Abstract

Porphyry copper deposits (PCDs) typically have large alteration haloes that extend several kilometers from economic mineralization providing a geochemical footprint potentially an order of magnitude larger than the deposit. The Paleocene (64±2 Ma) Los Morteros batholith comprises four granodiorite units and hosts four syn-mineralization porphyry units. These units are interpreted as the product of four magmatic differentiation cycles with three magmatic recharges. Alteration assemblages observed within the system include potassic, propylitic and phyllic, with intensities varying between weak to moderate for potassic and phyllic alteration, and weak to strong for propylitic.

Lithogeochemical characterization and quantification of alteration is an important exploration tool that has the potential to lead to exploration success. Two hundred and ninety-six surface rock samples were collected in a grid covering 65 km² centered over the Relincho PCD in the Atacama region, Chile to assess the suitability of surface rock lithogeochemistry as a medium for lithological and alteration characterization. Aqua regia ICP-MS, pressed pellet XRF, and fusion-ICP results, combined with shortwave infrared (SWIR) spectra, alkali feldspar staining, petrography and field observations were used to classify lithological units and identify and quantify alteration.

Data evaluation and modeling is completed through the use of exploratory data analysis, simple mass balances and molar element ratios (MER) complimented by hand and thin-section observations and SWIR analyses. Gain-loss variations are consistent with spatial element distributions indicating: the addition of SiO₂, K₂O, Ag, Cu and Mo and loss of CaO, Na₂O during potassic alteration; and the addition of Na₂O and loss of SiO₂ during propylitic alteration. Wavelengths of SWIR chlorite features indicate that chlorite is more Fe-rich proximal to mineralization and Mg-rich distally.

Simple and molar element ratios are used as proxies for the potassic, propylitic and phyllic alteration assemblages. From these ratios, alteration indices are calculated. The potassic index (K₂O/Th) and propylitic-phyllic index (((18Ca + 14Na + 25K)/(2Si + 7Al + 4(Fe + Mg)))) identify and quantify potassic, phyllic and propylitic alteration. Alteration
thresholds derived from probability plots indicate that these indices would identify the Relincho deposit as a potential PCD exploration target at a sample spacing of up to 2000 m.
Preface

This thesis was sponsored by Teck Resources Limited and its subsidiaries (Teck). The author and Mike Richard, formerly of Teck, identified the research scope and project area. The author, her supervisor (Dr. Craig Hart) and Paul Johnston of Teck Resources Limited identified the research objectives and strategy of the research. The thesis committee consists of Dr. Craig Hart, Dr. Peter Winterburn and Dr. James Scoates. Additional contributors include Dr. Paul Johnston, Dr. Liz Stock, Dr. Claire Chamberlain, Dr. Iain Dalrymple and Stephen Cook, all of Teck; Brian McNulty of MDRU; and Dr. Cliff Stanley of Acadia. This thesis is based on the analytical results of fieldwork performed by the author.

All sample descriptions and data interrogation results are the responsibility of the author unless otherwise noted. Samples were selected by the author for thin sections, alkali-feldspar staining, scanning electron microscope analysis, microprobe analysis, short-wave infrared analysis, and mineral quantification by Rietveld refinement, x-ray diffraction analysis, quantitative evaluation of minerals by scanning electron microscopy analysis and mineral liberation analysis.
## Table of Contents

ABSTRACT ........................................................................................................................................... ii
PREFACE ........................................................................................................................................ iv
TABLE OF CONTENTS ................................................................. v
LIST OF TABLES ........................................................................... ix
LIST OF FIGURES ........................................................................ x
LIST OF TERMS AND ACRONYMS .............................................. xii
ACKNOWLEDGEMENTS ................................................................ xiii
DEDICATION .................................................................................. xiv

### CHAPTER 1: INTRODUCTION: PROJECT SETTING AND OBJECTIVES  .......... 1
  1.1 Introduction ................................................................................................. 1
  1.2 Project Setting ............................................................................................ 5
  1.3 Historical Exploration .............................................................................. 7
  1.4 Regional Geology ..................................................................................... 10
  1.5 Research Objectives and Approach ........................................................... 12
  1.6 Thesis Overview ...................................................................................... 13

### CHAPTER 2: METHODOLOGY AND DATA QUALITY ASSESSMENT  .......... 14
  2.1 Introduction ................................................................................................. 14
  2.2 Field Methods ........................................................................................... 14
  2.3 Hand Samples: Shortwave Infrared, Petrography and Quantitative Mineralogy .......... 17
  2.4 Laboratory Methods .................................................................................. 18
  2.5 Data Quality Assessment .......................................................................... 19
  2.6 Data Analysis Methodologies ................................................................. 23
      2.6.1 Probability Plots .................................................................................. 23
      2.6.2 Tukey Plots ....................................................................................... 23
      2.6.3 Ranked Variable Plots ....................................................................... 24
      2.6.4 Bivariate Analysis ............................................................................ 24
  2.7 Elemental Gains and Losses ................................................................... 24
  2.8 Molar Element Ratios ............................................................................... 26
4.3.1 Staining, Field and Petrographic Observations ................................................................. 89
4.3.2 Shortwave Infrared Results .......................................................................................... 90
4.3.3 Molar Element Ratios ................................................................................................ 90

4.4 Interpretation of Alteration Processes ............................................................................ 96
4.4.1 Identification of Alteration Using Shortwave Infrared .................................................. 96
4.4.2 Identification of Alteration Using Lithogeochemistry ................................................ 98
4.4.3 Alteration Indices and Quantification ........................................................................ 100
4.4.4 Comments on Sample Spacing for Regional Exploration .......................................... 101
4.4.5 Using Alteration Indices as a Vector to Mineralization ............................................. 103
4.4.6 Comments on Alteration Indices ............................................................................. 106

4.5 Exploration Implications of Interpretations .................................................................... 106

CHAPTER 5: CONCLUSIONS AND IMPLICATIONS FOR EXPLORATION ......................... 108

5.1 Summary of Research Results ....................................................................................... 108
5.1.1 Rock Fertility Assessment ...................................................................................... 108
5.1.2 Alteration Characterization .................................................................................... 108
5.1.3 Quantifying Alteration Intensity on a Regional Scale ............................................. 109

5.2 Comparison of Methodologies ..................................................................................... 109
5.2.1 Gain-Loss versus Molar Element Ratios ................................................................. 109
5.2.2 Spatial Elemental Variability versus Molar Element Ratios ................................ 110
5.2.3 Simple Element Ratios versus Molar Element Ratios ......................................... 110

5.3 Research Shortcomings .................................................................................................. 111

5.4 Research Implications for Exploration ......................................................................... 111

5.5 Recommended Exploration Methodologies for Porphyry Cu-Mo Exploration .......... 112

5.6 Suggested Future Work ................................................................................................ 114

REFERENCES .................................................................................................................... 115

APPENDIX A: QUANTITATIVE MINERALOGY: A COMPARISON OF MINERAL LIBERATION, RIETVELD REFINEMENT, X-RAY DIFFRACTION, QUANTITATIVE EVALUATION OF MINERALS BY SCANNING ELECTRON MICROSCOPY AND WHOLE ROCK ANALYSES ........................................................................................................ 122
See Supplementary Materials and Errata Collection

APPENDIX B: SAMPLE DESCRIPTIONS AND PHOTOGRAPHS ..................................... 235
See Supplementary Materials and Errata Collection

APPENDIX C: THIN SECTION PHOTOGRAPHS ............................................................. 525
See Supplementary Materials and Errata Collection
APPENDIX D: TERRASPEC RESULTS
See Supplementary Materials and Errata Collection

582

APPENDIX E: ANALYTICAL RESULTS
See Supplementary Materials and Errata Collection

594

APPENDIX F: DATA QUALITY ASSESSMENT
See Supplementary Materials and Errata Collection

607

APPENDIX G: ELECTRON MICROPROBE RESULTS
See Supplementary Materials and Errata Collection

712

APPENDIX H: SCANNING ELECTRON MICROSCOPE RESULTS
See Supplementary Materials and Errata Collection

722
List of Tables

Table 1: Summary of certified values for reference materials ................................................. 22
Table 2: Summary of granodiorite unit properties .................................................................. 35
Table 3: Summary of porphyry unit properties ...................................................................... 38
Table 4: Summary of Tukey diagram observations ................................................................ 47
Table 5: Summary statistics for selected major oxides, heavy rare earth elements
and trace metals for the porphyry and granodiorite units ....................................................... 52
Table 6: Alteration gains and losses at Relincho and porphyry deposits with similar
characteristics .......................................................................................................................... 78
Table 7: Summary of alteration reactions between primary and alteration minerals
at the Relincho deposit .............................................................................................................. 84
Table 8: Summary of effective tools for the characterization of lithological units and
alteration assemblages ................................................................................................................. 113
List of Figures

Figure 1: Global map of porphyry belts ................................................................. 2
Figure 2: Schematic cross-section of porphyry formation in a subduction zone........ 3
Figure 3: Location of the Relincho deposit ............................................................ 6
Figure 4: Sample location map ............................................................................. 8
Figure 5: Photographs of the project area ............................................................. 9
Figure 6: Regional geology of the project area ..................................................... 11
Figure 7: Sample survey ....................................................................................... 16
Figure 8: Plots of mean versus mean percentage difference for selected analyte
duplicates ........................................................................................................... 21
Figure 9: Compositional matrix reduced to x and y vectors representative of the null
vector for customized Pearce element ratio plot ................................................. 29
Figure 10: Schematic geological map of the project area ....................................... 32
Figure 11: Photographs of the Cerrillos Formation andesite ............................ 34
Figure 12: Summary of the compositions of the granodiorite and porphyry units ... 36
Figure 13: Pictures of the contact breccia ............................................................. 40
Figure 14: Pictures of post mineralization dykes .................................................. 41
Figure 15: Spatial extent of weak alteration, with example photographs of alteration
assemblages ........................................................................................................... 43
Figure 16: Tukey diagrams by lithology ............................................................... 48
Figure 17: Major oxide and immobile element diagrams for granodiorite units...... 53
Figure 18: Radiometric diagrams distinguishing GRD1a from the GRD2, GRD3 and
GRD1b units ......................................................................................................... 54
Figure 19: Major oxide and immobile element diagrams for the porphyry units ..... 56
Figure 20: N-MORB normalized rare earth element diagrams of the granodiorite and
porphyry units .................................................................................................... 57
Figure 21: Magmatic evolution diagrams for the porphyry and granodiorite units.. 58
Figure 22: Hornblende fractionation diagrams .................................................... 60
Figure 23: Spatial Elemental Variability Plots ....................................................... 62
Figure 24: Bivariate Plots by Lithology ............................................................... 71
Figure 25: Population breaks based on probability plots ......................................................... 74
Figure 26: Spatial expression of alteration populations with alteration footprints .. 75
Figure 27: Elemental variability due to hydrothermal alteration ................................. 77
Figure 28: Shortwave infrared patterns indicative of potassic alteration ................. 83
Figure 29: Shortwave infrared patterns indicative of propylitic alteration .............. 91
Figure 30: General element ratio plots of feldspar-space ................................................. 93
Figure 31: Conserved element plots by differentiation cycle ........................................ 94
Figure 32: Pearce element ratio plots with spatial context .............................................. 95
Figure 33: Alteration indices and quantification ................................................................. 102
Figure 34: Alteration indices at 1000 m and 2000 m sample spacing .................. 104
Figure 35: Transects of alteration indices and Cu concentrations over the porphyry corridor ................................................................................................................ 105
## List of Terms and Acronyms

<table>
<thead>
<tr>
<th>Term or Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2bt</td>
<td>Secondary biotite</td>
</tr>
<tr>
<td>2CNK</td>
<td>(2Ca + Na + K)</td>
</tr>
<tr>
<td>apa</td>
<td>Apatite</td>
</tr>
<tr>
<td>bt</td>
<td>Biotite</td>
</tr>
<tr>
<td>Customized PER</td>
<td>Refers to the customized Pearce element ratio diagram: (2Si+7Al+4(Fe+Mg))/Ti vs (18Ca+14Na+25K)/Ti</td>
</tr>
<tr>
<td>Propylitic-phylllic index</td>
<td>Refers to the customized molar ratio: [(18Ca+14Na+25K)/(2Si+7Al+4(Fe+Mg))]</td>
</tr>
<tr>
<td>Feldspar space PER</td>
<td>Refers to the Pearce element ratio diagram: Al/Ti vs (2Ca+Na+K)/Ti</td>
</tr>
<tr>
<td>GER</td>
<td>General element ratio</td>
</tr>
<tr>
<td>hem</td>
<td>Hematite</td>
</tr>
<tr>
<td>HFSE</td>
<td>High field strength element</td>
</tr>
<tr>
<td>HREE</td>
<td>Heavy rare earth element</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>LREE</td>
<td>Light rare earth elements</td>
</tr>
<tr>
<td>mag</td>
<td>Magnetite</td>
</tr>
<tr>
<td>MER</td>
<td>Molar element ratio</td>
</tr>
<tr>
<td>MLA</td>
<td>Mineral liberation analysis</td>
</tr>
<tr>
<td>PCD</td>
<td>Porphyry copper deposits</td>
</tr>
<tr>
<td>PER</td>
<td>Pearce element ratio</td>
</tr>
<tr>
<td>Porphyry corridor</td>
<td>Outline of the multiple mineralized porphyry centers, as seen in Figure 4</td>
</tr>
<tr>
<td>Potassic index</td>
<td>K₂O/Th</td>
</tr>
<tr>
<td>Project area</td>
<td>The area covered by the sampling grid</td>
</tr>
<tr>
<td>PTS</td>
<td>Polished thin section</td>
</tr>
<tr>
<td>QEMSCAN</td>
<td>Quantitative evaluation of minerals by scanning electron microscopy</td>
</tr>
<tr>
<td>REE</td>
<td>Rare earth elements</td>
</tr>
<tr>
<td>Relincho Property</td>
<td>The area depicted by the property boundary in Figure 2</td>
</tr>
<tr>
<td>RR</td>
<td>Rietveld refinement</td>
</tr>
<tr>
<td>SWIR</td>
<td>Shortwave infrared, in this case Terraspec</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
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Acknowledgements

The author would like to thank her supervisor, Dr. Craig Hart, and her committee members Dr. Peter Winterburn and Dr. James Scoates for their contributions. The author would like to thank Teck Resources Limited for the opportunity to complete this thesis and for their financial support. Thank you to Acme Analytical Laboratories for their high quality analyses. The author would also like to thank Dr. Cliff Stanley, Dr. Liz Stock, Stephen Cook, Dr. Paul Johnston, Dr. Iain Dalrymple, Dr. Claire Chamberlain and Luis Nuehe for their considerable contributions. Thanks to all the others who helped out including, but not limited to Tansy O’Connor Parsons, Pim VanGeffen, Murray Allen, Thomas Bissig and Farhad Bouzari. And a special thanks to my peeps: Brian McNulty, Irene Del Real, Esther Bordet, Erin Looby, Erin O’Brien, Jeannie-kins, Victoria Sterritt, Gayle Febbo, Alfonso Luis Rodriguez Madrid, Sara Jenkins Newkirk, Aimée Campeau, Rupa Mukherjee, Madeleine Corriveau, Stanislawa Hickey, Allison Brand, Tucker, Lindsay McClaneghan, Jess Norris, my SnB group, Birgit Woods, Karen Furlong, Sarah Gordon and of course my family: the Greenlaws, Watsons, Wickmans and Takaichis for weddings, fondues, jam sessions, dog-sitting, wine nights, roadtrips and overall awesomeness over the past few years. Of course- a big thanks to my partner in crime, Mike Takaichi, for being so supportive in every way: I could not have done this without you.
To Michael: I love you dearly. I am so excited to be sharing my life with you.
Chapter 1: Introduction: Project Setting and Objectives

1.1 Introduction

Porphyry copper deposits (PCDs) account for nearly three-quarters of the world’s supply of Cu (Sillitoe 2010). Generally large-tonnage and low-grade, they are associated with convergent plate margins, frequently occurring in orogen-parallel belts with other PCDs of a similar age (Seedorff 2005; Singer et al. 2005; Corbett 2009; Sillitoe 2010) (Figure 1). Chile is well endowed with PCDs with a total resource, including production, of approximately 360 million tonnes of fine Cu identified in over 50 PCDs and prospects (Camus & Dilles 2001). As the world’s largest Cu producer, Chile annually exports approximately 33 % of the global supply of refined Cu, or 5.43 million tonnes (Mt), amounting to approximately US$ 42.7 billion, or 13.2 % of Chile’s gross domestic product, representing 53 % of the nation's exports in 2011 (BN Americas 2013).

A porphyry deposit comprises porphyritic textured intrusive bodies, in which phenocrysts, generally feldspar and quartz, occur in a fine-grained to aphanitic groundmass. These intrusive bodies are associated spatially, temporally and genetically with mineralization (Seedorff et al. 2005). Porphyry deposits form when increasing temperature due to the earth's thermal gradient dehydrates a subducting oceanic plate, releasing the less dense volatiles into the overlying mantle and causing partial melting (Richards 2003). The resulting hydrous basalt undergoes melting, assimilation, storage and homogenization (MASH) to produce a more silica-rich magma through magma differentiation by crystal fractionation (Hildreth & Moorbath 1988). Heat produced by the MASH zone causes further melting and assimilation of the surrounding rocks, facilitating the enrichment of volatiles and incompatible elements. Convection of this hydrated, evolving magma to hotter regions results in further partial melting of surrounding rocks (Figure 2; Richards 2003). The less dense, more evolved magmas rise with the volatiles to upper crustal levels where fractionation and interaction with crustal material occurs (Richards 2003).
Figure 1: Approximate location of global porphyry deposit belts, strongly coincident with subduction zones. The black box over Chile indicates the outline of the map in Figure 2. (Modified from Singer et al., 2005).
Figure 2: A schematic cross section of subduction arc showing dehydration of the subducting slab transferring volatiles causing partial melting of asthenosphere above. Magma pools at the asthenosphere-lithosphere boundary causing further partial melting in the MASH zone. Magmas rise to form batholiths. (Modified from Winter, J.D., 2001)
Magma pooled in the upper crust continues to fractionate and can produce a bubbly, buoyant mixture of evolved magma and contained volatiles. Following existing large, crustal-scale structures, this magma intrudes upward as dykes and plugs, some of which have a porphyritic texture. The volatile and incompatible element enriched fluids are released as they rise and cool typically at a depth of approximately 5-10 km (Richards 2011b). These fluids flow along fractures and permeate the host rock, depositing hypogene mineralization in the form of disseminated sulphides and stockwork veins (and native Au in the case of Au porphyry deposits), causing hydrothermal alteration of the host rock (Sillitoe 2010; Seedorff et al. 2005).

The dominant metal assemblage categorizes a porphyry deposits e.g. porphyry Cu-Mo deposit. The subducting slab is theorized to be the source of fluid-mobile elements including U, Pb, As, Sb, K, Sr, Ca, Cl, B, S and possibly Cu, Au and platinum group elements (PGEs) (Richards 2011b). Relatively high oxidation states, $f_{O_2} \geq FMQ +2$, in the mantle above the descending slab force S to be incorporated in the magma as sulphate, allowing sulphide-compatible elements (e.g. Cu and Mo) to be incorporated into the evolving melts and not bound as sulphides and potentially lost by sulphide segregation and settling (Richards 2011b, Pirajno 2009). Though it is unclear whether the source of Mo is mantle, crustal or both, it is in the MASH zone that Mo is likely introduced from the assimilation of Mo-bearing crustal material (Richards 2011a).

