A2. Digital appendix

SUMMARY OF DIGITAL APPENDIX FILES

The supplementary digital appendix on the supplied CD contains the following data files:

A2.1. Detailed thesis methodologies and data sources (below)

- a. Non-published reports and 3D Geological model usage
- b. Well logging and sampling
- c. Microscopy and photomicroscopy techniques
- d. Laboratory X-ray Fluorescence analysis
- e. Portable X-ray Fluorescence analysis
- f. Electron Microprobe of feldspars
- A2.2. A list of collected and provided samples from this research
- A2.3. Photograph clast size measurement data (>5000 measurements)
- A2.4. Laboratory X-ray Fluorescence (XRF) and portable XRF geochemistry (>1400)
- A2.5. Photomicrograph crystal size and volume measurement data (>2500 measurements)
- A2.6. EDS thin section analysis reports
- A2.7. Crystal Raman spectroscopy analyses (accessory data)
- A2.8. Crystal Electron Microprobe (EMP) data (accessory data)

A2.1. METHODOLOGIES AND DATA SOURCES

a. Non-published reports and Geological model usage

Geotechnical drilling reports for exploration and monitoring wells were provided for this research upon request to GNS Science on behalf of Contact Energy (e.g., Rosenberg et al., 2009b). These reports include a concise summary of well geology, primary and alteration mineralogy and drilling conditions. Their outcomes were used as a foundation for constraining field stratigraphy in detail (Rosenberg et al., 2009a) and were used with a 3D Geological Leapfrog model of Wairakei-Tauhara and physical descriptions. The 3D Geological model and a spreadsheet of drilling data were provided by Contact Energy. The model uses drilling results and structural data creating a 3D rendering of the field's geology (e.g., Alcaraz et al., 2011). Together with drilling reports, it provided an efficient method for assessing logged well stratigraphy.

b. Well logging and sampling

Samples from the wells used in this research were drilled for exploration and ground subsidence investigations by Contact Energy. Their stratigraphy was originally logged by GNS Science using the Rosenberg et al. (2009a) stratigraphic model (Ramirez et al., 2009; Rosenberg et al., 2009b). Earlier samples utilise the Grindley (1965) model. Continuous core was the preferred sample type over abundant cuttings chips (collected at 5 m intervals) for this investigation they preserved textures vital for detailed lithostratigraphic investigations. Cores are diamond drilled 6.3 cm diameter (HQ size) by 100 cm lengths stored as 5 m intervals in core sheds at the Wairakei Steam Field, Taupo. Continuous core from 14 wells were used in this research (TH18, THM12 – THM19, THM21, THM22, WKM14, and WKM15). All were drilled from within the field's resistivity boundary and were variably hydrothermally altered. Cored wells totalled ~ 5.4 km in length, of which ~4.2 km intersected the Huka Group. During physical examination and description, small core fragments for petrographic and geochemical analysis were sampled (Appendix A2.2). Collected samples were often loose or were otherwise cut from the core, bagged and labelled.

Wells were independently logged from high-resolution photographs supplemented with physical observations before original well logs from client drilling reports were available. Documented features included: matrix and clast lithologies, unit contact types, average apparent clast size, shape and

estimated lithic and pumice clast proportions. Resulting stratigraphic logs were similar to drilled logs, except when gradational contacts were involved (explained in Chapter 2).

c. Microscopy and photomicroscopy

Complementary to core logging, ~70 collected samples were thin sectioned, petographically logged and photographed. The altered volcaniclastic required resin impregnation before mounting and polishing. Primary mineralogy was sparse for most lithologies and described secondary mineralogy was pervasive, but beyond the scope of this research (SEE Steiner, 1977). Photomicroscopy was undertaken on all thin sections (utilised in Chapter 4) using methods outlined in Allen and McPhie (2003).

d. Laboratory X-ray Fluorescence analysis

Laboratory X-Ray Fluorescence were conducted at the University of Canterbury Geological Sciences Department using a Phillips PW2400 Sequential Wavelength Dispersive X-ray Fluorescence Spectrometer (lab XRF). Results are included in Appendix A2.4. Samples were first prepared by light crushing and removal of visible foreign lithic clasts. Remaining material was milled in an agate swing mill for 2 minutes following recommendation by Potts (1987). The methods of analysis are based on Norrish and Chappell (1967) and the Philips software/hardware manuals. Additional modifications have been made by the Geochemistry Lab at University of Canterbury to optimise analytical conditions (S. Brown, pers. comm. 2014). The spectrometer is calibrated using sets of certified international standards. The major chemistry is determined on fusion beads using a rhodium tube set at 50 KV/55mA whereas the trace chemistry is determined on pressed powder pellets using a rhodium tube set at 60KV/46mA. Ten major rock elements were analysed by fused disc (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O and P₂O₅). Sixteen trace elements were analysed by pressed powder pellet. (V, Cr, Ni, Zn, Zr, Nb, Ba, La, Ce, Nd, Ga, Pb, Rb, Sr, Th and Y).

