pXRF instrument was used to analyze the 1696 geothermal well cutting samples (such as those shown in Figure 2) provided by Mercury Ltd. The 40kV pXRF analyzer measures the low atomic number elements better than other pXRF models with higher energy beams that quantify high atomic number elements. A subset of 20 samples were analyzed using wavelength dispersive spectrometry (WDS)-XRF to validate elemental data from the pXRF. WDS-XRF analyses were carried out on fused beads for the major elements Si, Al, Ti, Mn, Fe, Na, Mg, K, Ca, P and S, which are measured as oxides. Samples were prepared in a 1:10 ratio with lithium borate flux. Pressed pellets were used for trace element analysis of the samples. The elements analyzed were Rb, Cs, Sr, Ba, Sc, V, Cr, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ga, Sn, Tl, Pb, As, Sb, S, F, Cl, La, Ce, Nd, Th, and U. Loss on Ignition (LOI) was determined from the weight change of the samples from drying overnight at 105 ^{o}C to heating at 1100 °C for 90 minutes. ioGAS® and Microsoft Excel were used to manage the data.

3. RESULTS AND DISCUSSION

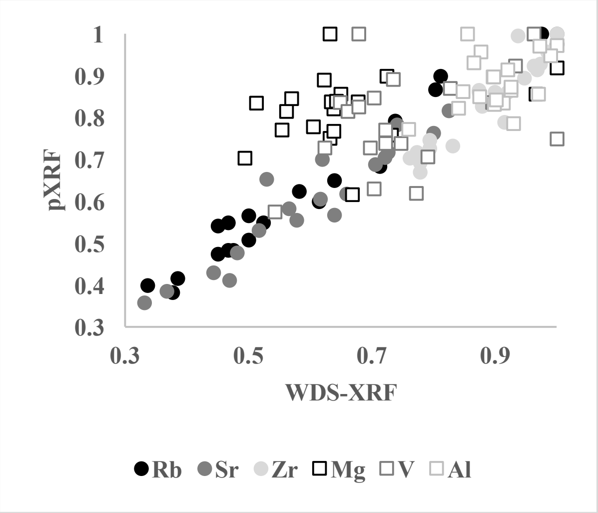

Figure 3: Normalized pXRF data validation with WDS-XRF.

Comparison of laboratory and pXRF results demonstrate that some elements are measured more accurately by pXRF than other elements. Figure 3 shows the comparison of six different elements. Results for the high atomic number elements (Rb r^2=0.96); Sr r^2=0.93; and Zr r^2=0.88) are clearly more accurate than low atomic number elements (Mg r^2=0.10, V r^2=0.15 & Al r^2=17), as is typical for pXRF