Hydrothermal alteration forms mineralogically distinct zones around the porphyritic intrusions that are controlled by increasing acidity and sulfidation state, and decreasing temperature of the hydrothermal fluids (Sillitoe 2010). The general spatial progression is from potassic, proximal to mineralization, through phyllic to propylitic alteration (Lowell & Guilbert 1970). Alteration related mineralogical changes are seen up to several kilometres away from porphyry related mineralization (Sillitoe 2010). Alteration significantly modifies the geochemistry of the host rocks making PCDs highly prospective targets for geochemical exploration (Sillitoe 1995). Ultimately the alteration ceases to have obvious, visible mineralogical effects and becomes cryptic, though is commonly still geochemically identifiable (e.g. Urqueta et al. 2009; Djouka-Fonkwe et al. 2012).
Lithogeochemistry of drill core material is recognized as a useful tool for exploration, fertility studies and characterization of various deposit types including PCDs worldwide (Stanley & Lang 1995; Ulrich & Heinrich 2002; Shen et al. 2009; Loucks 2014, etc.). Exploration using surface rock lithogeochemistry for PCDs, however, is not well documented in literature. The principal exception being the work by Urqueta et al., 2009 on the Collahuasi region of Chile, which successfully identified potassic, sericitic and argillic alteration through the use of molar element ratios (MERs) and relatively quantified alteration using indices derived from MERs.

The Relincho PCD in the Atacama region of Chile provides a unique opportunity to characterize the alteration assemblages and lithological units associated with mineralization using surface rock lithogeochemistry. Relincho is geologically well characterized (Cintis & Boivin 2003; Camus 2007; Teck Resources Limited 2007; Stanley & Johnston 2011; Johnston et al. 2012), yet the project area is not affected by large-scale mining operations or development. In addition, the deposit is unconcealed by overlying cover and has excellent outcrop exposure, thus giving full 2D access by foot or truck, making it an excellent candidate for surface rock lithogeochemical characterization. The results of this study will determine the feasibility of using surface rock samples as a regional lithogeochemical exploration tool.

1.2 Project Setting

The Relincho PCD (S 28.515°, W 70.312°) is of Paleocene age and located approximately 45 km east-northeast of Vallenar in the Atacama region of Chile (Figure 3; Teck Resources Limited 2007). Situated at the southern extent of a belt of Paleocene PCDs trending from southern Peru to central Chile, it is one of five such distinctly aged belts occurring parallel to and contained by the Andes (Figure 3; Vry et al. 2010). These belts formed as a result of the eastern migration of plutonism caused by contractional tectonism in the Andes spanning from the mid Cretaceous to Recent (Camus & Dilles 2001).
Figure 3: The Relincho Paleocene Cu-Mo porphyry deposit is located approximately 630 km northeast of Santiago at the southern end of a belt of Paleocene aged PCDs, which spans from southern Peru to central Chile. Five such distinctly aged PCD belts occur sub-parallel to the Andes, and young eastward (modified from Vry et al., 2010).
The property encompassing the Relincho PCD covers approximately 195 km² with elevations varying between 1500 and 3000 m above mean sea level (Figure 4). The term “project area” refers to the area covered by samples in Figure 4, which is centered over the Relincho PCD. The project area is located in a transitional desert, sparsely covered by sagebrush and wildflowers, with small trees limited to streambeds (Figure 5). Topographically the project area comprises small hills, interrupted by semi-dry streambeds, populated by wild donkeys and guanaco. As there is little in the way of vegetation, most of the property is accessible by truck, even areas without roads, allowing for excellent accessibility.

Blocky, generally small outcrops (one to six square metres) and angular boulders cover the hillsides. Host granodiorite and syn-mineralization porphyry units outcrop at surface. Minimal supergene transport of Cu and dominantly physical weathering (as opposed to chemical) are the result of a lack of precipitation. Weathered rinds are thin to non-existent and do not impact lithogeochemical results. Although there is minimal supergene transport of Cu, areas with surface exposure of sulphides have suffered oxidation to secondary copper minerals such as glassy limonite, malachite and azurite.

### 1.3 Historical Exploration

Artisanal mining operations, currently still active, date back to the early 1900s, with large-scale exploration starting in the early 1970s. More recently the Outokumpu company diamond drilled and sampled 35,000 m between 1993 and 1997, reporting a resource estimate of 112.2 Mt at 0.66 % Cu and 286 ppm Mo in 1995 (Cintis & Boivin 2003). Little exploration took place over the following decade as the property changed hands several times. The property was purchased in 2000 by Placer Dome; followed by Andes Pacific in 2002; optioned in 2003 by Lumina Copper Corp.; and finally transferred in 2006 to their subsidiary, Global Copper Corp. (Cintis & Boivin 2003).
Figure 4: Areal photograph showing sample locations, the porphyry corridor, and the Relincho property outline. Sample spacing is 250 m proximal to the porphyry corridor and 500 m distally. Thirty-four regional samples were taken at random spacing to assess background. The sample grid covers about 65 km². Contacts between Los Morteros granodiorite batholith and andesite of the Cerrillos Formation are approximated by white lines.
Figure 5: Photographs of the project area depicting the flora, fauna and outcrops. The lack of vegetation allows for easy vehicle access to outcrops. a. A photograph taken south of the project area looking northwest, with the Relincho camp visible in the lower left corner. b. Relincho camp, looking northeast. c. An example of a typical outcrop (sample Q-07), with the hammerhead pointing to the north. d. Wild donkeys native to the area. e. Guanaco native to the area.
From 2006 to 2008 Global Copper Corp. ran drilling programs to extend resources. Drilling continued into 2008, when Teck Cominco (now Teck Resources Limited) acquired Global Copper Corp., whose principal asset was the Relincho property. Since 2008, Relincho has undergone metallurgical studies, additional diamond drilling and further exploration. A feasibility report completed in the last quarter of 2013 reports 1,239.1 Mt at 0.37 % Cu, 0.017 % Mo Proven and Probable Mineral Reserves, and 397.0 Mt at 0.33 % Cu, 0.011 % Mo Measured and Indicated Mineral Resources (Teck Resources Limited 2014).

1.4 Regional Geology

Situated on the same Paleocene-Lower Eocene aged belt as the Carmen and Spence deposits, the Relincho PCD is hosted in Paleocene aged rocks, surrounded by Cretaceous volcanic units. Andesite of the Cerrillos Formation, into which the host granodiorite and mineralized porphyry units are intruded, formed during an extensional episode in the Early to Late Cretaceous (Camus 2007). The Cerrillos Formation consists of two units: a lower unit comprised of pyroclastic and sedimentary deposits and the upper unit comprised of andesitic to rhyolitic lavas (Camus 2007; Figure 6). Unconformably overlying the Cerrillos Formation are volcaniclastic breccias, conglomerates and sandstones of the Hornitos Formation (Reynaldo, et al., 2002), K-Ar dating on biotite indicates an age of 72.1 ± 1.2 Ma (Moscoso et al. 2010a). Extensional episodes in the Jurassic to Early Cretaceous formed a system of north-northwest striking basin-range faults (Reynaldo et al. 2002). These faults provided feeding structures for the emplacement of the Paleocene granodiorite of the Los Morteros batholith into both the Cerrillos and Hornitos Formations (Camus & Dilles 2001; Camus 2007). K-Ar dating on biotite of the Los Morteros batholith shows an age of 61.1 – 64.9 ± 2.9 Ma near the Relincho deposit (Moscoso et al. 2010a). The Los Morteros batholith outcrops over hundreds of square kilometres and hosts over a dozen known deposits (Moscoso et al. 2010b).
Figure 6: Regional geology of the area surrounding the Relincho deposit. Lithological units have been grouped by age for simplification. (Modified from Moscoso et al., 2010b)
On the project scale, the Los Morteros granodiorite dominates with the andesite of the Cerrillos Formation surrounding the project area (Figure 4). The four Paleocene porphyry units, also of the Los Morteros batholith, are associated with hydrothermal alteration and sulphide mineralization (Figure 4). Porphyry units are concentrated along a seven km long, northwest-southeast trending series of porphyry centers, hereon referred to as the “porphyry corridor” (Figure 4). Hydrothermal breccias often mark the contacts between the granodiorite and porphyry units. Barren, post mineralization, dacite dikes intrude all preceding units.

Potassic, propylitic and phyllic alteration at Relincho are defined by the following assemblages, with key minerals indicated in bold:

*Potassic Assemblage:* secondary biotite + K-feldspar + magnetite ±
  glassy limonite (from chalcopyrite)

*Propylitic Assemblage:* epidote + chlorite + hematite ± albite ± calcite ±
  pyrite

*Phyllic Assemblage:* chlorite + muscovite + quartz ± calcite ± hematite.

### 1.5 Research Objectives and Approach

The objectives of this thesis are:

- To characterize the lithological units using surface rock lithogeochemistry
- To characterize alteration assemblages using surface rock lithogeochemistry
- To quantify alteration using alteration indices identified through alteration characterization
- To identify key lithogeochemical indicators for recognizing areas of potential PCD mineralization
- To determine appropriate regional and follow up scale sample spacing strategies for identifying areas of potential PCD mineralization
- To propose appropriate analytical methodologies for PCD exploration

These objectives are achieved by first completing a two-month sampling survey centered over known mineralization (Figure 4) with the assistance of Luis Nuehe, an
employee of Teck Resources Limited. The survey covers 65 km² comprising an inner square grid with sample spacing of 250 m, surrounded by an outer grid with a sample spacing of 500 m. An additional 34 samples were taken regionally to assess background concentrations. Hand specimens were cut from each sample in the field and retained for petrography and alkali feldspar staining. Samples weighing approximately five kg were submitted for preparation and analysis at Acme Analytical Laboratories Limited (Acme) in Vancouver. Lithogeochemical results are interpreted using exploratory data analysis techniques such as probability, Tukey, ranked variable, univariate and bivariate methods; elemental gains and loss determinations; fertility assessment; and MER diagrams to determine the viability and suitability of surface rock lithogeochemistry as a regional scale exploration tool. Successful methods for using regional scale, surface lithogeochemistry for PCD exploration are summarized in the conclusions section for future exploration applications. Field, analytical and interpretive methodologies are summarized in chapter two.

It is important to note that geological mapping is not an objective of this thesis. A separate mapping program was initiated by Teck Resources Limited to achieve this goal. Point sample data has been collected and interpreted with few observations of contact relationships between lithological units. This data has been used to produce a schematic map of the project scale geology presented in Chapter two.

1.6 Thesis Overview

This thesis is divided into five chapters: (1) an introduction to the project setting, objectives, and regional geology; (2) descriptions of field and analytical methodologies, including a summary of the data quality assessment; (3) descriptions and discussions of the physical and chemical characteristics of the lithological units and alteration assemblages, including an interpreted magmatic evolution model and regional exploration applications; (4) descriptions and discussions of the geochemical attributes of the alteration assemblages, alteration indices and their regional exploration applications; and (5) a summary of the conclusions of chapters three and four and a discussion regarding suggested follow-up work and potential exploration applications.
Chapter 2: Methodology and Data Quality Assessment

2.1 Introduction

The purpose of this study is to use regional surface lithogeochemistry to characterize lithological units and alteration assemblages for applications in PCD exploration. As such a sample of each lithological unit present at 267 sites was collected for lithogeochemical characterization. In total 291 samples were collected over a 65 km² area. This section describes the field methods, petrography, analyses, data quality assessment procedures and interpretive methods involved in this characterization study.

A comparison of the mineral quantification methods: mineral liberation analysis (MLA); Rietveld refinement; X-ray diffraction (XRD); quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN); and whole rock data tabulated using the MINSQ spreadsheet (Herrmann & Berry 2002) was completed as a separate study using a subset of ten granodiorite samples. Appendix A presents the report and results from this comparison.

2.2 Field Methods

Sampling was completed over a two-month field season beginning in January of 2012. Centered over the porphyry corridor, sampling covers approximately 65 km² and consists of an inner grid with sample spacing of 250 m covering approximately 10 km² along the strike of the porphyry corridor, an outer grid with sample spacing of 500 m covering an additional 25 km², and regional sampling taken based on accessibility covering an additional 30 km² (Figure 4). Regional samples were taken in an attempt to ascertain background values. Every effort was made to obtain unaltered samples of each lithology, but the large footprint of the hydrothermal system made establishing a confident background baseline challenging.

All sample location information was collected, and is displayed in this thesis using the projection PSAD56, UTM zone 19S. Samples were collected in a grid pattern,
where each square is one square km organized alphabetically, then numerically, such that the sample name is representative of the sample location, e.g. LEG-A-04 is from the northwest corner of the sample area (grid A), and the northeast corner of grid A (Figure 7). Samples with double letters are from the small sample grid at the southeast end of the porphyry corridor; samples prefixed with a Z are regional samples.

Only outcrops were sampled in this survey. Outcrops were described in the field, noting location, lithology, alteration minerals, oxidation, veins, associated alteration haloes and contact relationships. A photograph was taken at each sample site. An in-situ outcrop sample, on average about six kg, was taken at each sample site. In cases where more than one lithology was identified at an outcrop, a sample representing each lithology was collected. Ten magnetic susceptibility measurements were taken using a KT-9 Kappameter for each sample on the outcrop with the maximum, minimum and average values recorded. The magnetic susceptibility values are assessed to determine if certain ranges are characteristic of a lithology or alteration assemblage. Each sample was tested for the presence of carbonates using 10 % hydrochloric acid. The intensity of the reaction to acid was recorded on a scale of one (least reactive) to three (most reactive) and prefixed as a reaction within the rock (R) or vein (V). This information is presented in Appendix B.

Care was taken to obtain representative samples of each outcrop. Any weathered portion of a sample was removed as much as possible in the field using a hammer to reduce the lithogeochemical impact of chemical weathering. Large (> 3 cm) veins were avoided when sampling to ensure that analytical results are representative of the host rock, and not diluted or biased by the composition of veins. Using a rock saw, each sample was cut into two parts:

1. A representative hand specimen, approximately 10 x 15 x 3 cm³ preserving the fresh and weathered surfaces for mineralogical observations, photographs, alkali feldspar staining, TerraSpec® work and polished thin sections;

2. Sample material submitted for geochemical analyses, approximately five kg once the hand specimen has been removed.
Figure 7: Map showing the one square kilometer grid pattern of the sampling survey. Each sample is named according to the location of the sampled outcrop, for instance LEG-I-08 would be from the center of the I square. All regional samples contain the prefix Z.
2.3 Hand Samples: Shortwave Infrared, Petrography and Quantitative Mineralogy

Hand samples were described in detail using a binocular microscope (Appendix B). Polished thin sections (PTS) from Vancouver Petrographics of 56 hand samples, selected based on lithology, alteration type/intensity, mineralization and texture, were photographed and described in detail (Appendix C). Vancouver Petrographics completed alkali feldspar staining on 268 samples by etching polished samples with hydrofluoric acid, and then dipping the sample in sodium cobaltinitrite, which stains K-bearing minerals, such as K-feldspar, yellow. Pictures of the stained samples are presented in Appendix B. Electron microprobe (EMP) (Appendix D) and scanning electron microscope (SEM) (Appendix E) work completed by the author at the University of British Columbia focused on characterizing feldspars, hornblende and biotite (primary and secondary) and also served to confirm petrographic observations. The 56 samples selected for PTS were submitted for XRD analysis at Acme in Vancouver; these results are found in Appendix A with the quantification method comparison.

Hand specimens were analyzed by shortwave infrared (SWIR) using a model TSP 350-2500 TerraSpec© instrument at the University of British Columbia. TerraSpec© spectra were processed using The Spectral Geologist© (TSG) software from AusSpec International Inc. Mineral speciation is based on best fit with a spectral library provided by the SpecMin® software. These mineral identifications were crosschecked manually by visual spectra comparison, rejecting any spectra identified as aspectral, null, wood or Teflon. In addition to mineral identification, the width, depth and wavelength of features occurring at 1930± 30 nm, 2205 ± 25 nm, 2254 ± 14 nm, and 2330 ± 30 nm were extracted to investigate the properties of: water chemically bound in clay minerals (1900); white micas (2200 nm); and chlorite (2250 nm, 2350 nm) (Halley 2008). Identified minerals and exported wavelength information is presented in Appendix F. For Terraspec© work a white polytetrafluoroethylene (Teflon) tile was measured every 20th sample as an absolute reflectance reference for calibration.
2.4 Laboratory Methods

After weathered portions and a representative hand sample were removed, approximately five kg of sample material remained for preparation and analysis at Acme. Samples were jaw crushed at the facility in Copiapo, Chile to nominally 80 % passing a 2 mm screen. All crushed material was sent to the Vancouver facility where a 500 g riffle split was disk mill pulverized by a labtechs LM2 in a 1000 cc capacity, high C steel composition bowl, to nominally 85 % passing 0.075 mm.

Samples were analyzed for:

1. Major oxides by a lithium metaborate/tetraborate fusion, dilute HNO₃ digestion of the fusion prill and inductively coupled plasma optical emission spectrometer (ICP-OES) finish on a 0.2 g sample split (Acme package 4A)
2. Trace elements by lithium metaborate/tetraborate fusion, dilute HNO₃ digestion of the fusion prill, with an inductively coupled plasma mass spectrometer (ICP-MS) finish on a 0.2 g sample split (Acme package 4B)
3. Trace elements by pressed pellet X-ray fluorescence (XRF) on a 7.5 g sample split (Acme package 2X)
4. Total carbon and sulphur by combustion furnace infrared C-S analysis (Leco) on a 1 g sample split (Acme package 4A)
5. Ultratrace-level analysis on 53 elements by Acme’s “aqua regia” (a solution of equal parts HCl, HNO₃ and H₂O) digest with ICP-MS finish on a 30g sample split (Acme package 1F30)
6. Samples exceeding 1000 ppm Cu were submitted for Cu and Mo assays by 4-acid (HClO₄, HNO₃, HF and HCl) digestion with an Atomic Absorption finish at Acme Analytical Laboratories in Santiago, Chile (Acme package 8TD).

Analytical results and package descriptions are shown in Appendix G.
2.5 Data Quality Assessment

All data quality plots are found in Appendix H, along with a summary of the data quality assessment.

Field duplicates, preparation duplicates, preparation blanks and certified reference materials (CRMs) were inserted at a rate of at least one in 20 samples, as per the data quality protocol of Teck Resources Limited. The author took field duplicates as independent samples from the same outcrop. Analytical results for the duplicates, blanks and CRMs along with a summary of the data quality assessment are found in Appendix H.

An Acme employee inserted the preparation duplicates, preparation blanks and CRMs at the instruction of the author. Preparation duplicates were taken during riffle splitting after crushing and prior to pulverization. Preparation blanks (G1) comprise barren granite inserted by an Acme employee prior to crushing. Five different CRMs were inserted at the weighing stage: ST-1; ST-2; 52C; GSP-2; and SY-4.