Glass fusion beads were prepared by fusing together approximately 1.3 g of rock powder with 6.98 g of flux (Li₂B₄O₇, Li₂O and La₂O₃ mixture) and a few grains of oxidant (NH₄NO₃) at 1030 °C for at least 15 minutes in Pt/Au crucibles. Loss on ignition (LOI) was calculated after fusion. Glass beads were formed by pouring the molten material into Pt/Au moulds which are cooled rapidly preventing recrystallisation of the original constituents. Pressed powder pellets (32 mm diameter) for trace element

analysis were prepared using approximately 8 g of rock powder and polyvinyl alcohol solution as a binder. Pellets are pressed in a hardened steel die at 3000 psi for 10 seconds.

e. Portable X-ray Fluorescence analysis

A portable X-ray Fluorescence spectrometer (pXRF) was used to provide non-invasive and rapid assessment on the distributions of major and trace elements in prepared (dried, sieved, milled), bagged and in situ unprepared samples. The non-invasive technique was a requirement for limiting sample destruction, thereby a near-complete core collection was retained. Current pXRF technology does not have the same accuracy or precision as conventional lab XRF, and is not capable of analysing some light elements (Chapter 4; Appendix A1.2). Over 5 field days, >1250 pXRF analyses were made on powder (dried and milled), collected hand samples (dried), in situ cores (moist) and cuttings samples (dry). Overall, pXRF was found to be a precise method with reproducible results. The accuracy of the results depended on sample type (grain-size and moisture) and its level of preparation. A site-appropriate mix of pXRF and lab XRF (~10 % of samples) is advantageous when assessing geochemical anomalies.





The pXRF used was a 40 kV Innov-X Alpha Series model A3500 (Fig. A2.1). The device was capable of analysing up to 26 (transition) metal elements (atomic number, Z, >21; Fig. A2.2) using Soil Mode with a beam size of ~0.7 mm at the port. Eight elements were repetitively detected in the prepared samples (Table A2.1; > 50 % machine pass rate). However, only Ti and Zr were used in Chapter 3.

Higher specification XRF (~50 kV) models capable of detecting lighter and a broader range of trace elements are suggested to be better suited to such detailed geochemical investigations (Fig. A2.2). Instrument contamination and calibration standardisation was carried out on every ~20 analyses as specified by the User's Manual ensuring quality results and reduced contamination.

hydrogen 1	Capabilities of pXRF on Huka Group samples													^{helium} 2 He			
1.0079 lithium 3	Li Be Analysed by 50 kV pXRF													fluorine 9	4.0026 neon 10		
6.941 sodium 11	9.0122 magnesium 12	10.811 12.011 14.007 15.999 18.998 aluminium silicon phosphorus sulfur chlorine 13 14 15 16 17												20.180 argon 18			
Na 22.990 potassium 19	24.305 calcium 20	Scandlum Unmilum Unmilum Imagenese Imagenese Color And Si P S CI And Si P S CI And And Si P S CI And Si P S Si P Si Si Si <												Ar 39.948 krypton 36			
839.098	Ca 40.078 strontium	Sc 44.956 yttrium 39	47.867	50.942 niobium 41	51.996 molybdenum	Mn 54.938 technetium 43	Fe 55.845 ruthenium	58.933 rhodium 45	S8.693 palladium	63.546	Zn 65.38	69.723	Ge 72.64	As 74.922 antimony	Se 78.96 tellurium	Br 79.904 iodine	83.798 xenon 54
Rb 85.468 caesium	Sr 87.62	Y 88.906	91.224	Nb 92.906 tantalum	Mo 95,96 tungsten	[98]	Ru 101.07 osmium	Rh 102.91 iridium	Pd 106.42	Ag 107.87 gold	Cd 112.41 mercury	In 114.82 thallium	Sn 118,71	Sb 171.76 bismuth	Te 127.60 polonium	126.90 astatine	Xe 131.29 radon
55 CS 132.91	56 X Ba 137.33		72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 🛣 Hg 203.59	81 TI 204.38	82 A Pb 207.2	83 Bi 208.98	84 Po [209]	85 At (210]	86 Rn [222]
87 Fr [223]	88 Ra [226]		104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 HS [277]	109 Mt [268]	110 DS [271]	111 Rg [272]							
			lanthanum 57	cerium 58	praseodymium 59	neodymium 60	promethium 61	samarium 62	europium 63	gadolinium 64	terbium 65 TL	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70	lutetium 71
			Ld 138.91 actinium	140.12 thorium	140.91	144.24 uranium	[145] neptunium	5 150.36 plutonium	LU 151.96 americium	GG 157.25 curium	158.93 berkelium	162.50 californium	164.93 einsteinium	167.26	168.93 mendelevium	173.05 nobelium	LU 174.97 lawrencium
			A C	232.04	Pa 231.04	92 ☆ U 238.03	Np [237]	94 Pu [244]	Am [243]	Cm [247]	Bk [247]	Cf [251]	ES [252]	Fm	Md [258]	102 No [259]	Lr [262]