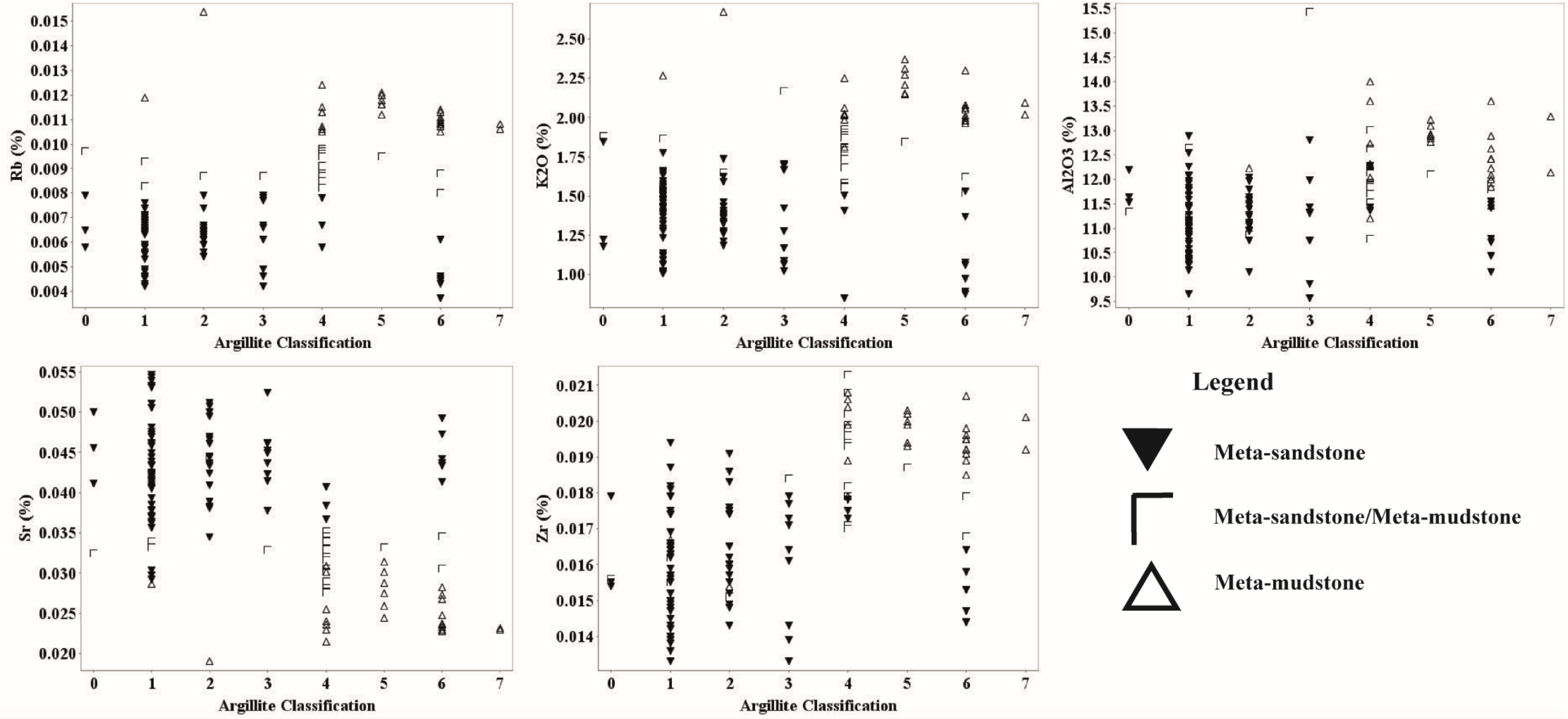

Figure 4: Comparison of Wallis (2011) visual logging classification versus Rb (and other elements) concentration. Wallis (2011) lithology scale is an arbitrary scale, ranging from 1 to 7, where 1 is sandstone and 7 is argillite. The Rb scale is also an arbitrary scale. Lithology based on Rb scale, sandstone = 0-0.008 ppm Rb; meta-sandstone/argillite mix = 0.008-0.010 ppm Rb, and argillite > 0.010 ppm Rb. The other elements are used to represent consistency with the Rb variatio