In general the preparation duplicates show better reproducibility than the field duplicates with reproducibility improving as concentration increases. Analytical results for all duplicate pairs are separated into ‘parent’ and ‘daughter’ samples which are plotted against each other with ± 10, 20 and 30 % error lines indicated to assess natural variability and to identify any contamination or sample mix-up in the lab. As per the protocol of Teck Resources Limited, field duplicates are expected to have 90 % of pairs fall within 30 % of each other at values greater than ten times detection limit, and preparation duplicates are expected to have 90 % of pairs fall within 20 % of each other for values greater than ten times detection limit. Based on these criteria the field duplicates show high natural variability (> 10 % of pairs plotting outside of ± 30 %) for U, Pb, Zn, Cu, Mo, Ag, As, Au, Cd, Sb, and Li. Preparation duplicates show a lack of reproducibility (> 10 % of pairs plotting outside of ± 20 %) for Au, Mo, and Cd. Elements such as Ag, Au and Mo commonly exhibit high natural variability because of the nugget effect. These elements tend to occur in concentrated nuggets that are non-uniformly disseminated resulting in poor analytical reproducibility.
To express the variability and bias visually, SiO₂, Al₂O₃, K₂O, TiO₂, Cu and Au are plotted on a mean versus mean percentage difference (MPD) diagram with ± 20 % and ± 30 % limits plotted (Figure 8). These plots indicate no obvious bias in the data, and emphasize the variability in Cu and Mo seen in the parent versus daughter duplicate plots in Appendix H. In practice no bias would be expected as the samples are analyzed at the same time, in the same batch with the same method. Some analytes are too close to or at the detection limits of the analytical techniques used to comment on natural variability or reproducibility, such as Sn, Ta, S, B, Hg, Se, Te, Re, Pd, and Pt; these elements are excluded from this study.

As per the protocols of Teck Resources Limited, blank sample (G1) concentrations are plotted with a line representing ten times the detection limit for each analyte (Appendix H), though this “blank” is a natural material, subject to natural variability. The G1 results are examined for any obvious outliers that could indicate carryover during preparation. Any erratic results for a sample have been investigated for consistent behavior between analytes and deemed a product of natural variability. If contamination were the source of an erratic result, it would be apparent in more than one analyte.

Five reference materials were inserted to assess data quality. Reference materials ST-1 and ST-2 are certified by and internal to Teck. They are weakly mineralized granodiorite from the Relincho property. Material 52C is ore and waste rock from an Au - Cu ± Mo porphyry in central western Australia commercially produced by OREAS. The USGS manufactured GSP-2 is a granodiorite from Silver Plume, Colorado. Diorite gneiss was used by CANMET to manufacture SY-4. Certified values for reference materials are summarized in Table 1.

All CRM analyses are plotted with the published certified values and accepted range of variation determined as three times the published standard deviation around the certified value and presented in Appendix H. Where values are not reported, published accepted means are used. Where no accepted values are given, analytical results are plotted without control limits. Plots are examined for results lying outside of the acceptance criteria, taking into account any discrepancy between the analytical method for the certified values and those used for the study sample results. Special
Figure 8: Duplicate pairs plotted as the mean versus the mean percentage difference (MPD) calculated as 100*(Original-Duplicate)/mean. Field duplicates are plotted as blue dots, and prep duplicates as green diamonds.
<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Cu (ppm)</th>
<th>Mo (ppm)</th>
<th>Au (ppb)</th>
<th>Al2O3 (wt %)</th>
<th>TiO2 (wt %)</th>
<th>SiO2 (wt %)</th>
<th>Na2O (wt %)</th>
<th>CaO (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSP-2</td>
<td>43</td>
<td>-</td>
<td>-</td>
<td>14.9</td>
<td>0.66</td>
<td>66.6</td>
<td>2.78</td>
<td>2.10</td>
</tr>
<tr>
<td>OREAS 52C</td>
<td>3440</td>
<td>267</td>
<td>346</td>
<td>15.3</td>
<td>0.64</td>
<td>59.7</td>
<td>3.47</td>
<td>3.45</td>
</tr>
<tr>
<td>ST-1</td>
<td>180</td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ST-2</td>
<td>760</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SY-4</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>20.69</td>
<td>0.287</td>
<td>49.9</td>
<td>7.10</td>
<td>8.05</td>
</tr>
</tbody>
</table>

**Table 1:** Summary of certified values for reference materials used for analysis. Plots of the reference material results are found in Appendix H.
attention is paid to the principle analytes used in this study, such as Cu, Mo, Au, CaO, Na₂O, K₂O, TiO₂, Al₂O₃, etc. Consistent low biases (for instance Fe, Mn, Pb and Cd for GSP-2) are considered an analytical artifact due to minor methodological differences between analytical techniques used in certification and those used in this survey. These samples were not submitted for re-analysis, as re-analysis by the same methodology would not correct for analytical method bias. In general the results for ST-1, ST-2, 52C and GSP-2 were consistent with certified results, with the exception of analytical biases.

SY-4 is only provided with a 95 % confidence interval, which is both inappropriate and incorrect to use for determination of acceptance criteria. Instead of using the confidence interval, values that are ± 5 % of the reported mean are used.

Failures for Ba, Cs, Hf, Th, Ta, Sr, La, Zr, Pr, Nd, Y, Ce, Sm, Gd, Lu, Cu, Zn, Ni, Be, Li, Co, Zn, and Ni are due: to incomparable analytical methods (e.g. Cu, Pb, Zn, Ni, etc.); detection limit proximity (e.g. U); and excessively tight control limits (e.g. Nb, Zr, etc.).

No significant data quality issues have been identified and this data has been deemed fit for purpose based on typical exploration data quality assessment procedures and parameters as defined by Teck Resources Limited.

2.6 Data Analysis Methodologies

2.6.1 Probability Plots

Data consisting of continuous variables, for example elemental concentrations and magnetic susceptibility values, have been assessed for multiple populations using probability plots, after assessing for normal distribution (Sinclair 1976). By plotting concentration on the y-axis, and units of normal probability on the x-axis, representative of the probability that a value will lie below the corresponding concentration, probability plots effectively shows the distribution of a population. Inflection points on a probability plot are indicative of a mixing of multiple populations (Sinclair 1976).

2.6.2 Tukey Plots

Tukey plots are used in chapter three for assessing and summarizing overall
compositional differences between lithological units. The plot boxes represents the “interquartile range” defined as the 50 % of data that lies between the first and third quartile (interquartile = Q3-Q1) of ranked data. Whiskers extend to the fifth and 95th percentiles. Outliers, displayed as hollow circles, fall outside of the fifth and 95th percentile. The mean is represented by a solid black dot, and the median a black line. Some elements are shown on a logarithmic scale (log) to better illustrate the range of the natural variability. Analytes such as Sn, Ta, S, B, Hg, Se, Te, Re, Pd, and Pt have been omitted from the Tukey plots, because their concentrations are too close to detection limit. La, Eu, Yb and Ce are plotted to represent the behavior of REEs. Population size for each lithology is indicated in the legend of the plots.

2.6.3 Ranked Variable Plots

Ranked variable plots, produced by the ioGAS software, are used in chapter three to visualize spatial compositional variations of GRD1a due to alteration processes. Each point is assigned colour and size representative of an equal portion of the sample population. Most analytes are plotted with 10 bins (i.e. 10 dots of a distinct colour and size). Analytes with a tighter concentration range, or samples close to detection limit contain fewer bins. Point size increases with increased concentration, colours are scaled on a cold (blue) to hot (red/pink) spectrum.

2.6.4 Bivariate Analysis

Plots of analyte versus analyte are used to assess correlations and differences between elements to aid in the characterization of the alteration assemblages and lithological units. This evaluation focusses on common geochemical associations (e.g. K-Rb, Ca-Sr, K-Tl, Zn-Cd, Ca-Eu, etc.), and relationships between ore and trace metals (e.g. Cu and Mo with the key traces As, Au, Ag, K, etc.). Samples in these plots are identified by lithology.

2.7 Elemental Gains and Losses

A comparison of fresh and altered whole rock compositions indicates which elements are gained and lost during the alteration process. In order to quantify
elemental variability, volume or mass changes resulting from hydrothermal alteration must be accounted for (Gresens 1967; Grant 1986; Appleyard 1980; MacLean & Barrett 1993). Using immobile element ratios as a proxy for mass and volume change, gains and losses are calculated using the formula:

\[ \Delta X = \left( \frac{X_{A}^{B}}{X_{B}^{B}} \right) * X^{B} - X^{A} \quad (1) \]

Where \( \Delta X \) is the mass change of the mobile analyte in g/100 g, (for concentrations in %) \( X_{A}^{B} / X_{B}^{B} \) is the ratio of the fresh (A) and altered (B) immobile analyte and \( X \) is the concentration of the mobile element for the fresh (A) and altered (B) samples (Warren et al. 2007). This equation is the mathematical equivalent to the equation put forth by Grant (1986), though by using immobile element ratios it is not necessary to know the fresh and altered rock densities (Warren et al. 2007). Ti is used as the immobile element (Hezarkhani 2011).

Elemental gains and losses induced by hydrothermal alteration have been determined for GRD1a using end members, selected based on observations and MER diagrams, to represent unaltered (fresh) rocks and those that display potassic, phyllic and propylitic alteration. Hand sample observations and a combination of element ratio plots identify samples:

**G-07a:** as fresh, as it plots on the line connecting (1,1) and (1,0), at the known composition of fresh plagioclase (around An45) on the plots (2Ca + Na + K)/Al versus 2Ca/Al and Na/Al; plots on the fresh line of Al/Ti versus (2Ca + Na + K)/Ti; and appears fresh in hand sample

**H-05:** as representative of potassic alteration, plotting with low Ca and Na and high K on the plots (2Ca + Na + K)/Al versus 2Ca/Al, Na/Al and K/Al, consistent with K-feldspar alteration of plagioclase; and confirmed by feldspar staining and hand sample observations
G-03: as representative of propylitic alteration, as it plots the farthest from the x = y control line, and closest to the epidote control line on the Al/Ti versus (2Ca + Na + K)/Ti; and confirmed by hand sample observations.

O-04: as representative of phyllic alteration; plotting with both low Ca and high K on the (2Ca + Na + K)/Al versus 2Ca/Al and K/Al, indicative of calcic zones of plagioclase altering to muscovite; and confirmed by thin section observations.

Photographs and descriptions of the selected samples are found in Appendix B and C.

2.8 Molar Element Ratios

Pearce and general element ratio (PER and GER) plots are used in chapter four to interpret alteration processes. Molar element ratio (MERs) is the collective term that encompasses both PER and GER. Molar combinations, stoichiometrically representative of minerals of interest, are plotted as axes to show trends indicative of a process, such as alteration (Pearce 1968).

A GER uses a compositionally suitable denominator (e.g. Al for examining feldspar systematics) to assess chemical variation relative to mineral nodes. Element ratios are presented on each axis that represent a mineral or group of minerals. Feldspar space is commonly examined using (2Ca + Na + K), abbreviated as 2CNK, on one axis, to accommodate for variability between feldspar end members anorthite, albite and orthoclase. The diagram 2CNK/Al versus Na/Al has mineral nodes representing albite (1,1), muscovite (1/3,0) and anorthite/K-feldspar (1,0). These mineral nodes are used to indicate both primary and alteration mineral composition. Mineral composition determines the node location. For example, albite with the end member composition NaAlSi3O8 [((2*0 + 1 + 0)/1), (1/1)] plots as (1,1). Neither of the end members anorthite (CaAl2Si2O8) nor K-feldspar (KAlSi3O8) contains any Na; therefore both plot as (1,0).

A conserved element is used in the denominator for PERs, which allows for mineral control lines (as opposed to nodes as in GER) to be used for interpreting
processes such as alteration. In order to use PER diagrams there must be a failure to reject the cogenetic hypothesis (Russell & Stanley 1990). The cogenetic hypothesis postulates that each rock unit, at some point, originated from a homogeneous system (Russell & Stanley 1990). To reject the cogenetic hypothesis, two potentially conserved elements (or oxides) are plotted against one another, treating each lithology separately. If the two elements are conserved the best-fit line will have a positive slope, pass through the origin, or cross the axis of the least conserved element, as well as intersect the analytical error ellipses (representing two standard deviations) of a statistically significant portion of samples (determined by population size, generally ~ 95 %) (Stanley, unpublished). If the elements are not conserved the slope of the best fit line will be negative, zero or infinite; or will not intersect an appropriate portion of the error ellipses. The conservation of Zr and TiO$_2$, both high field strength elements (HFSE) commonly determined as immobile elements for PER (e.g. Pearce 1987; Whitbread & Moore 2004; Urqueta et al. 2009), have been tested for each lithology; TiO$_2$ is deemed more conserved than Zr and is used as the immobile element for PER assessment (Figure 31).

The PER diagrams are generally designed to have a specific mineral, or group of minerals of interest represented by the $x = y$ (slope of the line - $m = 1$) control line (Stanley & Russell, 1989). Control lines are calculated using mineral compositions in the same way as nodes in GER plots, and are two-dimensional expressions of compositional planes into and out of the page representative of that mineral or groups of minerals. For example the plot Al/Ti versus 2CNK/Ti isolates all feldspar variation along the $x = y$ control line. This plot also displays control lines representing epidote ($m = 2$), muscovite ($m = 1/3$) and chlorite ($m = 0$). Any chemical difference due to feldspar composition (e.g. albitic alteration, or igneous K-feldspar) will be captured in the plane represented by the $m = 1$ line; chemical variability introduced by hydrothermal alteration to epidote (propylitic), muscovite (phylllic) or chlorite (propylitic and/or phyllic) will result in points plotting away from the feldspar control line, and towards their respective alteration mineral(s) control lines.

One advantage of PER over GER is that PER diagrams can be customized to maximize the visualization of a particular alteration process by using a selection of
suitable minerals, for instance minerals representing the primary composition, for axes calculations. These axes are calculated by first expressing the mineral compositions in a matrix, then calculating the null vector for that matrix, usually using mathematical software such as MATLAB® (modified from Stanley & Russell 1989) (Figure 9). This null vector is broken into an x and y component that defines a plane in space representing the compositional variability introduced by the minerals. Using the identified x and y components as the axes, this plane becomes the line identified by $x = y$. 
Figure 9: Compositional matrix of anorthite (An), pargasite (Hb), biotite (Bt), albite (Ab) and actinolite (Ac) reduced to x and y vectors representative of the null vector. These x and y vectors define a plane that is representative of compositional variability attribute to the primary mineral assemblage. Actinolite, pargasite, anorthite and albite are used to accommodate for compositional variations in feldspars and hornblende.
Chapter 3: Characterization and Evolution of the Lithological Units in a Calc-Alkaline Porphyry: A Case Study of the Relincho Cu-Mo Porphyry, Atacama, Chile

3.1 Introduction

Lithogeochemical sampling of surface rocks at a regional scale coupled with robust interpretation is used to characterize lithological units and alteration assemblages, as well as interpret potential magmatic evolution and source magma fertility. Mineralization at the Relincho PCD is hosted by Paleocene granodiorite of the Los Morteros batholith. Four Paleocene porphyritic units are spatially and genetically associated with Cu-Mo mineralization. Geochemistry is used to identify distinguishing features of the porphyry and granodiorite units for characterization, to understand the magmatic evolution of the lithological units, and to characterize alteration assemblages.

Characterization of the granodiorite and porphyry units using lithogeochemistry, petrography and field observations distinguishes four units of the granodiorite (GRD1a, GRD1b, GRD2 and GRD3), and four syn-mineralization porphyritic units (PQF1, PQF2, PFB, and PQB). An evolutionary model presented here suggests four magmatic differentiation cycles associated with three magma recharges resulting in an evolution from \([\text{GRD1b} + \text{GRD3}] \rightarrow \text{GRD1a} \rightarrow [\text{PQF1} + \text{PQF2} + \text{PFB} + \text{PQB}] \rightarrow \text{GRD2}\). Compositional overlaps within the porphyritic units prohibit further distinctions.

Results from the characterization are used for interpreting the magmatic fertility of the Los Morteros batholith. Magma fertility plots identify potentially Cu-Mo fertile source magmas from infertile based on water content of the source magma. The GRD1a, GRD2 and the porphyritic units are identified as potentially Cu-Mo fertile and likely from a high magmatic water content magma source, whereas the (interpreted) early granodiorite units \([\text{GRD1b} + \text{GRD3}]\) are infertile from a water-poor source magma.

Characterization of the alteration fluids is the initial step in understanding alteration processes and being able to relatively quantify alteration. Widespread, weak
to moderate intensity alteration associated with Cu-mineralization grades outward from mineralization from potassic proximally to phyllic and propylitic distally. Elemental gains and losses for potassic, propylitic and phyllic alteration are used to determine fingerprint elements for each assemblage that can be used regionally for exploration. Population breaks in key alteration elements distinguish samples affected by alteration from those unaffected.

### 3.2 Geological Setting

Early to Late Cretaceous andesite of the Cerrillos Formation host the Paleocene granodiorite of the Los Morteros batholith, which was emplaced via regional north-south striking extensional faulting formed during the Jurassic-Early Cretaceous period (Camus 2007) (Figure 4). This granodiorite hosts four Paleocene, syn-mineralization porphyritic units, emplaced along a seven km long, northwest-southeast striking series of mineralized porphyry centers, referred to as the porphyry corridor (Figure 4). Hypogene mineralization consists of veinlet-controlled and disseminated bornite, chalcopyrite, pyrite, and molybdenite. A 2000 m x 500 m surface exposure of mineralization is in the form of discontinuous copper oxide, oriented approximately northwest-southeast along the porphyry corridor (Teck Resources Limited 2007). Mineralization is related to a large-scale hydrothermal system that has an alteration surface expression of approximately 60 km².

### 3.3 Lithological Units

A project scale schematic geological map compiled from point data and regional geologic map are presented for general reference with the caveat that contacts between lithological units on the project scale map are approximated, being based on sample collection localities rather than detailed lithological boundary mapping (Figure 6, Figure 10). Descriptions are presented chronologically from oldest lithological unit to youngest. The andesite, granodiorite, porphyry, hydrothermal breccia and post-mineralization intrusive units are described, though only the granodiorite and porphyry units are characterized geochemically as they are related to the magmatic source of mineralization and its alteration effects.
Figure 10: Schematic geological map of the project area based on point data showing approximate contacts. Porphyry corridor is used for spatial context, note the spatial restrictions for the lithological units, namely GRD1a outcropping largely adjacent to or north of the porphyry corridor. GRD2, GRD3 and GRD1b outcrop predominantly to the south. Porphyry units are structurally controlled, outcropping near the porphyry corridor, or perpendicular to it.
3.3.1 **Andesite**

The Early Cretaceous, Cerrillos Formation andesite was emplaced subaerially (Martínez et al. 2013), with no flow structures observed in the project area. It is dark grey to brown, jointed to blocky, and resistant to weathering in outcrop, while appearing dark grey-green and homogeneous in hand sample (Figure 11a, b). The andesite is plagioclase-phyric and crowded (60% plagioclase phenocrysts) with a fine-grained groundmass and minor amounts of hornblende (less than 5%). Plagioclase crystals are 0.05 – 0.1 cm long and sub-angular (Figure 11c, d). The Cerrillos Formation andesite hosts the granodiorite and outcrops in the north and northwest region of the project area (Figure 4, Figure 10). Weak propylitic alteration is present in some of the andesite outcrops. This unit has not been characterized in this study due to its small spatial footprint in the project area and hence poor sample representation.