Figure A2.2. Periodic Table illustrating the elements analysed for by the pXRF model used (40 kV) and elements detected in the Huka Group compared to the greater capability elements analysed for by 50 kV pXRF models.

The count time of the pXRF is customisable between 30 and 120 seconds (s). Higher times yield the consistent (consistent) and most accurate (correct) results (Fig. A2.3). Detected concentrations varied with count time between elements. Those most affected elements (Ti and Co, Zn and Mn) improved total concentration values by 5 - 10 % between 30 and 90 s analyses. To achieve optimal data quality and a high number of analyses, prepared and dried hand samples types were analysed 2 - 3 times at 60 s and in situ core samples were analysed 3 times at 90 s. The repeated analyses were averaged for each sample as recommended by Potts et al. (1997) to improve precision and accuracy (Ross et al., 2014).



Figure A2.3. Graph illustrating the effect Innov-X Alpha Series model A3500 pXRF count time has on detection precision represented as the range in concentration for repeated tests. Two tests at each count time interval were repeated on six samples and results for each count time were averaged. Longer test times yielded more replicable concentrations.

Inhomogeneous and moist samples

Tests of the pXRF were conducted to identify the effect of sample type on detection and the effect of moisture on detection and concentration results. Comparing results of powder (n = 42) and hand sample (n = 39) should identify the effect of sample inhomogeneity. The milled powdered sample is considered homogeneous relative to the pXRF large beam size. Of the 7 elements detected at 60 s, repeat test variations of powder samples were 4 – 16 % (average 6 %). Hand samples were 9 – 25 % (average 16 %) with near constant (negligible) pXRF influence (Table A2.1). All core tests (n = 55) with variable moisture content were conducted at 90 s count time. Increasing the count time on *in situ* core from 60 s reduced the variation to between 7 – 21 %. This shows the high influence that count time can have on result accuracy even under suboptimal conditions.

Tested core samples had to remain moist during in situ testing to prevent desiccation. The effect of moisture on pXRF detection was tested by analysing 15 samples first when moist and then dried at 90 s. Several papers have quantified the effect of moisture by varying moisture content and fixing other parameters (e.g., Ge et al., 2005; Bastos et al., 2012). Most lithologies had sample measured moisture contents of ~5 wt. %. Tests on core samples indicate that elements are variably influenced by moisture.

Overall, between wet and dry tests the 7 elements varied by an average of -7 %, but with an averaged

SD 21 %. Element Ti was most susceptible with an averaged SD of 30 %. Moisture appears to be a

more significant factor influencing results than same sample repeat test variation.

Compared to lab XRF, pXRF returned lower concentration results (low accuracy; Fig A2.4), but follow the same trend (good precision). The lower accuracy is due to minor sample inhomogeneity in the powder and natural detection limits of the pXRF.

Table A2.1. Table demonstrating variations between prepared powders, dried hand samples and wet core sample types and count times capabilities on Huka Group samples. Pass rate is the number of tests per element that satisfies the pXRF detection criteria. "Mean conc. SD" is the averaged standard deviation over the average concentration of the element for the consecutive tests.

Minimum o (ppm)	letection @	Powder (60 s, n= 42)				Dry core (dry, 60 s, 1	n= 39)		Core (wet, 90 s , n=55)				
Element	Min. detected conc.	Machine error	Pass rate	Variations between tests	Machine error on test result	Total machine error variation	Pass rate	Variations between tests	Machine error on test result	Total machine error variation	Pass rate	Variations between tests	Machine error on test result	Total machine error variation
Ti	600	200	82%	16%	17%	7%	81%	23%	16%	5%	83%	21%	18%	7%
Mn	<117	16	100%	6%	8%	7%	100%	20%	8%	9%	100%	18%	4%	13%
Fe	4000	78	100%	2%	1%	7%	100%	20%	1%	17%	100%	18%	1%	27%
Zn	12	3	100%	11%	13%	7%	100%	18%	11%	8%	100%	19%	11%	10%
Rb	18	3	100%	4%	3%	10%	100%	12%	3%	8%	100%	17%	3%	15%
Sr	31	1	100%	3%	2%	9%	100%	9%	2%	7%	100%	16%	2%	11%
Zr	64	3	100%	5%	2%	8%	100%	10%	2%	5%	100%	10%	2%	11%
Mean				6%	7%	8%		16%	6%	9%		17%	6%	13%