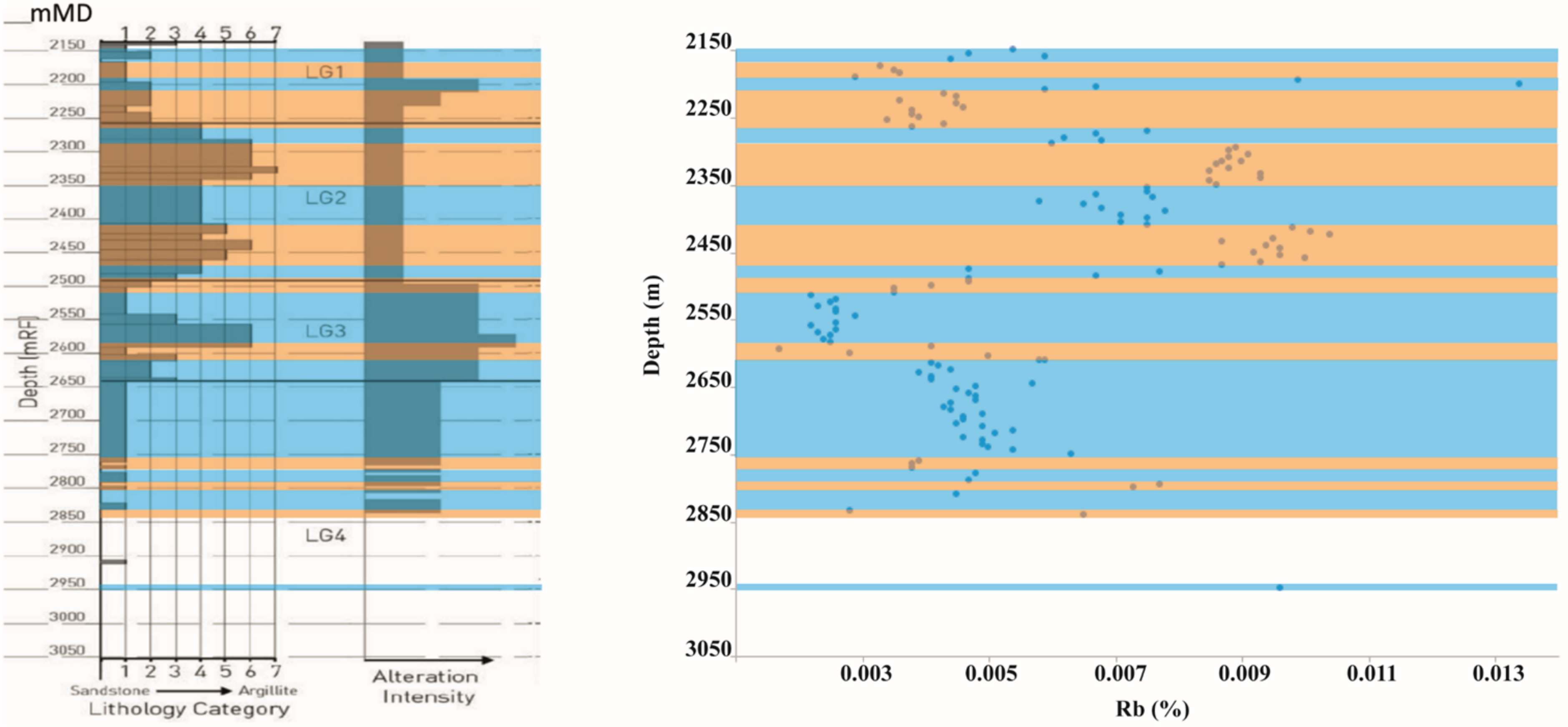

Figure 5: Wallis (2011) visual logged meta-sandstone and argillite classification superimposed with downhole Rb variation.

analysers. Therefore, the heavier elements were chosen to identify chemical thresholds.

It is important to note that changes in the composition of potentially fluid mobile elements (such as K, Rb and Sr) must be approached with a sense of caution, as it possible for concentrations of these elements to change during hydrothermal alteration. Figure 4 compares the visual classification scheme of Wallis et al (2011) to the measured Rb concentration of samples taken from the same intervals. The Wallis (2011) scheme defined a scale of 1-7 for argillite content, with 1 being meta-sandstone, 7 being meta-argillite, and the 2-6 representing a variation between these end-members. It is clear based on this classification scheme that argillite-rich samples (classification 5-7 on Figure 4) have elevated concentrations of Rb (>0.01%) and K (>1.9%) than meta-sandstone (classifications 1-3, Figure 4). Classification 4 shows a broad range of elemental concentrations. Therefore, we considered samples with greater than 0.01% Rb and 1.9% K to represent meta-mudstone lithologies. This compares to Price et al. (2015), who found Rb values between 0.0152-0.0171% and K concentrations in the range of 2.8% for argillite samples (Table 1).

Rb and K can be mobile in hydrothermal fluids and are associated with potassic alteration in hydrothermal alteration. However, K and Rb are also enriched in mudstones in the basement rocks (Price et al., 2015) due to the higher abundance of clay minerals in mudstone. While we acknowledge that there could be Rb and K concentration changes due to hydrothermal alteration, we consider that in these samples that Rb and K can be used as a proxy for the abundance of meta-argillite.

Table 1. Whole rock data comparison

Elements	Meta-mudstone	Meta-sandstone	Meta-mudstone	Meta-sandstone
	Price et al., 2015		From this study	
Rb	152-171 ppm	57-120 ppm	<0.010%	>0.008%
Sr	203-225 ppm	277-723 ppm	<0.035%	>0.030%
Zr	190-191 ppm	173-260 ppm	>0.019%	<0.017%
Al_2O_3	16.48-16.69%	13.15-17.10%	>2%	<1.5%
K_2O	3.33-3.40%	1.73-3.42%	<1.9%	>1.75%

When element concentrations are plotted against depth in well KA-50 (e.g. Rb, Figure 5), systematic changes are noted in the upper 2150-2650 metres, as the Rb abundances change in close response with visually logged changes in lithology. However, in the lower 2650-2850 metres, the Rb abundance is changing with no clear response in lithology. This could represent the difficulty in visually logging the finer drill cuttings typically recovered at greater depths.

The relative variability of Rb however does not translate to change in other immobile elements. We applied the Rb classified variations to other elements that are considered to be relatively immobile during hydrothermal alteration including Ti and Zr; the changes observed were not the same with Rb. There are clear chemical variations in both Ti and Zr within the wells.

Generally, some of the changes in geochemistry clearly correlate with logged changes in lithology. We coupled our geochemical data to the logged lithologies recently made down well KA-56 (Figure 6). Figure 6 shows that there are distinctive concentration thresholds for meta-sandstones, meta-siltstones and meta-mudstones. Using exclusively Rb concentrations as thresholds, we found that meta-sandstones had concentrations between 0-0.008%; meta-siltstones ranged between 0.008-0.0101% and meta-mudstones took values from 0.0101% and above, similar to the thresholds identified from the logging of Wallis et al (2011).