3.3.2 **Granodiorite Units**

The granodiorite units outcrop throughout the project area. They are spatially constrained in that GRD2 and GRD3 predominantly outcrop to the south of the porphyry corridor (Figure 10). In outcrop all granodiorite units appear similar: grey to pale brown-pink, competent, resistant to weathering and blocky when jointed.

Texture and mineralogy define three granodiorite units: GRD1, GRD2 and GRD3 (Table 2 and Figure 12a). Mineralogically the three units are comprised of varying quantities of plagioclase, quartz, hornblende and biotite with trace amounts of apatite, titanite, ilmenite, zircon, magnetite and in the case of GRD2 K-feldspar, as summarized in Table 2 and Figure 12a. In hand sample GRD1 has a characteristic homogenous, medium grained, idiomorphic texture. GRD2 is discernable by its hypidiomorphic texture, relative lack of mafic minerals and distinct pink colour due to the presence of igneous K-feldspar. Unit GRD3 has a relatively higher hornblende and biotite content than the other two units, and a distinguishing hypidiomorphic to sub-porphyritic texture. Igneous K-feldspar is only present in GRD2.
Figure 11: Pictures of the Cerrillos Formation andesite in a. outcrop, b. hand sample, c. polarized light thin section and d. cross-polarized light thin section.
<table>
<thead>
<tr>
<th>Code</th>
<th>Photograph</th>
<th>Granular Fabric</th>
<th>Protolith Composition</th>
<th>Hand Sample Colour</th>
<th>Lithology</th>
</tr>
</thead>
</table>
| GRD1a | ![Image](image1.png) | Idiomorphic, homogeneous | Medium grained | 60-75% plagioclase  
10-15% quartz  
10-15% hornblende  
5-12% biotite  
2-5% magnetite  
trace apatite  
Zr < 150 ppm | White-grey | Biotite-hornblende quartz diorite |
| n=97  | ![Image](image2.png) | Idiomorphic, homogeneous | Medium grained | 60-75% plagioclase  
10-15% quartz  
10-15% hornblende  
5-12% biotite  
2-5% magnetite  
trace apatite  
Zr < 150 ppm | White-grey | Biotite-hornblende quartz diorite |
| GRD1b | ![Image](image3.png) | Idiomorphic, homogeneous | Medium grained | 60-75% plagioclase  
10-15% quartz  
10-15% hornblende  
5-12% biotite  
2-5% magnetite  
trace apatite  
Zr > 150 ppm | White-grey | Biotite-hornblende quartz diorite |
| n=28  | ![Image](image4.png) | Idiomorphic, homogeneous | Medium grained | 60-75% plagioclase  
10-15% quartz  
10-15% hornblende  
5-12% biotite  
2-5% magnetite  
trace apatite  
Zr > 150 ppm | White-grey | Biotite-hornblende quartz diorite |
| GRD2  | ![Image](image5.png) | Hypidiomorphic | Fine-medium grained | 20-40% plagioclase  
15-30% K-feldspar  
35-55% quartz  
3-12% hornblende | Pink | Hornblende granodiorite |
| n=12  | ![Image](image6.png) | Hypidiomorphic | Fine-medium grained | 20-40% plagioclase  
15-30% K-feldspar  
35-55% quartz  
3-12% hornblende | Pink | Hornblende granodiorite |
| GRD3  | ![Image](image7.png) | Idiomorphic to sub-porphyritic | Fine-medium grained | 45-55% plagioclase  
5-12% quartz  
20-30% biotite  
10-15% hornblende up to 5% magnetite | White-grey | Hornblende-biotite quartz diorite |
| n=14  | ![Image](image8.png) | Idiomorphic to sub-porphyritic | Fine-medium grained | 45-55% plagioclase  
5-12% quartz  
20-30% biotite  
10-15% hornblende up to 5% magnetite | White-grey | Hornblende-biotite quartz diorite |

Table 2: Summary of granodiorite unit properties. Photographs are of the hand sample (top left), stained section (top right), polished thin section in polarized light (bottom left), and polished thin section in cross-polarized light (bottom right). Each photograph is of the same area of the same sample, to the same scale. Lithology classifications are based on quartz-alkali feldspar-plagioclase ternary classifications from Streckeisen, 1976 based on mineral composition from hand sample, thin section, feldspar staining and field observations. Note that the yellow staining in the GRD1b and GRD3 samples are from K-feldspar alteration, not igneous K-feldspar.
Figure 12: Compositional diagrams indicating variability of a. granodiorite units b. porphyry units, with ground mass depicted as solid colours and phenocrysts depicted as hatched, and c. the lithology of each unit, based on observed mineralogical compositions in accordance with the quartz - alkali feldspar - plagioclase ternary diagram presented by Streckeisen (1976).
The term “granodiorite” is used for consistency with current practices. Only GRD2 is a granodiorite sensu stricto as it is the only unit that contains igneous K-feldspar. Based on mineralogy the units are: biotite-hornblende quartz-diorite (GRD1); hornblende granodiorite (GRD2); and hornblende-biotite quartz-diorite (GRD3), in accordance with the quartz-alkali feldspar-plagioclase classification scheme presented by Streckeisen (1976) (Figure 12c). All granodiorite units exhibit some Cu-Mo mineralization, with GRD1 and GRD3 being the most mineralized and GRD2 least.

The granodiorite units have previously been identified in property scale maps as a single unit, however detailed observations made in this study have identified four distinct units. Geochemistry is used to further breakdown the GRD1 unit into GRD1a and GRD1b, which are visually indistinguishable. Further discussion is found in the “Geochemistry of Lithological Units” section of this chapter. With no contacts observed in the field and no prior subdivision of the granodiorite recorded, the contact relationships and relative ages of these units are unknown.

### 3.3.3 Porphyry Units

The porphyry units are isolated to outcropping within and near the porphyry corridor. Some offshoots to the north and south follow regional structures and are approximately perpendicular to the porphyry corridor (Figure 10). The four porphyry units are all similar in appearance in outcrop. In outcrop the porphyry units are beige-pink to light brown, massive, competent, resistant to weathering and blocky when jointed.

In hand sample the four units are distinguishable by texture and subtle variations in feldspar, quartz, hornblende and biotite content, as summarized in Table 3 and Figure 12b. PQF1 is aphanitic groundmass supported with phenocrysts of plagioclase, rounded quartz eyes, hornblende and biotite. PQF2 is distinguishable by the crowded phenocrysts of plagioclase, quartz eyes, hornblende and biotite, and the aphanitic groundmass. PFB has a distinct lack of quartz eyes, while containing crowded plagioclase, hornblende and biotite phenocrysts and a fine-grained groundmass. PQB is aphanitic groundmass supported, containing plagioclase, sub-rounded quartz eyes, hornblende and biotite phenocrysts.
<table>
<thead>
<tr>
<th>Code</th>
<th>Photograph</th>
<th>Phenocrysts Properties</th>
<th>Groundmass Properties</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQB</td>
<td><img src="image" alt="Image" /></td>
<td>45-65% phenocryst, sparsely crowded: 3-15% sub-rounded, 1 cm quartz eyes 20-45% plagioclase as 0.5 cm sub-angular to sub-rounded crystals 3-5% hornblende 5-10% biotite</td>
<td>35-55% aphanitic groundmass supported 55% quartz 45% K-feldspar</td>
<td>Hornblende-biotite monzogranite</td>
</tr>
<tr>
<td>PQF1</td>
<td><img src="image" alt="Image" /></td>
<td>55-65% phenocryst, crowded: 0-3% sub-angular, 0.2 cm quartz eyes 40-55% plagioclase as 1 cm sub-rounded and 0.2 cm sub-angular crystals 3-6% hornblende 4-10% biotite</td>
<td>35-45% fine-grained groundmass, phenocryst supported 55% quartz 45% K-feldspar</td>
<td>Hornblende-biotite granodiorite</td>
</tr>
<tr>
<td>PQF2</td>
<td><img src="image" alt="Image" /></td>
<td>60-75% phenocrysts, crowded: 5-7% rounded, 0.5cm quartz eyes 45-55% plagioclase as 1 cm laths or 0.5 cm sub-rounded crystals 3-5% euhedral hornblende 5-8% euhedral biotite</td>
<td>25-40% aphanitic groundmass, phenocryst supported 52% quartz 43% K-feldspar 5% slivers of biotite</td>
<td>Hornblende-biotite granodiorite</td>
</tr>
<tr>
<td>PFB</td>
<td><img src="image" alt="Image" /></td>
<td>55-65% phenocrysts, sparsely crowded: 5-12% rounded quartz eyes 25-45% plagioclase as 0.5 cm laths or 0.25 cm sub-rounded crystals 2-5% euhedral hornblende, 3-7% euhedral biotite</td>
<td>35-45% aphanitic groundmass supported 53% quartz 44% K-feldspar 3% biotite</td>
<td>Hornblende-biotite granodiorite</td>
</tr>
</tbody>
</table>

Table 3: Summary of porphyry unit properties. Photographs are of the hand sample (top left), stained section (top right), polished thin section in polarized light (bottom left), and polished thin section in cross-polarized light (bottom right). Each photograph is of the same area of the same sample, to the same scale. Lithology classifications are based on quartz-alkali feldspar-plagioclase ternary classifications from Streckeisen, 1976 based on mineral composition from hand sample, thin section, feldspar staining and field observations.
All four porphyry units contain K-feldspar and quartz in their groundmass. Mineralogically PQF1, PQF2 and PFB are hornblende-biotite granodiorite and the PQB is a hornblende-biotite monzogranite, in accordance with the classification scheme presented by Streckeisen (1976)(Figure 12c). All porphyry units show some Cu-Mo mineralization, with PQF1 being most strongly so, followed by PQF2, PFB and PQB.

Observed crosscutting relationships and mineralization aid in determining the relative ages of the porphyry units. Based on cross cutting relationships, PQB is the youngest porphyry unit. Mapping and age dating by Teck Resources Limited indicate that PQF1 is oldest, followed by PQF2, PFB and PQB. All four porphyry units are mineralized.

3.3.4 Hydrothermal Breccia

Hydrothermal breccia (BX) outcrops along the porphyry corridor (Figure 10). It is a polymictic, matrix supported breccia with angular to sub-angular granodiorite and/or porphyry clasts (0.5 – 3cm) depending on contact lithology, with a mafic rich matrix (Figure 13). The breccia unit is generally isolated to the area directly adjacent to porphyry – granodiorite contacts and typically contains mineralization in the matrix and clasts. This unit has not been characterized in this study due to limited spatial coverage and polymictic nature making them poor candidates for lithogeochemical assessment.

3.3.5 Post-Mineralization Dikes

Post-mineralization dikes (PM) follow northeast-southwest structures, outcropping as long, slender bodies (Figure 10). They intrude the porphyry and granodiorite units in the project area. The dykes are dacitic with textures ranging from fine-grained, idiomorphic to, more typically, porphyritic (Figure 14). Porphyritic dikes are groundmass supported with 15-40% sub-rounded plagioclase phenocrysts, 7-15% hornblende phenocrysts and 1-10% quartz eyes. This unit has not been characterized in this study due to poor spatial distribution and hence poor representation in the sample suite. Given that these dykes are post mineralization, lithogeochemical assessment of them would not add significant information as they post date alteration processes.
Figure 13: Pictures of the hydrothermal breccia in a. outcrop, b. hand sample, c. stained section d. polarized light thin section and e. cross-polarized light thin section.
Figure 14: Pictures of the post mineralization dikes in a. outcrop and b. hand sample.
3.4 Alteration

Alteration assemblages exhibited in the project area are potassic, propylitic and phyllic defined as:

*Potassic Assemblage:* secondary biotite + K-feldspar + magnetite + ± glassy limonite (from chalcopyrite weathering at surface)

*Propylitic Assemblage:* epidote + chlorite + hematite ± albite ± calcite ± pyrite

*Phyllic Assemblage:* chlorite + muscovite + quartz ± calcite ± hematite.

With key assemblage indicator minerals in bold. Potassic, propylitic and phyllic alteration affects all granodiorite and porphyry units, with the exception of PQB, which is not affected by potassic alteration. Late-stage, widespread chlorite alteration affects the entire project area.

Alteration intensities are described as: unaltered (< 15% replacement of the primary mineralogy by the alteration mineralogy); weak (15% ≤ replacement < 30%); moderate (30% ≤ replacement < 60%); or strong (≥ 60% replacement). A schematic alteration map based on hand sample, field and thin section observations indicates the extent of weak alteration (Figure 15). Alteration mineralogy shows an overall proximal to distal pattern of potassic (up to 200 m from the porphyry corridor) – phyllic (within 100 m of mineralization with structurally controlled outcrops distally) – propylitic (up to 2.5 km from the porphyry corridor) alteration progressing outward from the porphyry corridor. Cu sulphide mineralization is spatially related to potassic alteration. Propylitic alteration has the largest footprint. Patterns of overprinting alteration minerals indicate that the potassic alteration occurred first, followed by propylitic and phyllic, consistent with conventional porphyry models (Lowell & Guilbert 1970; Seedorff 2005; Sillitoe 2010).
Figure 15: Spatial extent of alteration assemblage and examples of minerals diagnostic of each assemblage. a. Spatial extent of weak alteration based on hand sample, petrography and field observations. The potassic alteration occurs in the porphyry corridor or within 200 m, with some structurally controlled distal expressions. Phyllic alteration is observed within 100 m of the porphyry corridor with some structurally controlled distal expressions. Propylitic alteration is expressed up to 2.5 km away. b. Potassic assemblage is defined by the presence of secondary biotite and K-feldspar. Moderate K-feldspar replacement of plagioclase, strong secondary biotite replacement of hornblende and K-feldspar haloes around glassy limonite veins is indicative of moderate intensity potassic alteration. Thin section photographs shows biotite replacement of a hornblende site being overprinted by chlorite alteration indicating propylitic or phyllic alteration overprinting of the potassic. c. Propylitic alteration is characterized by the presence of chlorite and epidote. Photographs indicate strong alteration of plagioclase and hornblende by epidote. The presence of K-feldspar indicates propylitic overprinting of potassic alteration. d. Phyllic alteration is defined by muscovite and chlorite. Thin section photographs show weak muscovite alteration of calcic zones in plagioclase, and weak calcite alteration of feldspar.
3.4.1 Potassic Alteration

Potassic alteration is generally constrained to in, or within 200 m of the porphyry corridor (Figure 15a). Secondary biotite and K-feldspar alteration are definitive of the assemblage (Figure 15b). Secondary biotite alters biotite and hornblende. It is identified by its well-developed shredded texture and distinct beer-bottle-brown colour. K-feldspar alteration tends to be incipient and difficult to identify in the field. Potassic alteration is associated with disseminated Cu-Mo mineralization in the form of chalcopyrite, molybdenite, and bornite, in addition to veins of chalcopyrite ± bornite ± molybdenite. Where oxidized, chalcopyrite has been changed to glassy limonite.

3.4.2 Propylitic Alteration

The propylitic alteration has the largest footprint of the alteration assemblages, extending up to 2.5 km away from the porphyry corridor (Figure 15c). Epidote and chlorite are diagnostic of the propylitic assemblage. Alteration intensities vary from weak to strong. Strong propylitic alteration is defined by strong replacement of hornblende and moderate replacement of plagioclase by epidote (Figure 15a). Albite replacement, where present, is weak and only apparent by an increased hardness of the plagioclase. Calcite, where present, replaces hornblende and/or plagioclase and/or is associated with veinlets. Pyrite has been largely destroyed by oxidation, though rusted pits are indicative of its existence.

In places, propylitic alteration overprints potassic alteration. These cases show incongruent mineral associations, such as epidote in the same sample as incipient K-feldspar alteration of plagioclase, or overprinting mineralogical textures such as chlorite overprinting secondary biotite.

Incipient to pervasive chlorite replacement of hornblende and biotite is a product of phyllic, propylitic and late-stage chlorite alteration. In order to differentiate between these alteration styles, epidote or muscovite must be identified in conjunction with chlorite to define alteration as part of either the phyllic or propylitic assemblage.

3.4.3 Phyllic Alteration

Phyllic alteration generally occurs within 100 m of the porphyry corridor with isolated, structurally controlled outcrops distally (Figure 15a). It is defined by the
presence of chlorite and muscovite with sporadic carbonate (Figure 15d). Muscovite alteration affects hornblende, biotite and calcic zones in plagioclase. The alteration of plagioclase by muscovite can resemble K-feldspar alteration, as it tends to be pink, though it is much softer than K-feldspar alteration. Quartz ± chlorite veins are also associated with phyllic alteration. The phyllic assemblage is not associated with supergene mobilization of mineralization, though it may contain pyrite, which has been oxidized and is now indicated by rusted vugs. Hematite is commonly associated with the phyllic assemblage and is interpreted to be a product of phyllic-related magnetite destruction.

Phyllic alteration locally overprints the potassic and/or propylitic assemblages. These cases show incongruent mineral associations, such as muscovite alteration of plagioclase adjacent to secondary biotite or epidote. Overprinting mineral textures, such as muscovite overprinting secondary biotite or chlorite, are also indicative of phyllic overprinting of potassic or propylitic alteration assemblages respectively.

3.5 Geochemistry of Lithological Units

Granodiorite units are distinctive geochemically from each other, though the porphyry units are much less so. Tukey, bivariate, univariate, immobile element, and REE plots along with radiometric imaging are used to differentiate and characterize the lithological units. Due to the incipient, widespread nature of alteration, most alteration is weak to moderate, and no samples are truly fresh. For the lithological characterization all sample results are used with no distinction between altered and fresh rocks. Summary statistics for diagnostic analytes are found in Table 5.

3.5.1 Granodiorite Units

Field observations distinguish three granodiorite units: GRD1, GRD2 and GRD3. Lithogeochemistry identifies two populations within the GRD1 unit: GRD1a and GRD1b. GRD1b is visually indistinguishable from GRD1a, though chemically GRD1b is more similar to GRD3. The granodiorite units, therefore, are separated into three geochemically distinct groups: GRD1a, GRD2 and [GRD1b + GRD3].
Tukey plots demonstrate the general compositional ranges between units (Table 4, Figure 16). These Tukey plots display 10% of samples as outliers, with the number of outliers being directly proportional to population size. As GRD1a has the largest sample population, it also has the most outliers (10). Relative standard deviations (RSD) calculated for selected elements gives a better indication of compositional variance within a unit (Table 5).

GRD2 and [GRD1b + GRD3] are the compositional end members of the granodiorite units. With respect to the other granodiorite units, GRD2 has higher concentrations of $K_2O$ and $SiO_2$ due to the igneous $K$-feldspar and elevated quartz content, not present in the other granodiorite units. [GRD1b + GRD3] shows elevated $TiO_2$, $Fe_2O_3$, $Cr_2O_3$, $MnO$ and $MgO$ relative to the other granodiorite units, consistent with a higher mafic mineral content in [GRD1b + GRD3]. GRD1a contains slightly more $Na_2O$ than the other granodiorite units, consistent with a more plagioclase dominant rock. All four units show some mineralization. Major oxide and immobile element plots show that GRD1a clusters tightly relative to other lithological units, generally between the compositions of [GRD1b + GRD3] and GRD2 (Figure 17). Generally speaking, GRD2 is slightly depleted and GRD1b slightly enriched in the light rare earth elements (LREEs) relative to GRD1a and GRD3 (Figure 20). REEs normalized to mid-ocean ridge basalt (N-MORB) show lower heavy rare earth elements (HREEs) concentrations in GRD1a and GRD2 relative to GRD1b + GRD3, consistent with hornblende fractionation in the source magma of GRD1a and GRD2 (Davidson et al. 2013). Negative Eu anomalies in [GRD1b + GRD3] and GRD2, but not in GRD1a (Figure 20) are associated with plagioclase fractionation and removal from the source magma (Davidson et al. 2013).