Figure A2.4. Comparison between lab XRF (dark grey point) and pXRF (light grey point) detected concentration in equivalent prepared Huka Group samples at varying sampled well elevations (mRL = meters relative to average sea level). Mean is the total averaged detected average values of pXRF compared to the lab XRF values. SD is the standard deviation between pXRF values and lab XRF values. pXRF is shown to be precise (high SD values), but lacks the accuracy of lab XRF as illustrated by constantly lower detected concentrations.

f. Electron Microprobe of feldspars

Limited petrological variations in the Huka Group restrict geochemical fingerprinting of minerals for unit identification. An attempt was made to fingerprint the feldspar zoning patterns using a combination of Scanning Electron Microscopy (SEM) Backscattered Electron images (BSE) for compositional variations and Raman spectroscopy for crystal structural states (Appendix A2.7). Following approaches by Müller et al. (2005), phenocryst zoning patterns were to be characterised in the vertically-defined MHFF pyroclastic (2 samples) and Waiora Ignimbrite units (7 samples) from core samples from two adjacent wells (WKM14, WKM15). Unit characterisation was made to assess the viability of the zoning fingerprint method for correlating less well defined units in the Waiora Volcaniclastics (8 samples).

Maps of feldspar zoning patterns on 17 carbon-coated thin sections were made at $50 - 150 \times$ magnifications using a JEOL 7000F Scanning Electron Microscope (15 kV, 0.59 nA at 4742 cps) at the University of Canterbury. Major elements in the compositional bands (SiO2, Na₂O, K₂O, CaO, Al₂O₃, FeO) were quantified by Electron Microprobe (EMP; Appendix A2.8). Analysis was made using a JEOL JXA-8600 Superprobe (15kV accelerating voltage, 20 µm beam diameter, 2×10^{-8} beam current, 60 s 15) at the University of Otago. Smithsonian Microbeam Standards including anorthoclase, microcline, labradorite plagioclase and hornblende were used for calibration. For most samples, points were analysed at areas corresponding with light or dark SEM-BSE zoning patterns. At least 2 points were analysed at the core and rim of smooth normal or reverse zoning patterns and up to 5 points on large (>800 µm) oscillatory zoned phenocrysts.

Gradational elemental changes (e.g., Na₂O and CaO ratios) and the geometry and chemistry of the zoning patterns (e.g., shape, width and complexity) were together anticipated to identify 'several common types' for characterising the unit (Müller et al., 2005). Analyses were made on crystal rims and cores (as determined by BSE maps). On large phenocrysts, intermediate measurements were also made between the core (mid-core) and rim (mid-rim). Microprobe weight percent totals out by ± 1 % were not included in the results (Appendix A2.8). Results confirm that feldspar phenocrysts in the MHFF (37 analyses) and analysed crystals from Waiora Volcaniclastics (104 analyses) consist of normally and complex oscillatory zoned andesine plagioclase (An% 55 – 40; Fig. A2.5). No expected common zoning types were able to be distinguished neither within individual samples (high intra-

sample variability) nor could correlation be made between laterally-equivalent samples (high intersample variability). Normally zoned feldspar phenocrysts in the Wairoa Ignimbrite (146 analyses) spanned a wider An% (~20 %An) with labradorite cores (66 %An) and andesine rims (43 %An; Fig. A2.5). Phenocrysts here were commonly more intact, euhedral and larger allowing multiple EMP measurements to accurately target different crystal regions.

Bignall et al. (1994) similarly found that wide variations in primary plagioclase compositions made them unsuitable for lateral ignimbrite correlation. High intra-sample variability may be attributed to differential and localised phenocrysts crystallisation conditions producing variable patterns over multiple generations of crystallisation from multiple sources. Furthermore, phenocrysts are mixed during eruption, transport and post-emplacement reworking further complicating intra- and intersample relationships. Mineral assemblages with diverse solid solution series are necessary when using mineral compositions as a volcanic fingerprinting tool (e.g., combination of plagioclase, amphibole, titanomagnetite; McHenry, 2005).



Figure A2.5. Ternary diagram of Huka Group feldspar compositions determined from 287 EMP analyses (Appendix A2.8). MHFF = Middle Huka Falls Formation.