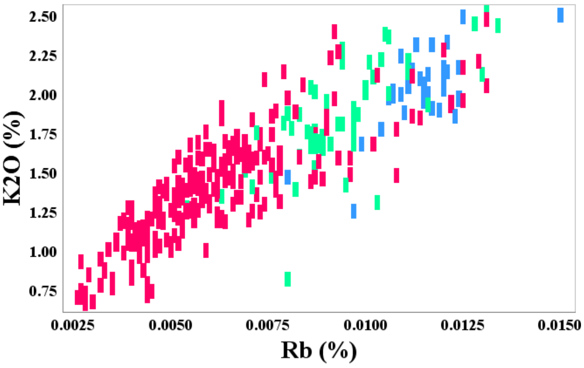

Figure 6: Recent logged classification of meta-sandstone (red), meta-siltstone (green) & meta-mudstone (blue) with K and Rb concentrations.

5. CONCLUSION

There is geochemical variation in the greywacke basement. The chemical variation correlates well to variations that have been defined using careful visual logging techniques, both in overall classification as well as downhole lithology changes. Typically, logged changes in lithology correlate to variations in chemical composition of samples. However, there are also some important discrepancies (e.g. non-coincidence of changes in Rb, Zr and Ti concentrations). The causes of these variations require a larger mineralogical and petrological data set as comparison, including quantified mineralogy via x-ray diffraction and/or petrographic approaches. Portable XRF shows significant promise to allow the rapid measurement and classification of samples collected from basement rocks and volcanic host rocks (*cf.* Mauriohooho et al., 2016) in order to refine the detailed stratigraphy and geology models of geothermal fields.

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REFERENCES

Adams, C.J., Mortimer, N., Campbell, H.J., Griffin, W.L.: Age and isotropic characterisation of metasedimentary rocks from the Torlesse Supergroup and Waipapa Group in the central North Island, New Zealand, *New Zealand Journal of Geology and Geophysics*, 52, (2009), 149-170

Bibby, H.M., Caldwell, T.G., Davey, F.J., and Webb, T.H. Geophysical evidence on the structure of the Taupo Volcanic Zone and its hydrothermal circulation: *Journal of Volcanology & Geothermal Research*, v. 68, pp. 29-58 (1995)

Jang, M. (2010). Application of portable X-ray fluorescence (pXRF) for heavy metal analysis of soils in crop fields near abandoned mine sites. *Environmental Geochemistry and Health, 32*(3), 207-16. doi:http://dx.doi.org.ezproxy.waikato.ac.nz/10.1007/s10653-009-9276-z

Liao, S., Tao, C., Huaiming, L., Zhang, G., Liang, J., & Yang W. Use of portable X-ray fluorescence in the analysis of superficial sediments in the exploration of hydrothermal vents on the Southwest Indian Ridge. *Acta Oceanologica Sinica, 36(7),* 66-76. doi:http://www.hyxb.org.cn/10.1007/s13131-017-1085-0

Mauriohooho, K., Barker, S.L.L., & Rae, A. (2016). Mapping lithology and hydrothermal alteration in geothermal systems using portable X-ray fluorescence (pXRF): A case study from the Tauhara geothermal system, Taupo Volcanic Zone. *Geothermics*, *64*, 125-134. doi:http://doi.org/10.1016/j.geothermics.2016.03.005

Mielke, P., Weinert, S., Bignall, G., & Sass, I. (2016). Thermo-physical rock properties of greaywacke basemenet rock and intrusive lavas from the Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research, 324(1),* 179-189. doi:http://dx.doi.org/10.1016/j.volgeores.2016.06.002

Milicich, S.D., Clark, J.P., Wong, C., & Askari, M. (2016). A review of the Kawerau Geothermal Field, New Zealand. *Geothermics, 59(2),* 252-265. doi:http://dx.doi.org/10.1016/j.geothermics.2015.06.012

Milicich, S.D., Wilson, C.J.N., Bignall, G., Pezaro, B., & Bardsley, C. (2013). Reconstructing the geological and structural history of an active geothermal field: A case study from New Zealand. *Journal of Volcanology and Geothermal Research, 262(1),* 7-24. doi:http://dx.doi.org/10.1016/j.volgeores.2013.06.004

Price, R.C., Mortimer, N., Smith, I. and Maas, R. 2015. Whole-rock geochemical reference data for Torlesse and Waipapa terranes, North Island, New Zealand. *New Zealand Journal of Geology and Geophysics*, vol. 58 pp 213-228

Wallis, I.C., McNamara, D., Rowland, J.V. and Massiot, C., The nature of fracture permeability in the basement greywacke at Kawerau geothermal field, New Zealand, Proceedings of the Thirty-Seventh Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, January 30 - February 1, 2012 SGP-TR-194

Wood, C.P., Brathwaite, R.L., and Rosenberg, M.D., 2001, Basement structure, lithology and permeability at Kawerau and Ohaaki geothermal fields, New Zealand: *Geothermics*, v. 30, p. 461-48