Radiometric K-eU-eTh imaging proves a useful tool for discriminating between the granodiorite units. Consistent with $K_2O$, Th and U variations in the geochemistry, the radiometric image shows a distinct boundary between the GRD1a in the north, a radiometric low, and GRD1b, GRD2, GRD3, and the porphyry units to the south, represented by a radiometric high (Figure 18a and b). This is a product of the low $K_2O$, Th and U concentrations in GRD1a relative to GRD1b, GRD2 and GRD3 (Figure 18a).
<table>
<thead>
<tr>
<th>Unit</th>
<th>Lower Concentration Range</th>
<th>Higher Concentration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRD2</td>
<td>SiO₂, K₂O, U</td>
<td>Fe₂O₃, MgO, MnO, Cr₂O₃, TiO₂, Ti, Li, Ni, V, Zr,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V, Sc, Rb, Zn, Ni, LREEs, HREEs</td>
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<tr>
<td>GRD1a</td>
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<tr>
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<tr>
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<td>HREEs, Zr, Y, V, Sc, Hf</td>
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</table>

**Table 4:** Summary of Tukey plot observations for distinguishing lithological units chemically.
Figure 16: Tukey diagrams are arranged by lithology in the order of interpreted chronology to assess compositional differences between lithological units, and overall compositional trends with magmatic evolution. Boxes represent the interquartile range defined as the 50% of the data lying between the first and third quartile. Outliers, shown as hollow circles are points beyond 1.5 * (Q3-Q1). Extreme outliers, hollow triangles, fall outside of 3.0 * (Q3-Q1). Whiskers extend to extreme values that are not outliers, i.e. fall within 1.5 * (Q3-Q1)). The mean is indicated as the solid black dot, the median as a black line. Some concentrations (Cu, Mo, Pb, Zn, Ag, Mn, Co, Bi, Mn, As, Au, Ce, Sb and Bi) are shown on a log scale to better represent the compositional spread. Population sizes are indicated in brackets next to the lithology above the plots.
Figure 16: Continued
Figure 16: Continued
Figure 16: Continued
<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$ wt%</th>
<th>K$_2$O wt%</th>
<th>Al$_2$O$_3$ wt%</th>
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<td>10%</td>
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</tbody>
</table>

**Table 5:** Summary statistics for major oxides, HREEs Cu and Mo for porphyry and granodiorite units.

Porphyry units have considerable compositional overlap, though some distinction can be made from the $K_2O$, Zr, Th, and the HREE concentrations. Granodiorite units are best distinguished using TiO$_2$, Zr, $K_2O$, U and Th.
Figure 17: Major oxide and immobile element plots for granodiorite units. 

a. Zr v TiO$_2$: GRD1a clusters tightly relative to other units. GRD2 contains the least Zr and TiO$_2$ of the granodiorite units, and GRD1b + GRD3 the most. 

b. K$_2$O v TiO$_2$: GRD1a clusters tightly relative to other units. GRD2 shows increased K$_2$O, consistent with igneous K-feldspar content. GRD3 + GRD1b have increased TiO$_2$, consistent with a higher mafic component. 

c. SiO$_2$ v MgO: GRD1a clusters tightly between GRD2 and GRD1b + GRD3. Relatively high SiO$_2$ and low mafic content apparent in GRD2 points. High MgO due to high mafic content in GRD1b + GRD3. 

d. K$_2$O v Al$_2$O$_3$: K$_2$O content generally increases from GRD1a to GRD1b + GRD3 to GRD2. High variability in Al$_2$O$_3$ in GRD 2 and GRD1b+GRD3. Summary statistics for these analytes are found in Table 3.
Figure 18: Radiometric analytes distinguish the GRD1a unit from the GRD2, GRD3 and GRD1b sub-units. **a.** Radiometric diagram of K₂O (wt%) versus Th (ppm) with U (ppm) for size show a tight cluster of GRD1a points with low Th, K₂O and U concentrations. Concentrations gradually increase in GRD3 and GRD1b, which have the highest U concentrations. GRD2 has the highest Th and K₂O concentrations, but lower U than GRD1b and GRD3. **b.** Radiometric image draped over an airphoto, with points coloured by granodiorite sub-unit and sized using the formula \( \frac{X_{K2O}}{\mu_{K2O}} + \frac{X_{U}}{\mu_{U}} + \frac{X_{Th}}{\mu_{Th}} \), where the sample content is divided by the mean of the entire granodiorite population (i.e. the mean of GRD1a, GRD1b, GRD2 and GRD3 combined). This plot emphasizes the spatial relationships between the granodiorite sub-units and the effectiveness of using a radiometric image to predict lithology.
3.5.2 Porphyry Units

The porphyry units generally lie within the compositional range defined by GRD1a and GRD2, and are least similar to the group [GRD1b + GRD3] (Figure 17, Figure 19 and Table 5). Major oxides SiO₂, TiO₂, Al₂O₃ and K₂O are useful for breaking out PFB and PQF1 as compositional end members of the porphyry units, with PQF2 and PQB falling between with considerable compositional overlap (Figure 19). From major oxide compositions, PFB is most similar to GRD1a; and PQF1 most similar to GRD2. PQB is distinguishable by its slightly elevated concentrations of P, Mn, Zn, Pb, Nb, Nd and Ta.

All four porphyry units have similar REE concentrations, with PQB having a slightly higher concentrations of REE, and PFB slightly lower (Figure 20). All porphyry units display the “spoon pattern” in normalized REEs, indicative of hornblende fractionation (Davidson et al. 2013). No porphyry unit shows a negative Eu anomaly which would be indicative of plagioclase fractionation (Davidson et al. 2013). In terms of REEs, the porphyry units are most similar to GRD1a. All porphyry units are mineralized, PQF1 most strongly, followed by PQF2, PFB and PQB (Table 5).

3.5.3 Magma Differentiation and Fertility Plots

Differentiation cycles and magmatic recharges can be interpreted from SiO₂ - TiO₂ variations (Loucks 2013). Ti is melt-incompatible and decreases with fractionation in a melt, while Si increases with fractionation. Magmatic recharges introduce Ti and other compatible elements causing an increase in Ti by addition and decrease in Si by dilution (Rohrlach & Loucks 2005). SiO₂ against TiO₂ and Zr are used to interpret magmatic differentiation cycles for the granodiorite and porphyry units (following the methods of Loucks 2013). SiO₂ against TiO₂ shows tight clusters proceeding from low SiO₂ and high TiO₂ to high SiO₂ and low TiO₂ of the following groups: [GRD1b + GRD3], GRD1a, porphyry units, and GRD2 (Figure 21a).

SiO₂ against Zr shows a similar progression from [GRD1b + GRD3], GRD1a, porphyry units, through GRD2. [GRD1b + GRD3] has the highest Zr content of the porphyry and granodiorite units, on average 190 ppm, and between 50 and 70 wt % SiO₂. GRD1a and the porphyry units contain around 120 ppm Zr and 60 to 72.5 wt% SiO₂. GRD2 has the highest SiO₂ content, between 70-77.5 wt%, and lowest Zr, on average 98 ppm.
Figure 19: Major oxide and immobile element plots for porphyry units using the same scale as the granodiorite plots to indicate composition variation between the units. 

a. Zr vs TiO\textsubscript{2} show some distinction between PQF1 and PFB, but much overlap between the PQF2 and PQB populations. 

b. K\textsubscript{2}O vs TiO\textsubscript{2} variability in K\textsubscript{2}O distinguishes PQF1 from PFB, but PQB and PQF2 overlap. 

c. SiO\textsubscript{2} vs MgO considerable compositional overlap, with PQF1 and PFB plotting as end members. 

d. K\textsubscript{2}O vs Al\textsubscript{2}O\textsubscript{3} considerable compositional overlap, with PQF1 and PFB plotting as end members. Summary statistics for these analytes are found in Table 3.
Figure 20: N-MORB normalized REE plots of granodiorite and porphyry units. HREEs distinguish GRD1b and GRD3 from GRD2 and GRD1b. PQF1 is generally REE depleted, relative to PQF2, PFB and PQB. PQB has elevated LREEs relative to the other porphyry units, with the exception of Eu. Depleted HREE concentrations in GRD1a, GRD2 and the porphyry units are indicative of hornblende fractionation from a hydrous melt. Negative Eu anomalies in GRD1b and GRD3 are indicative of plagioclase fractionation from an anhydrous melt. Normalization values from Sun & McDonough,1989.
Figure 21: The interpreted differentiation cycles are shown as numbered shaded areas, with numbered grey arrows showing recharges. 

a. SiO₂ v TiO₂: between populations there is an increase in TiO₂ and decrease in SiO₂ concentrations caused by the influx of fresh magma containing TiO₂, which decreases SiO₂ content by dilution and increase in TiO₂ by addition.

b. SiO₂ v Zr: GRD1b + GRD3 show increases in Zr concentration up to 65 wt% SiO₂, after which Zr concentration drops, consistent with infertile magmas. Magmatic recharge, seen between each population, results in SiO₂ depletion and a slight influx of Zr, which decreases with increasing SiO₂ concentration.
Fertility, or the potential for a magma to generate porphyry style mineralization, in a porphyry system is dependent upon a high magmatic water content source magma (Castillo 1999; Rohrlach & Loucks 2005). Water rich-source magmas can be distinguished based on the principle that hornblende preferentially partitions Y (and Mn) and plagioclase preferentially partitions Sr. A high magmatic water content magma fractionates hornblende in preference to plagioclase; therefore elevated Sr/Y ratios are indicative of mineral fractionation in high magmatic water content magmas (at the appropriate P and T conditions) (Rohrlach & Loucks 2005; Loucks 2013). Y against Sr/Y diagrams separate adakite-like rocks derived from a high magmatic water content, potentially fertile magma source, from “normal”, infertile, island-arc andesite-dacite-rhyolite rocks using a threshold derived from observations made on numerous other porphyry deposits of Sr/Y = 30, (Richards & Kerrich 2007). For the Relincho deposit, an asymptotic trend from a high Sr/Y and low Y, to low Sr/Y and high Y distinguishes the potentially fertile porphyry units, GRD1a and GRD2, from the infertile [GRD1b + GRD3] (Figure 22).

3.6 Elemental Variability Attributed to Alteration

Alteration intensity at the Relincho deposit is weak to moderate and is represented by minor compositional changes in the host rock. Gain-loss diagrams are calculated using one sample each to represent unaltered, potassic, propylitic and phyllic alteration composition, to summarize the materials transferred during alteration. Spatial plots of element variability in the GRD1a unit provide some insight as to the extent of element involvement in alteration. Bivariate analyses explore whether common elemental relationships exist. Probability plots are used to distinguish samples affected by alteration from those unaffected. The characterization of the alteration assemblages employs all of these results to determine how alteration can be identified on a regional scale and how it can be relatively quantification.
**Figure 22:** Magma fertility is indicated by hornblende fractionation from a water-rich melt. Y vs Sr/Y uses the threshold of Sr/Y=30 to represent hornblende fractionation. Hornblende sequesters Y as it fractionates, the remaining hydrous melt depleted Y, Sr is sequestered by plagioclase. Points plotting in the “adakite-like rocks” field are interpreted as more fertile than those plotting in the “normal andesite-dacite-rhyolite” field. Field outlines modified from Richards and Kerrich, 2007.
3.6.1 Spatial Element Variability

Ranked variable plots display equal sample populations as points of distinct colour and size, according to element concentration (Figure 23). To reduce the chemical variability introduced by plotting multiple lithological units, only GRD1a has been plotted spatially. Relative highs and lows are summarized with spatial reference to the porphyry corridor as within, adjacent (up to 500 m outside of the porphyry corridor) and distal (more than 500 m outside of the porphyry corridor):

- **Within**
  - High: \( \text{SiO}_2, \text{K}_2\text{O}, \text{Cu}, \text{Mo}, \text{Au}, \text{Ag}, \text{Rb}, \text{W}, \text{Bi} \)
  - Low: \( \text{CaO}, \text{Na}_2\text{O}, \text{P}_2\text{O}_5, \text{Al}_2\text{O}_3, \text{MnO}, \text{Sr} \)

- **Adjacent**
  - High: \( \text{CaO}, \text{MnO}, \text{Na}_2\text{O}, \text{Sr}, \text{Sb}, \text{Ba}, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{As}, \text{Ce}, \text{La}, \text{P}_2\text{O}_5 \)
  - Low: \( \text{K}_2\text{O}, \text{Cu}, \text{Au}, \text{Ba}, \text{Cd}, \text{Co}, \text{Ga}, \text{Mo}, \text{Ni}, \text{Pb}, \text{Rb} \)

- **Distal**
  - High: \( \text{Na}_2\text{O}, \text{Pb}, \text{Zn}, \text{Mn}, \text{Co}, \text{P}_2\text{O}_5, \text{Al}_2\text{O}_3, \text{Cr}_2\text{O}_3, \text{La} \)
  - Low: \( \text{Al}_2\text{O}_3, \text{Cu}, \text{Mo}, \text{Ni}, \text{SiO}_2, \text{Au}, \text{Cs}, \text{W}, \text{Li} \)

Elements are grouped by their Goldschmidt classification for interpretation, which categorizes elements by their geochemical affinity (Goldschmidt 1937). Lithophile elements (e.g. Li, Na, Mg, K, Ca, Rb, Sr, Cs, Ba, V, Cr, Zr, Al, Si, P) combine readily with O and tend to be elevated adjacent to the porphyry corridor, with the exception of K, Si, V and Rb, which are elevated within the porphyry corridor, and low adjacent to it. Chalcophile elements (e.g. Cu, Mo, Zn, As, Ag, Cd, Sb, Pb, Bi) combine readily with S. Cu, Mo, Bi and Ag are elevated within the porphyry corridor, though some chalcophile elements are elevated adjacent (Sb and As) or distal (Zn and Pb) to the porphyry corridor. Siderophile elements (e.g. Mn, Fe, Co, Ni, Au) combine readily with iron. Au is elevated in the porphyry corridor, though low adjacent and distally. Adjacent to the porphyry corridor Mn and Ni are elevated, with elevated Mn continuing distally.
**Figure 21**: Spatial plots of elemental variability for GRD1a with the porphyry corridor. Points are sized and coloured according to concentration, with each uniquely sized-coloured point representative of an equal number of samples.
Figure 21: Continued
Figure 21: Continued
Figure 21: Continued
Figure 21: Continued
Figure 21: Continued
Figure 21: Continued
Figure 21: Continued
3.6.2 Bivariate Analyses

Bivariate plots have been focused on elements pairs that exhibit geochemically similar behavior (e.g. Al₂O₃ – Ga, K₂O – Rb, CaO – Sr and Zn – Cd); identify lithological units (e.g. major element oxides, Eu, Th and Rb) or are potentially associated with mineralization (e.g. Cu and Mo versus trace and precious metals) (Figure 24). The porphyry and granodiorite units are distinguished by colour on the bivariate plots. Strong positive correlations are seen between Al₂O₃ – Ga, K₂O – Rb, K₂O – Th, CaO – Eu, and CaO – Sr. Lithological units cluster in these diagrams emphasizing the end member compositions of [GRD1b + GRD3] and GRD2 for the granodiorite units, and compositional end members PQF1 and PFB for the porphyry units. There is a weak correlation between Zn – Pb and Zn – Cd in the sample plots, though spatially there is a strong correlation between Zn – Pb – Cd. There is no correlation between Cu and Au, As, Ni, Pb, though Cu shows weak correlations with Ag, Mo and K₂O. Elevated Mo and Cu concentrations occurring predominantly in samples with over 2 wt % K₂O. Mo does not correlate with Au, Zn, Ag or As.

3.6.3 Probability Plots

Concentration breaks determined from probability plots are more representative than arbitrary concentration breaks, as they are indicative of distinct populations with fundamental compositional differences that could be due to lithology, alteration or mineralization (Sinclair 1976). Probability plots have been used to distinguish populations affected by alteration from those unaffected within the GRD1a unit (Figure 25). To minimize populations introduced by mixing lithological units, only GRD1a has been plotted. Once populations have been identified, they are plotted spatially to determine if they are consistent with field and hand sample observations. As GRD1a outcrops predominantly to the north, the alteration population footprints interpreted from GRD1a samples are truncated near the porphyry corridor. Elevated populations of K₂O/Th (> 0.32) and Cu (> 118 ppm) have a similar spatial extent to that of potassic alteration (Figure 26a). Low magnetic susceptibility (< 10.1) values resemble the phyllic alteration footprint, indicating magnetite destruction, giving a magnetically depressed zone in the system (Figure 26b).
Figure 22: Bivariate plots by lithology
Figure 22: Continued
Figure 22: Continued
Figure 23: Population separation based on probability plots with isolated populations indicated by shaded areas. 

a. Probability plot of magnetic susceptibility in GRD1a samples showing a small population change around 10.1. 

a. Depleted magnetic susceptibility are associated with phyllic alteration. 

b. K2O/Th probability plot of GRD1a samples showing a population break around 0.36. 

c. Cu probability plot of GRD1a with a break distinguishing background from samples affected by hydrothermal processes around 112 ppm. 

d. Cu probability plot of all granodiorite and porphyry units showing a population break at 282 ppm.
Figure 24: a. Potassic alteration showing strong spatial correlation with elevated GRD1a K₂O/Th, and Cu populations. b. Depleted magnetic susceptibility samples correlate with the outline of weak phyllic alteration in GRD1a.
3.6.4 *Elemental Gains and Losses*

Gain-loss diagrams summarize element transfer during alteration. This type of geochemical assessment is useful in identifying subtle changes in trace, generally mobile element chemistry, which can sometimes be cryptic and difficult to quantify with traditional methods, such as petrography. Altered and fresh samples are selected using a combination of hand sample observations and MER relationships to identify a representative sample of each alteration assemblage. Gains and losses are relative to volume change during alteration, which is approximated using immobile “element” ratios of the altered and fresh samples. TiO$_2$ is used as the immobile element to keep consistency with the PER interpretations. To minimize compositional variations due to lithology, only samples of GRD1a were used.

Elemental gains and losses from alteration of GRD1a are presented in Figure 27 and summarized in Table 6. The calculated gains and losses are summarized below with significant variations (> 1 g/100 g for oxides and > 10 mg/100 g for trace metals) indicated in bold:

- **Potassic alteration**
  Gains: SiO$_2$, K$_2$O, Zn, Ag, Cu, Al$_2$O$_3$, Fe$_2$O$_3$, MgO, Mo, Pb, Li
  Losses: CaO, Na$_2$O

- **Propylitic alteration**
  Gains: K$_2$O, Na$_2$O, Mo, Pb, Li
  Losses: SiO$_2$, Cu, Zn, Fe$_2$O$_3$, Al$_2$O$_3$, CaO, Ag, Li

- **Phyllic alteration**
  Gains: SiO$_2$, K$_2$O, Cu, Mo, Ag, Pb, Zn, Au, B
  Losses: Fe$_2$O$_3$, CaO, Al$_2$O$_3$, MgO, Na$_2$O, Li

The elemental variations associated with potassic, propylitic and phyllic alteration at the Relincho PCD are consistent with those observed at the trachydacite hosted Bajo de la Alumbrera porphyry deposit (Ulrich & Heinrich 2002); the diorite-granodiorite hosted Sungun porphyry deposit (Taylor & Fryer 1980); and various granodiorite related porphyry deposits in Turkey (Hezarkhani 2011) (Table 6).
Elemental gains and losses due to alteration of GRD1a are calculated using the formula $\Delta X = \left(\frac{X_B}{X_A}\right) \times (X^a - X^{ai})$, where $\Delta X$ is the mass change of the mobile analyte per 100 g, $X^a/X^{ai}$ is the ratio of the median values of the fresh (A) and altered (B) immobile analyte and $X$ is the median concentration of the mobile analyte for the fresh (A) and altered (B) populations (Warren et al. 2007). TiO$_2$ is used as the immobile analyte. a. gains and losses plots and b. summary of gains and losses.
**Table 6:** Summary of elemental gains and losses due to hydrothermal alteration at Relincho as compared to equivalent alteration assemblages at other porphyry deposits.

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<tr>
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<td>(N/A)</td>
<td>Fe₂O₃, Zn, K₂O</td>
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<td>Zn, Ni</td>
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<td>(N/A)</td>
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3.7 Interpretations of Magmatic Evolution, Fertility and Alteration Fluids

Major oxides, trace elements, REEs and hand sample observations are used to distinguish four porphyry units and four granodiorite units. These eight units are interpreted as the products of four differentiation cycles with three magmatic recharges. Porphyry and granodiorite units are identified as being sourced from a hydrous magma and are therefore potentially fertile, with the exception of GRD1b and GRD3.

Gain-loss observations are consistent with spatial plots of elements, showing increased concentrations of K, Cu, Si, Au and Ag in the porphyry corridor, with typical metal zonation of increased Zn, Mn and Pb distally. Population breaks within K₂O/Th, Cu and magnetic susceptibility identify the potassic (K₂O/Th and Cu) and phyllic (magnetic susceptibility) alteration assemblages.

3.7.1 Magmatic Evolution and Fertility

Based on major oxide, REE, and trace element plots there are eight distinct lithological units: [GRD1b + GRD3], GRD2, GRD1a, PQF1, PQF2, PFB and PQB. [GRD1b + GRD3] and GRD2 represent the compositional end members of the eight lithological units. Within the porphyry units PQF1 and PFB define the end member compositions, with much compositional overlap between the porphyry units. Tight clustering of GRD1a oxide and HFSE compositions (Figure 17 and Figure 18) is due to the homogeneous nature of the unit. Geochemical similarities between GRD1b and GRD3 imply that they are the same unit with variable mafic content and texture, resulting in the physical similarity between GRD1b and GRD1a. An interpreted compositional progression from [GRD1b + GRD3], through [GRD1a and PFB], [PQF2 and PQB], PQF1 and GRD2 is based on major oxide diagrams. The unit compositions trends from more primitive and mafic mineral rich (GRD1b + GRD3) through to more evolved, containing igneous K-feldspar (GRD2)(Figure 17 and Figure 19).

Cu-Mo fertility in PCDs is related to water content of the source magma (Rohrlach & Loucks 2005). Multiple differentiation and recharge cycles are required to concentrate Cu, Mo and volatile components, including water (Rohrlach & Loucks 2005). Influxes of fresh magma to the magma pooled in the upper crust introduce
additional water, volatiles and incompatible elements to the magma chamber, which accumulates in a cyclic manner (Rohrlach & Loucks 2005). When the magma ascends to a critical P level the fluids are exsolved from the magma along with other volatiles, which, if in an oxidized state (i.e. S as SO$_4^{2-}$ and not as S$^2$), has the capacity to carry metals (Richards et al. 2012). The reactions caused by these fluids interacting with the host rock and porphyry units result in the hydrothermal alteration and mineralization associated with PCDs (Winter 2001).

Four differentiation cycles with three magma recharges have been interpreted from SiO$_2$ versus TiO$_2$ and Zr plots. The interpreted evolution of the granodiorite and porphyry units is: [GRD1b + GRD3] → GRD1a → porphyry units → GRD2, where arrows represent magma recharges. TiO$_2$ concentrations are highest in [GRD1b + GRD3], which also has the lowest SiO$_2$ concentrations (Figure 21a). The TiO$_2$ concentration in [GRD1b + GRD3] decreases as the SiO$_2$ concentration increases. An interpreted magmatic recharge causes GRD1a to repeat the pattern exhibited by [GRD1b + GRD3], but with a starting composition between the maximum and minimum TiO$_2$ and SiO$_2$ concentrations of [GRD1b + GRD3]. A magma recharge between [GRD1b + GRD3] and GRD1a causes an increase in TiO$_2$ by addition of magma and a decrease in SiO$_2$ concentrations by dilution. Two more magma recharges are interpreted: between GRD1a and the porphyry units; and between the porphyry units and GRD2, as evidenced by the decrease in SiO$_2$ and increase in TiO$_2$ between the differentiation cycles (Figure 21a).

SiO$_2$ – Zr variations support these differentiation cycles by highlighting the same four distinct populations (Figure 21b). Zr concentrations in [GRD1b + GRD3] on average are higher than those of the other granodiorite units, with SiO$_2$ concentrations between 55 and 70 wt %. The process of mixing the fractionated and unfractionated magmas gives rise to compositions with a SiO$_2$ content around 65 wt % but with low Zr, as in GRD1a, porphyry units, and GRD3. Zr concentrations decrease with increasing SiO$_2$ concentration in GRD1a. A recharge dilutes the SiO$_2$ concentration for the porphyry units, and again for GRD2.

Strongly depleted HREEs with a spoon shaped pattern are indicative of hornblende fractionation and therefore of a hydrous melt (Richards & Kerrich 2007).
The overall HREE content of a melt is reduced as a result of hornblende fractionating from a hydrous melt and sequestering the middle HREEs during crystallization (Richards & Kerrich 2007) with, however an elevated tale in Yb-Lu. Depleted HREE concentrations in GRD1a, PQF1, PQF2, PFB, PQB and GRD2 produces the characteristic spoon shaped REE profile, indicating hornblende fractionation and therefore a high magmatic water content source magma with the potential for Cu fertility (Figure 20). GRD1b, GRD3 and GRD2 show a negative Eu anomaly, consistent with plagioclase fractionation (Loucks, 2013).

The fractionation of hornblende also partitions Y during crystallization as plagioclase fractionation partitions Sr. A Y versus Sr/Y plot is used to assess a high magmatic water content magma signature at Relincho and in fact test for Cu fertility in the PCD environment (Castillo, 1999, Rohrlach & Loucks 2005) (Figure 22). A threshold of Sr/Y=30 on the Y versus Sr/Y plot identifies GRD1a, PQF1, PQF2, PFB, PQB and GRD2 as originating from a high magmatic water content source magma and therefore potentially fertile, and [GRD1b + GRD3] as infertile (Rohrlach & Loucks 2005).

[GRD1b + GRD3] is also identified as being sourced from an infertile magma by SiO$_2$ versus Zr plots (Figure 21b). In a Cu-infertile magma Zr concentrations typically peak around 65 wt % SiO$_2$, as in the [GRD1b + GRD3] (Rohrlach & Loucks 2005; Loucks 2013). A product of anhydrous fractionation, this implies a decreased likelihood of Cu-Mo fertility in [GRD1b + GRD3] (Figure 21b)(Rohrlach & Loucks 2005; Loucks 2013).

The progression of [GRD1b + GRD3] → GRD1a → porphyry units → GRD2 is supported by the hand sample observations of the mineral composition becoming more evolved. The mafic component, hornblende and biotite, decreases as igneous K-feldspar content increases in the units, consistent with this proposed progression (Table 2, Table 3, and Figure 12).

3.7.2 Alteration Fluids

Alteration in the project area is generally weak to moderate. Given the weak to moderate intensity of alteration, the tight clustering of the GRD1a results implies a low water to rock ratio, or low reactivity of the minerals during alteration resulting in limited metasomatism (Figure 17 and Figure 18).
The spatial correlation between elevated Cu (> 112 ppm) in GRD1a and the extent of potassic alteration is supportive of a common source fluid, consistent with accepted porphyry models (Sillitoe 2010, Seedorff et al. 2005). Population breaks in magnetic susceptibility, K$_2$O/Th and Cu within the GRD1a results identified using basic statistics correspond spatially with alteration assemblages (Figure 25 and Figure 26). The influx of K during potassic alteration is evidenced by the correlation between the spatial expression of visible potassic alteration and elevated K$_2$O/Th (> 0.32) (Figure 26). Correlations between elevated Cu (> 118 ppm) populations and the potassic extent is evident of mineralization being associated with potassic alteration, consistent with current porphyry models (Sillitoe 2010, Seedorff et al. 2005). Low magnetic susceptibility populations (< 10.1) have a spatial correlation with phyllic alteration, implying that the phyllic alteration assemblage is magnetite-destructive and potentially visible in geophysical surveys (Figure 26). This is consistent with the oxygen rich environment created by phyllic alteration (Table 7) driving the oxidation of magnetite, resulting in the presence of hematite in phyllic-altered areas.

Calculated gains and losses are consistent with alteration reactions known to take place, based on primary and alteration mineral compositions (Table 7). Addition of SiO$_2$ and K$_2$O, and loss of CaO and Na$_2$O during potassic alteration is consistent with the alteration of anorthite to K-feldspar and hornblende to secondary biotite (Table 7). Gains in Cu, Mo and Ag are consistent with observed mineralization associated with potassic alteration. Propylitic alteration shows gains of Na, and K and losses of Si and Ca, consistent with alteration of plagioclase to albite, plagioclase to epidote, biotite to epidote and plagioclase to albite (Table 7). Phyllic alteration shows a gain of Si and K and loss of Ca relative to fresh samples, consistent with calcic zones of plagioclase altering to muscovite (Table 7). Phyllic related muscovite alteration of the mafic minerals biotite and hornblende result in a loss of both Fe and Mg (Table 7). The gain in Cu, Mo, Au and Ag in the phyllic assemblage could be due to variability in the levels of hypogene mineralization in the sample used to represent phyllic alteration. Elevated Pb and Zn in the propylitic and phyllic zones are common in porphyry deposits (Lowell & Guilbert 1970), however the gains and losses demonstrated by the samples are weak for Pb in particular. Despite this there are clear spatial indications of a Pb-Zn halo
Figure 28: SWIR results showing samples with a. potassic alteration footprint with white mica features between 2207.5 to 2209 nm and elevated Cu concentrations, b. wavelength of white mica features versus molar (Fe + Mg) with elevated Cu concentrations, c. potassic alteration footprint with SpecMin identified montmorillonite and siderite and d. SpecMin identified illite with the propylitic alteration footprint.
Table 7: Summary of primary and alteration mineral compositions and alteration reactions with gains and losses, where HB=igneous hornblende, BT=igneous Biotite, AN=anorthite (igneous feldspar), Alteration minerals: 2Bt=secondary biotite, KS=feldspar, EP=epidote, CL=chlorite, CA=calcite, AB=albite, MU=muscovite. Mineral compositions are simplified from compositions calculated from electron microprobe results.
around the porphyry. Gain-loss results at Relincho for the potassic, propylitic and phyllic alteration assemblages are consistent with equivalent alteration assemblages at other porphyry deposits in similar host rocks (Ulrich & Heinrich 2002; Hezarkhani 2011; Taylor & Fryer 1980) (Table 6).

The spatial element variability plots support the gain-loss calculations. When lithological variability is limited by only reviewing variability in GRD1a plots, areas affected by potassic alteration and possibly propylitic alteration are clear. Relatively high concentrations of K₂O, SiO₂, Cu, Mo, Ag, and Au and relatively low concentrations of CaO and Na₂O are consistent with gain-loss calculations for potassic alteration. Relatively high concentrations Na₂O adjacent to potassic alteration are consistent with propylitic alteration. Immediately adjacent to mineralization is elevated Mn, Zn and Pb, consistent gain-loss results for the phyllic assemblage, and with metal zoning presented by Lowell & Guilbert (1970).

3.8 Exploration Implications of Interpretations

Two methods for using surface sample lithogeochemistry for regional exploration of porphyry deposits have been identified:

1. Identifying prospective regions through the assessment of magma fertility by geochemical characterization of lithological units

2. Understanding alteration assemblages and identifying prospective areas through the use of simple element concentration plots.

The Relincho PCD is hosted in a set of four granodiorite (GRD1a, GRD1b, GRD2 and GRD3) units previously undifferentiated. Mineralization is associated with four syn-mineralization porphyry units: PQF1, PQF2, PFB and PQB. The interpreted magmatic evolution of this suite of rocks is: [GRD1b + GRD3] → GRD1a → [PQF1, PQF2, PFB and PQB] → GRD2 based on mineralogy and relationships displayed in the SiO₂ versus TiO₂ and SiO₂ versus Zr diagrams. All porphyry and granodiorite units, with the exception of
GRD1b and GRD3 are interpreted as sourced from a high magmatic water content magma, and therefore potentially Cu-fertile. These diagrams can be used to determine whether or not a source magma had the potential to generate mineralization, given the appropriate metal content, and P-T conditions of emplacement. This method can be used to quickly and relatively inexpensively identify regions of potential interest for follow-up exploration, even in areas with limited background knowledge of the lithological units and alteration.

Statistical population breaks in K$_2$O/Th, Cu and magnetic susceptibility within the GRD1a unit show strong correlation with potassic and phyllic alteration respectively. Elevated K$_2$O/Th and Cu populations show a strong spatial correlation with the potassic footprint, consistent with gain-loss, bivariate and spatial concentration diagrams. This is a logical observation as Cu-mineralization is commonly associated with potassic alteration in PCDs (Sillitoe 2010). K$_2$O/Th could be used on a regional scale to identify areas for PCD exploration. Low magnetic susceptibility populations are spatially consistent with the phyllic assemblage, indicative of magnetite destruction, consistent with hematite observed in phyllic-altered samples. This magnetic susceptibility low could potentially be visible in regional geophysical surveys as well. These statistical population breaks emphasize regions for exploration follow-up even with limited knowledge of the geological environment.

Gain-loss calculations assist in for regional exploration by identifying, which elements are associated with which alteration assemblage, and could be applied to identify areas of alteration. In the case of Relincho the chemical compositional change due to alteration is relatively insignificant making it difficult to apply the method without a thorough understanding of the local geology and alteration. To emphasize the effect of alteration, compositional end members identified using geochemistry and hand sample observations were used to represent the altered and unaltered compositions. Nevertheless, when the GRD1a geochemical results are reviewed spatially, typical high concentrations of K, Cu, Si, Mo and Au identify the area of mineralization and potassic alteration, showing classic distal elemental zonation such as elevated Zn and Pb around the deposit area.
Chapter 4: Recognizing Hydrothermal Alteration in a Felsic Environment: A Case Study of the Relincho Cu-Mo Porphyry, Atacama, Chile

4.1 Introduction

Alteration at the Relincho deposit is easily misidentified due to its weak intensity. Hand sample observations in combination with SWIR results and MERs applied to the porphyry and granodiorite samples identify key indicators for distinguishing alteration assemblages. Representative properties of the alteration assemblages are then used to calculate an alteration index for relative quantification of alteration intensity.

SWIR results aid in the characterization of potassic and propylitic alteration, but are less useful for the identification of phyllic alteration. Interpretations of SWIR analyses indicate that montmorillonite and siderite may be part of the potassic assemblage, and illite part of the propylitic. The wavelengths of identified chlorite features indicate that chlorite proximal to the porphyry corridor is Fe-rich, grading outwards to Mg-rich. White mica features show that elevated Cu concentrations (> 282 ppm) in samples with white micas are consistent with features occurring between 2207.5 and 2209 nm.

MERs, though ineffective for depicting potassic alteration at the Relincho deposit due to the chemical similarity between igneous and alteration minerals, depict even weak phyllic and propylitic alteration. GERs of feldspar space (2CNK/Al versus K/Al, 2Ca/Al and Na/Al) show losses in Ca associated with gains in K, interpreted to be a product of phyllic alteration. Feldspar space PER diagrams of (Al/Ti versus 2CNK/Ti) and customized PER diagrams ((2Si + 7Al + 4(Mg + Fe))/Ti versus (18Ca + 14Na + 25K)/Ti) effectively depict phyllic and propylitic alteration.

Effective simple and Pearce element ratios are used to calculate alteration indices and relatively quantify alteration intensity. This alteration index is used to calculate the minimum sample population required for regional PCD exploration.
4.2 Local Geology and Alteration

4.2.1 Lithological Units

Mineralization at the Relincho deposit is hosted in a Paleocene granodiorite of the Los Morteros batholith and associated with four Paleocene porphyritic intrusions (Figure 10). Mineralogy, texture and geochemistry distinguish four granodiorite units: GRD1a, GRD1b, GRD2 and GRD3 (Table 2, Figure 12); and four porphyry units: PQF1, PQF2, PFB and PQB (Table 3, Figure 12). Relative emplacement timing of the granodiorite units was not observed or deduced in the field, though based on evidence presented in Chapter three, three episodes of magma recharge drove four differentiation cycles resulting in the following progression from oldest (1) to youngest (4):

1- GRD1b + GRD3  
2- GRD1a  
3- Porphyry units (mineralization event)  
4- GRD2

This evolutionary progression is supported by petrographic observations of the mafic mineral content decreasing and K-feldspar content increasing from [GRD1b + GRD3] → GRD1a → porphyry units → GRD2 (Figure 12). It is important to note that only GRD2 and the porphyry units contain igneous K-feldspar (Figure 12).

4.2.2 Alteration

Alteration assemblages associated with mineralization are potassic, propylitic and phyllic with a late-stage, post mineralization chlorite alteration affecting the entire project area (Figure 15a). Mineralization is strongly associated with the potassic assemblage. Petrographic observations of overprinting mineral textures indicate that potassic alteration was followed by propylitic, then phyllic, consistent with general porphyry system models (Lowell & Guilbert 1970; Seedorff 2005). Alteration intensities are defined by the average replacement of primary minerals by alteration minerals as unaltered (< 15 % replacement of primary mineral by alteration mineral), weak (>15 %...
replacement < 30 %), moderate (30 % < replacement <60 %) and strong (60 % < replacement). The spatial footprint of weak potassic, propylitic and phyllic alteration based on hand sample and thin section observations is shown in Figure 15a. Alteration assemblages are defined by the presence of:

**Potassic:** \textit{secondary biotite + incipient K-feldspar} + magnetite ± epidote ± glassy limonite (from chalcopyrite);

**Propylitic:** epidote + chlorite + hematite ± albite ± calcite ± actinolite±pyrite;

**Phyllic:** chlorite + muscovite + quartz ± calcite ± hematite.

### 4.3 Results

Petrographic observations, including alkali feldspar staining, are used to support SWIR results and MER interpretations to characterize the alteration assemblages. The results of this characterization are used to calculate alteration indices.

#### 4.3.1 Staining, Field and Petrographic Observations

Based on field and petrographic observations, supported by rock staining for alkali feldspar, the spatial extents of weak alteration were established and presented in Figure 15. Alkali feldspar staining supports hand sample and field observations of the incipient nature of K-feldspar alteration of plagioclase and confirms the presence of igneous K-feldspar in GRD2 and the groundmass of the porphyry units as well as a lack of igneous K-feldspar in GRD1a, GRD1b and GRD3. Field and petrographic observations also indicate that alteration intensity is generally weak to moderate in phyllic or potassic alteration, and weak to strong in propylitic alteration. Weak phyllic alteration is best observed with a microscope, which shows the incipient nature of the selective muscovite replacement of calcic zones within plagioclase (Figure 15d).
4.3.2 Shortwave Infrared Results

SWIR results are processed by the software SpecMin® which compares the SWIR spectra to a spectral library to identify minerals. SpecMin® effectively identified minerals and features associated with the potassic and propylitic assemblages that could be used for regional characterization. Montmorillonite and siderite are weakly spatially associated with the potassic footprint, though not positively identified in hand sample (Figure 28). In samples that contain elevated Cu concentrations (Cu > 282 ppm for all porphyry and granodiorite units, Figure 25) and SpecMin® identified white micas (illite, muscovite, phengite and montmorillonite), elevated Cu concentrations strongly correlate with white mica with features between 2207.5 to 2209 nm (Figure 28b). SpecMin® chlorite with features in the range of 2330 ± 30 nm can be separated into three populations based on the wavelength location of features: 2335 to 2343 nm, 2343.5 to 2345.5 and 2346 to 2352 nm (Figure 29b). Plotted spatially, chlorite with higher wavelength features is proximal to the porphyry corridor. Illite is weakly associated with propylitic alteration (Figure 28c).

4.3.3 Molar Element Ratios

General and Pearce element ratios (GERs and PERs) are both molar element ratios (MERs) used to depict geochemical processes such as alteration (Stanley & Russell, 1989). In the accompanying GER and PER figures, unaltered to weakly altered samples are shown as dark points, and moderately to strongly altered samples as light points (Figure 30 and Figure 32). Feldspar composition is commonly examined using the molar sum of (2Ca + Na + K), summarized as 2CNK. Mineral nodes (GER) and control lines (PER) are calculated from simple mineral compositions. Mineral nodes are two-dimensional, whereas control lines are three-dimensional expressions of compositional planes into and out of the page representative of a mineral or group of minerals. Alteration intensity is proportional to a sample's position relative to unaltered composition and the alteration mineral node or control line. To simplify element ratio interpretation, end-member compositions of common primary and alteration minerals at the Relincho deposit have been summarized in Table 7.
Figure 29: TerraSpec results for chlorite and illite. 

a. Probability plot of the wavelengths of chlorite features showing population breaks by colour theoretically indicative of relative Fe and Mg concentrations. 

b. Spatial footprint of chlorite populations relative to the porphyry corridor showing the theoretical composition changing outwardly from Fe-rich to Mg-rich. 

c. SpecMin identified illite with the propylitic alteration footprint.
Test of the Cogenetic Hypothesis

Pearce element ratios differ from GERs in that they use a conserved element in the denominator. In order to use a conserved element, the PER methodology requires a failure to reject the cogenetic hypothesis, which postulates that each rock unit, at some point, originated from a homogeneous system (Russell & Stanley 1990). Two equally conserved elements plotted against each other yield a best-fit line with a positive slope that intersects the origin, if equally conserved, or the best-fit line will cross the axis of the less conserved element (Stanley & Madeisky, 1995). The conservation of TiO2 and Zr are tested for the four differentiation cycles identified in Chapter three (Figure 31). There is a failure to reject the cogenetic hypothesis for GRD1a, GRD2, and the porphyry units, with indications that Ti is slightly more conserved than Zr in GRD2. For this reason Ti is used as the conserved element in the PER plots (Figure 31b, c and d). There is a lack of conservation of Ti and Zr in units GRD1b and GRD3, resulting in a rejection of the cogenetic hypothesis (Figure 31a). The failure to reject the cogenetic hypothesis allows the use of PERs for GRD1a, GRD2 and the porphyry units, but not GRD1b and GRD3.

Molar Element Ratio Observations

Compositional variability in feldspar due to alteration and primary composition is depicted by the GER plots 2CNK/Al versus 2Ca/Al, Na/Al and K/Al (Figure 30). These plots indicate muscovite, K-feldspar, anorthite and albite nodes that can be used for interpretation of compositional variation due to alteration. Minimal fluctuation in Na concentration indicates that variability shown by 2CNK is from loss of Ca and gain of K during alteration, and from differences in primary mineralogy between lithological units.

Feldspar compositional variation is isolated in the plane represented by the $m = 1$ control line on the diagram 2CNK/Ti versus Al/Ti, hereon referred to as the feldspar space PER, emphasizing the effect of epidote (propylitic), muscovite (phyllic) and chlorite (propylitic and/or phyllic) alteration (Figure 32a). Unaltered samples lie approximately on the $m = 1$ line. Samples that have been phyllic altered plot below $m = 1$, toward the
Figure 30: General Element Ratio plots of feldspar space with dark points representing fresh to weakly altered samples and light points representing moderately to strongly altered samples. The combination of these two plots allows for the isolation of the source of the variability in the feldspar space. 

a. \( \frac{2(\text{Ca}+\text{Na}+\text{K})}{\text{Al}} \) vs \( \frac{2\text{Ca}}{\text{Al}} \), shows a depletion in Ca due to an alteration process.

b. \( \frac{2(\text{Ca}+\text{Na}+\text{K})}{\text{Al}} \) vs \( \frac{\text{K}}{\text{Al}} \), shows elevation of K due to alteration, also distinguishes the units with igneous K-feldspar (GRD2 and the porphyry units) and indicates that the loss of Ca from alteration coincides with a gain in K, due to muscovite alteration of plagioclase. 

c. \( \frac{2(\text{Ca}+\text{Na}+\text{K})}{\text{Al}} \) vs \( \frac{\text{Na}}{\text{Al}} \), shows little variability in the Na component indicating that alteration affects the calcic zones of plagioclase.
Figure 31: Conserved element plots by differentiation cycle. The mean value is indicated by the green dot, with analytical error indicated by the bars, the dashed line is the line of best fit. Samples plotting outside of the line of best fit +/- the calculated error are plotted in red. 

a. GRD2 samples indicate that both Zr and TiO$_2$ are conserved, failing to reject the cogenetic hypothesis, and indicates that TiO$_2$ is more conserved than Zr as the line of best fit intercepts the Zr axis. 

b. GRD1a shows two outliers in a population of 97, which is statistically acceptable. GRD1a fails to reject the cogenetic hypothesis and indicates that TiO$_2$ and Zr are equally conserved. 

c. Porphyry units have three outliers in a population of 108, which is statistically acceptable. The porphyry units fail to reject the cogenetic hypothesis and indicate that TiO$_2$ and Zr are equally conserved. 

d. GRD1b + GRD3 populations have eight outliers in a population of 42, which is not statistically acceptable, and a general best fit trend with a negative slope, thereby failing to reject the cogenetic hypothesis.
Figure 32: Pearce Element Ratio plots and associated spatial plots. PER plots show fresh samples as dark points and altered samples as light; shaded areas indicate point colours on the spatial plots. Spatial plots show strongly altered samples as larger points, weakly altered as medium, and fresh as small black dots, with lithology indicated by the point shape. Alteration intensity is based on the distance a sample plots from the trend of the fresh samples on the PER plot. Spatial plots of the alteration identified in the PER plots are consistent with hand sample and field alteration observations. GRD1b and GRD3 have not been plotted as those units failed the cogenetic hypothesis test. a. \((2\text{Ca}+\text{K}+\text{Na})/\text{Ti} \text{ vs } \text{Al/Ti with the } m=1 \text{ control line isolating compositional variability introduced by feldspar. Samples plotting towards epidote, muscovite and chlorite control lines are indicative of propylitic, phyllic or both types of alteration, respectively.} \) b. Spatial plot of propylitic and phyllic alteration, with intensity indicated by size. c. Customized PER plot of \((2\text{i}+7\text{Al}+4\text{(Fe+Mg)})/\text{Ti} \text{ vs } (18\text{Ca}+14\text{Na}+25\text{K})/\text{Ti} \text{ that isolates variability due to anorthite, albite, actinolite, pargasite and biotite in the } m=1 \text{ control line. Samples plotting near epidote, chlorite, muscovite and K-feldspar control lines indicate alteration. Igneous K-feldspar and lower mafic content results in GRD2 samples plotting to the upper right quadrant. The porphyry units plot between the GRD2 points and GRD1a on the } m=1 \text{ control line because of the increased K-feldspar and diminished mafic content relative to GRD1a. Four chemically distinct samples are labeled with photographs and the minerals which have affected their plotting space. Fresh samples plot close to the } m=1 \text{ control line. A sample with quartz veins associated with muscovite and chlorite alteration result in a sample plotting towards the x-axis.} \) d. Spatial plot of propylitic and phyllic alteration, with intensity indicated by size, based on the proximity of a sample to an alteration mineral control line.
muscovite (m = 1/3) and chlorite (m = 0) control lines. Propylitic altered samples plot above the m = 1 line toward the epidote (m = 2) control line. As epidote and chlorite lie on opposite sides of the m = 1 control line, the effect of propylitic alteration is understated by the chlorite content causing samples to plot towards m = 0.

The customized PER diagram has axes mathematically derived from simplified end member compositions of anorthite, pargasite, actinolite, albite and biotite (annite) (Figure 9). The diagram \([(2\text{Si} + 7\text{Al} + 4(\text{Fe} + \text{Mg}))/\text{Ti} \text{ versus } (18\text{Ca} + 14\text{Na} + 25\text{K})/\text{Ti}]\), hereon referred to as the customized PER, isolates the compositional variability of the primary mineralogy along the x=y plane, emphasizing the effect of potassic, propylitic and phyllic alteration (Figure 32b). Samples that have been propylitic altered plot above the m = 1 line toward epidote (m = 3/2), and phyllic altered plot below toward chlorite (m = 0) and muscovite (m = 25/27). Primary mineralogy controls the majority of samples plotting towards the K-feldspar (m = 25/13) line. Propylitic alteration is understated as epidote plots above the m = 1 control line and chlorite plots at m = 0, similarly, phyllic alteration is over-represented because of the bias introduced by the late stage chlorite alteration and chlorite associated with the propylitic assemblage. Hand sample observations should be made to ensure that points interpreted as propylitic altered are not the product of potassic alteration or primary K-feldspar mineralogy, as the K-feldspar line lies above the epidote line.

4.4 Interpretation of Alteration Processes

SWIR results in combination with MERs and simple element ratios from Chapter three are used to identify properties that can effectively distinguish alteration on a regional scale. Ratios that distinguish alteration are used to calculate an alteration index that relatively quantifies alteration.

4.4.1 Identification of Alteration Using Shortwave Infrared

Potassic Alteration

SWIR results indicate mineralogical patterns associated with the potassic alteration. Elevated Cu populations in samples with SpecMin® identified white mica, show a correlation between elevated Cu and white micas with features ranging from
2207.5 and 2209 nm (Figure 28c). The relatively high wavelength for white micas has been attributed to Tschermak substitution of \([\text{Al}^{3+}]^\text{vi} + \text{Al}^{3+}^\text{iv} \leftrightarrow \text{Fe}^{2+} \text{or Mg}^{2+}]^\text{vi} + \text{Si}^{4+}]^\text{iv}\) in illite and muscovite (Cohen 2012), though plots of molar Fe and Mg against wavelength of white mica features do not show a consistent pattern (Figure 28d). SpecMin® identified montmorillonite and siderite in potassically altered samples. Neither montmorillonite nor siderite were identified in thin section or hand sample, though montmorillonite can be associated with potassic alteration (Franchini et al. 2007) and siderite could either be associated with chalcopyrite or with an overprinting assemblage (Reynolds & Beane 1985; Rose 1970).

**Propylitic Alteration**

The spatial footprint of SpecMin® identified epidote, chlorite and illite are consistent with that of the propylitic assemblage. Epidote and chlorite identified by SpecMin® correspond spatially with the propylitic footprint, consistent with field observations (Figure 29a). Illite also shows a correlation with the propylitic footprint (Figure 29c). Illite and chlorite tend to interlayer, and though not identified in field or petrographic observations, illite is known to be associated with propylitic alteration (Franchini et al. 2007; Allen et al. 1996). Probability plots identify three populations based on the wavelength of features within the identified chlorite: 2335 to 2343 nm, 2346 to 2352 nm and 2343.5 to 2345.5 nm. Chlorite with features towards 2320 nm are theoretically more Fe-rich than those with features toward 2350 nm (Halley 2008). These populations have been interpreted as Fe-rich, intermediate and Mg-rich, respectively, though Fe and Mg fluctuations on this scale are not noticeable in geochemical results: EMP calculated chlorite compositions would confirm this pattern (Figure 29a). Chlorite is Fe-rich proximal to the porphyry corridor, transitioning through intermediate, and Mg-rich distally, according to this interpretation (Figure 29b).

**Phyllic Alteration**

The phyllic assemblage is not consistently represented by the SWIR results. SpecMin® software identified muscovite and chlorite, though they do not show spatial correlation with the phyllic alteration footprint. Feature properties such as wavelength
and depth for white micas and chlorite do not show any patterns that aid in the identification of phyllic alteration.

4.4.2 Identification of Alteration Using Lithogeochemistry

Potassic Alteration

Potassic alteration in felsic host rocks is not well characterized by MER plots due to the compositional similarity between alteration mineralogy and primary mineralogy. Secondary biotite is well developed in potassic-altered samples at Relincho, especially when replacing hornblende, though EMP results indicate that the compositional difference between primary and secondary biotite is minimal (Appendix D). K-feldspar replacement of plagioclase is weak to moderate even in samples with strong potassic alteration.

Primary mineralogy overshadows the K-feldspar alteration trends in the PER and GER diagrams (Figure 30 and Figure 32). Points trending towards the GER K-feldspar nodes are predominantly from the GRD2 and porphyry units representative of igneous K-feldspar as opposed to alteration (Figure 30a and b). In both PER diagrams the porphyry units plot high on the $x = y$ line because of the relatively high K from igneous K-feldspar and low Ti from lower mafic mineral content (Figure 32a & b). Epidote confounds the identification of K-feldspar alteration in the customized PER diagram by having a control line at $m = 3/2$, on the same side of the $x = y$ line as K-feldspar ($m = 25/13$). Epidote alteration is generally a stronger intensity than K-feldspar alteration, and dominates on this diagram. Potassic alteration is commonly overprinted by propylitic or phyllic alteration, which further confuses interpretations of potassic alteration, muting the effects of K-feldspar alteration by pulling samples toward the control lines of epidote ($m = 3/2$), chlorite ($m = 0$) and muscovite ($m = 25/27$) (Figure 32). The similarity of primary and alteration mineralogy in the granodiorite and porphyry units, combined with the alteration overprinting of the phyllic and propylitic assemblages makes interpretations and quantifications using MER diagrams difficult and inaccurate.
The simple element ratio of K$_2$O/Th discussed in Chapter three is a better indicator of potassic alteration than either the SWIR interpretations or the MERs. It is simple, fast and effective. Alteration indices are calculated using K$_2$O/Th for the relative quantification of alteration.

**Propylitic Alteration**

Feldspar space GER diagrams do not effectively represent propylitic alteration. Propylitic associated albite alteration, where present, is weak and does not produce significant geochemical variation. Albite alteration should result in a replacement of Ca by Na in plagioclase, which would be reflected by a loss of Ca and gain in Na in feldspar space GERs. Instead, Na concentration shows little variability, rendering the feldspar space GER diagrams ineffective at depicting propylitic alteration (Figure 30c).

Most effective for the interpretation of propylitic alteration are the feldspar space and customized PER diagrams (Figure 32a and c). In both diagrams points plotting above the m=1 line are indicative of epidote alteration, as confirmed by hand sample observations. The further a sample plots from the unaltered m = 1 composition, the more altered the sample is interpreted to be. The K-feldspar control line on the customized PER diagram lies above the epidote control line and can mask epidote alteration. The chlorite control line (m = 0) lies below the m = 1 control line resulting in a muted representation of propylitic alteration, as epidote lies above m = 1 and both are present in propylitic alteration (Figure 32a and c). Hand sample and petrography observations are beneficial to confirm that epidote alteration as the cause of trends towards the epidote line.

**Phyllic Alteration**

Phyllic alteration is commonly so weak that it is only evident through microscope petrography by the incipient muscovite alteration of calcic zones of plagioclase, yet the GER and PER diagrams readily identify the process of phyllic alteration. Trends towards the K-feldspar node on the GER diagram 2CNK/Al versus K/Al suggest that a gain in K in plagioclase is due to K-feldspar alteration (Figure 30a). When compared to the
diagram 2CNK/Al versus 2Ca/Al, the loss of Ca and gain in K is shown to be consistent with muscovite alteration of the plagioclase, with trends towards K-feldspar node controlled by primary mineralogy (Figure 30b). Petrography and staining confirms that the gain of K and loss of Ca is due to the incipient, selective alteration of calcic zones in plagioclase to muscovite (Figure 15c).

The feldspar space and customized PER diagrams depict the effect of phyllic alteration by isolating the control lines for chlorite and muscovite to below the x = y control line (Figure 32a and c). Unaltered samples plot along the m = 1 control line with points plotting closest to the chlorite control line (m = 0) being the most phyllic altered. Chlorite is associated with both the phyllic and propylitic assemblages, as chlorite lies below the m = 1 control line and epidote above, this could lead to an over-representation of phyllic altered samples, depending on the intensity of chlorite alteration versus epidote.

4.4.3 Alteration Indices and Quantification

Alteration intensity can be relatively quantified geochemically by using the lever rule on a MER diagram used to depict and constrain alteration processes, or by creating an alteration index.

Alteration is relatively quantified by observing the distance between a fresh sample (or the x = y control line for PER diagrams) and altered samples. For phyllic and propylitic alteration this quantification is most easily performed using the feldspar space or customized PER diagrams (Figure 32b and d). As the MER diagrams did not reflect potassic alteration, this method is not applicable to potassic alteration in this case.

Alteration indices can be calculated using a proven effective ratio. On a regional scale at Relincho the simple ratio K₂O/Th effectively represents potassic alteration, and the customized PER plot [(2Si + 7Al + 4(Fe + Mg))/Ti versus (18Ca + 14Na + 25K)/Ti] is effective for identifying propylitic and phyllic alteration. In order to quantify the alteration, populations of unaltered and altered samples are identified using probability plots of the ratios (18Ca + 14Na + 25K)/(2Si + 7Al + 4(Fe + Mg)), hereon referred to as the propylitic-phyllic index, and K₂O/Th, hereon referred to as the potassic index.
(Figure 33a and c). On a PER plot unaltered samples should lie on the line of $m = 1$. According to the probability plot of the propylitic-phyllic index unaltered samples lie between 0.94 and 1.04 (Figure 33a). Samples below 0.94 are considered phyllic-altered with P-04 identified as most altered as it has the lowest alteration index value. Samples above 1.04 are propylitic-altered with A-08 identified as most altered as it has the highest alteration index value. Using these two samples with 0.94 and 1.04 to represent an unaltered baseline for phyllic and propylitic alteration respectively, alteration intensity is calculated using equation (2). The probability plot for the potassic index indicates the unaltered population at and below 0.36, identifying H-05 as most potassically altered sample (Figure 33c).

Relative alteration quantification is calculated for each sample using the formula:

$$\frac{X - X_F}{X_A - X_F}$$

(2)

Where $X$ is the sample value, $X_F$ is the value for the fresh sample and $X_A$ is the value for the most altered sample identified by the alteration index. This creates a quantification that ranges between fresh (0) and most altered (1).

Spatial plots of the alteration indices show intensity as the size of the bubbles for the 256 granodiorite and porphyry samples over approximately 35 km$^2$ (Figure 33b and d). The alteration indices identify potassic, propylitic and phyllic alteration and correctly indicate increasing alteration intensity with proximity to the porphyry corridor.

**4.4.4 Comments on Sample Spacing for Regional Exploration**

Sample spacing used for this survey, approximately 250 m over known mineralization, and 500 m adjacent to mineralization, was adequate for the purpose of using lithogeochemistry to identify potentially fertile environments, characterize lithological units and identify alteration indices. Using only the porphyry and granodiorite samples and de-sampling the grid to a wider spacing allows for the assessment of the necessary sample spacing for target identification. Probability plots
Figure 33: Alteration indices calculated for propylitic-phyllic and potassic alteration of porphyry and granodiorite samples  

a. Propylitic-phyllic index probability plot indicates that samples below 0.94 are phyllic-altered, and samples above 1.04 are propylitic-altered 

b. Spatial plot using the propylitic-phyllic alteration index for point size, 

c. Potassic index probability plots indicate a population break around 0.36, indicating samples above 0.36 are potassic-altered and 

d. Spatial plot using the potassic alteration index for point size.
of the potassic and propylitic-phyllic alteration indices for each sample spacing set determines if this new set of samples will identify populations representative of potassic, propylitic or phyllic alteration.

Two examples of sample spacing are evaluated: a grid with 1000 m sample spacing for a total of 32 samples, and a grid with approximately 2000 m spacing with 7 samples (Figure 34). Thresholds interpreted from the probability plot of the entire survey are applied to the new sample populations to identify alteration. Over an area of approximately 35 km², the 1000 m spacing sampling grid identified 15 phyllic, two propylitic and 26 potassic altered samples, out of a sample set of 32 (Figure 34a and b). Alteration indices identified five phyllic; one propylitic; and three potassic-altered samples out of a sample set of seven, at 2000 m sample spacing (Figure 34c and d). The Cu and Mo concentrations are high in four of the five most potassic altered samples in the 1000 m sample spacing, but are low in the potassic-altered samples identified by the 2000 m spacing (Figure 34).

**4.4.5 Using Alteration Indices as a Vector to Mineralization**

To examine the alteration indices as an indicator of distance to ore both alteration indices are plotted for three transects over the deposit with Cu concentrations and the porphyry corridor indicated (Figure 35). There is little correlation between the alteration index and proximity to the porphyry corridor, nor is there much of a correlation between Cu concentration and the potassic indicator. The northern transect shows low, erratic potassic index values over the porphyry corridor consistent with low, erratic Cu concentrations, with a slight increase in potassic index values and Cu concentrations directly adjacent to the porphyry corridor. The propylitic-phyllic index does not show any trend (Figure 35b). The central transect shows relatively stable, high potassic index values over the porphyry corridor accompanied by highly erratic Cu concentrations, and relatively stable propylitic-phyllic index values. The southern transect shows a weak correlation between elevated potassic index values and Cu concentration, and still no correlation with the propylitic-phyllic alteration index.
Figure 34: Potassic and propylitic-phyllic alteration indices for porphyry and granodiorite samples at 1000 m and 2000 m sample spacing. Concentrations of Cu (red) and Mo (blue) in ppm are indicated adjacent to the 5 most potassic altered samples on the spatial plots. a. Propylitic-phyllic alteration indices at 1000 m sample spacing, b. Potassic alteration index at 1000 m sample spacing, c. Propylitic-phyllic alteration indices at 2000 m sample spacing, and d. Potassic alteration index at 2000 m sample spacing,
Figure 35: The propylitic-phyllic index \((18\text{Ca}+14\text{Na}+25\text{K})/(2\text{Si}+7\text{Al}+4(\text{Fe}+\text{Mg}))\), green) and potassic index \((\text{K}_2\text{O}/\text{Th})\), pink) alteration indices plotted with Cu concentrations (red) as transects across the porphyry corridor (grey box). Alteration index values are indicated on the left y-axis, Cu concentration values are on the right y-axis. a. Sample sites with porphyry corridor and transects North (N), Centre (C) and South (S) indicated, b. North transect showing a correlation between elevated Cu concentrations with elevated \(\text{K}_2\text{O}/\text{Th}\) values and no correlation with the customized alteration index. The \(\text{K}_2\text{O}/\text{Th}\) index seems to be higher adjacent to the porphyry corridor as opposed to within it. c. The centre transect does not indicate any consistent pattern between the alteration indications and Cu concentration, or proximity to the porphyry corridor. d. The south transect does not indicate any consistent pattern between the alteration indices and Cu concentration, or proximity to the porphyry corridor.
The lack of correlation between the alteration indices, Cu concentration and proximity to the porphyry corridor is potentially a product of inconsistent flow patterns of the hydrothermal fluids. The inconsistent flow could be a product of variations in permeability between lithological units, surface area of primary minerals, or due to the presence of structures, which form fluid pathways. The permeability in units with porphyritic texture is higher than those with the idiomorphic texture due to the porous nature of the groundmass. Grain sizes in the porphyry units are smaller and therefore a higher surface area, allowing for increased alteration of the surface areas. Northeast-southwest regional structures provide conduits for the alteration fluids resulting in uneven dispersal of alteration fluids.

Though the alteration indices are not suitable for calculating the distance a sample is from mineralization, the transects show that alteration indices behave independently from Cu concentration. This implies that areas identified as prospective by alteration indices, would not be identified by elevated Cu concentrations.

4.4.6 Comments on Alteration Indices

The propylitic-phyllic alteration index calculated for Relincho is similar to that calculated by Urqueta et al. (2009) for the Collahuasi epithermal cluster in Chile: 

$\frac{(18Ca+13Na)}{(2Si+7Al+4(Mg+Fe))}$. As at Relincho, the alteration indices identified propylitic alteration, but were unsuccessful as a tool for determining the distance to ore mineralization.

4.5 Exploration Implications of Interpretations

Lithogeochemistry of surface samples identifies potassic, propylitic and phyllic alteration at Relincho using SWIR, basic statistics and MER plots. Potassic alteration, though not evident in PER and GER plots due to the compositional similarity between primary mineralogy potassic alteration mineralogy, is consistent with elevated K₂O/Th populations. Propylitic alteration is optimally characterized using a combination of PER plots, which identify epidote alteration. Weak phyllic alteration is characterized using a combination of PER and GER plots. Even weakly altered samples with incipient muscovite alteration of calcic zones in plagioclase are evident in the PER and GER plots.
The potassic (K₂O/Th) and propylitic-phyllitic ((18Ca + 14Na + 25K)/(2Si + 7Al + 4(Fe + Mg))) alteration indices relatively quantify alteration intensity and determine necessary sample spacing. Using the Relincho deposit as a test, these indices could identify a blind target as an area for exploration follow-up using a sample spacing of up to 2000 m. Sample spacing of 2000 m identifies potassic, propylitic and phyllitic alteration even when Cu and Mo concentrations do not. Though the indices identify target areas, transects over the porphyry corridor indicate that the indices are not applicable for determining the distance to mineralization.

This ability to identify alteration assemblages through basic statistics and lithogeochemistry means that alteration fluid pathways could be mapped regionally, and in 3-dimensional models. Because of the predictable pattern of porphyry alteration haloes (Lowell & Guilbert 1970; Seedorf 2005; Sillitoe 2010), these population distinctions can be used to identify areas of interest for porphyry style mineralization, following alteration assemblages towards potassic alteration and potential mineralization.
Chapter 5: Conclusions and Implications for Exploration

5.1 Summary of Research Results

Surface lithogeochemistry, in combination with petrography and SWIR, were successfully used to characterize the lithological units and alteration assemblages at the Relincho PCD. Three effective methods have been identified in this study:

1. Rock fertility assessment for identifying regions of potential PCD mineralization;
2. Potassic, propylitic and phyllic alteration assemblage characterization through spatial element distributions, and simple and molar element ratios;
3. Quantifying alteration intensity on a regional scale through the application of alteration indices.

5.1.1 Rock Fertility Assessment

Four host granodiorite units and four porphyry units were distinguished based on mineralogy, texture and geochemistry. Magma evolution diagrams indicate that the granodiorite and porphyry units evolved in the following order: [GRD1b + GRD3] → GRD1a → [PQF1 + PQF2 + PFB + PQB] → GRD2. They are interpreted as the product of four differentiation cycles and three magma recharges (indicated by arrows), although evolution between the porphyry units is unclear. Fertility was assessed for each of these differentiation cycles. GRD1a, GRD2 and the porphyry units are identified as potentially fertile and [GRD1b + GRD3] potentially infertile, on the basis of N-MORB normalized REEs and Y versus Sr/Y properties, considered to be indicative of hornblende fractionation in high magmatic water content magmas.

5.1.2 Alteration Characterization

Lithogeochemistry of surface samples identifies potassic, propylitic and phyllic alteration using simple element ratios and MERs. The spatial footprint of elevated K2O/Th and Cu populations in the GRD1a unit serves as a proxy for potassic alteration. Propylitic and phyllic alteration are best characterized by the feldspar-space (Al/Ti
versus \((2\text{Ca} + \text{K} + \text{Na})/\text{Ti}\) and customized \(((2\text{Si} + 7\text{Al} + 4(\text{Fe} + \text{Mg}))/\text{Ti} \text{ versus } (18\text{Ca} + 14\text{Na} + 25\text{K})/\text{Ti}\) \) PER diagrams. The PER diagrams isolate propylitic alteration processes above the \(m = 1\) line, and phyllic alteration processes below. Phyllic and propylitic alteration can be visually, relatively quantified by assessing the distance between a point’s position and the fresh composition control line \((m = 1)\) on these PER diagrams.

### 5.1.3 Quantifying Alteration Intensity on a Regional Scale

Alteration indices are calculated from simple and molar element ratios to quantify potassic, propylitic and phyllic alteration. Using \(\text{K}_2\text{O}/\text{Th}\) as the potassic index and \(((18\text{Ca} + 14\text{Na} + 25\text{K})/(2\text{Si} + 7\text{Al} + 4(\text{Fe} + \text{Mg}))\) as the propylitic-phylllic index, five phyllic, one propylitic and three potassic altered samples are identified at a sample spacing of 2000 m.

### 5.2 Comparison of Methodologies

#### 5.2.1 Gain-Loss versus Molar Element Ratios

Gain-loss variations provide detailed information about alteration processes, though they can easily be miscalculated when in-depth knowledge of lithological units and alteration assemblages is lacking. It is imperative that gain-loss calculations be done using the same rock type for both altered and unaltered compositions. This can be difficult when separating lithological units geochemically, especially when there is limited background geological knowledge. Distinguishing attributes (e.g. REE and HFSE concentrations) must be examined to ensure the same lithological units are being compared. At Relincho there are very few samples that are unaltered, with almost all samples having undergone, at least, chlorite alteration to some extent. Field observations as well as MERs were relied upon to find least-altered and most-altered compositions to be used for the gain-loss calculations. Element variability is lost if the altered and fresh samples are not carefully selected. Weak alteration intensity and overlapping alteration assemblages at Relincho also complicated gain-loss variation interpretations. The gain-loss results showed illogical patterns when entire populations (i.e. all potassic altered GRD1a samples) were used for calculations.
Numerous lithological units can be plotted on MER diagrams simultaneously, as long as they are distinguishable on the plot. This, by default, increases the population represented by the diagram. MER diagrams indicate the process of alteration by showing a compositional trend from a primary mineral composition to an alteration mineral composition. Alteration intensity can be relatively quantified on an MER diagram by measuring the distance an altered point plots from the unaltered composition.

Though gain-loss diagrams can simultaneously express numerous analytes in one graph, they also require an in-depth knowledge of the host lithology and alteration intensity and are labour intensive. MER diagrams do not require in-depth background knowledge of the lithological units, beyond an understanding of what primary and alteration mineralogy is for the construction of the MER diagram. MER diagrams are more effective than gain-loss diagrams at displaying the alteration processes and the variability in alteration intensity. The MERs are more easily applied to large datasets with multiple lithological units.

5.2.2 Spatial Elemental Variability versus Molar Element Ratios

Spatial element variability is an effective means of identifying a prospective area for PCD exploration, especially in conjunction with the gain-loss variations. Spatial variability of trace metals such as Cu, Mo, Au, Pb and Zn show typical zonation of a PCD with Cu, Mo and Au elevated within the porphyry corridor and Zn and Pb elevated distally. The spatial variability indicates elemental trends but does not characterize an alteration process, or indicate alteration intensity as MER diagrams do.

5.2.3 Simple Element Ratios versus Molar Element Ratios

Simple and molar element ratios are both effective methods of quantifying alteration at the Relincho deposit. $\text{K}_2\text{O}/\text{Th}$ was superior to the MERs for displaying and quantifying potassic alteration, for this reason it was used as the potassic alteration index. MERs, however, were more effective and exhibiting and quantifying propylitic and phyllic alteration than simple ratios.
5.3 Research Shortcomings

This study focuses on regional scale lithogeochemical characterization. Though successful on the regional scale, by its very nature it lacks local detail:

- Sample spacing may have missed some important alteration indicators. Project geologists for Teck Resources Limited have reported strong potassic alteration proximal to mineralization, the extent of which was not observed in this sample set;
- Lack of lithological contact or vein relationship information. The contact relationships between some lithological units, in particular the granodiorite units, is not fully explored by this study, nor are veins characterized;
- Fresh samples were not obtained for most lithological units. Truly unaltered samples are nearly impossible to acquire over a hydrothermal system with an alteration footprint of 60 km². This leads to a potential bias in alteration calculations;
- A failure to uniquely characterize the porphyry units. The compositional overlap of the porphyry units would not allow for characterization;
- Lack of characterization of ore mineralogy. Due to destruction by oxidation, ore mineral assemblages are not described in detail.

5.4 Research Implications for Exploration

From a regional exploration perspective the surface rock lithogeochemistry successfully identified areas of potential mineralization. Sample spacing of 500 m is adequate for future surveys designed to characterize lithological units and alteration assemblages, provided that adequate sample populations for each lithology are acquired. Alteration indices suggest that sample spacing up to 2000 m can be used for identifying areas of potential PCD fertility.

Alteration indices for the potassic, propylitic and phyllic assemblages could have applications for mapping alteration fluid pathways regionally. The indices could also be applied to existing databases or as a prospecting tool for identifying potential regions
for porphyry style mineralization. Potassic and propylitic-phylic indices could be applied to granodiorite dominant regions using thresholds of K2O/Th > 0.36 for potassic alteration and \(((18\text{Ca} + 14\text{Na} + 25\text{K})/(2\text{Si} + 7\text{Al} + 4(\text{Fe} + \text{Mg})) < 0.94\) for potassic, and \(((18\text{Ca} + 14\text{Na} + 25\text{K})/(2\text{Si} + 7\text{Al} + 4(\text{Fe} + \text{Mg})) > 1.04\) for propylitic.

5.5 Recommended Exploration Methodologies for Porphyry Cu-Mo Exploration

The most effective analytical methodologies were aqua regia, ICP-MS and fusion ICP-OES (Table 8). These two analytical methods provide all the trace element, major oxide, HFSE and REE data necessary for an in-depth lithogeochemical interpretation. Commercial XRD results were of limited value to the extent that they were not used in the interpretation. Fusion ICP-OES trace element results proved to be of equal or better quality than the pressed pellet XRF results, with detection limits on average an order of magnitude lower. SWIR interpretations are complimentary to the dataset, but not necessary. Although proven as a useful tool for alteration mapping at many other deposits (e.g. SWIR interpretations at the Pebble PCD by Harraden et al. (2013)) they were not particularly effective at the Relincho deposit, possibly due to weak alteration intensity. Interpretations were laborious and yielded results that were largely replaceable by hand sample observations or geochemistry.

The most effective interpretive methodologies for PCD exploration at the Relincho deposit were rock fertility assessment, and simple and molar element ratio characterization of alteration assemblages (Table 8). The assessment of GRD1a, GRD2 and the porphyry units as potentially fertile would identify the area as a candidate for follow-up geochemical investigation. Alteration indices produced from simple and molar element ratios, with population breaks determined from probability plots, quantified alteration and could be applied to regions of a similar geological setting for PCD exploration, or to map alteration intensity of known mineralization and map fluid pathways. Magmatic evolution and Tukey diagrams help to characterize lithological units, but are not necessary for regional exploration. Gain-loss diagrams aid in characterizing alteration assemblages, but are potentially inaccurate when there is limited knowledge of the lithological host units.
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**Method** | **Purpose** | **Necessary** | **Complimentary** | **Nonessential** |
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**Table 8:** Summary of effective analytical and interpretive tools for the characterization of lithological units and alteration assemblages
5.6 Suggested Future Work

A thorough mapping program would glean much about the alteration fluids and lithological units. By examining the veins associated with each assemblage, more could be understood about alteration fluid timing and composition. Prior to this study the four granodiorite units had not been differentiated. Studies of the temporal relationships of the four granodiorite units could benefit property scale exploration.

Fluid inclusion and isotope work could be considered for further characterization of the alteration fluids. Fluid inclusions can be used to determine relative temperature, pressure, salinity and gas composition of the different alteration fluids, allowing for a better understanding of alteration fluid composition and compositional evolution (Kamilli & Ohmoto 1977; Arancibia & Clark 1996; Ulrich et al. 2001; etc.). Isotope work using C, H, O and S could be used to distinguish one alteration events (Ulrich et al. 2001; Cohen 2012; Djouka-Fonkwe et al. 2012; etc.). Sulphur isotopes could be used in the drill core, although not in surface samples as surficial processes have destroyed sulphides.

The results of this study could be applied to an in-depth characterization of alteration on a deposit scale using the existing, extensive database of drill core. Alteration indices derived from this study could be applied to drill core results to produce a three-dimensional model of the alteration.

Spatial elemental variability, probability diagrams, SWIR and MERs can be employed for the characterization of a variety of rock types and deposit styles. SWIR results are known to have many successful applications for alteration characterization, particularly at deposits with clays as alteration minerals (Cohen 2012; Barker et al. 2013; Harraden et al. 2013; etc.). Probability plots distinguish between samples affected by a process, such as alteration or mineralization, from those unaffected, as such could be applied to any deposit style (Sinclair 1976). Molar element ratio diagrams describe processes. By changing the minerals used to calculate the axes, MER diagrams could be used to model and quantify alteration for any alteration-associated mineralization.
References


